

Series Editor
Saul Patai

The chemistry of functional groups

Edited by
Frank R. Hartley

The chemistry of
organophosphorus compounds

Volume 2 Phosphine oxides, sulphides,
selenides and tellurides



**THE CHEMISTRY OF ORGANOPHOSPHORUS
COMPOUNDS
VOLUME 2**
Phosphine oxides, sulphides, selenides and tellurides
Edited by
Frank R. Hartley
The Cranfield Institute of Technology, England

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- 1 Structure and bonding in tertiary phosphine chalcogenides**
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- 8 Coordination chemistry of phosphine chalcogenides and their analytical and catalytic applications**
T.S. Lobana

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organophosphorus compounds

Volume 2

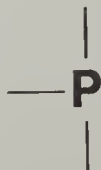
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The chemistry of **organophosphorus compounds**

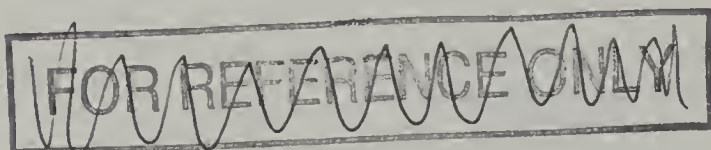
Volume 2

Phosphine oxides, sulphides, selenides and tellurides

Edited by

FRANK R. HARTLEY

*Cranfield Institute of Technology
Cranfield, UK*



1992

JOHN WILEY & SONS

CHICHESTER — NEW YORK — BRISBANE — TORONTO — SINGAPORE

An Interscience® Publication

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New York, NY 10158-0012, USA

Jacaranda Wiley Ltd, G.P.O. Box 859, Brisbane,
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John Wiley & Sons (Canada) Ltd, 22 Worcester Rd,
Rexdale, Ontario M9W 1L1, Canada

John Wiley & Sons (SEA) Pte Ltd, 37 Jalan Pemimpin #05-04,
Block B, Union Industrial Building, Singapore 2057

Library of Congress Cataloging-in-Publication Data

(Revised for vol. 2)

The Chemistry of organophosphorus compounds.

(The Chemistry of functional groups)

'An Interscience publication.'

Includes bibliographical references and indexes.

Contents: v. 1. Primary, secondary, and tertiary phosphines, polyphosphines, and heterocyclic organophosphorus(III) compounds — v. 2. Phosphine Oxides, sulphides, selenides, and tellurides.

1. Organophosphorus compounds. I. Hartley, F. R.

II. Series.

QD412.P1C444 1990 547'.07 89-22591

ISBN 0 471 92607 8 (v. 1)

Ref 547.07

03692355

British Library Cataloging in Publication Data

A catalogue record for this book is available from the British Library

ISBN 0 471 93056 3

Typeset in Times 9/10 pt by Thomson Press (India) Ltd, New Delhi and
Printed and bound in Great Britain by Biddles Ltd, Guildford, Surrey

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Foreword

The Chemistry of Organophosphorus Compounds is a multi-volume work within the well established series of books covering *The Chemistry of Functional Groups*. It is proposed to cover the extensive subject matter in four volumes.

Volume 1 covers primary, secondary and tertiary phosphines ($\text{PR}_3\text{H}_{3-n}$, $n = 1-3$), polyphosphines [both $\text{P(C)}_n\text{P}$ and $\text{R(P)}_n\text{R'}$, $n > 1$] and heterocyclic compounds containing phosphorus.

Volume 2 covers phosphine oxides, sulphides, selenides and tellurides.

Volume 3 will cover phosphonium salts, phosphonium ylides and phosphoranes.

Volume 4 will cover phosphinous, phosphonous, phosphinic and phosphonic acid compounds and their halogen derivatives R_2PY , RPY_2 and $\text{R}_2\text{P(X)Y}_2$, where Y = halogen and X = O, S or Se.

For many years the nomenclature used in organophosphorus chemistry was extremely frustrating, with different compounds being given the same name by different authors. The nomenclature has, however, now been rationalized and is summarized in Volume 1, Chapter 1, Section IV.

In common with other volumes in *The Chemistry of the Functional Groups* series, the emphasis is laid on the functional group treated and on the effects which it exerts on the chemical and physical properties, primarily in the immediate vicinity of the group in question, and secondarily on the behaviour of the whole molecule. The coverage is restricted in that material included in easily and generally available secondary or tertiary sources, such as *Chemical Reviews* and various 'Advances' and 'Progress' series, as well as textbooks (i.e. in books which are usually found in the chemical libraries of universities and research institutes) is not as a rule repeated in detail, unless it is necessary for the balanced treatment of the subject. Therefore, each of the authors has been asked *not* to give an encyclopaedic coverage of his or her subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself or herself to a reader who is assumed to be at a fairly advanced postgraduate level. With these restrictions, it is realised that no plan can be devised for a volume that would give a complete coverage of the subject with no overlap between the chapters, while at the same time preserving the readability of the text.

The publication of the Functional Group Series would never have started without the support of many people. This volume would never have reached fruition without the help of Mr Mitchell and Mrs Perkins with typing and the efficient and patient cooperation of several staff members of the Publisher. Many of my colleagues in England, Israel and elsewhere gave help in solving many problems, especially Professor Saul Patai, without whose continual support and encouragement this work would never have been attempted.

Finally, that the project ever reached completion is due to the essential support and partnership of my wife and family, amongst whom my eldest daughter provided both moral support and chemical understanding in the more difficult areas of the subject.

Cranfield, England

FRANK HARTLEY

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List of abbreviations used

abd	azobisisobutyl diacetate
Ac	acetyl (MeCO)
acac	acetylacetone
Ad	adamantyl
aibn	azobisisobutyronitrile
all	allyl
an	acetonitrile
An	anisyl
Ar	aryl
ATP	adenosine triphosphate
bipy	2,2'-bipyridine
BSA	bovine serum albumin
btsa	<i>N,O</i> -bis(trimethylsilyl)acetamide
Bu	butyl (also <i>t</i> -Bu or Bu ^t)
Bz	benzyl
cd	circular dichroism
cod	cycloocta-1,5-diene
cp	cyclopentadienyl
mCPBA	<i>m</i> -chloroperoxybenzoic acid
CPMAS	cross-polarization magic angle spinning
Cy	cyclohexyl
dbn	1,5-diazabicyclo[5.4.0]non-5-ene
dbso	dibenzoyl sulphoxide
dbu	1,8-diazabicyclo[5.4.0]undec-7-ene
DDPN ⁺	deamino diphosphopyridine nucleotide
diop	2,3- <i>o</i> -isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
dme	1,2-dimethoxyethane
dmf	dimethylformamide
dmg	dimethylglyoximate
dmpe	bis(1,2-dimethylphosphino)ethane
dmsO	dimethyl sulphoxide
DNA	deoxyribonucleic acid
dpbO ₂ }	Ph ₂ P(E)(CH ₂) ₄ P(E)Ph ₂ E = O, S
dpbS ₂ }	

dpbSe ₂	$\text{Ph}_2\text{P}(\text{E})(\text{CH}_2)_n\text{P}(\text{E})\text{Ph}_2$ $\text{b}, n = 4$ $\text{e}, n = 2$ $\text{m}, n = 1$ $\text{p}, n = 3$ $\text{E} = \text{O}, \text{S}, \text{Se}$
dpeO ₂	
dpeS ₂	
dpeSe ₂	
dpmO ₂	
dpmS ₂	
dpmSe ₂	
dppO ₂	$\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{PPh}_2$ $\text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{PPh}_2$ diphosphopyridine nucleotide dihydronicotinamide adenine dinucleotide bis(1,4-diphenylphosphino)butane bis(1,2-diphenylphosphino)ethane bis(1,1-diphenylphosphino)methane bis(1,3-diphenylphosphino)propane diphenyl sulphoxide
dppS ₂	
dppSe ₂	
dpmPS	
dpmPSe	
DPN ⁺	
DPNH	
dppb	electron transfer followed by chemical reaction followed by further electron transfer enantiomeric excess electron paramagnetic resonance electron spin resonance
dppe	
dppm	
dppp	
dpso	
ECE	flavine adenine dinucleotide flavine mononucleotide Fourier transform
ee	
epr	
esr	
FAD	benzoylacetone benzoyltrifluoroacetone dibenzoylmethane di(2-ethylhexyl)phosphoric acid dimethylglyoxime dithizone (3-mercapto-1,5-diphenylformazan) hexyl hexafluoroacetylacetone hanging mercury drop electrode hexamethylphosphoramide hexamethylphosphorotriamide highest occupied molecular orbital 8-hydroxyquinoline high-performance liquid chromatography 1-phenyl-3-methyl-4-acylpyrazol-5-one 1-phenyl-3-methyl-4-benzoylpyrazol-5-one 1-phenyl-3-methyl-4-butyrylpyrazol-5-one 1-phenyl-3-methyl-4-(3,5-dinitrobenzoyl)-pyrazol-5-one 1-phenyl-3-methyl-4-octanoylpyrazol-5-one 1-phenyl-3-methyl-4-stearoylpyrazol-5-one 1-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one pivaloyltrifluoroacetone
FMN	
FT	
Hba	
Hbfa	benzoylacetone benzoyltrifluoroacetone dibenzoylmethane di(2-ethylhexyl)phosphoric acid dimethylglyoxime dithizone (3-mercapto-1,5-diphenylformazan) hexyl hexafluoroacetylacetone hanging mercury drop electrode hexamethylphosphoramide hexamethylphosphorotriamide highest occupied molecular orbital 8-hydroxyquinoline high-performance liquid chromatography 1-phenyl-3-methyl-4-acylpyrazol-5-one 1-phenyl-3-methyl-4-benzoylpyrazol-5-one 1-phenyl-3-methyl-4-butyrylpyrazol-5-one 1-phenyl-3-methyl-4-(3,5-dinitrobenzoyl)-pyrazol-5-one 1-phenyl-3-methyl-4-octanoylpyrazol-5-one 1-phenyl-3-methyl-4-stearoylpyrazol-5-one 1-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one pivaloyltrifluoroacetone
Hdbm	
H ₂ dehp	
H ₂ dmg	
H ₂ dz	benzoylacetone benzoyltrifluoroacetone dibenzoylmethane di(2-ethylhexyl)phosphoric acid dimethylglyoxime dithizone (3-mercapto-1,5-diphenylformazan) hexyl hexafluoroacetylacetone hanging mercury drop electrode hexamethylphosphoramide hexamethylphosphorotriamide highest occupied molecular orbital 8-hydroxyquinoline high-performance liquid chromatography 1-phenyl-3-methyl-4-acylpyrazol-5-one 1-phenyl-3-methyl-4-benzoylpyrazol-5-one 1-phenyl-3-methyl-4-butyrylpyrazol-5-one 1-phenyl-3-methyl-4-(3,5-dinitrobenzoyl)-pyrazol-5-one 1-phenyl-3-methyl-4-octanoylpyrazol-5-one 1-phenyl-3-methyl-4-stearoylpyrazol-5-one 1-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one pivaloyltrifluoroacetone
Hex	
Hhfa	
hmde	
hmpa	benzoylacetone benzoyltrifluoroacetone dibenzoylmethane di(2-ethylhexyl)phosphoric acid dimethylglyoxime dithizone (3-mercapto-1,5-diphenylformazan) hexyl hexafluoroacetylacetone hanging mercury drop electrode hexamethylphosphoramide hexamethylphosphorotriamide highest occupied molecular orbital 8-hydroxyquinoline high-performance liquid chromatography 1-phenyl-3-methyl-4-acylpyrazol-5-one 1-phenyl-3-methyl-4-benzoylpyrazol-5-one 1-phenyl-3-methyl-4-butyrylpyrazol-5-one 1-phenyl-3-methyl-4-(3,5-dinitrobenzoyl)-pyrazol-5-one 1-phenyl-3-methyl-4-octanoylpyrazol-5-one 1-phenyl-3-methyl-4-stearoylpyrazol-5-one 1-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one pivaloyltrifluoroacetone
hmpt	
HOMO	
Hox	
HPLC	benzoylacetone benzoyltrifluoroacetone dibenzoylmethane di(2-ethylhexyl)phosphoric acid dimethylglyoxime dithizone (3-mercapto-1,5-diphenylformazan) hexyl hexafluoroacetylacetone hanging mercury drop electrode hexamethylphosphoramide hexamethylphosphorotriamide highest occupied molecular orbital 8-hydroxyquinoline high-performance liquid chromatography 1-phenyl-3-methyl-4-acylpyrazol-5-one 1-phenyl-3-methyl-4-benzoylpyrazol-5-one 1-phenyl-3-methyl-4-butyrylpyrazol-5-one 1-phenyl-3-methyl-4-(3,5-dinitrobenzoyl)-pyrazol-5-one 1-phenyl-3-methyl-4-octanoylpyrazol-5-one 1-phenyl-3-methyl-4-stearoylpyrazol-5-one 1-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one pivaloyltrifluoroacetone
Hpmap	
Hpmbp	
Hpmbup	
Hpmdbp	benzoylacetone benzoyltrifluoroacetone dibenzoylmethane di(2-ethylhexyl)phosphoric acid dimethylglyoxime dithizone (3-mercapto-1,5-diphenylformazan) hexyl hexafluoroacetylacetone hanging mercury drop electrode hexamethylphosphoramide hexamethylphosphorotriamide highest occupied molecular orbital 8-hydroxyquinoline high-performance liquid chromatography 1-phenyl-3-methyl-4-acylpyrazol-5-one 1-phenyl-3-methyl-4-benzoylpyrazol-5-one 1-phenyl-3-methyl-4-butyrylpyrazol-5-one 1-phenyl-3-methyl-4-(3,5-dinitrobenzoyl)-pyrazol-5-one 1-phenyl-3-methyl-4-octanoylpyrazol-5-one 1-phenyl-3-methyl-4-stearoylpyrazol-5-one 1-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one pivaloyltrifluoroacetone
Hpmop	
Hpmsp	
Hpmtfp	
Hpva	

Hpvta	dipivaloylacetone
Htbfa	thiobenzoyltrifluoroacetone
Htfa	trifluoroacetylacetone
Htfma	1,1,1-trifluoro-5-methylhexane-2,4-dione
Htta	1,1,1-trifluoro-3-(2-thenoyl)acetone
IP	ionization potential
LC ₅₀	concentration causing lethality to 50% of the population
LD ₅₀	dose causing lethality to 50% of the population
lda	lithium diisopropylamide
lp	lone pair of electrons
LUMO	lowest unoccupied molecular orbital
M	metal
Me	methyl
mibk	methyl isobutyl ketone
MNDO	modified neglect of diatomic overlap
NADP	nicotinamide adenine dinucleotide phosphate
nba	<i>N</i> -bromoacetamide
nbs	<i>N</i> -bromosuccinimide
NHN	nicotinamide ribose monophosphate
Np	naphthyl
OAc	acetate
ord	optical rotatory dispersion
Pe	pentenyl
Pen	pentyl (C ₅ H ₁₁)
pes	photoelectron spectroscopy
Ph	phenyl
phen	1,10-phenanthroline
ppa	polyphosphoric acid
ppm	parts per million
Pr	propyl (also <i>i</i> -Pr or Pr ^{<i>i</i>})
R	any radical
RNA	ribonucleic acid
SCE	standard calomel electrode
SCF	self-consistent field
tbp	trigonal bipyramid (when referring to a structure) or <i>tert</i> -butyl peroxide (when referring to a chemical)
tbpo	tri- <i>n</i> -butyl phosphate
tfa	trifluoroacetic acid
tfb	tetrafluorobenzobicyclo[2.2.2]octatriene
thf	tetrahydrofuran
tht	tetrahydrothiophen
tmeda	<i>N,N,N',N'</i> -tetramethylethylenediamine
tmpo	2,2,6,6-tetramethylpiperidine-1-oxyl

Tol	tolyl ($\text{CH}_3\text{C}_6\text{H}_4$)
topo	tri- <i>n</i> -octyl phosphate
tos	tosyl
TPN	triphosphopyridine nucleolide
VSEPR	valence shell electron pair repulsion
X	halide

CHAPTER 1

Structure and bonding in tertiary phosphine chalcogenides

D. G. GILHEANY

Department of Chemistry, St. Patrick's College, Maynooth, Co. Kildare, Ireland

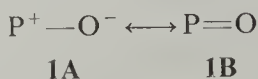
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1. INTRODUCTION

The general features of bonding to phosphorus were discussed in Volume 1¹, including likely bonding schemes and the strengths of single and double bonds to phosphorus. Using these, the gross features of the structure and bonding of phosphine chalcogenides are readily predicted and understood. Taking the oxides as an example, phosphorus has five electrons available for bonding, so five bonds to phosphorus are possible, while oxygen is normally divalent and double bonds are allowed. Hence, *if we ignore the octet rule*, there is no problem in predicting the correct structure: phosphorus will have four ligands via three single bonds and one double bond to oxygen, with all electrons used. From the recently rehabilitated² valence shell electron pair repulsion (VSEPR) theory, the four ligands are expected to have tetrahedral geometry with the bond to oxygen being stronger than the others and rather polar because of the difference in electronegativity between oxygen and phosphorus. These predictions are borne out completely by measurement of the bond lengths and angles (detailed in Section III), vibration frequencies and dipole moment (Section IV.A). The strength of the PO bond is illustrated by the experience of practical chemists that its formation drives the very useful Wittig and Arbusov reactions and the reactions of life itself.

Of course, it is not that simple. First, there is the problem of the octet rule, and second, on the LCAO-MO model there are, at first sight, not enough orbitals on phosphorus. Indeed, much of the previous discussion of the bonding in phosphine oxides, (and sulphides and selenides) has centred on how to overcome these difficulties, in particular with respect to the nature of the PO bond. Thus the standard discussion of the PO bond in previous reviews of this topic³⁻¹³ has been in terms of a combination of two different descriptions, often *via* a resonance between structures **1A** and **1B**:



Structure **1A** avoids the problem of violation of the octet rule, but there is evidence (Section IV.A) that there is not a full positive charge on phosphorus or negative charge on oxygen, so structure **1B** is allowed to contribute. In this case the number-of-orbitals problem is overcome by invoking a suitable virtual d orbital on phosphorus in an overlap scheme such as that in Figure 1. The conventional phrase is often used³⁻¹³ that 'there is expansion of the octet on phosphorus to allow backbonding from oxygen lone pairs into low-lying empty d orbitals'. In turn, this explains the difference between phosphine oxides and amine oxides in that the first-row element does not have easily accessible d

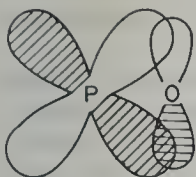


FIGURE 1. The now outdated and misleading view of the π -type orbital overlap in phosphine oxides

orbitals. Hence a discussion of the bonding in phosphine oxides leads on to the differences between the first and subsequent rows of the Periodic Table.

It is shown below that work over the last 10–15 years has rendered this description untenable¹⁴. First the d-orbitals concept is now redundant at best, and inaccurate and misleading at worst, because d orbitals are not required for there to be backbonding. As described in Section II, it has recently been confirmed beyond doubt by Magnusson¹⁵ that the importance of d functions in *ab initio* calculations on these systems does not mean that they have a valence role. Second, at a deeper level, doubt has been cast on the description of the PO bond as a single bond with some backbonding, the rival description being a formal triple bond. As we shall see in Section IV, this latter issue is not yet settled and is part of a developing general controversy about the nature of multiple bonding.

Hence the investigation of the bonding in phosphine oxides (and sulphides and selenides) calls for an examination of some the most basic concepts in valency and bonding theory in the context of one of the most important bonds in practical chemistry and the processes of life. The following quotations are from two recent papers which are discussed in Section IV.D.3 and illustrate the controversial nature of the subject:

‘These studies emphasize the importance of partial ionic bonding in second row hypervalent species... Due to the ionic character of the bonding, the *electronic* octet rule is far from being violated. This emphasizes the robustness of the Lewis octet concept’.

A. E. Reed and P. v. R. Schleyer¹⁶

‘Contrary to much previous experience based on molecular orbital calculations, generalized valence bond calculations exhibit six bonds to P and S atoms in the presence of electronegative ligands. One must conclude that this is strong evidence that such molecules violate the Lewis–Langmuir octet rule’.

R. Messmer¹⁷

Even the representation of the bond from oxygen to phosphorus in tertiary phosphine oxides is contentious. Practical chemists usually just write a double bond, $R_3P=O$, but a number of other descriptions and representations have been advocated as the following chronological list illustrates: ‘somewhere between a single and triple and only by chance it happens to be a double bond’¹⁸; ‘a partial triple bond’¹⁹; ‘a resonance between single and triple bond structures, the double bond being rejected on symmetry grounds’²⁰; ‘the dipolar structure dominates and the double bond structure contributes but little’²¹; ‘a formal triple bond’¹⁷. In Section IV.F, we discuss the representation of the PO bond and argue that the continued use of the double bond formula is perfectly reasonable and unrelated to the controversy as to where exactly the bonding electrons are.

II. NON-INVOLVEMENT OF d ORBITALS

The description of the structure and bonding in phosphine oxides has been connected intimately with the concept of virtual d-orbital involvement in bonding in the Main

Group of the Periodic Table. Since, as we shall see, it is only recently that this concept has been discredited, a short overview of the subject is warranted.

The elegance, economy and widespread applicability of the valence bond (VB) and molecular orbital (MO) methods have made them nearly universal in both the qualitative and quantitative discussion of bonding and other molecular properties²². In particular, a version of the MO method, the linear combination of atomic orbitals (LCAO) scheme²², provides the most commonly used framework for the discussion and interpretation of the bonding. In these methods atoms are considered to offer, for bond formation, the outermost valence orbitals (those which are occupied in the atom). Thus hydrogen has one atomic orbital (AO) available for bonding, the first-row elements boron to neon have four, the transition metals six, and so on. In this way, early explanations were provided for s and p bonds in the first row of the Periodic Table from lithium to fluorine. In 1931 Pauling²³ showed how, by introducing appropriate hybrids of s and p orbitals, the characteristic valence angles and bond lengths in compounds of carbon, oxygen and nitrogen could be explained. Although the rough qualitative picture obtained by bonding with these orbitals was satisfactory in most cases, some important difficulties arose.

A particular qualitative difficulty concerned the existence of the so-called 'hypervalent molecules'. In these there seem to be more bonds from the central atom than would be permitted on the basis of Langmuir's octet rule. Thus, in the valence bond picture of, for example, the SF₆ molecule, sulphur forms six σ bonds using six equivalent d²sp³ hybrids²⁴. However, the d functions used are virtual, not being occupied in the aufbau description of the ground-state sulphur atom. It is then said⁵ that SF₆ is characterized by 'outer d-orbital participation in the bond' or that there is an 'expansion of the valence shell of sulphur by promotion of an electron(s) into a low-lying vacant d orbital(s)'. Similar considerations applied to PF₅. The concept of d orbitals was then found convenient to describe two other π -type phenomena exemplified in phosphorus chemistry³ by (i) the structure and stability of phosphine oxides and ylides (especially compared with their nitrogen analogues) and (ii) the shortening of formally single bonds such as the PO bonds in phosphates. These latter two phenomena involve d orbitals in π -type overlap with adjacent p orbitals⁵.

In this way, the possession of 'low-lying' d-orbitals came to be seen as a fundamental difference between first- and second-row elements of the Periodic Table, explaining, for example, why silicon tetrafluoride hydrolyses readily whereas carbon tetrafluoride does not²⁵. Since the work of Pauling²³, there have been many papers dealing with the participation of d-orbital basis functions in molecular orbitals for systems containing non-transition elements. Because of their more elaborate symmetry, d orbitals may form more kinds of bonds than can s and p orbitals and detailed and elaborate schemes were built up to use d orbitals to explain the various phenomena²⁶⁻³⁰. This early work is well summarized in a number of reviews^{5,31-33}, the most useful of which is that of Mitchell⁵.

At the outset, a distinction has to be made between inner and outer d orbitals³⁴. This refers to the principal quantum number of the d orbital in relation to that of the other valence electrons. *Inner* d orbitals have a principal quantum number one less than that of the other valence electrons. Thus, in the first transition metal series it is the 3d, 4s and 4p orbitals that are involved and the charge cloud for these d electrons lies mostly within that of the s and p electrons. Since these d orbitals are occupied in the ground-state atom, they are clearly required for description of the molecular wavefunction, and the question of their inclusion does not arise. This is the case for bonding in the transition metals³⁵ and will not be discussed further. *Outer* d orbitals, on the other hand, have the same principal quantum number as that of the other valence shell electrons. The question of their involvement in bonding is much more problematic since they are not occupied in the ground state of the atom under consideration. Indeed, the concept was never fully

accepted by the chemical community, including Pauling²⁴, and, from an initially small group of dissenters³⁶⁻⁴³ among whom it is probably fair to single out Rundle³⁹, the concept has now become redundant, at least among theoretical chemists. Its popularity probably peaked around about 1970 with the review by Mitchell⁵ and the advent of the first *ab initio* calculations on these systems (see Section II.B).

A. Alternative Models

The first reservation that has to be entered about virtual d-orbital involvement in bonding is that there are alternative explanations of all the phenomena involved. One of the initial successes of the hybridization theory of bonding as proposed by Pauling^{23,24} was the prediction of molecular stereochemistry in that bond directions are determined by the relative orientations of a set of hybrid orbitals on the central atom which are used to form bonds to the ligand atoms and to hold unshared electron pairs. However, during the 1950s it was shown by Gillespie that the successful prediction of molecular geometry does not require explicit reference to the bonding involved because the well known and useful VSEPR model^{35,44} explains the geometry of most molecules. Also, at about the same time, a simple and reasonably easily understood model was developed which explains the bonding in non-octet (hypervalent) compounds and which does not require the use of d orbitals. This is the three-centre bond model proposed at various times by Pimental^{36,37}, Rundle^{38,39}, Havinga and Wiebenga^{40,41}, Pitzer⁴² and Musher⁴³ and their coworkers and developed in detail by Rundle³⁹ and Musher⁴³. Bonding is envisaged as partly ionic, which removes the need to involve the d orbitals and explains why fluorine is a crucial ligand in hypervalence. Better still, this model explains well the bonding in other systems where the d orbital concept is lacking, e.g. noble gas derivatives^{45,46} and the interhalogen compounds⁴¹. As we shall see in Section IV, there is also a simple alternative to the d orbital concept as applied to $d\pi-p\pi$ systems.

Second, from the 1950s to 1970s there were a multitude of experimental and theoretical investigations, none of which confirmed unequivocally the validity of the concept of d-orbital involvement. This is well documented in the book by Kwart and King⁴⁷, the problem being that no study could distinguish d-orbital involvement from an alternative explanation. Indeed, it appeared that the d orbital theory might fit into Popper's category of an unfalsifiable theory⁴⁸. Examples of phenomena which were investigated without definitive results are (i) bond length data in the series of ions XO_4^{n-} ($X = \text{Si, P, S and Cl}$), which are all short relative to values reasonably expected for single bonds^{30,35,49}, and (ii) the planarity of trisilylamines⁵⁰⁻⁵³. Probably the last example where a determined effort was made to prove d orbital involvement is the detailed study of a cyclic conjugated sulphone by Fraenkel and coworkers⁵⁴. Even in 1986, after all the work that had gone before⁴⁷, these workers felt able to claim that their study implicated p-d bonding 'unequivocally and for the first time'⁵⁴. However, in the light of the results discussed below, it seems likely that all they did, which was still significant, was to show that cyclic conjugation occurred in their system.

B. Theoretical Studies

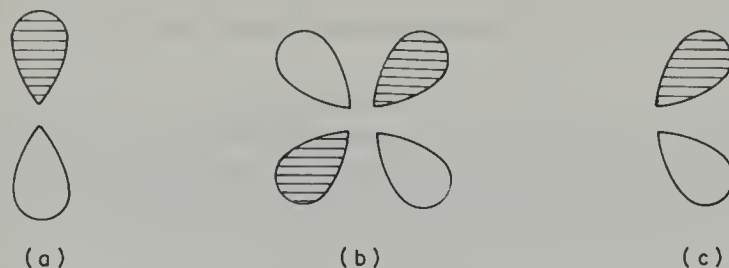
Since the experimental work had been so very contradictory, it was hoped that calculations might lead to a more definitive answer. Indeed, the early theoretical work was encouraging because it had concentrated on certain issues concerning the suitability of the valence atomic d orbitals for their task⁵⁵⁻⁶³. Two issues of concern were the size and energy of the d orbitals. First, the d orbitals are too large to overlap effectively with their potential s and p partners^{34,56}. By consideration of the factors affecting the size⁵⁷, namely unpaired electron spin assignments^{34,58,59}, the number of promoted

electrons^{34,59,60} and the formal charge on the central atom⁵⁹, it was shown that this objection could be overcome. In particular, the contraction of the d orbitals in a field of strongly electronegative ligands provided a neat explanation of why fluorine is able to induce the largest valence of a central atom. As regards the energies of the d orbitals, which are too high in the isolated atom for effective hybridization with s and p orbitals⁵, it was also shown that a field of electronegative ligands could reduce the energies to reasonable values^{57,62,63}.

In about 1970, with the advent of full *ab initio* calculations on these molecular systems, more detailed investigation of the bonding became possible. For example, early descriptions of the bonding in phosphine oxides (see Section I) involved either semipolar bonds without reference to d orbitals or ordinary covalent bonds constructed from appropriate hybrids that involve d orbitals. Since the former corresponds to a zero population of d orbitals and the latter to a population of unity, it was expected that an analysis of the d populations of the calculated wavefunctions would indicate which was correct. Indeed, the first calculations appeared to confirm the importance of d orbitals because, when d functions were left out, very inaccurate results were obtained and also their addition caused very large energy decreases. Certain calculations in particular had a very strong influence, at least on the community of practical phosphorus chemists⁶⁴, e.g. the extended Hückel studies of ylides and phosphoranes by Hoffmann and coworkers⁶⁵⁻⁶⁷ and the *ab initio* STO-3G studies by Van Wazer and coworkers on ylides and phosphine oxides^{68,69}. This despite the specific warning of Hoffmann and coworkers⁶⁷ on the *deus ex machina* aspect of d orbitals.

However, there were two problems which confused the theoretical analysis of these systems, namely the incompleteness of most of the basis sets used and the requirement for polarization functions. Initially it was not well recognized that if the s and p basis sets used in the calculations were not saturated, that is, addition of further s and p basis functions still gave energy lowering, then the added d functions would make up the difference and lead to an overestimation of the importance of d orbitals. Differences in the basis set then lead to large differences in the importance of d orbitals from populations of 0.3 to greater than 1. Although the evidence for this was present from the start (see Section IV.D.2), it was only later that it was stated explicitly¹⁹. The difficulties were further compounded by the well known dependence of population analysis on basis set¹⁹.

However, even if the sp basis is saturated and the population analysis is foolproof, there is still a crucial role for d functions in the calculation of molecular properties and most calculations, especially on second-row elements, will require their inclusion^{1,15,70-73}. This is because they act as polarization functions^{15,34,71}. Early in the development of quantum chemistry it was known⁷⁴ that a proper description of the σ bond in H_2 requires the use of a $p\sigma$ basis function on the proton. The purpose of this function is to polarize the wavefunction (see below) and thus permit the charge distribution to change shape, becoming more localized along the bond axis. This requirement is now routine⁷⁵ and for first- and second-row elements the polarization functions needed are d functions. To illustrate the effect of these polarisation functions, consider an electron in a 2p state of a fixed hydrogen atom³⁴ (Figure 2a). Application of a steady fixed electric field in the z-direction would polarize the charge and pull it in the z-direction. The final perturbed shape is shown in Figure 2c. It can be seen that the charge cloud, and hence the wavefunction, of the perturbed state can be approximated by a superposition (Figure 2b), of some amount, λ of d orbital character on the original p orbital³⁴. Hybrids of this kind, involving a small amount of d character, will often be the easiest way of expressing perturbations or polarizations of p orbitals, for example in molecules containing a large dipole moment or in strained-ring compounds⁷¹. The d orbitals mixed in by this process are not suggested to have any independent existence. In fact, it can be shown^{15,34} that the d contribution which expresses the polarization of a 2p orbital

FIGURE 2. Polarization of a p orbital. $(a) + \lambda(b) = (c)$

is a 2d orbital and its function is merely to be of about the same size as the orbital it perturbs and to have the appropriate symmetry to provide the angular flexibility needed to direct the electron density efficiently into regions between bonded atoms.^{15,71}

Needless to say, many theoretical workers were uneasy about ascribing a valence role to such polarization functions. During the 1970s there were a number of attempts to define circumstances in which one could say which role was taken by the d functions. For example, Coulson³⁴ distinguished between *polarisation* (d population < 0.1) and *participation* of d orbitals in bonding, where one or more complete d orbitals are used, and Ratner and coworkers^{76,77} drew a similar distinction between the *qualitative* and *quantitative* necessity for d orbital inclusion in a basis set, while noting that the whole question is to some extent an artifact of the very convenient atom-centred LCAO method. Then, during the 1980s, it gradually became clear to the majority of theoretical workers that the maximum d population was about 0.3 in most cases and that it has no valence role. Examples of this conclusion are in calculations on, among many others, oxy- and thio-carbanions^{78,79}, sulphur tetrafluoride^{80,81} and, especially significant, the volte-face of Cruickshank⁴⁹ on the oxyanions of second-row atoms. There was a minor renaissance⁸²⁻⁸⁴, but it is now clear beyond doubt through the very recent work of Magnusson, discussed below, that the d orbital concept is redundant. Good recent leading references to this literature are the paper by Magnusson¹⁵, that of Reed and Schleyer¹⁶ which, since they treat phosphine oxides, is discussed in detail in Section IV.D.3.a, and the general review by Kutzelnigg¹⁴ on bonding in Main Group compounds, which is indispensable.

C. Calculations by Magnusson

Many workers have studied the variation of the use of d functions in a calculation in order to determine their valence role and concluded that it was not large⁸⁵. For example, Grein and Lawlor⁸⁶ showed that the use of bond functions⁸⁷ replicated the beneficial effect of d functions in calculations on H_3NO . However, the recent study by Magnusson¹⁵ is so comprehensive and gives such an unequivocal conclusion that it surely must be the final word on the subject. Therefore, we reproduce below the main conclusions in some detail.

Magnusson¹⁵ reported calculations for a very large number of compounds of first- and second-row elements, both normal valent and hypervalent, all at a comparable level. The basis set was of double zeta quality and the experimental geometries were used. Single and multiple sets of five Gaussian d functions were added to the basis sets of all atoms except hydrogen (p function). The exponents of the d functions on the central atom were optimized in all cases, as were those on selected peripheral atoms. The possibility of basis set superposition error was checked and avoided and also the results

were compared with those obtained by adding Slater-type functions. The results are given below.

i. The most important observation is that the optimum d function exponent for any element changes very little from one compound to another, even those as different as H_2S and SF_6 . Hence there is no support for the view that diffuse d orbitals on the central atom take part in bonding after being contracted by an electronegative ligand field; for example, there is no sign of any progressive contraction across the SF_2 , SF_4 , SF_6 sequence¹⁵.

ii. There are large energy depressions for many other types of molecule than the allegedly hypervalent species and there is no clear demarcation between them and the normal-valent compounds. In fact, when the energy depressions are measured *per bond* they show only limited variation. This suggests that the involvement of d functions is characteristic of the bond rather than the compound that contains it, and that the extra involvement of d functions in hypervalent molecules is because they have more bonds¹⁵.

iii. There are also energy depressions on the addition of d functions to the basis sets of peripheral atoms. The energy increment per added function is much greater for the central atom but *per bond* there is no difference¹⁵.

iv. There are also energy depressions in compounds of first-row elements and when the results are obtained at the same basis set level the contrast between second- and third-shell behaviour is less spectacular than usually reported¹⁵.

v. There is a strong response in the optimum exponent and d function energy increment to change in bond length. The optimum d function exponent on the peripheral atom also changes¹⁵.

vi. Finally, there is no difference in the role of d functions between normal-valent and hypervalent compounds. They facilitate the transfer of electronic charge into the internuclear bonding region at the expense of the outer parts of the valence wavefunction. Hence the occupations of the higher order functions are strongly dependent on the degree of charge transfer from the central atom and the number of electron pairs formally arranged around the central atom. In short, their purpose is to respond to the rapidly varying molecular potential in the space between the nuclei¹⁵.

We also leave the final word on this with Magnusson¹⁵: 'accordingly, any resemblance between d functions in molecular wavefunctions and the valence d orbitals of excited second-row atoms is an artifact of the electronic structure model; they should not be called d orbitals'.

III. STRUCTURE

Structure in organophosphorus chemistry was last reviewed comprehensively in 1974 by Corbridge⁹, but work on tertiary (and other) phosphine chalcogenides was not well developed at that time. Thus the material presented below is mostly from the intervening period. The usual general publications⁸⁸⁻⁹¹ also give some relevant data but, again, the coverage is not complete. The structures of tertiary phosphine oxides, sulphides, selenides and the few tellurides are first discussed using the data in Tables 1-3. Then these compounds are compared and contrasted with other phosphorus derivatives and non-phosphorus compounds not strictly relevant to this chapter, in particular the parent tertiary phosphines, halogenophosphoryl derivatives and amine and arsine chalcogenides using the data in Tables 4 and 5.

Although a high proportion of available structures are included in Tables 1-3, they are not comprehensive and readers requiring data on particular compounds should also refer to *Chemical Abstracts*. Readers should also refer to the original publications for

detail of the structural determinations, error limits and the other molecular dimensions of the compounds quoted.

A. Bond Length–Bond Angle Relationships

The idea that bond length and bond angle are related can be helpful in the analysis of trends in the structures of molecules. It is especially useful in the case of a tetrahedral disposition of ligands around a central atom where most of the space around that atom is occupied. Then the introduction of either bulky or more electronegative groups will lead to a change in both bond angle and bond length. Thus, for example, the bond angle between bulky groups will have to be larger, so all ligand(s) will not be able to approach as close to the central atom and their bond length will be larger. On the other hand, a more electronegative group will require a shorter bond length to the central atom, forcing the other ligand(s) closer together and reducing their bond angle. The structure of the molecule then reflects the balance between these two effects.

Used carefully, the concept can reduce the number of experimental correlations that have to be explained. Obviously there are limitations on its use, e.g. (i) if the space around the central atom is not fully occupied, then bond angle can increase while maintaining bond lengths, for example in the tricoordinate phosphines¹ and perhaps in the later rows of the Periodic Table where the central atom is relatively large, and (ii) if the space around the central atom is already very crowded, as in tetrahedral derivatives of the small first-row atoms, then the size effect may be more dominant.

B. Phosphine Oxides

Table 1 gives some structural data for tertiary phosphine oxides, mostly determined using X-ray diffraction. As befits such an easily crystallized and thereby useful¹⁴⁸ compound, there are no less than eight reported X-ray crystal structure determinations on triphenylphosphine oxide^{96–99,149}, most of which are detailed in Table 1. This is because there are at least two crystal modifications and there have been temperature variation studies. Note the fairly large changes in structural parameters as the *R* value falls from 7.8 to 3.5. Only in one case, trimethylphosphine oxide, were both X-ray and electron diffraction used, with only moderate agreement between the methods (the difference was not caused by intermolecular contacts in the crystal⁹³). A number of useful generalizations may be made from Table 1.

The PO bond length is usually in the range 147.5–149.0 pm (the figure of 146 pm, derived from the first study⁹⁸ on triphenylphosphine oxide, which was widely quoted^{92,94} into the mid-1980s, is clearly in error). This PO distance is almost insensitive to molecular environment. It increases by only 1 pm on metal complexation of the triphenyl derivative¹⁰⁰ (Table 1) or on hydrogen bonding^{9,150}, although the trialkyl derivatives are affected by a larger amount by the latter change⁹. Similarly, the PO length is little changed by electronegative substituents, α,β -unsaturation or inclusion in a tricyclic ring structure (Table 1). It is possible that alkyl-substituted phosphine oxides have a PO bond length marginally shorter than aryl analogues, which could be due to a bond length–bond angle relationship, but there are not enough data to be sure. This PO bond length may be compared with those in HPO⁹¹ (151.2 pm), diatomic PO⁹¹ (147.6 pm) and a typical PO single bond (160 pm; bridging bond in P₄O₁₀⁸⁹). Clearly the PO bond has high multiple character.

The PC bond length is normally in the range 179–181 pm. From the limited data available, there is a strong effect of electronegative substituents to increase the PC distance, the extreme example being the tris(trifluoromethyl)-substituted case. Also, it is possible that P—C(alkyl) is less than P—C(aryl) by about 1 pm but, again, there are

TABLE 1. Structural data^a for some tertiary phosphine oxides

Molecule	Method ^b	$r(\text{P}=\text{O})$	$r(\text{P}-\text{C})$	$\angle \text{OPC}$	$\angle \text{CPC}$	R^c	Ref.
$\text{Me}_3\text{P}=\text{O}$	E	147.6	180.9	114.4	104.1	5.2	92
	X	148.9	177.1	113.1	105.9	6.5	93
$\text{Bu}_3^t\text{P}=\text{O}$	E	159.0	188.8	106.1	112.9	9.7	94
$(\text{CF}_3)_3\text{P}=\text{O}$	E	147.6	189.7	114.2	104.3	—	95
$\text{Ph}_3\text{P}=\text{O}$	X^d	148.3	179.2	112.3	106.5	6.0	96
	X^e	148.4	180.3	112.3	106.6	4.5	97
	X^f	146	176	111.7	107.1	7.8	98
	$\text{X}^{f,g}$	149.1	180.3	112.4	—	3.5	99
	$\text{X}^{e,g}$	149.4	180.0	112.4	—	3.6	99
$\text{Ph}_3\text{P}=\text{O}$ complexes	X^h	150	179	111	—	—	100
$(2\text{-MeC}_6\text{H}_4)_3\text{P}=\text{O}$	X	147.4	181.0	112.9	106.0	7.5	101
$(4\text{-ClC}_6\text{H}_4)_2\text{Ph}_2\text{P}=\text{O}$	X	148.5	180.5	111.9	107.0	4.7	102
$(4\text{-BrC}_6\text{H}_4)_2\text{Ph}_2\text{P}=\text{O}$	X	149.7	180.8	112.0	106.9	6.4	103
$(\text{C}_6\text{F}_5)_2\text{Ph}_2\text{P}=\text{O}$	X	147.4	179.6	—	—	—	104
$\text{Me}_2\text{PhP}=\text{O}$	X	147.4	178.9	113.9	105.5	4.3	105
			181.5 ⁱ	111.9 ^j			
$\text{ClCH}_2\text{Ph}_2\text{P}=\text{O}$	X	149.3	183.2	113.9	105.6	5.3	106
			180.4 ⁱ	112.6 ^j			
$\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2$	X	149.1	181.9	112.0	106.8	6.3	107
			179.4 ⁱ				
$\text{Ph}_2\text{P}(\text{O})\text{C}\equiv\text{CP}(\text{O})\text{Ph}_2$	X	148.1	179.4	114.4	103.7	3.9	108
			180.8 ⁱ	112.9 ^j	108.5 ^k		
$\begin{array}{c} \text{Ph}_2\text{P}(\text{O}) \quad \text{CH}_2\text{Cl} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{ClCH}_2 \quad \text{P}(\text{O})\text{Ph}_2 \end{array}$	X	148.5	184.3	112.5	106.3	3.3	109
			180.0 ⁱ				
7-Phosphanorbornene derivative ^l	X	148	186.7	116.8	84.3	7.0	110
			181.1 ⁱ	111.1 ^j	112.9 ^m		
1-Phosphanorbornane derivative ⁿ	X	148.7	178.3	—	96.2	5.4	111

^a $r(\text{P}-\text{X})$ = bond length in pm; $\angle \text{XPY}$ = bond angle in degrees; mean values are quoted, unless indicated otherwise.

^bE = electron diffraction; X = X-ray crystallography at room temperature, unless indicated otherwise.

^cReliability index = $100 \times$ conventional R for both X and E, except where indicated otherwise; see original papers for definitions.

^dMonoclinic, space group $P2_1/a$.

^eMonoclinic, space group $P2_1/c$.

^fOrthorhombic, space group $Pbca$.

^gPerformed at 100 K.

^hAverage of 62 fragments from the Cambridge Crystallography Database.

ⁱ $\text{P}-\text{C}_{\text{Ph}}$.

^j $\text{O}-\text{P}-\text{C}_{\text{Ph}}$.

^k $\text{C}_{\text{Ph}}-\text{P}-\text{C}_{\text{Ph}}$.

^l5-Cyano-1,4,7-triphenyl-7-phosphabicyclo[2.2.1]hept-2-ene-7-oxide.

^m $\text{C}_{\text{Ph}}-\text{P}-\text{C}_{\text{ring}}$.

ⁿ1-Phosphabicyclo[2.2.1]heptane-1-oxide.

not enough data to be sure. There is a small but definite decrease in PC length (1 pm) on metal complexation at oxygen. There is a consistent deviation of the bond angles from the tetrahedral values with CPO higher (112–114°) and CPC lower (104–107°). This is consistent with the shorter PO distance relative to the PC distance.

Note the totally anomalous nature of the structure of tri(*tert*-butyl)phosphine oxide.

The remarkable features of the structure of Bu_3^tPO are (i) the much greater length of the PO bond (159.0 pm) compared with all other oxides, making it essentially a single bond length, (ii) the greater length of the PC bond (188.8 pm) and (iii) the reversal of the angle deviation from tetrahedral (CPC is greater). Obviously the great bulk of the *tert*-butyl groups must be at least partly responsible for this anomalous structure. For example, the CPC angles in the parent phosphine¹³⁶ (109.9°) are already one of the highest known and could hardly be expected to decrease on oxidation. However, it should be pointed out that there is no steric requirement for the PO bond to be so long because the oxygen atom is well separated from its neighbouring carbon atoms and from the methyl group atoms⁹⁴. The long PO bond length has therefore also been attributed⁹⁴ partly to the electron-releasing properties of the *tert*-butyl groups. In any event, it seems reasonable to regard the bonding in the molecule as purely $\text{Bu}_3^t\text{P}^+ - \text{O}^-$.

Brock and coworkers⁹⁹ made a very careful study of both forms (monoclinic and orthorhombic) of triphenylphosphine oxide at low temperature. They found that there do not appear to be any important differences between the molecular dimensions in the two crystals. Even some small structural trends are shared by the two molecules; for example, of the three PC distances, 179.8, 180.3, 180.8 pm in the orthorhombic and 179.7, 180.2, 180.2 pm in the monoclinic structure, the smallest is to the phenyl ring whose plane is most nearly perpendicular to the PO bond (see also Section V).

C. Phosphine Sulphides

Table 2 gives some structural data for tertiary phosphine sulphides. Only in the case of trimethylphosphine sulphide was more than one method used to study the structure

TABLE 2. Structural data^a for some tertiary phosphine sulphides

Molecule	Method ^b	$r(\text{P}=\text{S})$	$r(\text{P}-\text{C})$	$\angle \text{SPC}$	$\angle \text{CPC}$	R^c	Ref.
$\text{Me}_3\text{P}=\text{S}$	M	193.6	181.4	114.4	—	<0.2	112
	E	194.0	181.8	114.1	104.5	4.8	92
	X	195.9	179.8	113.2	—	5.0	113
$[(\text{Me}_3\text{P}=\text{S})_3\text{Cu}]\text{ClO}_4$	X	199.4	179.3	111.6	—	11	113
$(\text{Me}_3\text{P}=\text{S})\text{Cr}(\text{CO})_5$	X	199.0	179.2	112.4	106.4	6.5	114
$(\text{cyclohexyl})_3\text{P}=\text{S}$	X	196.6	183.9	110.9	108.0	5.8	115
$(\text{cyclopropyl})_3\text{P}=\text{S}$	X	193.9	178.5	113.4	104.9	6.0	116
$\text{Ph}_3\text{P}=\text{S}$	X	195.0	181.7	113.1	105.7	4.6	117
$(2\text{-MeC}_6\text{H}_4)_3\text{P}=\text{S}$	X	194.8	181.9 ^d	112.6	106.1 ^e	9.0	101
$(3\text{-MeC}_6\text{H}_4)_3\text{P}=\text{S}$	X	193.6	181.5	112.3	106.5	8.0	118,119
$(4\text{-ClC}_6\text{H}_4)\text{Ph}_2\text{P}=\text{S}$	X	194.9	180.7	112.9	105.9	5.2	120
$(4\text{-BrC}_6\text{H}_4)\text{Ph}_2\text{P}=\text{S}$	X	195.0	181.6	113.1	105.7	5.1	121
$(4\text{-CH}_3\text{C}_6\text{H}_4)\text{Ph}_2\text{P}=\text{S}$	X	194.8	179.4	113.7	105.2	6.7	122
$\text{Ph}_2\text{P}(\text{S})\text{C}\equiv\text{CP}(\text{S})\text{Ph}_2$	X	192.3	176.3	113.8	101.8	4.0	123
			179.5 ^f	114.9 ^g	108.3 ^h		

^a $r(\text{P}-\text{X})$ = bond length in pm; $\angle \text{XPY}$: bond angle in degrees, mean values are quoted, unless otherwise noted.

^bE = electron diffraction; X = X-ray crystallography at room temperature.

^cR = reliability index = $100 \times$ conventional R for both X and E, except where indicated otherwise; see original papers for definitions; percentage error for M.

^d $d(\text{P}-\text{C})$ range = 177.3–187.0 pm.

^e $\angle \text{CPC}$ range = 101.5–110.6°.

^f $\text{P}-\text{C}_{\text{Ph}}$.

^g $\text{S}-\text{P}-\text{C}_{\text{Ph}}$.

^h $\text{C}_{\text{Ph}}-\text{P}-\text{C}_{\text{Ph}}$.

and, again, agreement was only moderate, although the gas-phase methods are in good agreement.

The PS bond length is in the range 194–195 pm. However, unlike the oxide, this shows variation with environment. Metal complexation causes it to increase by about 5 pm while conjugation appears to cause a decrease of about 2 pm. Again, it may be that P—C(alkyl) is less than P—C(aryl), but there are not enough data. This PS bond length may be compared with that of a typical PS single bond of about 208–210 pm (208.5 pm for bridging bond in P_4S_{10} ^{89,90}). Hence the PS bond also has high multiple character.

The PC bond length in phosphine sulphides is in the range 181–182 pm, somewhat longer than in the oxides. Once again there is a more noticeable change (decrease of 2 pm) on metal complexation at oxygen. The deviation of the bond angles from the tetrahedral values is similar to that in the oxides (CPS, 112–114°; CPC, 104–107°). The structure of the fairly bulky tricyclohexylphosphine sulphide shows, to a lesser extent, the same trends as tri(*tert*-butyl)phosphine oxide of longer bond lengths and equalization of bond angles.

D. Phosphine Selenides

Table 3 shows data from nearly all structural studies of tertiary phosphine selenides. Again, X-ray crystallography has been the method of choice and, again, only the trimethyl derivative has been studied by other methods with only slightly better agreement between them than for the oxides and sulphides.

The PSe bond length is normally in the range 209–211 pm. However, there is not enough variation in the groups attached to phosphorus to make generalizations on trends in the PSe bond length, although it is noticeable that, as usual, bulky groups increase it. Other discernible trends (e.g. shortening of PSe with electronegative substituents) may not be crystallographically significant. This PSe bond length may be compared with the PSe single bond length of 224 pm (bridging bond in P_4Se_3 ⁸⁹) and again it is apparent that the PSe bond has high multiple character.

The PC bond length in phosphine selenides is variable, covering the range 178–185 pm with more values in the upper part of the range (181–184 pm). Comparison of the trimethyl and triphenyl derivatives strongly suggests that P—C(alkyl) is less (by 4 pm) than P—C(aryl), but other data in Table 3 contradict this. The deviation of the bond angles from the tetrahedral values is similar to that in the oxides and sulphides (CPSe, 112–114°; CPC, 104–107°). Again, the structure of the fairly bulky tris(2,4-dimethoxyphenyl)phosphine selenide shows, to a lesser extent, the same trends as tri(*tert*-butyl)phosphine oxide of longer bond lengths and equalization of bond angles. However, the tris(trimethoxyphenyl) derivative is anomalous in this respect in that crowding is avoided by a marked asymmetry of the substituents¹³⁰.

Allen and coworkers¹²⁹ advanced two arguments for the shortening of the P—C bond in the 2-furyl derivative; a π -type interaction with the substituent or the lower steric demand of the 2-furyl group. Given that the CPC angle is also narrowed (a bond length–bond angle relationship), it seems more reasonable to prefer the steric argument.

E. Phosphine Tellurides

To date there appear to be structural data for only one tertiary phosphine telluride¹³⁷. Unfortunately, this is the tri(*tert*-butyl) case (included in Table 4). We have already noted the totally anomalous nature of the structure of tri(*tert*-butyl)phosphine oxide. Comparison of these (Table 4) shows that the same unusual structural characteristics are present in the telluride as in the oxide. Thus the CPC angle is greater than the TePC angle and the PC bond length is very long (same length as in the oxide), in contrast to all other tertiary phosphine chalcogenides. There must therefore be a strong suspicion

TABLE 3. Structural data^a for some tertiary phosphine selenides

Molecule	Method ^b	$r(\text{P}=\text{Se})$	$r(\text{P}-\text{C})$	$\angle \text{SePC}$	$\angle \text{CPC}$	R^c	Ref.
$\text{Me}_3\text{P}=\text{Se}$	E	209.1	181.6	113.8	104.8	9.1	124
	X	211.1	178.6	113.1	105.7	4.8	125
	N	—	—	—	105.0	± 0.2	126
$\text{Ph}_3\text{P}=\text{Se}$	X	210.6	183.0	113.1	106.0	7.0 ^d	127
$(2\text{-MeC}_6\text{H}_4)_3\text{P}=\text{Se}$	X	211.6	183.4	112.7 ^k	106.4	6.7	101
$(3\text{-MeC}_6\text{H}_4)_3\text{P}=\text{Se}$	X	210.9	182	112.3	106.7	11	119
$(3\text{-CF}_3\text{C}_6\text{H}_4)_3\text{P}=\text{Se}$	X	209.4	181.5	113.1	105.6	5.4	128
$(2\text{-furyl})_3\text{P}=\text{Se}$	X	209.4	177.8	115.0	103.5	3.8	129
$(2,4\text{-(MeO)}_2\text{C}_6\text{H}_3)_3\text{P}=\text{Se}$	X	213.5	184.3	111.1 ^e	107.9 ^f	5.2	130
$(2,4,6\text{-(MeO)}_3\text{C}_6\text{H}_2)_3\text{P}=\text{Se}$	X	211.9	182.7 ^g	112.8 ^h	106.2 ⁱ	6.4	130
$\text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{P}(\text{Se})\text{Ph}_2$	X	210.0	184.3	114.9	104.6	4.4	131
			181.1 ^j	113.1 ^k	105.5 ^l		
$\text{Ph}_2\text{PCH}_2\text{P}(\text{Se})\text{Ph}_2$	X	210.3	182.6	113.6	105.0	3.9	132
			181.3 ^j				
$\text{PhMePrP}=\text{Se}$	X	211.9	182.3	113.1	105.7	4.8	133
			180.0 ^j				
			185.4 ^m				
$\text{Ph}_2\text{P}(\text{Se})\text{C}\equiv\text{CP}(\text{Se})\text{Ph}_2$	X	209.7 ⁿ	178.3	112.7	102.6	6.3	134
			183.2 ^j	114.5 ^k	108.8 ^l		

^a $r(\text{P}-\text{X})$ = bond length in pm; $\angle \text{XPY}$ = bond angle in degrees; mean values are quoted, unless indicated otherwise.
^bE = electron diffraction; X = X-ray crystallography at room temperature; N = NMR in liquid crystal (nematic) phase.

^cR = reliability index = $100 \times$ conventional R for both X and E, except where indicated otherwise; see original papers for definitions.

^d $R = R_w$.

^e $\angle \text{SePC}$ = average of 106.2, 110.0 and 117.0°.

^f $\angle \text{CPC}$ = average of 102.1, 110.5 and 111.0°.

^g $r(\text{P}-\text{C})$ = average of 180, 182 and 186 pm.

^h $\angle \text{SeCP}$ = average of 103.6, 116.3 and 118.5°.

ⁱ $\angle \text{CPC}$ = average of 97.8, 108.7 and 112.0°.

^j $\text{P}-\text{C}_{\text{Ph}}$.

^k $\text{Se}-\text{P}-\text{C}_{\text{Ph}}$.

^l $\text{C}_{\text{Ph}}-\text{P}-\text{C}_{\text{Ph}}$.

^m $\text{P}-\text{C}_{\text{Pr}}$.

ⁿ $r(\text{P}-\text{C})$ = average of 212.4 and 206.9 pm.

that the PTe bond length of 236.8 pm is not typical of tertiary phosphine tellurides. In fact, analogy with tri(*tert*-butyl)phosphine oxide suggests that it is significantly too long. If it were too long by the same percentage as in the oxide (6.7%), then the true length would be about 222 pm.

Against this it must be said that the PTe distance found in the other phosphine tellurides examined is, in some cases, of the same order of magnitude as this. There have been four other crystal structures reported, yielding five phosphine telluride PTe distance measurements¹⁵¹⁻¹⁵³ of 228.8, 232.2, 232.7, 235.4 and 235.6 pm. The 235.6 pm value is for the trismorpholino derivative, which, it could be argued, is crowded, leading to longer bond lengths. On the other hand, the trismorpholinophosphine selenide analogue had a normal PSe bond length¹⁵⁴. The other reported structures all involve phosphorus with two nitrogen ligands in a four-membered ring; again, it could be argued that this is an unusual situation. It would be helpful to know if tri(*tert*-butyl)phosphine selenide has a longer than usual PSe bond. Even with this uncertainty, it should be noted that a PTe bond length of 236.8 pm corresponds to a bond order of 1.5 calculated^{24,137} using the covalent radii of Schomaker and Stevenson.

TABLE 4. Comparison of structural data^a for some tertiary phosphine chalcogenides R₃P=Y

Molecule	Method ^b	<i>r</i> (P=Y)	<i>r</i> (P—C)	∠ YPC	∠ CPC	<i>R</i> ^c	Ref.
Me ₃ P	E	—	184.7	—	98.6	—	135
Me ₃ P=O	E	147.6	180.9	114.4	104.1	5.2	92
Me ₃ P=S	E	194.0	181.8	114.1	104.5	4.8	92
Me ₃ P=Se	E	209.1	181.6	113.8	104.8	9.1	124
Bu ⁱ ₃ P	X	—	191.9	—	109.9	—	136
Bu ⁱ ₃ P=O	E	159.0	188.8	106.1	112.9	9.7	94
Bu ⁱ ₃ P=Te	X	236.8	189.6	108.7	110.2	6.9	137
Ph ₃ P	X	—	182.8	—	103.0	—	138
Ph ₃ P=O	X	148.4	180.3	112.3	106.6	4.5	97
Ph ₃ P=S	X	195.0	181.7	113.1	105.7	4.6	117
Ph ₃ P=Se	X	210.6	183.0	113.1	106.0	7.0	127
(2-MeC ₆ H ₄) ₃ P	X	—	183.5	—	101.7	4.5	101
(2-MeC ₆ H ₄) ₃ P=O	X	147.4	181.0	112.9	106.0	7.5	101
(2-MeC ₆ H ₄) ₃ P=S	X	194.8	181.9 ^d	112.6	106.1 ^e	9.0	101
(2-MeC ₆ H ₄) ₃ P=Se	X	211.6	183.4	112.7	106.4	6.7	101
(3-MeC ₆ H ₄) ₃ P	X	—	183.5	—	101.7	10.7	119
(3-MeC ₆ H ₄) ₃ P=S	X	193.6	181.5	112.3	106.5	8.0	118, 119
(3-MeC ₆ H ₄) ₃ P=Se	X	210.9	182	112.3	106.7	11	119
(4-ClC ₆ H ₄)Ph ₂ P=O	X	148.5	180.5	111.9	107.0	4.7	102
(4-ClC ₆ H ₄)Ph ₂ P=S	X	194.9	180.7	112.9	105.9	5.2	120
(4-BrC ₆ H ₄)Ph ₂ P=O	X	149.7	180.8	112.0	106.9	6.4	103
(4-BrC ₆ H ₄)Ph ₂ P=S	X	195.0	181.6	113.1	105.7	5.1	121
Ph ₂ P(O)CH ₂ P(O)Ph ₂	X	149.1	181.9	112.0	106.8	6.3	107
			179.4 ^f				
Ph ₂ P(Se)CH ₂ P(Se)Ph ₂	X	210.0	184.3	114.9	104.6	4.4	131
			181.1 ^f	113.1 ^g	105.5 ^h		
Ph ₂ PC≡CPh ₂	X	—	176.5	—	100.2	6.1	139
			183.2 ^f		102.8 ^h		
Ph ₂ P(O)C≡CPh ₂	X	148.1	179.4	114.4	103.7	3.9	108
			180.8 ^f	112.9 ^g	108.5 ^h		
Ph ₂ P(S)C≡CPh ₂	X	192.3	176.3	113.8	101.8	4.0	123
			179.5 ^f	114.9 ^g	108.3 ^h		
Ph ₂ P(Se)C≡CPh ₂	X	209.7 ⁱ	178.3	112.7	102.6	6.3	134
			183.2 ^f	114.5 ^g	108.8 ^h		

^a*r*(P—X) = bond length in pm; ∠ XPY = bond angle in degrees; mean values are quoted, unless indicated otherwise.

^bE = electron diffraction; X = X-ray crystallography at room temperature.

^c*R* = reliability index = 100 × conventional *R* for both X and E, except where indicated otherwise; see original papers for definitions.

^d*d*(P—C) range = 177.3–187.0 pm.

^e∠ CPC range = 101.5–110.6°.

^fP—C_{Ph}.

^gY—P—C_{Ph}.

^hC_{Ph}—P—C_{Ph}.

ⁱ*d*(P—Se) = average of 212.4 and 206.9 pm.

F. Comparison of Phosphine Chalcogenides

First, from the discussions in the previous sections, the contraction in PY distance from a standard single bond to that in R₃PY is similar for oxides, sulphides and selenides, being in the range 6.5–7.5%. Within that range, the oxides have the largest contraction

(7.5%), sulphides are next (7.2%) and selenides have least (6.7%). Hence the three types of compound probably have similar PY bond orders with minor differences in the order $O > S > Se$.

Tables 4 and 5 show comparisons of the structures of phosphine chalcogenides with the parent phosphines and other pnictogen chalcogenides. A number of interesting trends may be gleaned from these comparisons. As mentioned in previous sections, there is little variation in either CPY or CPC angles in the chalcogenides and it can be seen from Table 4 that all are larger than in the parent phosphines. This is attributed in the valence shell electron pair repulsion (VSEPR) theory to greater repulsion from the lone pair than from the oxo, sulphido or seleno ligand.

The PC bond length calculated²⁴ by the Schomaker–Stevenson equation is 184 pm, which, not surprisingly, is the typical PC bond length in tertiary phosphines. Also in tertiary phosphines $P-C(\text{alkyl})$ is slightly larger than $P-C(\text{aryl})$, which is probably a bond length–bond angle relationship since alkyl CPC angles are less than aryl CPC angles¹. The following related observations were taken from Tables 4 and 5:

(i) The PC bond length decreases on formation of the chalcogenide. However, it can also be seen that the fall is greatest for oxides (-4 pm), is less for sulphides (-2.5 pm) and may be less again for the selenides (-1 pm, although this is not consistent). From Table 5, it can be seen that there are similar decreases in the PF and PCl bond lengths in the series $F_3P > F_3PS > F_3PO$ and $Cl_3P > Cl_3PS > Cl_3PO$. These decreases may be attributed to the increase in the effective electronegativity of the phosphorus atom due to its extra positive charge in the chalcogenides which is in the order $O > S > Se$ (see Section IV.A). The detailed differences in the lengths of the PA bond in A_3PY molecules

TABLE 5. Comparison of structural data^a for some pnictogen chalcogenides $A_3Pn=Y$

Molecule	Method ^b	$r(Pn=Y)$	$r(Pn-A)$	$\angle YPnA$	$\angle APnA$	Ref.
$Me_3P=O$	E	147.6	180.9	114.4	104.1	92
$F_3P=O$	E	143.6	152.4	—	101.3	140
$Cl_3P=O$	E	144.9	199.3	—	103.3	140
$(MeO)_3P=O$	E	147.7	158.0	—	105	141
$Me_3P=S$	E	194.0	181.8	114.1	104.5	92
$F_3P=S$	E	186.6	153.8	117.9	99.6	142
$Cl_3P=S$	E	188.5	201.1	—	101.8	140
Me_3N	M		145.1		110.9	91
$Me_3N^+ \cdots O^-$	X	138.8	147.7			143
F_3N	M		136.5		102.4	91
$F_3N=O$	E/M	115.9	143.2	117.4	100.5	144
F_3P	E		157.0		97.8	145
$F_3P=O$	E	143.6	152.4	—	101.3	140
$F_3P=S$	E	186.6	153.8	117.9	99.6	142
Cl_3P	E		203.9		100.3	146
$Cl_3P=O$	E	144.9	199.3	—	103.3	140
$Cl_3P=S$	E	188.5	201.1	—	101.8	140
Me_3As	E		196.4		96.0	124, 147
$Me_3As=O$	E	163.1	193.7	112.6	—	92
$Me_3As=S$	E	205.9	194.0	113.4	—	92

^a $r(Pn-A)$ = bond length in pm; $\angle APnA$ = bond angle in degrees.

^bE = electron diffraction; X = X-ray crystallography at room temperature; M = microwave spectroscopy.

have been interpreted as evidence of strengthening by a π -bonding component in some cases¹²⁴.

(ii) Most interestingly, the only exception to (i) (which is strongly in the other direction) is for the PC bond to an alkyne carbon. This is difficult to explain.

(iii) Also difficult to explain is that P—C(alkyl) is probably less than P—C(aryl) for all the chalcogenides although, as noted above, there are not enough data to be sure. There is no apparent bond length–bond angle relationship in this case.

(iv) There is a consistent variation in PO and PS bond lengths in that they decrease over the series $\text{Me}_3\text{PO} > \text{Cl}_3\text{PO} > \text{F}_3\text{PO}$ and $\text{Me}_3\text{PS} > \text{Cl}_3\text{PS} > \text{F}_3\text{PS}$. These shortenings again suggest a polarity effect which may be discussed in terms of the VSEPR theory; with more electronegative groups the electron pairs of the bonds are displaced away from phosphorus allowing the oxo or sulphido ligand to approach closer^{140,155}. However, an exception may be trimethylphosphate, which has the same PO bond length as trimethylphosphine oxide, although this may be a steric effect since the terminal PO bond length in P_4O_{10} ⁸⁸ is 139 pm.

For the nitrogen analogues the following comments and comparisons are derived from Table 5:

(i) The NO bond length in trimethylamine oxide is close to the NO single bond length in hydroxylamine (145.3 pm)⁹¹, while the NO length in trifluoroamine oxide is very significantly shorter and must be accorded the status of a double bond.

(ii) There is a much larger decrease in the NO distance from the trimethyl to the trifluoro compound than in the analogous PO distance. Undoubtedly this is due both to the increased electronegativity and a strong steric effect at the small nitrogen atom.

(iii) There is an *increase* in both NC and NF bond lengths on formation of the oxide. This is the opposite of the trend noted above for the phosphine oxides. However, again, the extra factor is the small size of the first-row atom so that the ligands are already close together and the additional oxygen means they have to move apart.

IV. BONDING

For the reasons outlined in the Introduction (Section I), studies of the bonding in phosphine oxides, sulphides and selenides have concentrated on the nature of the PO bond, and to a lesser extent the PS and PSe bonds. Particular issues which have been of concern are (i) the great strength of the PO bond, (ii) the exact distribution of the electron density in the PO bond, (iii) the difference between the PO bond in phosphine oxides and the NO bond in amine oxides and (iv) the difference between the oxides and the sulphides and selenides.

A. Other Experimental Observations

From the bond lengths reported in Section III, it is clear that the phosphoryl (and thio- and seleno-phosphoryl) bond has high multiple character. In the case of the oxides, since the bond length is shorter than in HPO and of the same order as diatomic PO, the bond order lies between double and triple. Some other physical measurements support this conclusion and provide further insights.

1. Bond energies

Strong multiple character is also suggested by the paltry number of bond energies that are available for phosphine oxides and sulphides, a selection of which are given in Table 6. It can be seen that the PO bond dissociation energy is usually in the range 536–577 kJ mol^{−1} (128–139 kcal mol^{−1}) with the electronegatively substituted com-

TABLE 6. Bond dissociation energies^a and stretching frequencies^b in some phosphine chalcogenides A₃P=Y

Molecule	<i>D</i> (P=O)	<i>ν</i> (P=O)	Molecule	<i>D</i> (P=S)	<i>ν</i> (P=S)	Molecule	<i>ν</i> (P=Se)
H ₃ PO	464 ^c	1240 ^d					
Me ₃ PO	582	1170 ^{e,f}	Me ₃ PS		567 ^f	Me ₃ PSe	441 ^g
Pr ₃ PO	577	1166	Pr ₃ PS	383	550		
Ph ₃ PO	536	1195	Ph ₃ PS		637 ^g	Ph ₃ PSe	561 ^g
F ₃ PO	540 ^h	1418 ^f					
Cl ₃ PO	510 ^h	1298 ^f	Cl ₃ PS	293 ⁱ			
P ₄ O ₁₀	577	1400					
P ₄ O ₆	360 ^j						
(EtO) ₃ PO	619 ^h	1272	(EtO) ₃ PS	379	608		
(EtO) ₃ P	385 ^j						
PO diatomic	586 ^k	1218 ^f					

^a*D*(P–Y) in kJ mol^{–1} (kcal mol^{–1}), from ref. 156 unless indicated otherwise.^b*ν*(P–Y) in cm^{–1}, from ref. 156 unless indicated otherwise.^cCalculated, from ref. 14.^dMatrix isolated species from ref. 157.^eActually 1169–1180 cm^{–1}.^fFrom refs 158 and 159.^gFrom ref. 7.^hFrom ref. 14.ⁱQuoted in ref. 3.^jDissociation energy of PO single bond.^k± 84 kJ mol^{–1}.

pounds at the higher end of the range. In agreement with chemical experience, however, both methyl and halogen substituents have a higher bond energy than unsubstituted phosphine oxide.

In general, these bond energies are of the same order as that in diatomic PO while a PO single bond energy is about 360–385 kJ mol^{–1} (86–92 kcal mol^{–1}). The difference of about 200 ± 20 kJ mol^{–1} can be taken as an indication of the extra energy in the phosphoryl bond over that in a PO single bond.

In a useful exercise, Kutzelnigg¹⁴ developed a series of *σ* and *π* ‘increments’ for various multiple bonds which were derived by a combination of calculation and the limited experimental results. His value for the *π* increment of the PO bond (155 kJ mol^{–1}) is in rough agreement with the figure of 200 ± 20 kJ mol^{–1} derived above, given the many approximations that have to be made and the limited experimental data. The *σ* increment for the PO bond was given as 335 kJ mol^{–1} whereas for the NO bond the *σ* increment was 188 kJ mol^{–1}, with a *π* increment of 368 kJ mol^{–1}. Note that, as expected¹, *π* bonds formed by the second-row element are weaker than its *σ* bonds whereas it is the opposite for the corresponding first-row element.

Kutzelnigg¹⁴ also calculated the bond dissociation energy for H₃PO (464 kJ mol^{–1}), H₂FPO (531 kJ mol^{–1}) and H₃NO (222 kJ mol^{–1}) and, while obviously subject to some calculational inaccuracy (see Section IV.C.1), they can be helpful for comparison. Unfortunately, the experimental results for amine oxides are almost non-existent with the only reasonably reliable one¹⁴ being a bond dissociation energy of 276 kJ mol^{–1} for the NO bond in F₃NO.

Based on these limited comparisons, it can be seen that the NO bond energy in trifluoroamine oxide is larger than the corresponding single bond whereas the strength of the PO bond lies between those for a double and a triple bond. Also, the bond energy of the PS bond is noticeably less than that of the PO bond, but a suitable single PS

bond energy does not appear to be in the literature. It should be noted that the PO bond energy is expected to be greater than the NO bond energy. This is because in structure **1A** (see Section I) an electron is removed from phosphorus and the ionization potentials of R_3P are lower than those of R_3N . In addition, there will be interelectronic repulsions of the valence electrons around the small first-row atom.

2. Infrared spectroscopy

The strength and polarity of the PO bond in phosphine oxides is attested to by the very strong and diagnostic PO stretching frequency which occurs in the range $1100\text{--}1400\text{ cm}^{-1}$, usually near 1200 cm^{-1} , and Table 6 includes the values for some representative compounds. These frequencies and the derived force constants have been used^{3,160} to derive bond orders of about two for the PO bond, although this is variable for reasons discussed below. The PS stretching frequency is much lower than that of the oxide, as are the PSe frequencies^{7,161}, possibly indicating lower bond orders.

Other useful information can also be derived from infrared spectroscopy^{3,162}. Indeed the only experimental study of unsubstituted phosphine oxide is an infrared spectrum of the matrix isolated species¹⁵⁷ which is discussed in Section IV.C.2. The value found in this study for the PO stretch (1240 cm^{-1}) is included in Table 6. There is a well established^{3,6,158,162}, approximately linear¹⁶³, relationship between PO stretching frequency and electronegativity of substituent, which can be seen qualitatively in Table 6. The more electronegative the substituent, the higher is the wavenumber and the higher is the PO bond force constant, in qualitative agreement with the trend of the bond energies.

There is one other interesting observation in Table 6. As mentioned in the previous section the bond energies of both methyl- and halogen-substituted phosphine oxides are higher than that of the unsubstituted compound. However, the PO stretching frequencies of alkyl- and aryl-substituted phosphine oxides are *lower* than that in the unsubstituted molecule whereas the halogen- and oxygen-substituted cases are *higher*. This suggests that the methyl group stabilizes the phosphoryl bond while decreasing its force constant and leads to the difficulties in assigning bond orders from infrared spectra, referred to above. This observation is in agreement with the theoretical studies of substituted phosphine oxides and is discussed further in Section IV.D.5.

3. Dipole moments

Phosphine chalcogenides have significant dipole moments, some of which are given in Table 7. As can be seen, for the tertiary derivatives the polarity increases in the series oxide < sulphide < selenide. However, when this is converted into charge separation across the PY bond the order becomes^{92,164} oxide > sulphide \approx selenide, in line with

TABLE 7. Dipole moments^a of some tertiary phosphine chalcogenides

Molecule	$\mu(P=O)$	$\mu(P=S)$	$\mu(P=Se)$
$Me_3P=Y$	4.29	4.73	
$Ph_3P=Y$	4.51	4.88	5.17
$F_3P=Y$	1.74	0.63	
$Cl_3P=Y$	2.42	1.42	

^a μ in D, from refs 164 and 165 and references cited therein.

electronegativity considerations. As might be expected, dipole moments show an inverse relationship with substituent electronegativity^{164,166}. The reduced charge separation found for the trihalo derivatives has been taken as evidence of increased backbonding¹⁶⁴. The fact that substituent electronegativity has a greater effect on the charge separation in sulphides than in oxides suggests that there is less multiple character in the PS bond¹⁶⁴.

It has long been argued^{92,167} that the PO bond moment is smaller than expected for the purely coordinate structure 1A. Thus, if the structure were 1A, then the expected bond moment should be

$$\begin{aligned}\text{electronic charge} \times \text{bond length} &= (1.602 \times 10^{-19} \text{ C}) \times (1.49 \times 10^{-10} \text{ m}) \\ &= 2.39 \times 10^{-29} \text{ C m} = 7.15 \text{ D}\end{aligned}$$

However, the actual bond moment, derived by measurement on the triphenyl derivative at the time of the original discussion¹⁶⁷, was 3.5 D, only about 50% of the theory, so a full electron has not been transferred from phosphorus to oxygen. A similar calculation for the NO bond, using available data from trimethylamine oxide, gave 6.66 D as the maximum theoretical value while the actual value was 4.3 D, 65% of the theory. This was then be taken as evidence of a greater amount of backbonding of electron density from oxygen to phosphorus than from oxygen to nitrogen. However, this argument can be criticized^{21,168} because any two charges as near as a bond length will be polarized towards each other and the bond moment will be less. In fact, this may well be the case for the amine oxides and it is possible that the difference between them and the phosphine oxides is just the greater polarizability of phosphorus. Indeed, the reduction in expected bond moment for phosphine sulphides is greater again (about 30% of the theory), in line with the greater polarizability of sulphur. Recent, more sophisticated, measurements and calculations¹⁶⁹ gave the limits for the PO bond moment as 3.26–4.72 D and the PS moment as 3.65–4.85 D. Hence the issue remains unclear.

4. Magnetic resonance spectroscopy

Nuclear magnetic resonance (³¹P, ¹H and ¹³C) confirms that there is a high degree of positive charge at phosphorus in the tertiary chalcogenides and that there is multiple binding^{161,170–173}. Thus, in the ³¹P spectra of the oxides, the phosphorus atom is strongly deshielded relative to the parent phosphine, typically by about 30–40 ppm, but it can be much more¹⁷⁰; for example, for the triphenyl case $\Delta\delta \approx 37$ ppm whereas for the trimethyl case $\Delta\delta \approx 100$ ppm. In a comparison of a number of bisphosphine chalcogenides, Grim and Walton¹⁶¹ found that the charge developed at the phosphorus atom increased in the order oxide (+0.29) < sulphide (+0.47) < selenide (+0.52), in agreement with the dipole moments. Since this is not the order expected on the basis of the electronegativity of the chalcogens, they concluded that there was more backbonding for the oxide than the sulphide or selenide.

Other evidence for multiple bonding is provided by, among others, (i) ³¹P chemical shift anisotropies, which show stronger shielding in the direction of the P=X bond^{174–176}, (ii) ³¹P–⁷⁷Se coupling constants¹⁷⁷ and (iii) ¹⁷O nuclear quadrupole double resonance¹⁷⁸.

5. Photoelectron spectroscopy

The core and valence ionization potentials of some phosphine chalcogenides are given in Table 8. From the core values we expect information on the degree of charge on the atom concerned¹⁸⁰, whereas the first ionization potential in these molecules corresponds to the loss of an electron from a chalcogenide lone pair^{19,68,69,179,184,185}. For our purposes it is unfortunate that core potentials tend to be large and show only a small

TABLE 8. Core^a and valence^b ionization potentials^c for some phosphine chalcogens and related molecules

Molecule	P(2p)	O(1s)	S(2p)	Se(3p)	1st IP
Me ₃ P	135.9				
Me ₃ PO	137.8	536.1			9.9
Me ₃ PS	137.5		166.9		8.48
F ₃ P	141.8				
F ₃ PO	143.0	539.1			13.52
F ₃ PS					11.05
Me ₃ NO		537.7			8.43
F ₃ NO		542.0			14.11
H ₂ O		539.8			12.91
Cl ₃ P	139.6				
Cl ₃ PO	140.9	537.8			11.93
Cl ₃ PS	140.5				
Ph ₃ P	131.1				
Ph ₃ PO	132.8	531.1			
Ph ₃ PS	132.6		162.0		
Ph ₃ PSe	132.6			160.8	
Ph ₃ PBF ₃	132.2				
Ph ₄ P ⁺ Cl ⁻	133.0				

^aFrom refs 179–183; more accurate comparisons of molecules would be possible using data from one source only, but no one source covers the full range of molecules given.

^bFrom refs 179 and 184.

^cIn eV; although some of these values are very precise, the accuracy is ca ± 0.3 eV.

variation with environment. Also, although there are valence ionization energies for a good number of phosphoryl derivatives in the literature^{186–188}, the data for tertiary phosphine oxides are sparse. However, some useful trends can be discerned from Table 8.

As expected, phosphorus core ionization energies in the chalcogenide derivatives are higher than those for the parent phosphine, reflecting a high positive charge at phosphorus^{180,190}. Conversely, in most cases, the oxygen core potentials are lower than that for water, for example, with the striking exception of F₃NO. The elevation of the phosphorus value for the triphenylphosphine chalcogenides is about half that in tetraphenylphosphonium salts, indicating that there is not as great a positive charge at phosphorus in the former. In the few cases where comparison of chalcogenides is possible, the elevation for the sulphides and selenides is similar and less than that in the oxide, indicating a greater charge at phosphorus in the latter, as expected. Comparison of analogous phosphine and amine oxides shows that there is a larger negative charge on oxygen in the former, in agreement with electronegativity predictions. The same trends as these were found in the X-ray K emission spectra of triphenylphosphine and its oxide^{190,191}. Finally, there is a change of about 2 eV in the P(2p) core potential on formation of phosphine oxides but the analogous change in N(1s) for amine oxides is much larger (4 eV), which could be taken to indicate backbonding in the phosphorus derivatives¹⁸¹.

Similar conclusions can be drawn from the valence ionization potentials. First, although not shown in Table 8, there is an overall stabilization of orbital energies in the X₃P moiety in X₃PY compared with those in the parent X₃P species¹⁸⁴. This corresponds to a charge transfer from the X₃P group to the Y atom¹⁸⁴. From Table 8, the first ionization potential of tertiary phosphine oxides and amine oxides is less than that in water. This is consistent with an increased negative charge at oxygen. The

exceptions are the trifluoro derivatives, which may be taken as evidence of extensive backbonding or may be solely due to electronegativity¹⁸⁸. Also, the first ionization potential of trimethylphosphine oxide is greater than that in trimethylamine oxide, indicating a lesser charge at oxygen in the phosphine oxide. Finally, the first ionization potential of sulphides is less than that of the analogous oxide, in line with electronegativity.

B. Qualitative Considerations

To summarize the experimental observations so far: the phosphoryl bond is strong, short and polar and, whereas the sulphur and selenium analogues are similar, they are not quite as strong and are more polar. Most estimates of bond order give the PO bond as greater than two and the PS and PSe bonds as less than two. As mentioned in the Introduction (Section I), the standard description of the PO bond to account for these observations has been in terms of a resonance hybrid of structures **1A** and **1B**. The extra bond in the case of **1B** is formed by backbonding of lone-pair electron density from oxygen into suitable acceptor orbitals on phosphorus. Qualitatively, there are some obvious problems with this description.

First, the double bond formalism clashes with the octet rule. Until fairly recently, it was usual^{3-13,192} to sidestep this issue by saying that this indicated that 'an expansion of the octet is required', which is a euphemism for saying that the octet rule is broken by these compounds. Also, until recently, there was a smoothly made connection^{3-13,192} that this indicated that 'the low-lying atomic d orbitals are involved in hybridization at phosphorus'. We now know (Section II) that there is no role for valence d orbitals in bonding within the Main Group of the Periodic Table.

Second, the structures **1A** and **1B** are not mutually exclusive. For example, consider the overlap of oxygen lone pairs with suitable receiving orbitals on phosphorus. No matter what receiving orbitals are envisaged (either the d orbitals or some other combination—see below), the overlap would be highly unsymmetric with most of the electron density near oxygen²⁹. Hence the double bond structure **1B** would necessarily lead to a polar molecule anyway. Alternatively, one could consider that the PO bond is a pure σ single bond formed by donation of the phosphine lone pair into a vacant p orbital on O (preserving the octet at phosphorus). Then the phosphorus carries a full positive charge and the oxygen a full negative charge. The proximity of these two opposite charges must surely lead to a strengthening of the PO link via an ionic type of attraction. It has been often implied²¹, but has not been shown explicitly, that this does not account fully for the shortened PO distance and the increased bond strength.

A final difficulty is that there may be more than one way of having a π -type backbonding interaction from oxygen to phosphorus. In the case of d orbitals it was always recognized that this was the case^{14,19,193}, because there are two d orbitals of appropriate symmetry which could overlap with two oxygen lone pairs. This is obscured by the double bond formula **1B** and so a triple bond formula naturally arises¹⁹. An alternative description is as a resonance between structure **1A** and a triple bond²⁰. The description 'partial triple bond' is also reasonable^{14,19} on the basis that the bond order is between two and three. This latter view involves one σ bond and two half π bonds and has become common recently^{14,16}. Note that a formal triple bond from oxygen to phosphorus in these compounds would imply that phosphorus carries a negative charge and oxygen a positive charge, perhaps providing a qualitative rationalisation of the reduced PO bond moment discussed in Section IV.A.3, if indeed it really is reduced.

Of these difficulties the d orbital issue is easiest to deal with qualitatively. This is because there is available a perfectly reasonable alternative set of acceptor orbitals on phosphorus. We have already described¹ the backbonding in transition metal phosphine

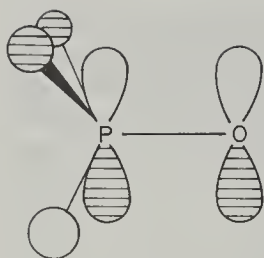


FIGURE 3. View of the bonding in phosphine oxide, showing one of the π backbonds formed by overlap of a lone pair on oxygen with an antibonding orbital of e symmetry on the H_3P moiety

complexes which is not into phosphine d orbitals but into the phosphine LUMO which is of σ^* type^{194–197}. The backbonding in phosphine chalcogenides can be considered to be exactly analogous. In an AH_3 moiety there is a set of two antibonding orbitals with the e symmetry required to accept electron density from the oxygen lone pairs. These are the orbitals labelled $2e$ in Figure 3 in ref. 1 or Figure 9.6 in ref. 198. In the case of Me_3PO , H_3PO and F_3PO these are the $7e$, $3e$ and $7e$ sets, respectively (see Figure 5 in ref. 1). This alternative to d orbital involvement in the backbonding in phosphine oxides is shown in Figure 3. Some additional useful insights are provided by this analysis.

The structure of F_3NO was always very inconvenient for those who advocated the involvement of d orbitals to explain the structure of phosphine oxides. It will be recalled from Section III.F (Table 5) that the NO distance in this molecule is extremely short and must be accorded the status of a double bond and 'rightly or wrongly, few chemists would invoke the 3d-orbitals of nitrogen to explain the bonding'¹⁹⁹. Thus its stability was 'somewhat surprising'²⁰⁰. Now that backbonding does not have to be into d orbitals there is no problem. Indeed, the NF bond is lengthened (see Table 5), consistent with population of the antibonding orbitals. The orbitals of F_3NO were analysed in detail by Grein and Lawlor⁸⁶, who concluded that the $3e$ orbital of NF_3 was the suitable acceptor orbital.

The energies of these antibonding acceptor orbitals are also interesting and those derived from a SCM- $X\alpha$ DV calculation¹⁹⁵ are detailed in ref. 1 (Figure 5 and Table 13 therein). In H_3P the $3e$ orbital is the LUMO at 0.88 eV whereas in F_3P the $7e$ orbital is the LUMO at -1.05 eV, but in Me_3P the lowest unoccupied orbital of e symmetry is the $7e$ orbital which is the NLUMO at 0.85 eV, the LUMO being $9a_1$ at 0.43 eV. Thus the appropriate acceptor orbital for the F_3P moiety of F_3PO is at significantly lower energy than that in H_3PO and Me_3PO , in agreement with greater backbonding leading to a stronger PO bond in F_3PO .

It should be noted that the idea of backbonding into antibonding orbitals to explain the bonding in phosphine oxides has been around for a long time. It is essentially the same as the concept of hyperconjugation or 'double-bond/no bond resonance'^{180,199}.

For the other qualitative difficulties with the description of the PO bond, we must hope that they will be answered by accurate calculation. However, as we shall see, they have not yet been satisfactorily resolved.

There is one further qualitative insight which is of value. There is a formal analogy between the semipolar bond, e.g. in H_3PO , and the bonding situation in phosphoranes such as H_3PF_2 , just as H_2CO and H_2CF_2 are formally related^{14,16}. In this way the PO bond can be viewed as analogous to the three-centre, two-electron bond developed by Rundle³⁹ to explain the bonding in phosphoranes. Note that this three-centre, two-electron bond model is not incompatible with some degree of backbonding.

C. Survey of *Ab Initio* Calculations on Phosphine Chalcogenides

At the outset, it is important to delineate what useful results should be expected from calculations on phosphine chalcogenides. Two objectives may be identified: (i) an

understanding of the nature of the PO bond and (ii) predictions of the structure and properties of those members of the series which are not yet known molecules. It can be seen that these are much more ambitious objectives than in the case of, for example, calculations on the parent phosphines¹.

We have already discussed extensively¹ how calculations on phosphines have become reliable only in the last few years. The factors responsible for this (e.g. basis set inadequacy and lack of geometry optimization) apply with increased force to calculations on phosphine chalcogenides. Thus, for example, a calculation on phosphine oxide is likely to be at least 50% more difficult than phosphine owing to the increase in the number of electrons. However, an additional consideration for the chalcogenides is the increased need for polarization functions, due to the charge differences within the molecule, so that the actual increase in difficulty is even greater. Given the increased expectations for such calculations, we should not be too disappointed if they do not fulfil one or other of the objectives set out above.

1. Survey of calculations

Table 9 gives the results (total energy, geometry and dipole moment) of selected calculations on phosphine chalcogens (mainly oxides). It also includes amine oxides for comparison. The literature has been surveyed as far as the end of 1990. Owing to the extra computation required, the total number of calculations is less than for the phosphines but the quality is better. This is probably because investigators undertook studies only if they had the facilities to do so; for example, most workers took care to include polarization functions. Nevertheless, even for H_3PO , only a limited number include correlation corrections in MO treatments.

It is very difficult to assess the usefulness of the calculations whose results are reported in Table 9. In such an assessment, it is usual to examine the accuracy of predicted geometric, or other, parameters and whether the total energy has been minimized. Neither procedure is foolproof; sometimes geometry is predicted well at basis set levels which give poor results for other properties and the energy test must be carefully applied because, for example, augmenting the basis set for the inner shells has a significant effect on the total energy without improving the properties associated with the valence shell¹⁸. However, in this case, these difficulties are compounded by the fact that the most studied molecule, H_3PO , was unknown until recently and is very unstable. Hence its geometry is not available for comparison and the only information to date is the infrared spectrum of the matrix-isolated species¹⁵⁷. This problem is discussed in detail in Section IV.C.2. It is appropriate to discuss separately the usefulness of the calculations for the two objectives mentioned above.

a. Prediction of unknown species. As regards the prediction of the structure and properties of unknown species, we may be fairly confident of reasonable accuracy in some of the latest calculations. Even so, perusal of Table 9 shows that the agreement of theory and experiment can, at best, only be described as modest. This is not surprising because it is expected¹ that basis sets of at least double zeta quality with polarization terms, full geometry optimization and some form of electron correlation will be necessary for the detailed description of compounds of third-row elements, and very few such calculations have been reported for phosphine oxides. It can be seen from Table 9 that the best split-valence and double zeta calculations are only just about adequate to describe consistently the geometric parameters of these molecules. Even then there are some worrying basis set effects; for example, the difference in predicted dipole moment for phosphine oxide between the 6-31G* and DZ + P basis sets²⁰¹ which are normally of comparable quality²². Basis set effects on the structure of phosphine oxide and fluorophosphine oxide have been studied in detail by two groups^{201,207}. Also, there is

TABLE 9. Results of *ab initio* calculations on phosphine and amine chalcogenides $A_3E=Y$

Molecule	Calculation ^a	Energy ^b	$r(E=Y)^c$	$r(E-A)^c$	$\angle YEA^d$	μ^e	Ref.
$H_3P=O$	STO-3 G	-412.3567	165.6	138.3	118.7		201
	3-21 G	-415.0830	157.9	140.5	117.2	4.60	201
	3-21 G#	-415.2070	147.0	139.1	117.5		192
	3-21 G*	-415.2961	146.0	139.3	117.8	3.46	201
	4-31 G*	-416.8795	146.0	139.8	117.4		202
	6-31 G*	-417.3068	146.4	139.3	117.0	4.18	16, 201, 203, 204
	6-31 G**		146.5	139.6	116.9	4.19	205, 206
	DZ	-417.1831	160.5	140.5	116.0		207
	DZ + P	-417.3342	147.4	139.3	115.8	5.14	201
	TZ + P		145.6	139.2	116.0	4.22	206, 208
	> DZ + P + C ^f	-417.5378				3.87	19
	TZ + P ^g + C ^h	-417.7140					208
	STO-2 G#		142.1	139.0 H	117.2 H		209
$FH_2P=O$				148.4 F	118.8 F		
	3-21 G	-513.4178	154.1	138.8 H	117.3 H	4.23	201
				161.5 F	114.5 F		
	3-21 G*	-513.7179	145.1	138.9 H	116.9 H	3.13	201
				154.2 F	115.7 F		
	> DZ + P	-515.9874	146.7	139.0 H ⁱ	108.3 H ⁱ	4.14	19
$MeH_2P=O$				157.8 F	117.3 F ⁱ		
	6-31 G* ^j	-516.2075					209
	6-31 G* ^j + C ^k	-516.6631					209
	STO-2 G#		141.7	138.5 H	118.2 H		209
				181.4 C	115.9 C		
	3-21 G*	-454.1131	146.5	138.1 H	116.1 H	4.28	210
				178.9 C	119.0 C		

TABLE 9. (continued)

Molecule	Calculation ^a	Energy ^b	$r(E=Y)^c$	$r(E=A)^c$	\angle YEA ^d	μ^e	Ref.
F ₃ NO	4-31 G	-426.7288	118.7	141.2	117.2	0.88	215
	4-31 + BF	-426.9059	117	136	116.6	1.20	86
	DZ + BF	-427.4232	118	136	116.9	1.23	86
	DZ + BF + CI	-427.7633	116	143	117.4	0.52	86
	6-31 G*	117.2	117.2	135.0	116.3		16
	GVB-SOPP	120					17
Me ₂ NO	EXPT ^m		115.8	143.1	117.1	0.04	144, 216
	STO-3G	-244.9079	158.2	147	109.5		214
	4-31 G	-247.6864	146.6	147 ⁱ	109.5 ⁱ	5.2	214
	EXPT ^m		138.8	147.7		5.0	143, 217

^a All self-consistent field, contracted Gaussian-type basis sets and geometry optimized by the gradient method unless indicated otherwise. Symbols STO-3 G, DZ, TZ, 3-21 G, 4-31 G and 6-31 G have their usual meanings²²; * = a set of six d-type polarization functions added to basis set; # = a set of five d type functions added; P = other combinations of d functions added; BF = bond functions added as polarization functions; CI = with electron correlation by configuration interaction; C = with correlation by other methods; GVB-SOPP = generalized valence bond calculation employing the strong orthogonality and perfect pairing approximations.

^b Total electronic energy in hartree; 1 hartree = 27.2 eV = 2625 kJ mol⁻¹.

^c Bond length in pm; H, C or F identifies atom A.

^d Bond angle in degrees; H, C or F identifies atom A.

^e Dipole moment in debye.

^f CEPA-PNO method; coupled electron pair approximation with pair natural orbitals.

^g Two uncontracted d sets on P and one on O, one p set on H with added diffuse functions.

^h Double substitution coupled cluster method—ACCD form.

ⁱ Assumed.

^j Geometry optimized at STO-2 G# level.

^k Correlation using Möller-Plesset perturbation theory.

^l Two d sets on P.

^m From Tables 1-5 and 7.

ⁿ Single d function on P.

^o At STO-2 G# geometry.

^p Single d set on N.

^q At the geometry found for F₃NO by GVB-SOPP method.

no consistent trend in the errors in the prediction of geometric parameters, except of course the dramatic increase in bond lengths for both second- and third-row elements if polarization functions are omitted.

Notwithstanding the above comments, we may say with reasonable confidence that if the structure of phosphine oxide is determined in the future, the values will be $r(\text{PO}) = 146.0 \pm 0.5$ pm, $r(\text{PH}) = 139.4 \pm 0.2$ pm and $\angle \text{HPO} = 116.5 \pm 0.5^\circ$. Similar predictions can be made for other unknown species in Table 9. The bond length of 146 pm may be compared with those in HPO^{91} (151.2 pm), diatomic PO^{91} (147.6 pm) and a typical single PO bond (160 pm; bridging bond in P_4O_{10} ⁸⁹). Also, the PO length in H_3PO is about 2 pm shorter than in substituted phosphine oxides (Section III, Table I) which is almost certainly a bond length–bond angle effect wherein oxygen can approach closer to phosphorus as the angle between the other ligands decreases. A similar effect is probably responsible for the shortening of the PH bond length from that in parent phosphine¹ (PH = 142 pm, HPH = 93.5°).

b. Nature of the PO bond. In this case we must be less sanguine. The results in Table 9 do not lead to total confidence in the usefulness of the calculations for the elucidation of the nature of the PO bond, a problem which has already proved intractable. They are only just about able to predict geometries with confidence, so we may feel legitimately mistrustful of their ability to describe the distribution of electron density in the region of the PO bond. More seriously, all theoretical studies so far on the nature of the PO bond have used either the 6–31G*.DZ + P or inferior levels of calculation and most have been on phosphine oxide. From Table 9 it can be seen that the lowest energy achieved so far for phosphine oxide is about 0.4 hartree below that at the 6–31G* or DZ + P levels. This is about twice the energy of the PO bond and was achieved by electron correlation. Hence, again, it is perfectly legitimate to feel uneasy as to whether the electron distribution in the PO region can be adequately described at these levels. Even with correlation, the computed PO strengths are significantly low; for example, Schmidt and Gordon²⁰ estimated the PO bond strength in F_3PO to be 467 kcal mol^{–1} (at the 6–31G* level with correlation by third-order Møller–Plesset theory using the 6–31G* geometry) whereas the experimental value¹⁵⁶ is 542 kJ mol^{–1}, an error of about 14%.

A further point is that the problem is made extra difficult by not being a comparative one. Often it is possible to obtain useful results at modest levels of calculation by comparing sets of molecules. In the determination of the PO bond, however, an absolute result is sought, namely its electron distribution. Even comparison with amine oxides may not be real since they may very well be different entities.

2. Infrared spectrum of phosphine oxide

As mentioned above, unlike the situation in the parent phosphines¹, there is a problem with comparison of theory and experiment for phosphine oxides. This is because it is only recently that good calculations could be done on anything other than $\text{H}_3\text{P}=\text{O}$ and, unfortunately, until recently this was an unknown molecule. Even now the only experimental study that has been reported is the infrared spectrum of the matrix-isolated species¹⁵⁷. Two groups have attempted to calibrate the theory with this experimental^{204–206}. However, this is more problematic than, for example, comparison of computed and measured molecular geometry data because of the extra step involved in computing the infrared spectrum.

Table 10 shows the comparison of experimental and calculated wavenumbers in the infrared spectrum of $\text{H}_3\text{P}=\text{O}$. Usually computed wavenumbers are considerably higher (10–15%) than experimental values and this can be seen clearly in Table 10 at all the

TABLE 10. Comparison^a of experimental and calculated vibrational frequencies (cm⁻¹) in the infrared spectrum of H₃P=O

Mode	Experimental ^b ν_E	3-21 G# ^c			6-31 G* ^d			6-31 G** ^e			TZ + P ^f			TZ + P + A ^g		
		ν_C	Δ		ν_C	Δ	Δ_{sc}	ν_C	Δ	Δ_{sc}	ν_C	Δ		ν_C	Δ	
PH a_1	2359	2687	328		2694	335	46	2647	288	23	2594	235		2500	141	
PH e	2372	2644	272		2666	294	7	2618	246	-16	2573	201		2490	118	
PO a_1	1240	1437	197 ^h		1397	157	16	1389	149	10	1361	121		1341	101	
HPH a_1	1144	1287	143 ^h		1284	140	11	1282	138	10	1263	119		1245	101	
HPH e	1114	1238	124		1246	132	-22	1238	124	0	1235	121		1213	99	
HPO e	853	976	123		958	105	-13	959	106	7	933	80		922	69	

^a ν_E = experimental vibration frequency; ν_C = calculated harmonic vibration frequency at the indicated level of theory; Δ = $\nu_C - \nu_E$; Δ_{sc} = $\nu_C - \nu_E$ after scaling of the calculated value—see text.

^b From ref. 157.

^c From ref. 192.

^d From ref. 204.

^e From ref. 205.

^f From ref. 206.

^g A = with anharmonicity correction; from ref. 206.

^h These frequencies interchanged from the assignment in the original work—see text.

levels of theory studied. Traditionally this difficulty has been addressed by using a scaling procedure; theoretical and experimental values are compared for related species for which data is available (e.g., PH_3 and $\text{F}_3\text{P}=\text{O}$ in this case) and scale factors are computed to adjust the theoretical wavenumbers for the unknown species. Scaling procedures attempt to remove systematic errors which may be due, for example, to basis set incompleteness, neglect of electron correlation or neglect of anharmonicity considerations^{205,218,219}. Table 10 includes scaled values for two of the theory levels.

Returning to the question of the quality of the calculations, as can be seen from Table 10, after scaling, the predicted frequencies are accurate to about 20 cm^{-1} in most cases. Schneider and coworkers²⁰⁴ were non-committal about the quality of the scaled 6-31G* results, being fairly content with the PO modes but less than satisfied with the PH stretching modes (2359 and 2372 cm^{-1}), whereas Person and coworkers²⁰⁵ considered that the scaled 6-31G** results were spectacularly good. However, it can also be seen from Table 10 that there is still a substantial difference in absolute terms between theory and experiment because, even after including a correction for anharmonicity, the calculated wavenumbers at the triple zeta plus polarization level are still approximately 5–10% higher than the experimental values. This reviewer concludes that better than TZ + P and substantial consideration of correlation effects will be necessary for satisfactory agreement between experiment and theory for the infrared spectrum of $\text{H}_3\text{P}=\text{O}$. This reinforces the conclusions of the previous section on the usefulness of these calculations for determining the nature of the PO bond.

A subsidiary, but significant, issue is that there is inevitable uncertainty as to the frequency of the PO stretch in H_3PO due to strong mode mixing from the H_3P bending mode²⁰⁵. For consistency because of this, in the 3-21G# column in Table 10, the values for PO stretch (1437 cm^{-1}) and HPH bend (1287 cm^{-1}) (both a_1 modes) are the reverse of those in the original work. Incidentally, and ironically, Schmidt and coworkers¹⁹² used this calculated value of 1287 cm^{-1} to argue that the PO bond fell far short of a double bond in comparison with the calculated value of 1498 cm^{-1} for the PO bond in the HPO molecule. With the revised assignments, this argument would lead to the opposite conclusion.

The PO force constant derived from the infrared spectrum¹⁵⁷ is $9.53 \times 10^2\text{ N m}^{-1}$. This may be compared with the force constants for the PO bonds in¹⁵⁷ H_2POH ($4.39 \times 10^2\text{ N m}^{-1}$), HPO ($8.67 \times 10^2\text{ N m}^{-1}$) and diatomic PO ($9.24 \times 10^2\text{ N m}^{-1}$). This confirms that the PO bond is stronger than a single or double bond and is comparable to, or greater than, the bond strength in diatomic PO.

3. Population analyses

A widely used device in the analysis of wavefunctions is population analysis²². This seeks to find, among other properties, regions of charge build-up, orbital occupancy and bond order. There are a number of methods available for this purpose²², that of Mulliken being the most commonly used for phosphorus compounds. Others used have been that of Ahlrichs and coworkers^{220,221} and the natural population analysis²²² based on the natural bond orbitals (see Section IV.D.1). A slightly different approach is the calculation of integrated spatial electron populations (ISEP) for regions bounded by minima in the projected electron density functions²¹. These methods were developed later than the Mulliken method and all claim to be better.

Table 11 gives a comparison of some results from the various population analyses which have been applied to phosphine oxides and related molecules. Population analysis, especially the Mulliken method, has been subject to much criticism^{14,16,22,222} as being basis set dependent and giving unphysical results. In fact, as noted by Kutzelnigg¹⁴, a difficulty with most population analyses of this kind (based on the LCAO method) is

TABLE 11. Population analyses^a from *ab initio* studies of A₃E = Y compounds and related molecules

Molecule	Method ^b	Calculation ^c	<i>q</i> E	<i>q</i> Y	<i>q</i> A	<i>p</i> EY	Ref.
H ₃ P=O	M	6-31 G*	0.92	-0.72	-0.07	0.56	203
	M	> DZ + P	1.33	-0.97		0.71	19
	M	TZ + P	0.84	-0.97	0.04		208
	M	TZ + P + C	0.72	-0.86	0.05		208
	H	> DZ + P	1.12	-0.78		1.78	19
	N	6-31 G*	1.51	-1.16	-0.12	0.73	16
	I	3-21 G*	1.83	-1.53	-0.10		201
	I	6-31 G*		-1.53			201
	I	DZ + P		-1.58			201
H ₂ POH	M	> DZ + P	0.58	-0.56		0.35	19
H ₃ NO	M	> DZ + P	0.39	-0.76		0.35	19
	N	6-31 G*	-0.46	-0.74	0.40	0.84	16
H ₂ NOH	M	> DZ + P	0.08	-0.48		0.60	19
H ₂ FP=O	M	STO-2 G#	1.24	-0.65	-0.40 F		209
	M	> DZ + P	1.82	-1.01		0.80	19
	H	> DZ + P	1.40	-0.77		1.94	19
	I	3-21 G		-1.23	-0.81 F		201
	I	3-21 G*		-1.51	-0.86 F		201
	M	STO-2 G#	1.03	-0.69	-0.78 C		209

^a*q*E/Y/A = net atomic charge on E/Y/A; H, C or F identifies A atom; *p*EY = overlap population of EY bond.

^bType of population analysis: M = Mulliken, H = Heinzmann-Ahrichs, N = natural population, I = ISEP; see text for explanations.

^csee footnote *a* in Table 9.

that any resolution of the charge density in a molecule into atomic contributions is not unique. Thus one seeks not to analyse the population of an individual molecule (which is not very meaningful) but to compare different molecules with the same or comparable AO basis sets and, so long as the basis sets are balanced¹⁴, one hopes that reliable results may be obtained.

Examination of Table 11 shows the expected strong dependence on basis set of Mulliken populations. Note, for example, the variation for H₃PO even among the higher quality basis sets. Also, as expected, there is wide variation among the different methods of population analysis, both for atomic charges and overlap populations. However, it is clear that the PO bond is strongly polarized, phosphorus having a net charge near 1.0 whereas oxygen has charge of about -1.0. It should be emphasized that the absolute values in Table 11 have no useful meaning, especially the overlap populations, but comparisons may be valid. Thus, with care, other conclusions can be drawn from Table 11 which will be discussed in the following sections.

D. Detailed *Ab Initio* Studies of the Bonding

Given the comments in Section IV.C.1 on the usefulness of the calculations reported so far, the reader will not be surprised that a single picture has not yet emerged of the nature of the PO bond. That is not to say, however, that there are no definite statements in the literature on this topic. In fact, as intimated in Section I, the debate on the nature of the PO bond has recently been vigorous with two apparently contradictory viewpoints being proposed. These may be termed the σ/π -bond description and the Ω -bond description, neither of which, of course, involves much discussion of the involvement of

d orbitals. These two alternatives are described below, but first it is necessary to fill in some background for readers who are not theoreticians and to dispose of the d orbital issue.

1. Localization procedures

Before we can describe the studies which have been done on the PO bond, it is necessary to mention the concept of delocalized and localized MOs. The LCAO-MO description of chemical bonding²² leads to a set of molecular orbitals formed by the overlap of atomic orbitals centred at different atoms. These MOs are then classified as bonding, non-bonding or antibonding, depending on whether their energy is less than, equal to or greater than that of the constituent AOs. Each of the MOs is completely delocalized about all the constituent atoms and may only be occupied by two electrons of opposite spin. To express this, the ground-state wavefunction is described by a Slater determinant of the MOs. From this wavefunction can be calculated the properties of the molecule, e.g. electron probability density, dipole moment and geometry. However, this description is significantly deficient in one very important respect: as it stands, it is inconsistent with the existence of individual bonds in the molecule. The idea of a chemical bond between a pair of atoms in a molecule, which is approximately transferable between molecules, is fundamental to chemistry, so this is a grave deficiency indeed.

However, it is possible to reconcile the MO method with reality. This is because it is possible to convert the Slater determinant of MOs, by a unitary transformation, into another Slater determinant containing a set of MOs corresponding to localized bonds. These are the *localized* MOs as opposed to the original *canonical* MOs from the LCAO-MO method. Although this transformation does not change the value of the total electronic ground-state energy, the orbital energy values are shifted. In fact, there are an infinite number of such transformations possible²², many of them corresponding to localized MOs, so that one needs a procedure or criterion for generating them consistently. Three such procedures are:

(i) that which generates the *energy-localized* MOs, originally suggested by Lennard-Jones and Pople²²³ and developed by Edmiston and Reudenberg²²⁴; the LMOs are defined as that set of orbitals which minimizes inter-orbital repulsion and exchange energy;

(ii) that which generates the *exclusive* MOs due to Foster and Boys^{225,226}, usually called the Boys LMOs, defined as that set which maximizes the sum of the squares of the distances between the orbital centroids;

(iii) a more recent method is that of the *natural localized molecular orbitals* developed by Reed and Weinhold²²⁷, which are derived from a natural bond-orbital analysis proposed by Foster and Weinhold²²⁸. The natural bond orbitals correspond more closely to the picture of localized bonds and lone pairs as basic units of molecular structure, are much easier to calculate and give results usually in good agreement with the other LMO methods²²⁹.

Of these methods, that of Boys probably has been in greater use especially for systems containing second-row atoms because of its ease of computation. All three methods have been applied to phosphine oxides, more commonly that of Boys. Normally the different localization methods give similar results but not in the case of phosphine oxide, as we shall see.

An interesting point about these localization methods is that they sometimes lead to 'banana bonds'. For example, the energy-localized MOs for N₂ are three equivalent curved bond orbitals spaced 120° apart from one another, the 'banana bonds', whereas

the canonical MOs are the familiar σ bond and two π bonds²². A similar result may be obtained for the alkene and carbonyl groups using the Boys method¹⁸. Thus localization procedures tend to obscure σ/π separability, which has also been a useful concept in chemistry. This aspect is often avoided by a preliminary examination of the canonical orbitals, especially the HOMO, to see if it has π properties and is already strongly localized; if it has, it is then excluded for the localization procedure. For example, the HOMO of ethylene is excluded in the localization procedure to preserve the familiar σ/π description of the carbon—carbon double bond²².

Note that both these difficulties (absence of identifiable bonds and then loss of σ/π separability) are artifacts of the framework chosen for solution of the Schrödinger equation—the LCAO–MO method.

2. Insignificance of *d* orbitals

Phosphine oxide calculations are a very good example of the trend mentioned in Section II whereby the significance of *d* orbitals appeared to change during the 1970s. In 1970 three sets of calculations indicated that *d* orbitals were significant in the electronic description of phosphine oxide^{69,185a,230}. This was on the basis that leaving out the *d* functions leads to large energy increases for the species. Although all groups reported that *d* orbitals were important there were, with hindsight, significant differences in the degree of importance. Thus, for example, Hillier and Saunders^{185a} found a *d* population of > 1 for H_3PO at the STO-3G* level, while Demuyne and Veillard²³⁰ found that it was 0.36 at $> \text{DZ} + \text{P}$. Also, Marsmann and coworkers⁶⁹ noted that the *d*-orbital radii found, by optimization, were similar to those of the *s* and *p* orbitals but, in their opinion at that time, this merely showed that there was no problem involved in achieving good overlap of these orbitals. This bias towards one viewpoint at the time is not surprising, given the preconditioning towards it that had occurred in the previous two decades and the apparent confirmation of it in the calculations.

By 1979 the situation had changed, even though the calculations were similar. Thus, in the course of a comprehensive study, discussed further below, Wallmeier and Kutzelnigg¹⁹ repeated the observation of Demuyne and Veillard²³⁰ that the *d* population in H_3PO is 0.3 at the $> \text{DZ} + \text{P}$ level. However, they showed (convincingly by both Mulliken and Heinzmann–Ahlrichs population analysis) that the *d* functions used were not true valence orbitals. For example, the Mulliken *d* population with a saturated *sp* basis is 0.3, which is comparable to that found in H_3PF_2 (0.2), but the *d* population in H_2POH is only smaller by a factor of 2. Further, the energy lowering due to the presence of *d* functions is roughly proportional to the *d* population (in line with the considerations of Section II above). They concluded¹⁹ that 'the traditional valence AOs of *s* and *p* type are, when appropriately deformed, able to describe the bonding in all molecules in this paper. They are slightly poorer for the electron-rich molecules but even for them there is no indication of a valence extension'.

Wallmeier and Kutzelnigg¹⁹ also demonstrated that phosphine oxides are a good example of *d* functions making up any deficiencies in the *s* and *p* basis and that, to obtain consistency in *d* function contribution, basis sets must be used which are saturated for *s* and *p* basis functions (i.e. there should be no further energy lowering on adding more *s* and *p* basis functions). However, in retrospect, their more important finding was that the use of *d* functions is essential to obtain an accurate description of these molecules. For example, they found for H_3PO that, on addition of *d* functions, there was a strong energy lowering, amounting to 218 kJ mol^{-1} (52 kcal mol^{-1}). Also, the PO bond length optimized without *d* functions (160 pm) was close to that of a single bond (calculated as 167 pm in H_2POH), while the optimized bond length with *d* functions (147 pm) was in good agreement with experimental values¹⁹ (see Table 9). As discussed in Section II,

this need for d functions in phosphine oxide calculations is because the PO bond is very polar so that there is a rapidly varying potential between the nuclei, which cannot be described accurately by a wavefunction which includes only atom-centred s and p functions.

These early conclusions by Wallmeier and Kutzelnigg¹⁹ have been confirmed in detail by the later studies, two of which deserve mention. Magnusson¹⁵ included calculations on phosphine oxides in his general study of hypercoordinate molecules (described in Section II) and they followed the same general pattern whereby there is no role for valence d orbitals. Reed and Schleyer¹⁶ addressed the same problem in their recent study of hypervalent molecules (discussed further in Section IV.D.3.a). They showed that the depletion of the Y lone-pair orbital population in A_3XY systems was not matched by a corresponding increase in the central atom d orbital population.

Finally, an interesting psychological observation can be made about the influential paper by Wallmeier and Kutzelnigg¹⁸. Although they demonstrated that there is no valence role for d orbitals in phosphine oxides, nevertheless they used arguments based on them, in the same paper, to explain several aspects of the bonding. This reluctance on their part to abandon the concept, even though they had disproved it, shows how convenient the idea had been up to that time.

3. *The two alternative views of the bonding in phosphine oxide*

All of the detailed theoretical studies of the PO bond to date show, in agreement with experimental observation, that the PO bond has high multiple bond character and is highly polarized^{16,17,19–21,68,69,185,192,201,203,230,231}. From Table 9, the optimized PO bond length for H_3PO (146 pm) is in good agreement with the experimental value for the substituted compounds. From Section III this is less than the bond length in the PO molecule (147.6 pm) or the HPO molecule (151.2 pm), both of which must have multiple character, and is distinctly shorter than a PO single bond (160 pm).

The results of population analyses (Table 11) are consistent with the picture that about one electron is transferred from phosphorus to oxygen. The polarity of the PO bond is significantly larger in H_3PO than in H_2POH , where it is only determined by the difference in electronegativity. Also, there is significant PO overlap as measured by overlap populations. There is no problem in reconciling these population results because if there was overlap of oxygen lone pairs with suitable receiving orbitals on phosphorus it would be highly unsymmetrical with most of the electron density near oxygen, as discussed in Section IV.B. In fact, the detailed studies (see the references at the start of this section) show that the presence of backbonding does not attenuate the charge-transfer characteristic of a semipolar bond and that backbonding means that the π AOs of oxygen are strongly polarized towards the H_3P moiety^{16,17,19–21,68,69,185,192,201,203,230,231}.

Although we know that the PO bond is multiple and highly polar, there is still strong disagreement about the exact electron distribution in it. As mentioned above, there are two viewpoints, described below. It turns out that phosphine oxides are part of the overall dichotomy between the σ/π and bent bond descriptions of multiple bonds²².

a. One σ bond and two half π bonds (backbonding/negative hyperconjugation). This might now be described as the traditional view, having become so over about the last 30 years with the dominance of the molecular orbital method. It has been discussed qualitatively in Section IV.B. The bond can be viewed^{20,192} as a donor–acceptor or Lewis acid–base interaction with backbonding superimposed. The lone pair of electrons from phosphorus forms a σ bond to oxygen which completes its octet. Then there are two possibilities. The resulting extra charge density on oxygen may go into suitable acceptor orbitals on phosphorus, forming a double bond (or rather a partial triple bond)

by a π -type interaction called backbonding^{14,16,19}, as shown in Figure 3. The suitable orbitals are now known^{15,16,19} not to be d orbitals but a set of antibonding orbitals of e symmetry on the R_3P moiety (see Section IV.B). This can be viewed as a resonance between single and triply bound structures²⁰. The alternative possibility^{21,201} is that the two opposite charges on adjacent atoms interact in an ionic bond and strengthen the PO link so that it is multiple (essentially structure 1A with some polarization of the charges towards each other).

There has never been any doubt, from the earliest to the most recent calculations, that there is a polarization of the charge at oxygen (the lone pairs) towards phosphorus^{14,16,19-21,69}. It is the interpretation of this polarization which has proved difficult because, as already pointed out, any double bond between phosphorus and oxygen must be highly polar, so that it is difficult to distinguish between ionic and covalent bonding here. Most workers have interpreted the polarization as indicating backbonding, but, for example, Streitwieser and coworkers^{21,201} took the view that it is nothing more than the polarization of the charges in an ionic bond. They asserted, but did not show, that this view was consistent with the reduced dipole moment because the charges are not spherically symmetric about the nuclei²⁰¹. Similar sentiments were raised by Wallmeier and Kutzelnigg¹⁹ who stated at one point in their paper, but again did not show, that the polarity of the PO bond was inconsistent with double bond character. However, later in the paper, they invoked backbonding to form a partial triple bond.

Most recently, Reed and Schleyer¹⁶ did a very useful broad general study of the bonding in A_3XY species. They used calculations at the 6-31G* level and population analyses using the natural population method. They formalized the view that the backbonding is into empty σ^* orbitals on the R_3P moiety and placed the phenomenon in the context of the more general idea of negative hyperconjugation. Hyperconjugation is the interaction of filled σ orbitals and empty π^* orbitals, e.g. the σ_{CH} bonds of the CH_2 group of cyclopentadiene with the π^* orbitals of the diene. Negative hyperconjugation is then the converse, i.e. electron donation from π to σ^* orbitals as in π_C to σ_{CF}^* donation in the $FCH_2CH_2^-$ anion²³².

There was one irritating difficulty with Reed and Schleyer's results¹⁶. A consequence of negative hyperconjugation in A_3XY should be relatively increased XA bond lengths. This is indeed found to be the case for, for example, F_3CO^- and in F_3NO . However, the PF bonds are shortened in F_3PO and F_3PS and in most tertiary phosphine oxides relative to the parent phosphine (see Section II). Therefore, Reed and Schleyer had to look for other factors which influence PA bond lengths and they proceeded to invoke the greater importance of d orbitals(!) for second- as opposed to first-row atoms. They then attempted to measure the relative importance of negative hyperconjugation and d orbital involvement by examining the ratio between the depletion of the lone-pair occupancy and the d orbital population on the central atom. They found that the depletion was relatively high and the d orbital population low. They therefore concluded that the bonding was a partially ionic σ bond and partial π bonding which occurs mainly through negative hyperconjugation and only secondarily through overlap with extra valence shell d orbitals.

This reviewer was surprised by the readiness of Reed and Schleyer¹⁶ to invoke valence d orbitals as an explanation for the bond length contraction in phosphine oxides relative to the parent phosphines, especially since one of the thrusts of their paper was that the traditional dsp^3 and d^2sp^3 models are now invalid. Also, as they pointed out, d functions serve to polarize existing valence orbitals to lead to a better wavefunction for the system. This is equivalent to saying that if negative hyperconjugation occurs then d functions will be required in the LCAO-MO calculation. In fact, it is just as reasonable to argue that the need for d functions in the LCAO-MO treatment indicates that negative

hyperconjugation is occurring. Hence it cannot be strictly valid to compare the amount of negative hyperconjugation with the d population since they are already related.

There are other explanations which can be resorted to before valence d orbitals need to be invoked. One such is the bond length–bond angle relationship. Thus unsubstituted and both fluoro- and methyl-substituted phosphine oxides have decreased P—ligand bond lengths compared with their parent phosphines but all also have increased bond angles, and all of the variation is of the same order (about 5 pm and 5–6°; compare Tables 4 and 5 with Tables 2–4 in ref. 1). It is commonplace to argue¹, in the case of Main Group compounds, that an increase in bond angle is related to a decrease in bond length, because as the ligands move apart from each other (bond angle increases from 90° towards 109.5°) they can approach closer to the central atom (see also Section III.A). That the first-row compounds do not follow the same pattern can be ascribed to the already crowded environment around the small central atom.

b. Three Ω bonds (banana bonds/bent multiple bonds). This might be termed the unorthodox view, the valence bond method having been somewhat in disuse until recently. There is neither a σ nor a π bond. The PO bond is a formal triple bond with the three curved regions of electron density disposed between P and O in a symmetrical fashion (at 120° to each other in Newmann projection along the PO coordinate, Figure 4A). This description arises in both the MO and VB theoretical analyses of phosphine oxides described below. In both cases the electron density of the bonds is found to be strongly displaced towards oxygen and the remaining lone pair on the oxygen atom is found to be directed away from phosphorus along the PO axis.

These curved bonds have been termed ‘bent multiple’ bonds²⁴ and ‘banana’ bonds²², while more recently the terms ‘ τ bond’ and ‘ Ω bond’ have been coined by VB workers^{233,234}. Since the term Ω bond has been used in connection with phosphine oxides already, and since the Greek letter is reminiscent of their shape, we shall use it in the following discussion. The term τ bond has been used for the specific case where the banana bonds occur in pairs, as in alkenes²² and phosphorus ylides²³⁴.

i. Boys localization. In SCF–HF/LCAO–MO calculations, the Boys localization procedure for phosphine oxides gives the Ω -bond description, shown as a contour plot in Figure 5, at all levels of theory studied. Guest and coworkers²³¹ were the first to describe banana bonds for H_3PO , Me_3PO , F_3PO , Cl_3PO and F_3PS at the STO-3G* level. Then Wallmeier and Kutzelnigg¹⁹ found the same at the >DZ + P level, after

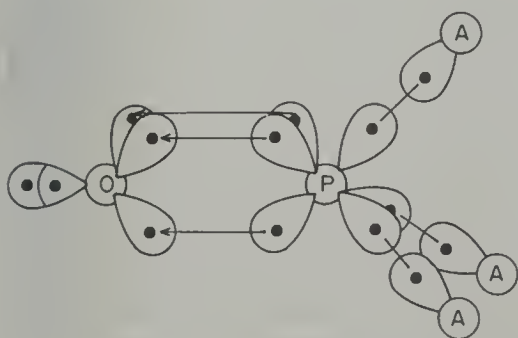


FIGURE 4A. The Ω bond model of the bonding in phosphine oxides, A_3PO . Adapted from Messmer¹⁷

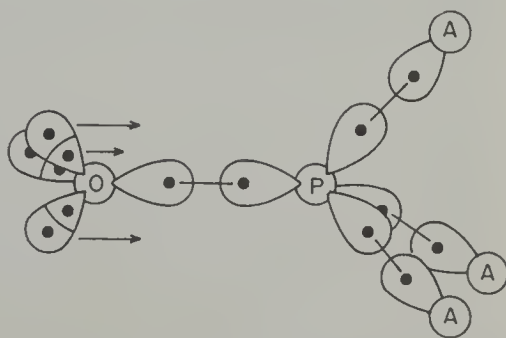


FIGURE 4B. The triple backbond model of the bonding in phosphine oxides, A_3PO . Adapted from Messmer¹⁷. The backbonds are shown by the arrows

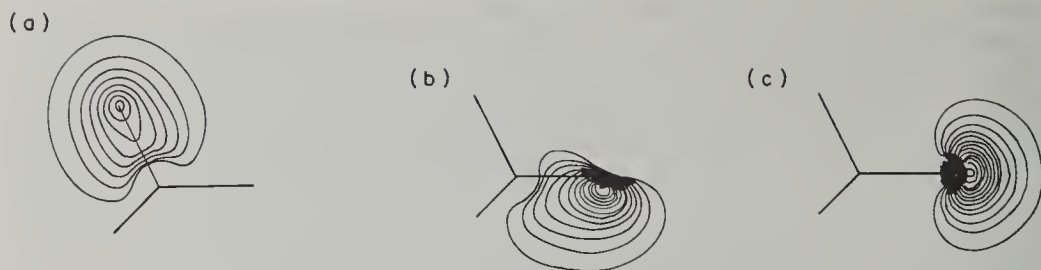


FIGURE 5. Contour plots of the Boys localized bonding orbitals of H_3PO . (a) One of three PH bonds; (b) one of three banana bonds (note that it is strongly polarized towards oxygen); and (c) the single oxygen lone pair. At the 3-21 G# level, one phase only shown, increment between all contours is $0.05 \text{ bohr}^{-3/2}$. Adapted from Schmidt and coworkers¹⁹²

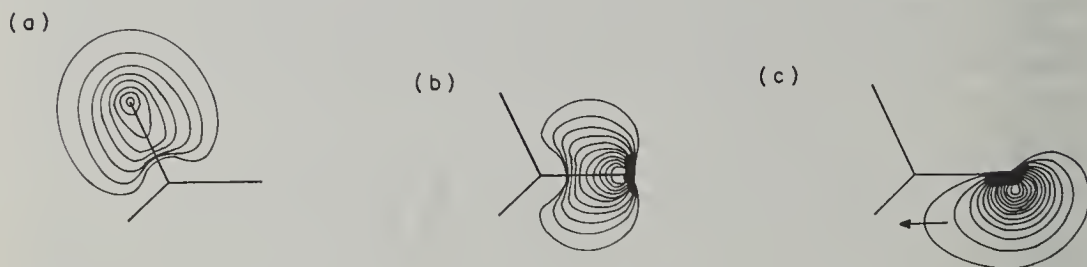


FIGURE 6. Contour plots of the energy-localized bonding orbitals of H_3PO . (a) One of three PH bonds; (b) the PO σ bond; and (c) one of three oxygen lone pairs (note the backbonding towards phosphorus, shown by the arrow). At the 3-21 G# level, one phase only shown, increment between all contours is $0.05 \text{ bohr}^{-3/2}$. Adapted from Schmidt and coworkers¹⁹²

noting that there was no natural choice of a plane of symmetry to impose a σ/π separability. Recently, Molina and coworkers²⁰³ found the same result at the 6-31G* level.

Schmidt and coworkers¹⁹² found an even more interesting result. This was that, for H_3PO , the energy localization procedure gave a different result from the Boys procedure. The energy localized orbitals at the 3-21G# level for H_3PO are shown in Figures 4B and 6. They are three equivalent PH bond, one strong PO σ bond and three equivalent orbitals on oxygen whose character is principally lone pair. This is similar to a representation using structure 1A except that each of the lone pairs possesses some tendency to back-donate electron density to phosphorus. This result is different¹⁹² from the Boys result at the same level of theory, which is in terms of banana bonds as shown in Figures 4A and 5, whereas usually the two procedures give similar results. Even starting each procedure with the localized orbitals from other procedure gave the same end result¹⁹². The energy-localized result described above is in accord with the picture of the PO bond as arising from strong σ donation enhanced by some degree of π backbonding, except that the back-donating lone pairs are staggered with respect to the PH bonds, which would be inimical to negative hyperconjugation.

It is noticeable that whenever a localization procedure gives banana bonds, the result is not taken seriously²². This is not reasonable, since it has the same energy as a σ/π description, but it is understandable, because it is outside the familiar realm of textbook

chemistry. In just the same way, those workers who obtained this result for phosphine oxide were often reluctant to take it fully on board; some comments were: 'should not be taken too literally'¹⁹, 'overly complicated'¹⁹², 'a very peculiar electronic distribution'²⁰³. Most notable was the reaction of Schmidt and coworkers¹⁹² who had performed both localization procedures and chose to reject the banana bond description without any justification other than to say that they favoured the alternative. This was in spite of the fact that on increasing fluorine substitution the energy-localized orbitals reverted to the banana bond description (see Section IV.D.5).

ii. *Generalized valence bond calculations.* Very recently a new approach to the bonding in these compounds has been published¹⁷ based on the generalized valence bond (GVB) method.

The GVB method was developed from about 1970 by Goddard and coworkers²³⁵. The GVB wavefunction is much simpler than a VB wavefunction and so easier to calculate. However, it is still computationally difficult and, as usual, approximations have to be made. There are two such approximations, called the strong orthogonality (SO) and the perfect pairing (PP) restrictions, first proposed by Hurley and coworkers²³⁶ and developed by Goddard and coworkers²³⁵. Usually they are both applied (SOPP). The method is claimed to be a substantial improvement beyond Hartree-Fock theory in that it is the most general independent particle model and provides a unique set of localized orbitals with which to interpret the bonding^{17,235}. There are very few valence bond studies of hypervalent molecules^{61,81,234}.

During the late 1980s Messmer and coworkers^{233,237-239} started to explore the utility of GVB methods on simple systems, both with and without the SOPP restrictions. In most cases they found that the description of multiple bonds is in terms of Ω bonds. For example, in the description of difluoroacetylene the three Ω bonds may be thought of as the overlap of three sp^3 hybrids on each of the carbons²³⁷. These Ω bonds are very similar to the banana bonds often given by localization procedures in MO theory, except that in this case they are the only result which minimises the energy of the system. One interesting aspect of these studies was that the GVB-SOPP results may give different results from the full GVB method. For example, tetrafluoroethylene is described by the traditional σ/π representation in GVB-SOPP but by a two Ω -bond representation (τ bond) in the full GVB treatment²³⁹. Schulz and Messmer²³⁹ have tried to develop guidelines on when the full GVB will give the same results as GVB-SOPP.

Very recently, these studies using the GVB-SOPP method have been applied to Main Group (N, S, and P) oxides^{17,240}. It is found that in F_3PO the oxygen forms a triple bond to the phosphorus atom using three Ω bonds, very similar to the Boys localization results from MO theory shown in Figures 4A and 5. The phosphorus atom assumes a pseudo-octahedral distribution of orbitals about its core and the orbitals are strongly polarized towards the surrounding atoms.

It should be noted that, although the idea of Ω bonds now appears unorthodox, it is not at all new. In fact, Pauling introduced it in 1931²³ to explain *E/Z* isomerism in alkenes in the same paper which developed the sp^3 model and it is discussed at length in the third edition²⁴ of *The Nature of the Chemical Bond*, where he notes that the description was used by nineteenth century chemists to explain why the carbon-carbon double bond is not fully twice the energy of the single bond. However, the σ/π representation predominated later because it could be quantified fairly easily through MO theory²².

Although this reviewer finds the triple bond description for the PO bond to be fairly convincing and appealing, some reservations do have to be entered about the GVB-SOPP results reported above. First, full GVB gives Ω bonds for $F_2C=CF_2$ whereas GVB-SOPP gives a σ/π description, so it is just conceivable that it could be other way

around for F_3PO . Messmer¹⁷ has argued against this possibility but he cannot yet rule it out completely. Also, many of the systems reported so far have fluorine as ligands (e.g. $FC\equiv CF$, $F_2C=CF_2$, F_3NO , F_3PO) and in the case of the amine oxides the result was different with hydrogen ligands (see Section IV.D.4). Hence there is the possibility that the result will be different for phosphine oxide or tertiary phosphine oxides. Again Schulz and Messmer²³⁹ have indicated that change in ligand is not important, but only in references to unpublished material. More seriously, an examination of Table 9 shows that the few results available from GVB-SOPP calculations do not compare favourably with those from other calculational methods. For example, for F_3PO , the predicted PO bond length is 147 pm compared with the experimental result of 143.6 pm while the 6-31G* value was 142.5 pm.

A final point is that both the Boys localization results and the GVB-SOPP results for F_3PO are inconsistent with negative hyperconjugation. Examination of Figure 5 shows that the three Ω bonds are staggered with respect to the other phosphorus—ligand bonds, giving an octahedral disposition of electron pairs around phosphorus. This is the arrangement expected on the basis of the Pauli exclusion principle, but it would minimize the overlap of the orbital interaction required for negative hyperconjugation.

4. Comparison of phosphine oxides and amine oxides

Tables 9 and 11 also include for comparison results from calculations on ammonia oxide and other amine oxides. It is to be expected that differences between these results and those for phosphine oxides should reflect fundamental differences between first- and second-row elements. There are some anomalous results reported in Table 9. Note, for example, that most of the calculations on F_3NO are hopelessly inaccurate with the single GVB-SOPP result being particularly bad. The worst predictions are for the NF bond length and the dipole moment and only when correlation is included are the results reasonable, although the NO bond length is still overestimated. Indeed, we can be much less confident in predicting the geometry of ammonia oxide than we were above for phosphine oxide.

The observations to be explained, which may or may not be related, include:

- (i) the lower dipole moment of phosphine oxides compared with amine oxides;
- (ii) the PO bond in H_3PO and R_3PO is stronger and shorter than a PO single bond whereas in H_3NO and R_3NO the NO bond (length ca. 140 pm) is like an NO single bond²⁴¹;
- (iii) the PO bond in F_3PO is qualitatively similar to that in H_3PO whereas the NO bond in F_3NO is a double bond on the criteria of length and strength;
- (iv) the PA bond lengths in A_3PO are all shorter than those in A_3P whereas the NA lengths in A_3NO are longer than in A_3N , with the contrast being especially marked for the fluoro derivatives (compare Tables 4 and 5 with Tables 2–4 in ref. 1).

Many of the theoretical studies of phosphine oxides also include comparison with amine oxides^{16,17,19,203,242} and there is greater unanimity about the bonding in amine oxides. All find that the NO bond in amine oxides is weaker than in phosphine oxides, in agreement with the chemical experience that amine oxides are oxidizing agents and phosphines are reducing agents. There is a general picture from population analyses^{14,19,242} (Table 11) that ammonia oxide and tertiary amine oxides are singly bound with a semipolar bond and no backbonding, equivalent to the representation $R_3N^+-O^-$. The presence of backbonding in the phosphine oxides and its absence in the amine oxides then explains the lower than expected dipole moment in phosphine oxides.

The difference between R_3NO and F_3NO is also explained because it is found that

there is backbonding in the fluorine derivative. As observed in Section IV.B, now that backbonding does not have to be into d orbitals there is no problem about it for nitrogen compounds. The likely acceptor orbitals for back-donation in F_3NO were analysed by Grein and Lawlor⁸⁶, who concluded that the $3e$ orbital of NF_3 was the most suitable. A similar picture was found in the Boys localized molecular orbitals of H_3NO at the 6-31 G* level²⁰³, which were found to be composed of one centroid along the NO bond with the remaining ones around oxygen, in contrast to the result found by the same workers²⁰³ for phosphine oxide outlined in the previous section.

Also similar were the GVB-SOPP calculations¹⁷ on F_3NO and H_3NO , which gave results different from each other and from F_3PO . We have seen in Section IV.D.3.b that the result for F_3PO was three Ω bonds. The result for F_3NO was different. In this case there is a σ bond from nitrogen to oxygen and the three lone-pair orbitals on oxygen are strongly polarized towards nitrogen as in Figures 4B and 6, yielding three equivalent backbonds, amounting overall to a second bond between oxygen and nitrogen in accord with the short length (116 pm) of the NO bond in F_3NO . The result for H_3NO was different again. This time there is again a σ bond but the lone pairs on oxygen are not polarized towards nitrogen; there is no backbonding, in agreement with the longer bond lengths in substituted amine oxides. It should be mentioned that the concept of backbonding used here is different from the same idea in MO theory, because it is not based on atomic orbitals. Therefore, in order for electrons on one atom to backbond to another atom there is no need to invoke vacant atomic orbitals on the acceptor atom. The only requirement, for example for the oxygen lone pairs in F_3NO to backbond to nitrogen, is that there be sufficient space for them, provided by the polarization of the NF bond orbitals towards fluorine. In the case of H_3NO the NH bond orbitals are not polarized towards the ligands as in F_3NO and so there is no room for backbonding electron density.

Messmer¹⁷ contended that the fundamental difference between first- and second-row atoms is reflected in these different results from the GVB-SOPP calculations on F_3PO and F_3NO , described above. The nitrogen atom in F_3NO prefers to form four primary bonds (the backbonding is regarded as secondary) whereas the phosphorus atom in F_3PO forms six. This is a direct consequence of the greater core size in the second row.

There is one point where the unanimity breaks down, namely on the issue of where the backbonding is directed in F_3NO . What we have referred to as the traditional view would see it as going into suitable acceptor orbitals on nitrogen, the most likely being the σ^* NF antibonding orbitals. This is negative hypereconjugation and is consistent with the increased length of the NF bonds relative to F_3N . However, this agreement with the NF bond length may be coincidental, as pointed out in Section IV.D.3.a, because there is not a similar lengthening in F_3PO relative to F_3P . On the other hand, examination of the GVB-SOPP version of the backbonding in F_3NO , shown in Figures 4B and 6, shows that it is inconsistent with negative hypereconjugation. This is for just the same reasons as in F_3PO discussed in the previous section; the donating oxygen lone pairs are staggered with respect to the NF bonds.

In addition, Messmer¹⁷ offered a simple and reasonable explanation of the trends in bond lengths found to the other ligand, i.e. the lengthening of the NF bonds in F_3NO relative to F_3N and the shortening of the PF bonds in F_3PO relative to F_3P . This is based on the bond length-bond angle relationship referred to in the previous section and on the small size of first-row elements. Thus, in going from F_3N to F_3NO the added oxygen contributes polarizable lone pairs which may contribute electron density to screen the nitrogen core. When the lone pairs approach closer to the small core, the resulting increased Pauli repulsions with the NF bonds produce a lengthening in these bonds. In the case of F_3P and F_3PO , the difference lies in the larger size of the phosphorus core, which means that it can form more bonds because there is more room. Then,

because the oxygen polarizes orbitals away from P there is a reduction in Pauli repulsions with the PF bonds resulting in the shortening of these bonds.

5. Bonding in substituted phosphine oxides

Parent phosphine oxide is known only in matrix isolation experiments¹⁵⁷ and yet the formation of the PO bond drives the synthetically useful Wittig and Arbusov reactions and some of the processes of life itself. The most obvious question to be answered here then is why carbon, oxygen and fluorine substituents all stabilize phosphine oxide. The obvious answer is that decomposition by tautomerism of a hydrogen atom is prevented by any substitution. However, calculations have shown that the answer is more subtle than that, because there is a general effect of substitution to increase the PO bond strength^{14,19,20,204,210,213}.

Schmidt and Gordon²⁰ quantified this effect in detail in a comparison of substituent effects on the PO bond and some of their results are given in Table 12. They found both an increase in bond strength and a decrease in bond length on substitution (except for an Si substituent) at all levels of theory studied, including calculations with electron correlation. The effect increases with increasing electronegativity of the substituent but there is a limit to the ability of increasing electronegativity to increase bond strength. For example, from Table 12 it can be seen that in the series H, CH₃, NH₂ the bond strength increases significantly but remains nearly constant for OH and falls off slightly for F. There is a similar pattern with multiple substitution. Note that the experimental bond energy of F₃PO is 542 kJ mol⁻¹, so these computed bond strengths are too low; however, it is assumed that the calculated values are internally consistent.

Schmidt and Gordon²⁰ also compared the effect of substitution on H₃PO with respect to a Mulliken population analysis. They found that the substituents withdrew electron density from phosphorus, the amount of the withdrawal being consistent with electronegativity (F > OH > NH₂ > CH₃). The charge at oxygen was also reduced by a smaller amount. Even so, there was still a large positive charge on phosphorus and negative on oxygen. They also derived the PO bond order by Mulliken population analysis for some of the substituted phosphine oxides given in Table 12. It can be seen that the bond orders increase roughly as the computed bond strengths, i.e. with increasing

TABLE 12. Effect of substitution on PO bond lengths and strengths and orders at various basis set levels^a

Molecule	$d(\text{P}=\text{O})^b$	Bond strength ^c			Bond order ^d
		3-21 G#	6-31 G*	MP3/6-31 G*	
H ₃ PO	142.3	377	423	531	1.58
H ₂ (CH ₃)PO	141.7	423	460	565	1.66
H ₂ (NH ₂)PO	142.0	494	519	628	
H ₂ (OH)PO	141.8	485	527	640	1.69
H ₂ FPO	141.1	481	515	628	1.74
HF ₂ PO	141.0	540	565	686	
F ₃ PO	140.9	523	540	657	

^aAll at STO-2 G# geometry from ref. 20; see Table 9, footnote a, for terminology.

^bSTO-2 G# computed bond lengths in pm.

^cEnergy for the dissociation of the phosphine oxide to phosphine and ¹D oxygen in kJ mol⁻¹ using the indicated calculation; ¹D oxygen is about 190 kJ mol⁻¹ above the triplet ground state.

^dDerived from a Mulliken population analysis at the 3-21 G# level.

electronegativity of the substituent. This was found to be due to an increased amount of backbonding²⁰.

Two groups have argued that the stabilizations by fluoro and methyl substituents are caused by different mechanisms. Schneider and coworkers²⁰⁴ studied a series of $A_3P=Y$ molecules ($A = H, CH_3, F$; $Y = O, S$) at the 6–31 G* level, the results of which are shown in Table 13. It can be seen that the substitution of H by both F and Me causes an increase in the $P=Y$ bond energy but only F substitution causes an increase in stretching force constant. As noted in Section IV.A.2, this is confirmed by experimental observations. They say that this shows that methyl stabilization is by a different mechanism, because the higher $P=O$ and $P=S$ bond strengths in the trimethyl compounds are shown by this to be not directly related to inherent properties of the PO and PS bonds, but must rather be caused by changes in the R_3P moiety. Wallmeier and Kutzelnigg¹⁹ studied fluorine substitution in detail, using the population analyses shown in Table 11. They found that the binding energy of the PO bond in $H_2P(O)F$ is larger than that in H_3PO . Also, the overlap population or bond order is significantly (25%) larger in $H_2P(O)F$ than in H_3PO , which confirms that fluorine substitution stabilizes the PO bond. A similar result was found for double fluorine substitution and they noted that both were in line with the results for the triply substituted compound reported by Serafini and coworkers²¹³.

Both Schneider and coworkers²⁰⁴ and Wallmeier and Kutzelnigg¹⁹ advanced the same mechanisms for the different ways that fluorine and methyl substituents stabilize the PO bond. Thus fluorine increases π backbonding by electron withdrawal from phosphorus, which becomes more positive, giving more opportunity for electron donation from oxygen lone pairs. On the other hand, methyl groups stabilize the partial positive charge on phosphorus in R_3PY so we must look for another effect. A possibility is that steric hindrance destabilizes Me_3P relative to H_3P to a greater extent than Me_3PY relative to H_3PY , because of the change in the angles at phosphorus (see Table 4 and Table 2 in ref. 1). Hence, since PO bond dissociation in R_3PO leads to R_3P , this gives a higher bond dissociation energy for the methyl-substituted compound.

Von Carlowitz and coworkers²¹⁰ compared bond lengths in methylphosphine and methylphosphine oxide and the effect of fluoro substitution thereupon, and some of the results are shown in Table 14. They found that there was a remarkably large variation (decrease of 10 pm) in PC bond length from methylphosphine to difluoromethylphosphine

TABLE 13. Calculated and experimental bond energies and calculated force constants for $P=Y$ in $A_3P=Y$ compounds

Molecule	$D_0(P=Y)^a$	$D_0(P=Y)^b$	f^c
$H_3P=O$	426		9.423
$F_3P=O$	539	540	11.812
$Me_3P=O$	537	582	9.144
$H_3P=S$	226		4.210 ^d
$F_3P=S$	269	293 ^e	6.093 ^d
$Me_3P=S$	324	383 ^f	3.917 ^d

^aIn kJ mol^{-1} at 6–31 G*, from ref. 204.

^bBest available experimental comparison from Table 6.

^cScaled stretching force constant in $\text{mdyn } \text{\AA}^{-1}$, using scale factors optimized for PH_3 and $F_3P=O$.

^dThese are not directly comparable, see ref. 204.

^e $D_0(P-S)$ in Cl_3P-S .

^f $D_0(P-S)$ in $(C_3H_7)_3P-S$.

TABLE 14. Effect of fluoro substitution on calculated bond lengths in methylphosphine and methylphosphine oxide^a

Bond length ^b	CH ₃ PH ₂	CH ₃ PF ₂	CH ₃ POH ₂	CH ₃ POF ₂
P—C	185.3	179.9	178.9	175.3
P=O			146.5	143.1
P—F		157.8		153.9

^aFrom ref. 210.^bIn pm, using 3-21 G* basis set.

oxide. This was made up from two increments. There was the fall (5 pm) in PC on change from phosphine to the oxide explained by the bond length–bond angle relationship (see Section III.A), but there was also a decrease of about 5 pm on substitution of two fluorines for two hydrogens. They commented²¹⁰ that ‘these extremely large structural variations are presumably due to the withdrawal of negative charge from the phosphorus atom and the consequent shrinkage of bonds to other electronegative substituents’. Thus, in all cases, replacement of one substituent by a more electronegative one results in a shortening of all of the other P—X bonds.

Finally, Schmidt and Gordon²⁰ found a very interesting result of substitution on the derived energy-localized orbitals. Methyl and silyl phosphine oxides still have the three lone-pair orbitals on oxygen and one PO σ bonding orbital as described in Section IV.D.3.b for parent phosphine oxide, Figures 4B and 6. For hydroxy and fluoro phosphine oxides, the lone-pair orbital *trans* to the substituent becomes so involved in backbonding that it tips inward and the localization procedure leads to the formation of two banana bonds from it and the σ bond. For the trifluoro compound two lone pairs tip in, leading to three banana bonds, Figures 4A and 5.

6. Bonding in phosphine sulphides

Some of the studies of phosphine oxides have included phosphine sulphides for comparison^{16,20,231}. It is found that the sulphides are qualitatively similar to the oxides, except that they have a relatively weaker PS bond and are less polar. Schmidt and Gordon²⁰ studied H₃PS and derived a bond order (from Mulliken population analysis) of 1.32 for H₃PS compared with 1.58 for H₃PO. As in the oxide, electronegative substituents act to increase the PS bond strength. One additional result was that the weakness of the thiophosphoryl bond was also due to a weakening of the PS σ bond. This was derived from Mulliken population analysis of atomic charges, P = 0.481 and S = -0.457, compared with P = -0.922 and O = -0.719. They commented²⁰ that ‘sulphur’s diminished ability relative to oxygen to hold a large negative charge has decreased the charge separation in the PX bond considerably and thus weakened the formally ionic donor σ bond’.

Guest and coworkers²³¹ did an STO-3G* calculation at assumed geometry on F₃PS with Boys transformation of the resulting canonical orbitals. They found essentially the same features for the PS bond as for the PO bond, including banana bonds. The PS bond polarity was slightly less and the phosphorus component to the bond involved slightly smaller 3d and 3p contributions.

E. Empirical Calculations

Since the initial study of Wagner¹⁶² there have been only a few empirical or semi-empirical studies of phosphine oxides. The earlier ones reported detailed

examinations of the bonding^{162,199,243-245} and concluded that the PO bond is multiple and polar, but were much taken with the influence (or lack thereof) of d orbitals. Later studies²⁴⁶⁻²⁵², mainly by Soviet workers, used these methods (HMO, CNDO) to predict atomic charges and dipole moments, in some cases to explain or predict extractive capability or donation ability. The SINDO method was applied to phosphine oxide by Jug and Schulz²⁵³ in their general study but gave poor results (PO = 149 pm, PH = 142 pm).

F. Summary of Bonding and Comments on the Formula of Phosphine Oxides

Previous general discussions³⁻¹³ of the bonding in phosphine oxides have been couched in terms of a resonance between two possible limiting structures $\text{H}_3\text{P}=\text{O}$ and $\text{H}_3\text{P}^+ - \text{O}^-$. This view will have to be given up. It is too simplistic because, as we have seen, the presence of a multiple bond between phosphorus and oxygen is not inconsistent with a high degree of polarity. More important, this view reduces the significance of the P=O formulation without conveying in return the true complexity of the bonding. A subsidiary point is that if the Ω bond description (Section IV.D.3.b) turns out to be the correct one, the formula $\text{R}_3\text{P}^+ - \text{O}^-$ would be misleading because it implies that there is a σ bond between P and O.

The satisfactory formulation of the PO bond is difficult because we are accustomed to formulae from the first row of the Periodic Table. In the first row there is a fortuitous correspondence between bond strength, number of electron pairs and valence. This is one of the indirect consequences of the small size of these elements. Thus, for the common multiple bonds of organic chemistry, $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$ and $\text{C}=\text{O}$, the two (or three) lines carry three different implications at the same time: (i) that the bond is twice (or three times) the strength of a single bond between the elements concerned, (ii) that there are two (or three) electron pairs in the region between the elements and (iii) that it is possible to have an addition reaction wherein one (or two) ligand(s) is (are) added to each of the atoms involved in the bond.

This all breaks down in the second and higher rows. In the case of PO, we have a double-strength, highly polar bond composed of three (or more) electron pairs (by both of the descriptions in Section IV.D.3). Hence the PO bond can be viewed as either a double bond $\text{P}=\text{O}$ or a triple bond $\text{P}\equiv\text{O}$. If we wish to have one formula to represent the PO bond, we must choose which information is the most important to convey. If we consider that it is more important to convey the information that the PO bond contains three electron pairs then we should use the $\text{P}\equiv\text{O}$ formula, but if we consider that it is more important that the strength of the bond be specified then we should use the $\text{P}=\text{O}$ formula.

This reviewer proposes that a utilitarian view be taken. Strength and, especially, valence are the things that matter in practical chemistry (i.e. how much energy will be required for the bond to react and how many things can be attached to it in an addition reaction). Hence the formula $\text{X}_3\text{P}=\text{O}$ is the most useful. In addition, it also has the merit that it is currently in common use. However, until now, practical chemists have been made to feel uneasy about its correctness. The above analysis shows that their instincts were correct.

Sometime in the future, better calculations will determine the electronic distribution in the PO bond. For now, the best we can say is that the nature of the PO bond will probably be one of the following:

either

'The PO bond is a double strength bond, formulated as $\text{P}=\text{O}$. This representation also implies (i) that there are three electron pairs between P and O composed of a σ bond between P and O and two π backbonds between lone pairs on O and acceptor

orbitals on P which are antibonding in character with respect to the other ligands on P as shown in Figure 3 and (ii) that the electron density of the bonds is strongly skewed towards O so that there is a high degree of positive charge on P and negative on O'.

or

'The PO bond is a double strength bond, formulated as $P=O$. This representation also implies (i) that there are three electron pairs between P and O composed of three Ω bonds from P to O as shown in Figure 4A and (ii) that the electron density of the bonds is strongly skewed towards O so that there is a high degree of positive charge on P and negative on O'.

or

'The PO bond is a double strength bond, formulated as $P=O$. This representation also implies (i) that there are four electron pairs between P and O composed of a σ bond between P and O and three backbonds from lone pairs on O to the P atom as shown in Figure 4B and (ii) that the electron density of the bonds is strongly skewed towards O so that there is a high degree of positive charge on P and negative on O'.

Finally, is the octet rule broken by phosphine oxides? As the quotations in the Introduction imply, the answer is yes and no. This reviewer would argue that it may not be broken technically because the electron density is skewed towards O so that P is not receiving a full half share of each electron pair. Reed and Schleyer¹⁶, for example, are careful to say that the *electronic* octet rule is not broken. However, there is a strong case that it is broken in spirit because phosphorus is participating in more than four electron pair bonds.

V. CONFORMATION

There have been a number of studies, both experimental and theoretical, on the conformations of tertiary phosphine oxides. Of particular concern have been the *trans/gauche* ratio (see Figure 7) about the PC bond and the orientation of the aromatic rings in the triaryl derivatives.

A number of workers have examined the conformations about the PC bond of trialkylphosphine chalcogenides using various physical techniques, including infrared spectroscopy, dipole moments, Kerr effects and NMR²⁵⁴⁻²⁵⁹. The conclusion is that in solution there is a mixture of the *trans* and *gauche* forms with the *gauche* form usually preferred, the ratio depending on the substituents and the solvent, while only the *gauche* form remains in the solid state, at least in the case of ethyldimethylphosphine sulphide²⁵⁴.

For the triaryl derivatives, the most detailed study was that of Brock and coworkers⁹⁹ at low temperatures on both forms of triphenylphosphine oxide (monoclinic and

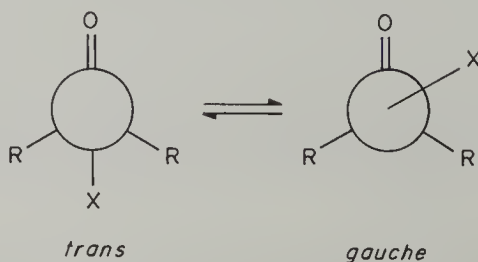


FIGURE 7. The *trans* and *gauche* conformers of a tertiary phosphine oxide

orthorhombic). In both structures the normal to one phenyl ring (A) is roughly (within 30°) parallel to the PO bond while the other two ring normals (B and C) are roughly perpendicular to this bond. A similar observation was made for triphenylphosphine sulphide¹¹⁷. As already noted in Section III.B, the smallest PC bond in both structures is the one to ring A, perhaps an indication of delocalization of the aromatic π system into the PO π^* orbital^{99,260}. In solution, however, no difference has been found in the orientation of the phenyl rings by a variety of methods, including infrared and ultraviolet spectroscopy, dipole moment and Kerr constant²⁶¹⁻²⁶⁵. The introduction of *ortho*-substituents on the aryl rings causes some minor changes in conformation^{101,266-268} and, as expected, rotation of the rings is slowed on the nmr time scale^{267,268}.

In a particularly careful and interesting study of a very large number of published X-ray crystal structures, Bye and coworkers¹⁰⁰ mapped the reaction path for stereoisomerization of triphenylphosphine oxide derivatives. Their description of the interconversion is repeated here. The equilibrium structure of an isolated $\text{Ph}_3\text{PO}-\text{X}$ fragment is close to a symmetric propeller shape with all three phenyl rings rotated from the respective CPX planes in the same sense and by approximately the same amount, about 40° . Then, starting with a molecule with positive torsion angles, the stereoisomerization path begins by rotation of one ring, say A, toward 90° (perpendicular to its CPX plane) coupled with a rotation of the other two rings in the opposite sense (toward 0°) and by half the amount of ring A. As the reaction proceeds, the rotation of the other two rings B and C becomes out of step, with one, say B, rotating less, leading to a mirror-symmetric structure with torsion angles of ca 90° , 10° and -10° . At this point ring A has rotated by $+50^\circ$, ring B by -30° and ring C by -50° . In the second part of the path, the roles of rings B and C are interchanged, so the path ends at the enantiomorphic structure with torsion angles of 140° , -40° and -40° equivalent to -40° , 40° and 40° .

The more complicated cases of mixed alkyl and aryl phosphine chalcogenides have also been studied by many workers. The orientation of the aryl ring(s) follows the same trends as in the triaryl compounds mentioned above. In the solid phase one aryl ring is usually roughly parallel with the PO bond^{105,106,122} whereas in solution the non-coplanarity increases^{269,270}. As regards the *trans/gauche* ratio, the same results were found as above, namely that the *gauche* conformer is the preferred form in solution, the preference increasing with increasing size of the substituent groups, and the preference becomes total in the solid state^{106,271-274}.

Theoretical methods have also been applied in the study of the conformations of phosphine oxides, mainly of the molecular mechanics type^{209,275-278}. The results generally agree with the experimental work and there have been a number of predictions of a similar nature for species previously not studied experimentally. It is considered that in the *gauche/trans* equilibrium (Figure 7), the *trans* form is favoured by dipole-dipole interactions and the *gauche* form by steric considerations^{255,272,278}.

In studies of the conformations of 2-(diphenylphosphinoyl)-[1,3]-dithiane, Juaristi and coworkers²⁷⁹⁻²⁸¹ discovered the existence of a strong $\text{S}-\text{C}-\text{P}$ anomeric effect. This is shown by the predominance of the conformer of the dithiane ring, which places the phosphinoyl group in the axial orientation. The analogous diphenylthiophosphinoyl derivative also shows the same effect to a lesser extent²⁸². Similar observations on this system and on the 1,3,5-trithiane derivatives were made by Mikolajczyk and coworkers²⁸³⁻²⁸⁷.

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Structure and stereochemistry of secondary and tertiary phosphine chalcogenides

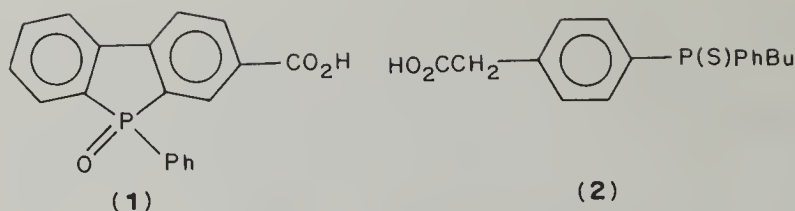
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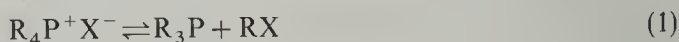
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I. INTRODUCTION

The stereochemistry of phosphorus chalcogenides, and of phosphorus compounds in general, is a subject that is essentially only 30 years old. This is despite the fact that



methylethylphenylphosphine oxide was first resolved by Meisenheimer¹ in 1911 using (+)-bromocamphorsulphonic acid as the resolving agent. He subsequently resolved benzylmethylphenylphosphine oxide in the same way in 1926^{2a}, but it was to be many years before another phosphine oxide, the dibenzphosphole **1** was resolved^{2b}. In 1944 Davies and Mann³ resolved the sulphide **2**. These isolated instances apart, it was generally held that the stereochemistry of phosphorus (and arsenic, antimony and bismuth) would be uninteresting, since any conversion to the trivalent form would result in racemization owing to inversion in the same way as was known to occur for nitrogen. It was further held that the equilibrium (equation 1) was a mobile one and would prevent any useful stereochemical studies of quaternary compounds. Although ample evidence to the contrary existed, the notion persisted until it was demolished entirely by Horner's isolation of stable enantiomeric phosphines by the electrolytic cleavage of resolved quaternary salts. This discovery stimulated an enormous amount of interest in the stereochemistry not only of phosphorus, but also of many other elements, and the field is now so large that it is doubtful if it could be usefully reviewed as a whole.



This chapter is restricted to a consideration of the stereochemistry of chalcogenides of tertiary and secondary phosphines. It will be very largely concerned with oxides and sulphides, since very little work has appeared on selenides and tellurides^{4a}. Indeed, simple tellurides, R₃P₂Te, are unstable compounds and decompose at room temperature unless kinetically stabilized by bulky groups, such as *tert*-butyl^{4b}.

Strictly, there are three classes of phosphine chalcogenides, primary, RP(X)H₂, secondary, R₂P(X)H, and tertiary, R₃PX, in addition to the parent compounds H₃PX. These last are unknown, although H₃PO and its tautomer H₂POH have been detected as reaction products in an argon matrix^{5a}. Theoretical considerations indicate they should be stable, probably in the tautomeric form H₂PXH^{5b}. Phosphine oxide has been suggested⁶ to account for the formation of tertiary phosphine oxides in the attempted base-catalysed alkylation of alkyl phosphinates, ROP(O)H₂. Primary phosphine chalcogenides, although known, have been little studied and no stereochemical or structural information is available.

In the stereochemical discussion which follows, the terms inversion and retention of configuration refer only to the non-chalcogen atoms on phosphorus in order to avoid the confusion which may arise in discussion if the Cahn-Ingold-Prelog nomenclature is strictly adhered to. Put another way, the chalcogen atom is considered always to be the atom of lowest priority in the RS system when discussing configurational changes (or lack of them) at phosphorus.

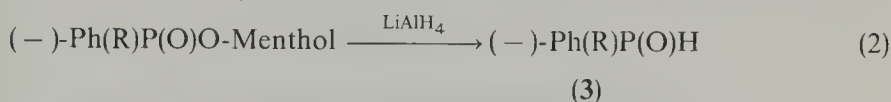
II. SECONDARY PHOSPHINE CHALCOGENIDES R¹R²P(X)H (X = O, S, Se)

A. Preparation

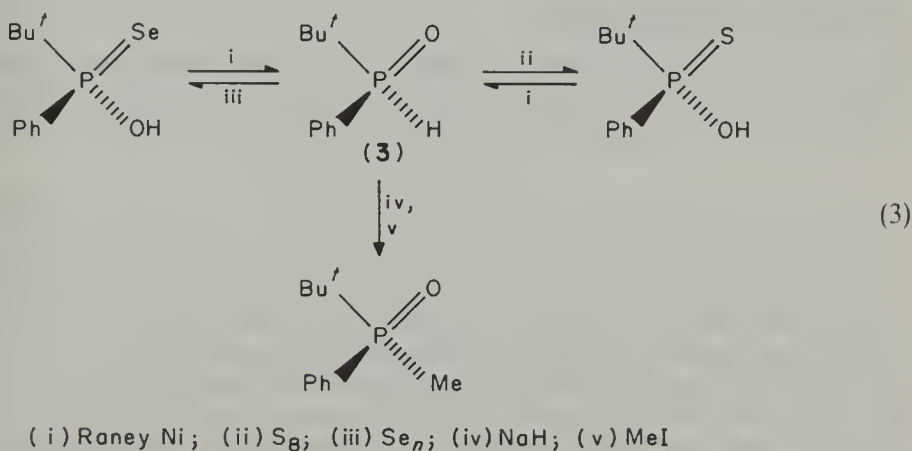
Secondary phosphine chalcogenides are reasonably well known, although little structural information is available. Methods for their preparation are limited and most do not lend themselves to resolution. Nevertheless, secondary phosphine oxides and sulphides

have been obtained in optically active form. The first example⁷, benzylphenylphosphine oxide (**3**; R = PhCH₂), was obtained by lithium aluminium hydride reduction of one enantiomer of (–)-menthyl benzylphenylphosphinate (equation 2). Shortly after, β-naphthylphenylphosphine oxide (**3**, R = 2-naphthyl) was similarly obtained⁸. Both compounds had extremely low rotations ($\alpha_D - 0.52^\circ$ and -0.59° , respectively) and nothing is known of the optical purity of either sample.

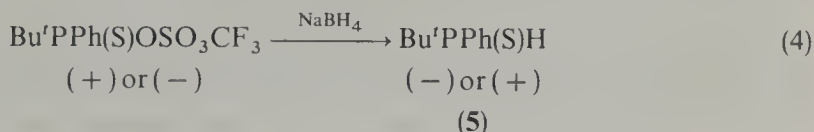
However, Campbell and Way^{2b} and Mislow and coworkers (**3**)⁹ had found that lithium aluminium hydride causes racemization of tertiary phosphine oxides, so it must be considered unlikely that a high degree of stereoselectivity would be obtained in the reduction of the esters. Both groups presented evidence that the observed rotation was in fact due to chiral phosphorus, but the subsequent preparation of (–)-phenyl-*tert*-butylphosphine oxide^{10a} (**3**; R = *t*-Bu, $\alpha_D - 28.8$) suggests that optical purities for **1** (R = PhCH₂ or 2-naphthyl) were low. Michalski and Skrzypczynski^{10a} obtained **3** (R = *t*-Bu) by two routes (equation 3) and assigned absolute stereochemistry on the basis of its stereospecific alkylation to give the tertiary oxide₄ whose absolute stereochemistry had previously been established by correlation¹¹.

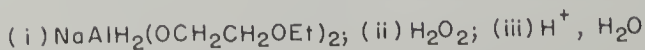
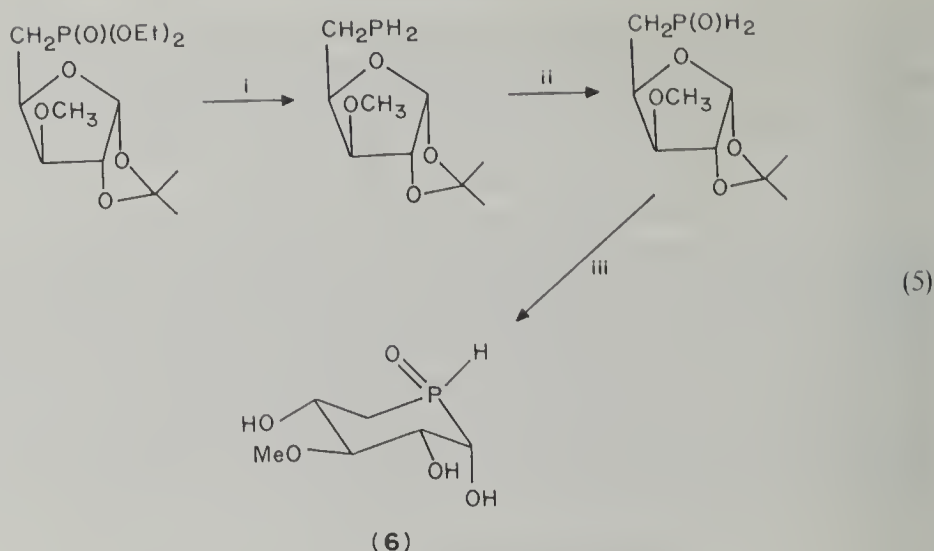


The sequence shown in equation 3 also serves to establish the stereochemistry of the addition of S and Se to secondary phosphine oxides as proceeding with retention. It is notable that the anion formed from **3** (R = *t*-Bu) retains its stereochemical integrity. This fact, together with the general observation that thiophosphinic acids are readily synthesized and usually readily resolvable, suggests that desulphurization of resolved thiophosphinates followed by base-catalysed alkylation or Michael-type addition reactions may well prove a useful general route to chiral tertiary phosphine oxides.



The same Polish workers^{10b} prepared the sulphur analogue, **5**, by reduction of a mixed anhydride (equation 4): Only the mixed anhydride with trifluoromethanesulphonic acid gave chiral products, presumably because the triflate anion is an excellent leaving group and substantially reduced the risk of stereomutation of the intermediate. Both

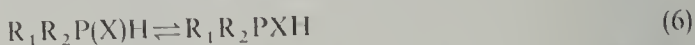




enantiomers were obtained with apparently good optical purity. There is good evidence that the reduction step proceeds with inversion in an $\text{S}_{\text{N}}2$ type of reaction. A cyclic secondary phosphine oxide, 6, has been prepared as part of a phosphasugar study¹¹. Its synthesis is shown in reaction 5. The stereochemistry at phosphorus was not assigned and some doubts have been cast on its homogeneity.

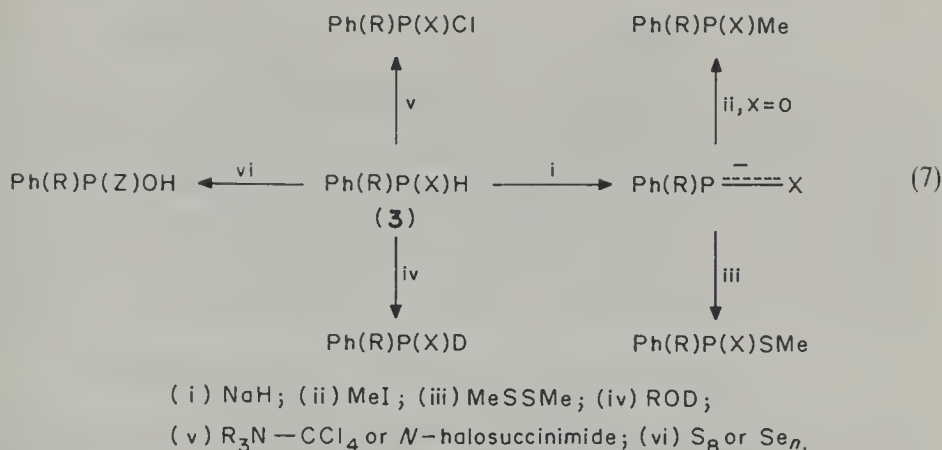
B. Reaction Stereochemistry

Like other classes of phosphorus compounds containing the structural feature P(X)H , secondary phosphine chalcogenides exist in a tautomeric equilibrium (equation 6); although, in general, evidence for the phosphorus(III) form is indirect and little is known



of the factors influencing the equilibrium. However, the small amount of chemical evidence available suggests that the conversion does not alter the stereochemistry. Thus, deuterium exchange is rapid even with the absence of a catalyst and produces no evidence of racemization. The same behaviour has been observed¹² with isopropyl methylphosphinate, MeP(O)(H)OPr^i . Similarly, deprotonation of 3 ($\text{R} = t\text{-Bu}$) does not afford a racemic product although this is reported for base treatment of 3 ($\text{R} = \text{PhCH}_2$). Both 3 ($\text{R} = t\text{-Bu}$) and 5 may be converted to the corresponding halides or thiomethyl compounds with retention of stereochemistry and 3 ($\text{R} = t\text{-Bu}$) reacts with sulphur or selenium also with retention. Equation 7 summarizes the known transformations, all of which proceed with retention of configuration.

Conditions for racemization are unclear. Emnick and Letsinger⁷ reported that both acids and bases racemized 1 ($\text{R} = \text{PhCH}_2$), although the related isopropyl methylphosphinate is stable to acids and not to bases¹². Since tertiary phosphine oxides are stable to alkali and the secondary phosphine chalcogen anions retain their stereochemistry, base-catalysed inversion seems unlikely. Acids, however, do isomerize tertiary phosphine oxides, presumably via a phosphorus(v) intermediate, and this type of reaction seems more likely for the secondary analogues also, although it does not appear to have been reported, except indirectly in the preparations of 3 ($\text{R} = \text{PhCH}_2$) or



2-naphthyl). The stereochemistry of the reversible addition of ethylphenylphosphine oxide to carbonyl compounds has been described¹³, but otherwise the use of secondary phosphine chalcogenides in synthesis has been little studied.

III. TERTIARY PHOSPHINE CHALCOGENIDES, $\text{R}^1\text{R}^2\text{R}^3\text{P(X)}$ ($\text{X} = \text{O}, \text{S}, \text{Se}$)

A. Structure

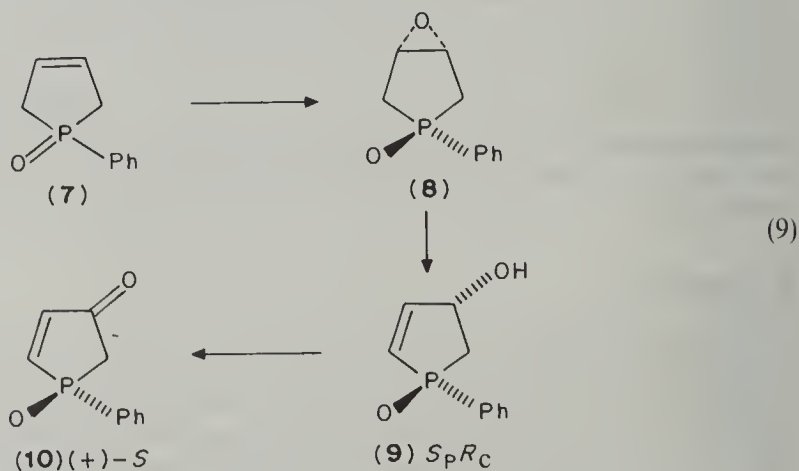
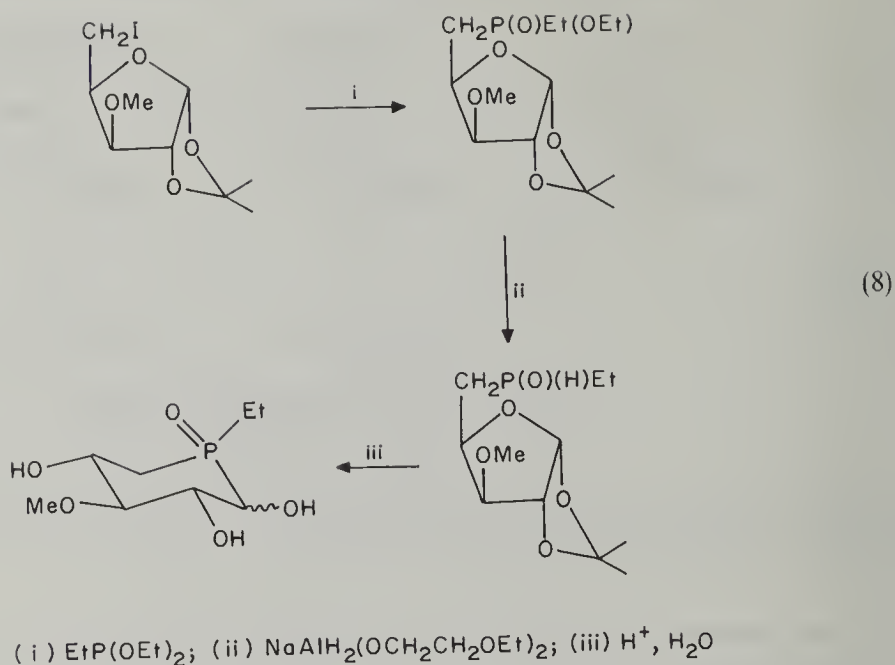
Because of their chemical stability and the fact that they are usually crystalline solids, this class of organophosphorus compounds has received much stereochemical attention. There is a wealth of structural data available, both in the solid state (in 1990 the Cambridge Crystallographic Data Base contained more than 250 structures of tertiary phosphine chalcogenides) and in solution, for oxides, sulphides and selenides, but very little for tellurides. Cyclic and acyclic compounds are well represented. Solid-state structures show a tetrahedral geometry at phosphorus with the XPC angle greater than for a regular tetrahedron, possibly owing to a repulsive interaction between the $\text{P}=\text{X}$ and $\text{P}-\text{C}$ bonds.

B. Preparation

1. Cyclic compounds

Although stereoisomerism arising from cyclic phosphine chalcogenides was not reported until the early 1960s¹⁴, it rapidly became commonplace and *cis-trans* isomers have been observed and characterized for oxides and sulphides of cyclic phosphines of virtually every ring size that has been studied¹⁵. Nowadays failure to observe this type of stereoisomerism in cyclic systems would require comment. The preparative heterocyclic chemistry of tertiary phosphine chalcogenides is very extensive and cannot be surveyed here. A good book¹⁵ is available and cyclic phosphines have been reviewed in Volume 1 of this work¹⁶. In general, oxidation or sulphuration of cyclic phosphines affords the corresponding chalcogenides in a stereospecific manner with retention and with the number and ratio of isomers formed being the same as are present due to the pyramidal phosphine. The diastereoisomers are usually readily separated by normal techniques. Many X-ray structures have been determined¹⁵.

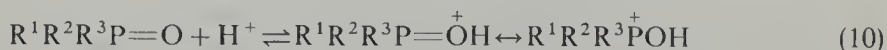
Chiral cyclic phosphine oxides are rare, the major examples being phosphinoyl sugars, which have been studied largely by Inokawa and coworkers¹⁷. Several X-ray structures of these have been determined¹⁸ and, since, the absolute stereochemistry of



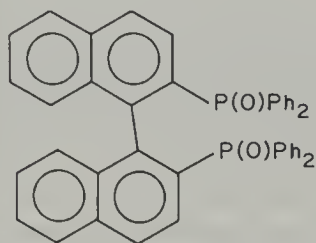
the carbocyclic portion of the ring is known, these constitute determinations of absolute stereochemistry at phosphorus, independent of correlation. Equation 8 shows one such route to this class of compounds. Another chiral cyclic phosphine oxide, 3-oxo-1-phenyl-2-phospholene-1-oxide **10**, was obtained by Bodalski and coworkers¹⁹ from the readily accessible 1-phenyl-3-phospholene-1-oxide (**7**) (reaction 9). Stereospecific epoxidation followed by base-catalysed rearrangement gave the (\pm) -alcohol **9** which was resolved using camphanyl chloride to give the (+)-isomer, whose absolute configuration was determined by X-ray diffraction as $S_P R_C$. Oxidation afforded the chiral ketone, **10**, stable under the reaction conditions and hence probably of high optical purity.

2. Acyclic compounds

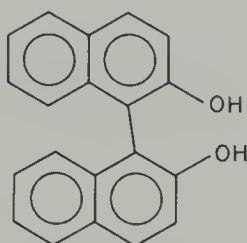
a. Resolution methods. Chiral phosphine oxides were first obtained by resolution using (+)-bromocamphorsulphonic acid^{1,2}, a method relying on protonation of the phosphoryl oxygen and separation of the salts by recrystallization. Tartaric acids and their derivatives have also been used²⁰. The method can be, and usually is, extremely tedious and very laborious, but in Meisenheimer's hands it yielded ethylmethylphenyl- and benzylmethylphenyl-phosphine oxides of good optical purity. Part of the difficulty is that phosphine oxides are not very basic and the position of the equilibrium (equation 10) under normal circumstances would lie predominantly on the phosphine



oxide side. Nevertheless, the method is occasionally useful and has been used by Nyori and coworkers²¹ for the resolution of 2,2'-bis(diphenylphosphino)-1,1'-dinaphthyl (**11**). The related compound, (+)- or (-)-2,2'-dihydroxy-1,1'-dinaphthyl (**12**), has been successful in the resolution of phosphine oxides by diastereoisomeric complex formation²². Although simple and giving excellent yields and purity, the method appears extremely sensitive to spatial factors. Thus, it resolved EtMePhP(O) but not MePrPhP(O). Tartaric acid has also been used successfully in the resolution of phosphine oxides. Very high yields and virtually complete enantiomeric separations have been obtained chromatographically for phosphine oxides using a column with a bonded stationary phase of 3,5-(NO₂)₂C₆H₄CONHCHPhCONH(CH₂)₃^{23a}, with normal stationary phases on a cyclodextrin column^{23b} or using Pirkle's chiral stationary phase^{23c}. A range of organophosphorus compounds can be resolved on a column of optically active poly(trityl methacrylate)²⁴. In view of the present availability of very efficient chromatographic processes, the development of a range of columns would seem to be the most hopeful area for convenient resolutions in the future.



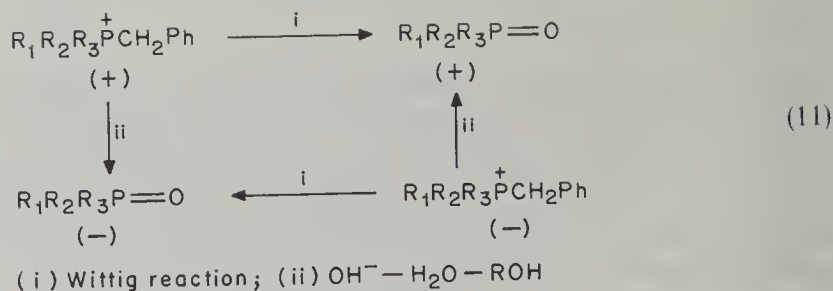
(11)



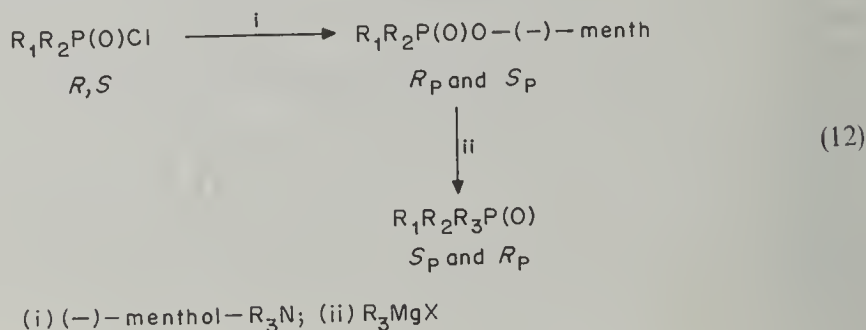
(12)

Although Davies and Mann³ resolved the phosphine sulphide **2** nearly 50 years ago, there has been no reported interest since then. Sulphides are much weaker protic bases than oxides and the acid-base approach will not be successful here. No resolution of a selenide has been described. The sulphur chalcogenides are commonly obtained by stereospecific synthesis from the phosphine²⁵ using a range of reagents; selenides are similarly prepared. Sulphides may also be prepared from the oxides with predominant (acyclic) or complete (cyclic) retention of configuration using B₂S₃ as a reagent²⁶.

b. Synthesis. McEwen and coworkers²⁷ resolved the first acyclic phosphonium salt (benzylethylmethylphenyl) using the dibenzoyl hydrogentartrate anion and converted



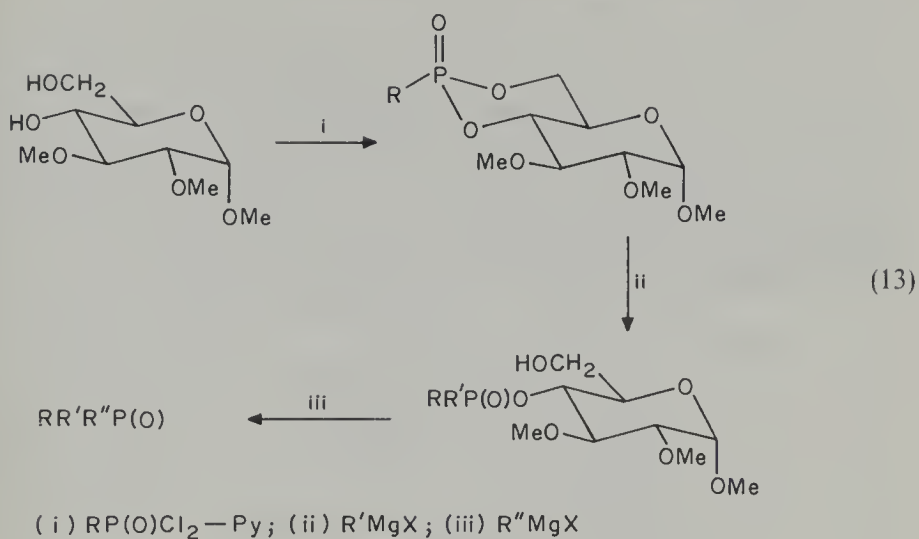
the enantiomeric salts into the corresponding oxides by either alkaline hydrolysis (inversion) or the Wittig olefination reaction (retention) (equation 11). As a general method this is restricted by the stereochemical complications which can arise in the alkaline hydrolyses of phosphonium salts²⁸, the fact that the benzyl group will not necessarily be the only group participating in the Wittig reaction and by difficulties in the preparation and resolution of the phosphonium salts.



Mislow and coworkers²⁹ separated the diastereoisomeric esters of phosphinic acids and $(-)$ -menthol, in itself a difficult and low-yielding process, and converted them into phosphine oxides by stereospecific Grignard reactions (equation 12). The reaction is believed to proceed with inversion since Hudson and Green³⁰ had earlier shown that transesterification of phosphinate proceeds with inversion. Until recently, this method was the most widely used, despite the practical difficulties. $(-)$ -Menthol is almost invariably the resolving agent, although cholesterol was briefly tried³¹. The use of organolithiums in place of Grignards does not produce any great improvement and often gives products of lower optical purity. If the chiral starting ester is a resolved cyclic phosphonate, then the reaction has the advantage that by altering the sequence of the two Grignard displacements enantiomeric phosphine oxides may be obtained from the same starting material³² e.g. by interchanging steps ii and iii in equation 13.

Inch and coworkers³² successfully used carbohydrate diols as the asymmetric unit (equation 13) and noted that the cyclic phosphonate was readily separated into its diastereoisomers, which is often not the case for acyclic phosphinates. Further, the assignment of absolute configuration to the starting phosphonate is more straightforward in view of the well established correlations in the carbohydrate field. However, the reaction suffers from the same disadvantages as the phosphinate method in terms of sluggish reactions and low yields.

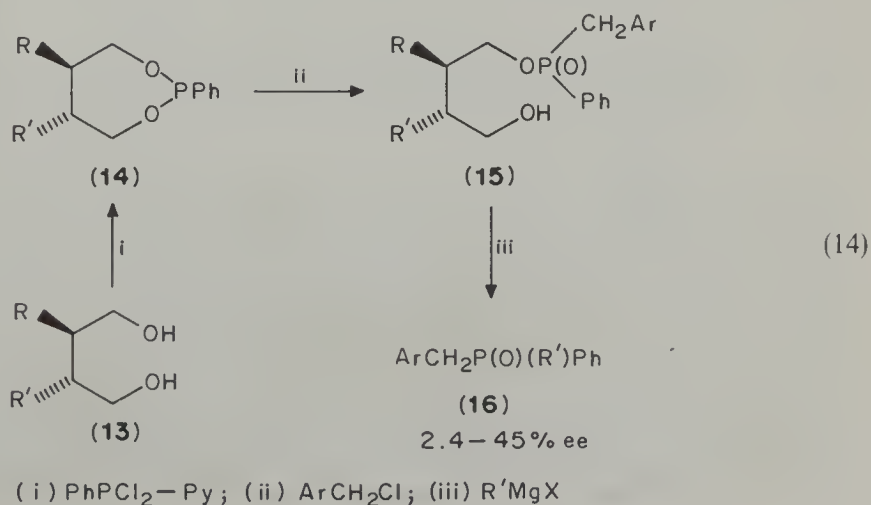
Some variations on this theme have appeared in recent years which seek to overcome some of the problems by using other stereospecific reactions. Kato and coworkers³³ began with the isomerically pure diol **13** and prepared the cyclic phosphonates (**14**),

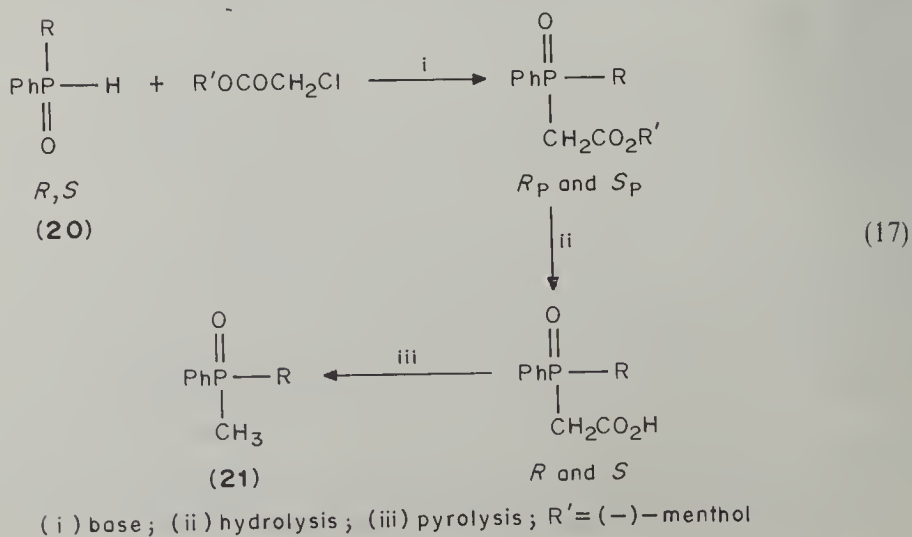
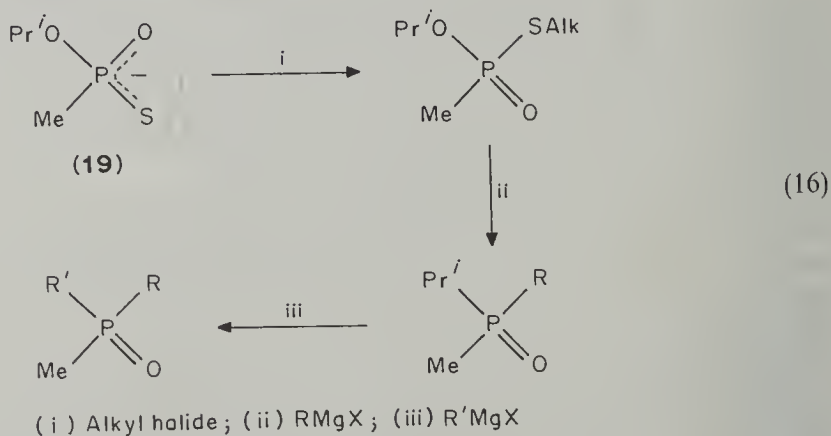
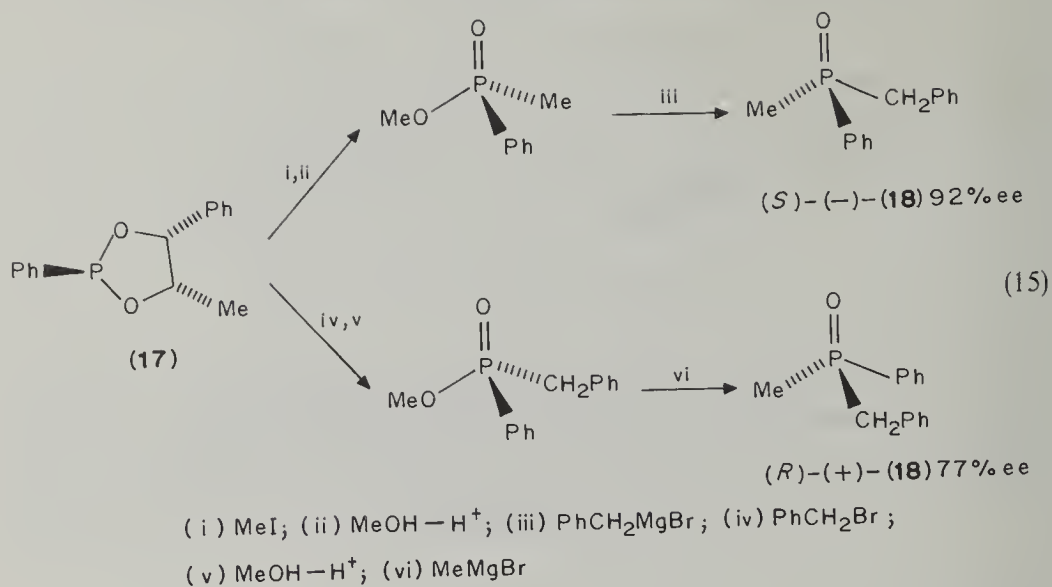


which underwent the Michaelis–Arbuzov reaction (retention) to give the benzyl phosphonate (**15**), which was then subjected to a Grignard reaction (reaction 14). However, the optical purities of the products were not high. Similarly, Juge and Genet³⁴ opened the ring of the readily accessible chiral 1,3,2-dioxaphospholan **17** by Arbuzov alkylation and, after transesterification, Grignard reaction gave the phosphine oxides (**18**) (reaction 15). By varying the order of addition of the substituents they obtained either enantiomer with good enantiomeric excesses.

A variation of this approach (reaction 16) utilizes the readily resolvable *O*-alkyl monoesters of alkylphosphonothioic acids (**19**). The stereochemical consequences here are less certain, particularly as displacement of the thio group may be sensitive to subtle variations of reaction conditions and structure³⁵; generally, however, displacement of a thiolate group at phosphorus proceeds with retention, not inversion as is the case for alkoxy groups.

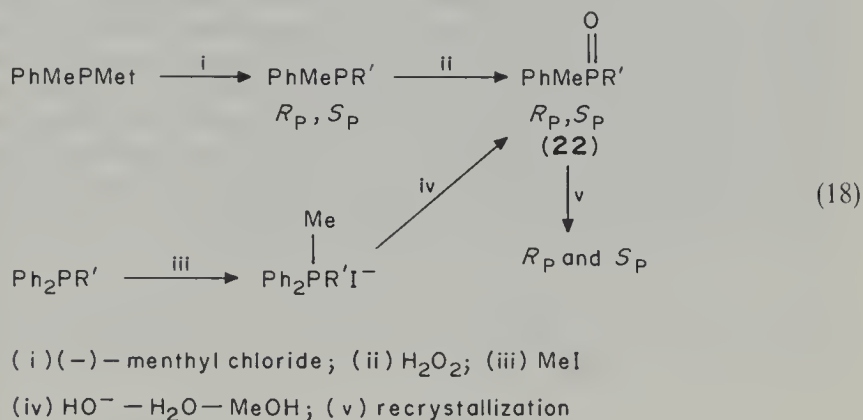
An alternative approach avoids the often vexatious Grignard reaction altogether (reaction 17). Alkylation of the secondary phosphine oxide (**29**) with (–)-menthyl chloroacetate, separation of the diastereoisomers, hydrolysis and decarboxylation afford



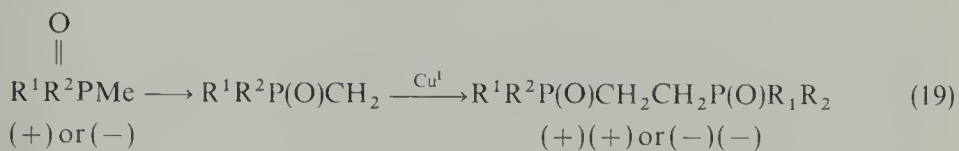


the chiral methyl oxides (**21**) with essentially 100% enantiomeric excess. Provided that the secondary phosphine oxide is available, this seems a general and useful route to a range of compounds of good chiral purity.

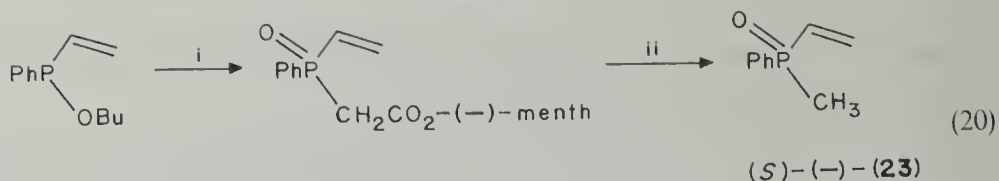
In an alternative approach, two groups have prepared diastereoisomeric phosphines by the reaction of alkali metal phosphides with optically active halides (reaction 18) followed by oxidation and separation of the mixtures^{36,37}. Elimination was a serious side reaction with the substitution procedure. A variant is to prepare the phosphines from diphenyl phosphide and then to quaternize and hydrolyse the salts with alkali³⁸. Crystal structures have established the absolute stereochemistry at phosphorus in the menthylmethylphenylphosphine oxides (**22**)^{37,38}.



All the foregoing syntheses involve a separation of diastereoisomers, and this is very often tedious, difficult and, worse still, unpredictable. An alternative approach is to start from a phosphine oxide already resolved and to elaborate it further using reactions which do not affect the stereochemistry at phosphorus. An initial step in this direction was taken by Mislow and coworkers³⁹, who showed first that deprotonation of carbon attached to chiral phosphorus left the stereochemistry there unaffected and used this reaction to prepare and oxidatively couple the anions to make chiral diphosphine dioxides (reaction 19). This reaction is important since it provides a route to chiral diphosphines⁴⁰, which are very valuable as chelating agents in homogeneous transition metal catalysis.



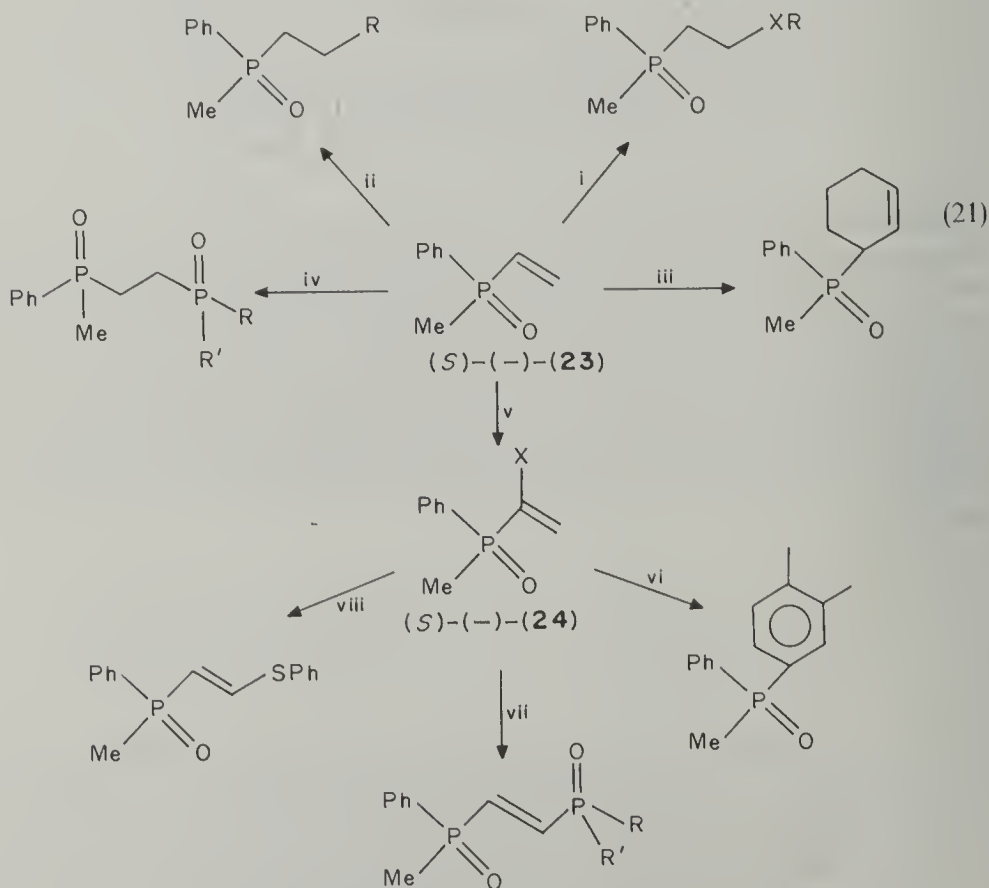
A much more flexible approach, however, has been developed recently by Pietrusiewicz and coworkers⁴¹. They have established a good preparative route (reaction 20) to (–)-(*S*)-methylphenylvinylphosphine oxide (**23**) of high optical purity. Unlike most other oxides, **23** contains a reactive site at which a great deal of chemistry can be carried out without affecting the stereochemistry at phosphorus. Vinyl phosphine oxides, particularly those unsubstituted at the β-carbon, are excellent Michael acceptors and **23** readily adds alcohols⁴², amines^{43,44}, alkyl groups^{45,46} (as the cuprates), thiols⁴² and secondary phosphine oxides⁴⁷. The alkene will undergo Diels–Alder⁴⁵ and related⁴⁸ cycloaddition reactions. By halogenation and dehydrohalogenation, **23** is converted to the α-halovinyl oxide (**24**), which will in turn undergo a number of addition–elimination



(i) $\text{ClCH}_2\text{CO}_2(-)-\text{menth}$; (ii) LiCl , H_2O , Me_2SO

reactions as well as cycloadditions⁴⁸; some of these transformations are summarized in equations 21. The addition of secondary phosphine oxides is of particular interest since it results in diastereoisomer formation if the secondary oxide is chiral and hence the effective resolution of another tertiary oxide. Similarly, the α -halovinylphosphine oxide **24** affords chiral *trans*-ethene-1,2-bisphosphine oxides⁴⁹. It is clear that this approach is versatile and flexible and represents the first systematic development of an active chemistry of this class of compounds as distinct from preparing examples.

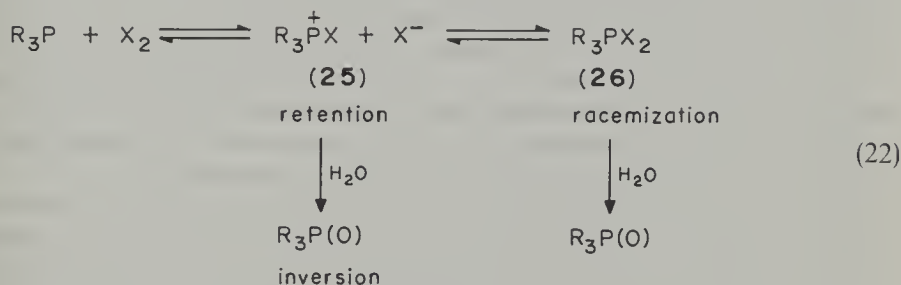
Much less work has been done with chiral sulphides and selenides. However, a method exists for converting oxides to sulphides stereoselectively with retention using boron



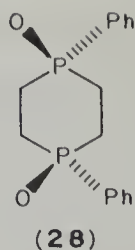
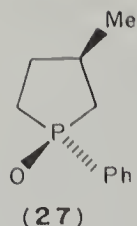
(i) RXH ; (ii) Bu_2CuLi ; (iii) $\text{CH}_2=\text{CHCH}=\text{CH}_2$; (iv) $\text{RR}'\text{P(O)H}$;
 (v) X_2 , base; (vi) 2,3-dimethylbutadiene; (vii) $\text{RR}'\text{P(O)H}$, base;
 (viii) RSH , base

sulphide, B_2S_3 ⁵⁰. The more commonly used phosphorus pentasulphide causes racemization⁵¹.

The simplest and most straightforward method of obtaining isomerically pure chalcogenides is to treat the corresponding phosphine with an oxidising agent or with sulphur or selenium reagents. These last two methods work well, the reaction proceeding cleanly and essentially stereospecifically with retention at phosphorus. A common method of determining stereoisomer distribution in mixtures of diastereoisomeric phosphines is to convert them to their sulphides, which are air stable and usually crystalline. Oxidation, however, is not so straightforward and stereochemical integrity can easily be lost. Stereochemical results can vary with the reagent⁵²⁻⁵⁵ and solvent^{52,53} and may depend on whether the phosphine is cyclic or not. Retention, inversion and racemization have all been observed in the formation of phosphine oxides from phosphines. In particular, any reaction proceeding via a phosphorane can lead to partial or complete racemization because of ligand reorganization in the intermediate. This process does not require a symmetrical intermediate and is normally very rapid at ambient temperature. Halogens⁵⁵, pseudo-halogens⁵⁵, 'positive' halogen compounds⁵¹ and mono- or dialkyl-peroxides⁵³ will, in general, give either racemization via a phosphorus(V) intermediate (26) or inversion [via displacement on an initially formed phosphorus(IV) intermediate (25)], depending on whether a nucleophilic solvent is absent or present. Polar solvents will usually favour polar intermediates such as 25 and hence are less likely to lead to loss of optical activity, although this can be brought about by a reversible S_N2 processes. Bistrimethylsilyl peroxide oxidizes phosphines to their oxides cleanly and with retention⁵⁶.



Perhaps the most general oxidant is aqueous hydrogen peroxide, which affords the oxide with retention and relatively few side-reactions^{54,57}. It is occasionally difficult, however, to separate unreacted peroxide from the product. Aerial oxidation, although sometimes very clean, can result in P—C bond cleavage and should be avoided. Polish workers have used an unusual class of reagents, the selenoxides, $RR'SeO$, which convert phosphines, their sulphides or their selenides, into the corresponding oxides with variable stereochemical results⁵⁸. For Me_2SeO , the reaction proceeds with inversion for acyclic compounds and retention for cyclic compounds, but other selenoxides are less specific and the steric result may also vary with the solvent. Oxides may also be obtained from the other chalcogenides by oxidation, but the stereochemical results are not promising. For example, N_2O_4 , a reagent widely used for oxidizing phosphites to phosphates, converts sulphides to oxides with overall retention but partial racemization⁵⁹. This reagent will even induce racemization in phosphine oxides, e.g., 27, and hence its value as an oxidant in stereochemical work is dubious. Other oxidants, e.g. $KMnO_4$, do not look much more promising, retention with partial racemization being the general rule^{54a}. These results presumably reflect the formation of pentacovalent species from the chalcogenide and oxidant with the degree of racemization being a function of the lifetime of the intermediate. Enantiospecific oxidation of phosphenes has been reported to be unsuccessful³⁶.



In general, claims in the literature for oxidation with complete retention or inversion should be treated with caution since, though this may well be the case in the quoted examples, it would be unwise to assume that the statement is generally true.

C. Determination of Stereochemistry

1. Cyclic compounds

This is a large field and a great deal of principally spectroscopic work has been done to elucidate diastereoisomerism and conformation. Much of this relates to oxa-, thia- or aza-heterocycles and is outside the scope of this chapter. Rings which are carbocyclic, except for the phosphorus atom, are less amenable to ^1H NMR for reasons of spectral complexity^{60b}. Lanthanide shift reagents can sometimes simplify the spectra sufficiently for them to be useful, although several instances are known of conformational equilibria being disturbed by the reagent. Lanthanides complex at the phosphoryl oxygen even when alternatives sites, such as carbonyl, are available. These reagents have been used successfully for rigid systems such as phosphetane oxides⁶¹ or bicyclic oxides^{62,63}. Sulphur and selenium complex poorly with lanthanides, making the shift reagents of little use in stereochemical assignments for these chalcogenides.

The principal spectroscopic tool is ^{13}C NMR, for which well established Karplus-type angular dependencies, $^nJ_{\text{PC}} (n = 1, 2 \text{ and } 3)$ are available^{15,60a}. Such relationships do not, however, establish the geometry at phosphorus and for this reliance must be placed on chemical shift trends and X-ray analysis. However, for those cyclic oxides where the proton spectra are resolved, $^2J_{\text{PCH}}$ is related to the dihedral angle OPCH with the *anti* orientation having a smaller magnitude than the *gauche* orientation¹⁷. This appears to be reliable since, although relatively few examples have been reported, they are mainly from the well established carbohydrate field. The range of values for $^2J_{\text{PCH}}$ is considerable and it would be unwise to make an assignment without having both isomers at hand.

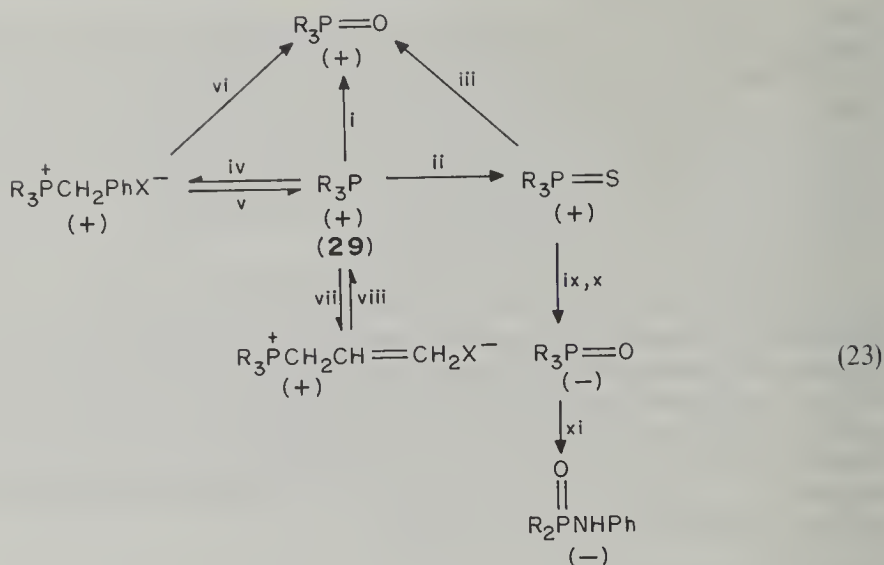
Since the steric (or volume) requirements of oxygen, sulphur, and selenium at phosphorus are not large and since the increased length of the phosphorus—carbon bonds (compared with carbon—carbon bonds) diminishes non-bonded interactions further, influences on the carbon chemical shift are usually related to the orientation of the exocyclic carbon substituent at phosphorus. In general, the carbon substituent on phosphorus of the more crowded isomer (usually the axial substituent in phosphinanes) absorbs upfield of its less crowded partner. This effect is independent of ring size, although the magnitude may vary considerably and would be expected to diminish in large rings. No consistent variation is observed in $^1J_{\text{PC}}$ for axial or equatorial disposition of the substituent. There is no useful correlation between ring geometry and phosphorus chemical shift, although in restricted classes of compounds a correlation may be observed. There are differences in both chemical shifts and coupling constants for axial and equatorial selenium^{60c} and the developing field of ^{17}O spectroscopy appears very promising, since both chemical shift and $^1J_{\text{P}^{17}\text{O}}$ seems very sensitive to geometry^{60d}.

Dipole moments have also been used, particularly for rings with more than one phosphinyl group, and the technique is one of the few methods available for isomer determination in large rings⁶⁴. Generally, conformational bias in phosphorus heterocycles is considerably less than is found in their carbocyclic analogues, presumably because of the increased bond lengths to phosphorus in comparison with the same distances to carbon. These resulting small energy differences are reflected in at least one instance¹⁵ of both conformers being found in the same crystal and in conformational preferences in solution varying with solvent.

In phosphinane chalcogens the chalcogen atom will normally occupy the axial position^{15,65} unless steric factors elsewhere on the ring dictate otherwise. Strongly electronegative groups on phosphorus may alter this preference. There is no reason to suppose that the rings do not undergo rapid flipping, however, the *cis*-diphosphinane **28** shows only a single absorption in its ³¹P NMR spectrum⁶⁶ and, in general, separate peaks for conformers are only seen at low temperatures. Absolute configurations at phosphorus have been assigned in the phosphasugar series and substantiated by X-ray structures^{17,18}. The only other example is compound **10**, whose configuration was also established by X-ray techniques¹⁹.

2. Acyclic compounds

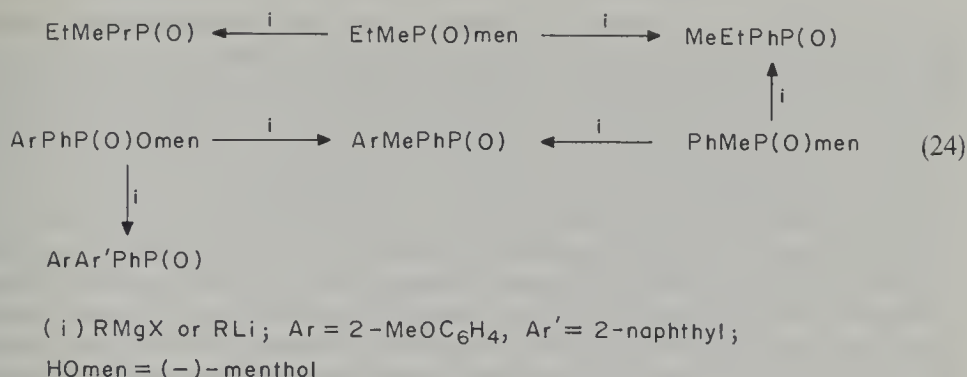
The initial steps in this field were taken by McEwen and coworkers²⁷, who first resolved an acyclic phosphonium salt and, with both enantiomers available, were able to construct the simple cycle (equation 11) which established that alkaline hydrolysis and the Wittig reaction proceeded with opposite stereochemistries. Since it was very likely that the Wittig olefination proceeded with retention, they suggested that alkaline hydrolysis went with inversion. Shortly thereafter, Horner and coworkers⁵⁴ established the basic principles on which assignments of the steric consequence of reaction now depend, using resolved tertiary phosphines as the starting point. Benzylation of a phosphine and its regeneration by electrolytic cleavage proceed without affecting the stereochemistry at phosphorus; similarly, allylation of a phosphine and its regeneration by removing the allyl group with cyanide ion leave the configuration at phosphorus unaffected. Since the latter reaction, in particular, proceeds by reaction remote from phosphorus, it is overwhelmingly probable that alkylation proceeds with retention. Oxidation and sulphuration are similar to alkylation in involving the lone pair on phosphorus, and it follows that they too should proceed with retention; hence the steric course of alkaline hydrolysis and the Wittig reaction of phosphonium salts are as proposed by McEwen and coworkers. Sulphides may be converted to oxides with inversion by alkylation at sulphur, which necessarily proceeds with retention at phosphorus, followed by hydrolysis, hence addition of sulphur to a phosphine proceeds with retention as expected. Benzylmethylphenylphosphine oxide undergoes a Wittig–Horner reaction with benzaldehyde-*N*-phenylimine to give *N*-phenylmethylphenylphosphinamide, whose optical rotatory dispersion curve had the same sign as the starting oxide, thus lending strong support to the notion that the Wittig reaction proceeds with retention. Most Wittig reactions are now believed to proceed via a phosphorane and should theoretically be capable of stereomutation at phosphorus; such a process might result in racemization, but it is difficult to see the net steric result being inversion. These reactions and a number of others shown in equations 23 (largely due to Horner and coworkers) are used to establish the stereochemistry of phosphine chalcogenides in general. It would be unwise, however, to assume that these reactions always apply, and there are many instances of reversal of the expected results. Thus the stereochemical consequence of the alkaline hydrolysis of a phosphonium salt is sensitive to the nature of the leaving group, and the size and nature of the substituents^{28,67–69}. Small or strained rings may give



- (i) H_2O_2 ; (ii) S_8 ; (iii) KMnO_4 -Py; (iv) PhCH_2X ;
 (v) cathodic reduction; (vii) Wittig, (viii) $\text{CH}_2=\text{CHCH}_2\text{X}$;
 (viii) CN^- ; (ix) MeI ; (x) aq. OH^- ; (xi) Wittig

unexpected results; phosphetanes, for example, react predominantly with retention at phosphorus⁷⁰ and the 7-phosphanorbornene system undergoes a range of reactions unprecedented in less strained or acyclic systems⁷¹. The stereochemistry of none of these pathways can be assumed on the basis of results with unrelated systems.

The ability to determine absolute stereochemistry spectroscopically would be very desirable but has attracted relatively little attention. Small chemical shift differences have been observed for enantiomeric phosphine oxides in both ^{31}P and ^1H NMR spectra when they are in the presence of a chiral solvent; thus Mislow and coworkers⁶⁸ used (+)-1-phenyl-2,2,2-trifluoroethanol (Pirkle's reagent) to determine the optical purity of *tert*-butylmethylphenylphosphine oxide. The same group established the absolute configuration at phosphorus in the diastereoisomerically pure methyl phosphinates from their proton spectra⁷² and hence, by inference, the configurations of the phosphine oxides prepared from them by Grignard reaction²⁹. Pirkle and coworkers⁷³ found small differences (1.4–3.2 Hz at 100 MHz) in the chemical shift of the methyl group of the enantiomers of three phosphine oxides using (+)-1-phenyl-2,2,2-trifluoroethanol as cosolvent. With more modern higher field instruments, these differences will be amplified considerably. More recently, Moriyama and Bentrude³⁵ have shown that *tert*-butylphenylthiophosphinic acid gives better separation (3.0–10.6 Hz at 90 MHz) of enantiomeric groups in the proton NMR and suggest it may be generally useful for this purpose. Two groups have used chiral shift reagents, (*R*)-(-)-*N*-3,5-dinitrobenzyl-1-phenylethylamine and (+)- or (-)-1-phenylethylamino-3,5-dinitrobenzamide, to determine stereochemical purity by proton NMR on the basis of chemical shift differences, usually of a methyl group^{74,75}. These differences are not large, however, typically only 0.01–0.02 ppm. It might be expected that ^{31}P NMR differences would be greater and, although they have been observed⁷⁶ with lanthanide shift reagents, no stereochemical use of them has been described, possibly because of difficulties in quantifying the peak heights.

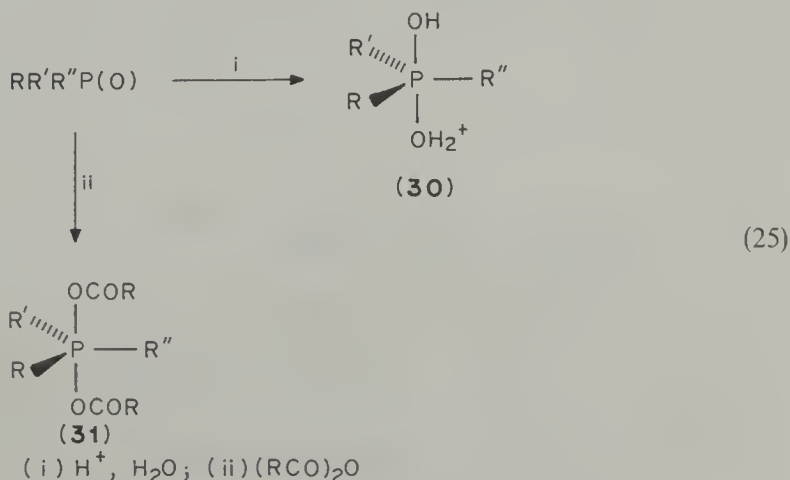


Other physical methods have not been much used, although diarylmethylphosphine oxides have been correlated with sulfoxides by circular dichroism. The method is limited by the need for an appropriate chromophore⁷⁷. Chemical methods of configurational correlation are uncommon, largely as a consequence of the limited chemistry that has been studied for groups attached to phosphorus. Conversion of methylphenylvinylphosphine oxide to ethylmethylphenylphosphine oxide by hydrogenation is one example⁴¹. By utilizing relay compounds, Lewis and Mislow⁷⁸ ingeniously correlated trialkyl- and triaryl-phosphine oxides (equation 24). Conformational analysis of acyclic compounds has received a reasonable amount of attention primarily for phosphine oxides. Normal methods for study are dipole moment variation and proton NMR spectroscopy. The subject has been reviewed⁷⁹.

D. Reaction Stereochemistry

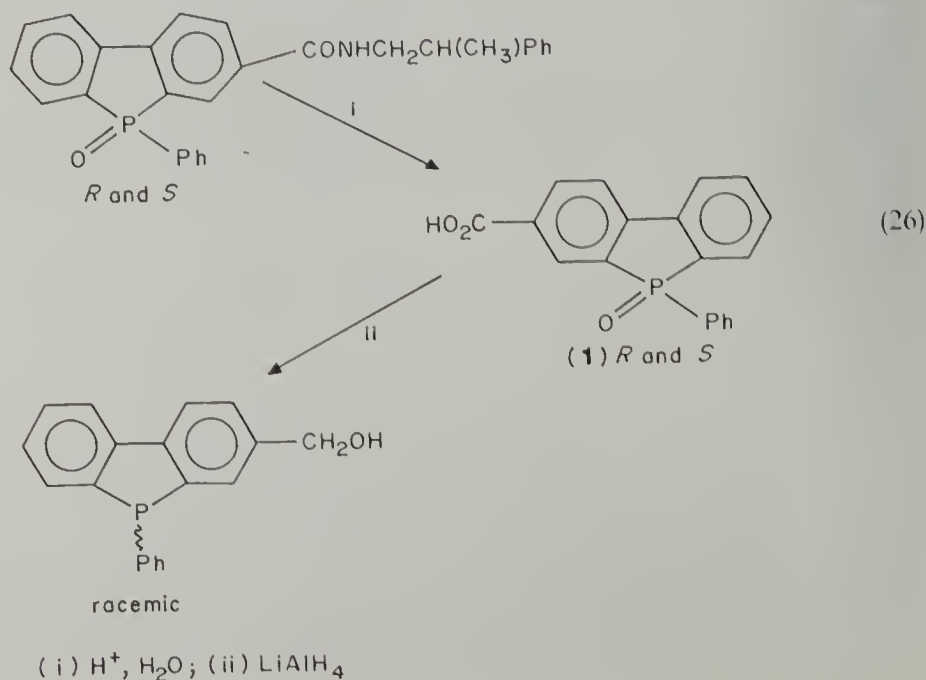
1. Oxides

The phosphoryl group is normally regarded as being particularly stable and its formation is believed to constitute a strong driving force for a reaction. In fact, its dissociation energy does not differ all that greatly from that of a carbonyl group and its apparent lack of reactivity seems more a reflection of its reduced polarity, generally attributed to backbonding between oxygen and phosphorus, than any inherent great stability. The oxygen is sufficiently basic to allow its protonation with reasonably strong acids which, if they are chiral, will allow resolution. Whether a hydroxy phosphonium



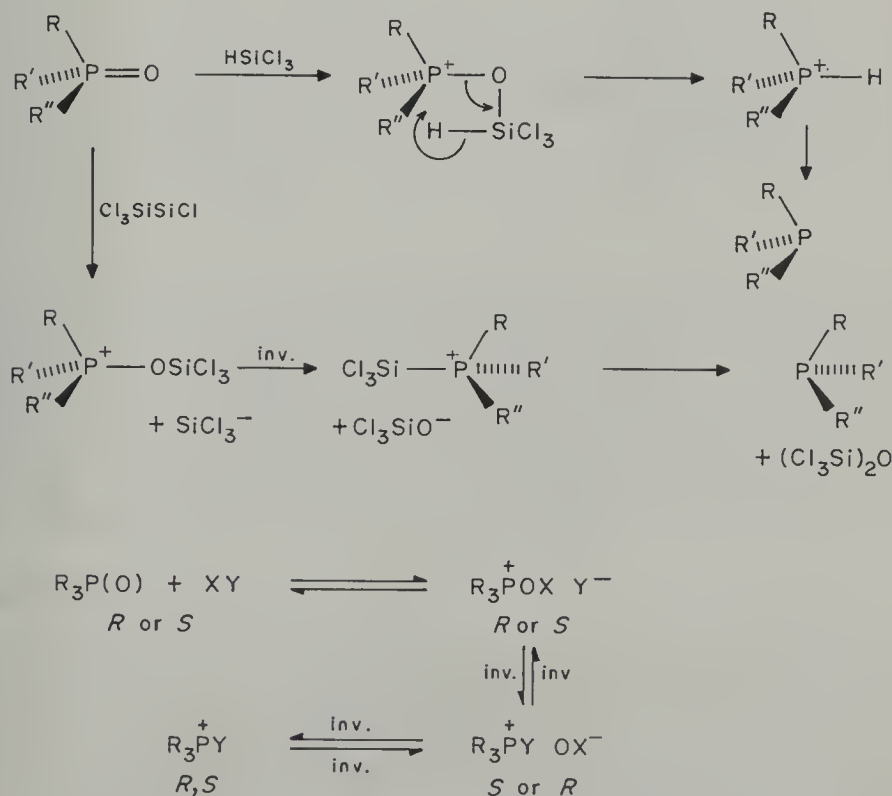
salt exists under these conditions or a strongly hydrogen-bonded complex is not known. With sufficiently powerful alkylating agents, usually trialkyloxonium salts, alkoxyphosphonium salts are formed with, of course, retention of configuration at phosphorus⁸⁰. These salts, like their sulphur analogues, undergo alkaline hydrolysis with complete inversion of configuration; attack at carbon does not seem to occur and has been excluded by isotopic experiments. Under vigorous acid conditions such as refluxing aqueous hydrochloric acid, racemization at phosphorus in phosphine oxides occurs, accompanied by ^{18}O exchange^{81,82}. This suggests the formation of a pentacovalent species **30**, which is essentially symmetrical under aqueous conditions. A similar result is obtained by heating the phosphine oxide with a carboxylic acid anhydride to give, presumably, the diacycloxyphosphorane **31**. However, a symmetrical intermediate is not essential for racemization of a pentacovalent species as ligand reorganization can produce inversion without bond breaking, as is evidenced by obtaining the same result with hydrogen chloride in dry dioxane⁸². Racemization may also be brought about by N_2O_4 ⁵⁹, a reaction whose mechanism is not obvious but which presumably also involves reversible formation of a phosphorane.

Stereoisomerism also occurs with Lewis acids, e.g. phosphine oxides are racemized by lithium aluminium hydride⁹, presumably via reversible formation of a phosphorus(V) species. This accounts for the failure of Campbell and Way²⁶ to reduce their resolved phosphine oxide (equation 26) to an optically active phosphine and the general failure of this reducing agent to give stereospecific reduction of phosphine oxides. However, like most reactions of phosphorus compounds, stereochemical generalizations are difficult to maintain. Thus, the resolution of **1** involved the preparation and separation by crystallization of the diastereoisomeric amides of the acid with (–)-phenylethylamine. The enantiomers were regenerated by vigorous acid hydrolysis, which appears to have had no effect on the optical purity since both enantiomers were obtained with equal and opposite rotations²⁶. Further, phosphine oxides with *tert*-butyl substituents have been reduced by lithium aluminium hydride with overall retention⁸³. These reactions



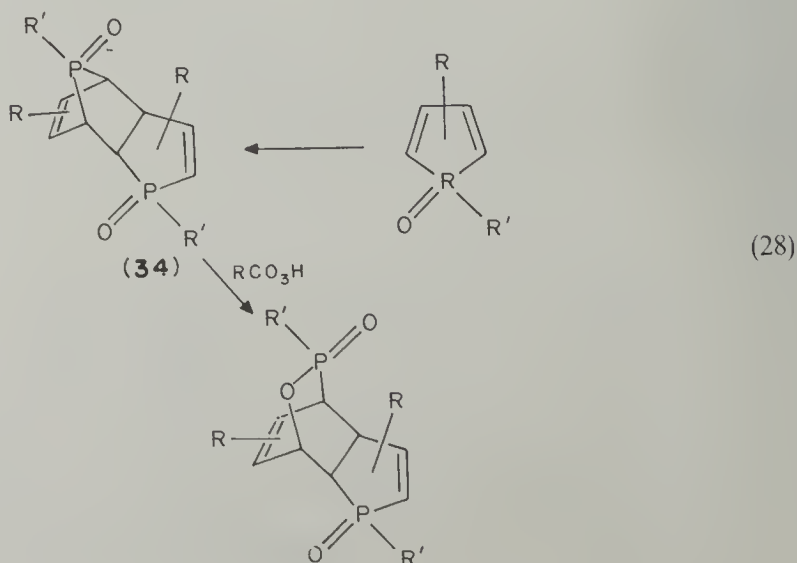
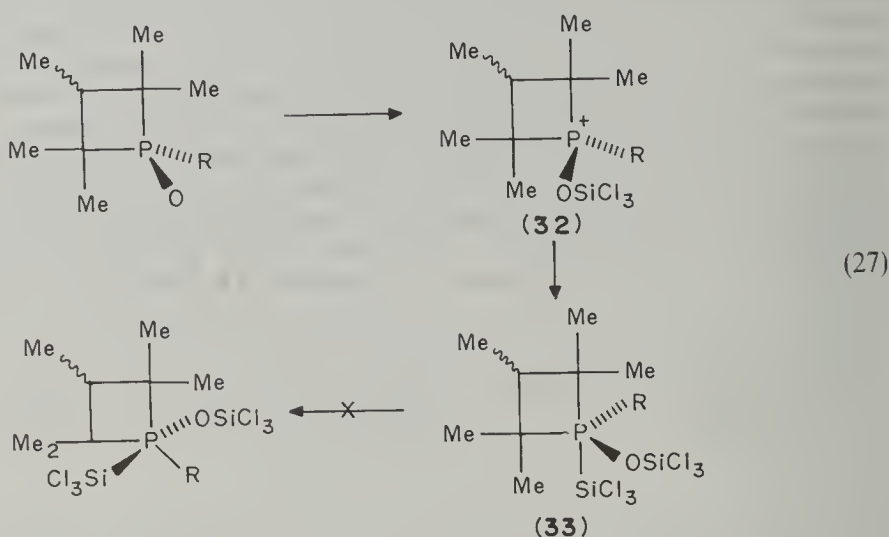
suggest that the racemization process may be subject to both ring and substituent effects. The combination of lithium aluminium hydride and cerium(III) chloride reduces phosphine oxides readily but non-stereoselectively⁸⁴.

Reduction of phosphine oxides proceeds fairly readily with a variety of silanes containing a silicon—hydrogen bond under mild conditions unlikely to produce thermal epimerization of the product phosphine. The inexpensive and readily available trichlorosilane converts phosphine oxides to phosphines with different stereochemical consequences, depending on the presence or absence of amines in the reaction mixture⁸⁵. In the absence of an amine the reaction proceeds with predominant retention, as it does also in the presence of pyridine; in the presence of triethylamine, inversion is observed. It was soon realized⁸⁶ that the steric result was affected by the base strength of the amine used and that with strong bases reduction was being brought about by decomposition products of the trichlorosilane. This observation led to the introduction of hexachlorodisilane as a reducing agent⁸⁶ and this was found to reduce phosphine oxides to phosphines of good optical purity with inversion at phosphorus. Experimental conditions are critical with hexachlorodisilane, however, since extended reaction times beyond that necessary for reduction may result in extensive racemization of the product phosphine. Some racemization of the phosphine oxide may occur; both processes may result from the reversible formation of pentacovalent phosphorus species or alternatively via reversible substitutions on an intermediate phosphonium salt. The latter proposal is supported by the fact that phosphine oxides may be racemized by silicon tetrachloride, acetyl chloride, or phosphorus trichloride when the solvent acetonitrile is used, which should favour polar intermediates. Suggested mechanisms for silane reductions and racemizations are outlined in Scheme 1. Other silanes, such as phenyl- or diphenyl-silane,

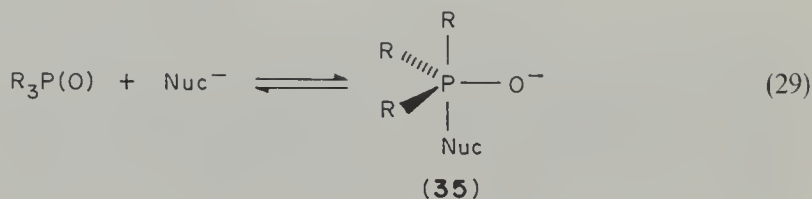


SCHEME 1

are also commonly used and, as would be expected from the initial studies on trichlorosilane, these reductions also proceed with retention. All silane reductions are frequently non-stereospecific and varying degrees of racemization are observed. It seems that a general principle where maximum stereoselectivity is important is to minimize exposure of the product phosphine to the reducing agents and their oxidation products. Phosphetane oxides are reduced with retention, regardless of the silane used, reflecting the constraints imposed by the four-membered ring on the intermediates. Initial reaction of a phosphetane oxide will give a phosphonium cation (32), particularly susceptible to further attack to give a phosphorane (33) because of the relief of the severe angular distortion at phosphorus (ca 20° from tetrahedral) in the four-membered ring when it is incorporated into trigonal bipyramidal geometry. Permutational isomerisation of such an intermediate is blocked by the inability of the four-membered ring to lie in the equatorial plane, since the four-membered ring could not accommodate a 120° angle at



phosphorus (equation 27). Similarly, phosphetane oxides alkylated at oxygen undergo hydrolysis with retention rather than inversion and this has been shown by isotopic techniques to proceed via attack at phosphorus⁸⁷. This type of behaviour is common with phosphetanes and reflects a generally increased reactivity of the phosphoryl group as a consequence of ring strain. All phosphetane oxides currently available have their reactivity masked by heavy substitution on the ring, a consequence of the limited methods of preparation available, and a simpler, less crowded system, should display a diverse and interesting chemistry. The bicyclic phosphine oxides, e.g. **34** (equation 28), readily available by either dimerization or Diels–Alder cycloaddition of intermediate phosphole oxides, possess a severely strained bridging phosphorus which exhibits a remarkable range of reactions many of which are often unprecedented, and usually unexpected, on the basis of less strained derivatives⁷¹. Angular distortion in these structures is of the same order as in phosphetanes, i.e. about 20° from the tetrahedral. Attempted oxidation of the double bond in the ring resulted in oxygen insertion in to the P—C bond⁸⁸, a reaction analogous to the Bayer–Villiger reaction, which is general for strained bicyclic systems⁷¹ and also occurs with phosphetanes⁸⁹. The phosphorus may be epimerized by the action of water or amines, a reaction in striking contrast to the otherwise inert behaviour of the phosphoryl group towards nucleophiles in unstrained systems. For example, prolonged refluxing with aqueous alkali or alcoholic alkoxides does not affect the stereochemistry at phosphorus⁸² in acyclic systems. It does not follow, however, that nucleophilic attack has not occurred under those conditions, since in the expected intermediate (**35**, equation 29) the oxygen ligand may be effectively locked in the radial plane of the pentacovalent species.



Apart from the foregoing, relatively few reactions of the phosphoryl group are known whose stereochemical consequences have been examined. Allylic optically active phosphine oxides are thermally stable, unlike the sulphides, e.g. resolved allylmethylphenylphosphine oxide showed no loss of optical activity after 12 h at 200 °C⁹⁰. The phosphoryl group may be converted to thiophosphoryl, B₂S₃ giving retention and P₂S₅ racemization⁵¹; removal of proton from carbon adjacent to phosphorus does not affect the stereochemistry there³⁹. When a chiral phosphinoyl group migrates in a carbonium ion rearrangement, it does so with retention of configuration at phosphorus⁹¹.

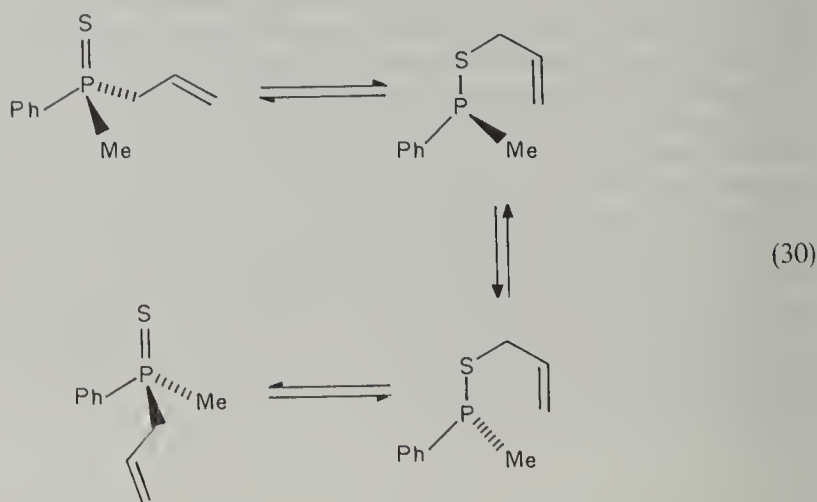
2. Sulphides and selenides

Little chemistry has been done with selenides and even less of stereochemical interest. Like sulphides, they are converted by selenoxides into phosphine oxides with a stereochemical result depending on the selenoxide and the reaction conditions⁵⁸.

Sulphides are much less basic towards protons than oxides, but since they are softer bases they alkylate more readily and alkaline hydrolysis of the resulting thioalkylphosphonium salts affords the oxides with inversion at phosphorus^{54a,79}. Reduction of sulphides with hexachlorodisilane proceeds, unexpectedly, with high retention of

stereochemistry at phosphorus⁷⁹, in marked contrast to the behaviour of oxides. The reason for this difference is obscure and, as in the case of phosphine oxide reduction, a clearer understanding is hampered by difficulties in identifying the silicon by-products. Once again, in contrast to phosphine oxides, optically active sulphides are reduced to the phosphine by lithium aluminium hydride with retention of configuration⁹².

Allylic phosphine sulphides may be racemized thermally, presumably via allylic rearrangement to a trivalent thiophosphinite which then undergoes thermal inversion⁹³ (equation 30). This is supported by the facts that the activation energy of the process is



similar to the activation energies for the thermal inversion of phosphines and also that allylic thiophosphinites are known to undergo thermal allylic rearrangement to the corresponding sulphides^{93,94}. Conversion of phosphine sulphides to oxides is brought about by a range of oxidizing agents and with variable stereochemical results, but usually overall retention is observed.

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CHAPTER 3

Electrochemistry of organophosphorus(V) compounds

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I. INTRODUCTION

The pivotal role played by electrochemistry in unravelling the chemistry of reactive phosphorus intermediates of organophosphorus(V) compounds is discussed in this chapter. These intermediates are either free radical anions or cations undergoing cleavage reactions or geometrical isomerizations or biochemical energy transductions. In several ways the cleavage reactions are similar to the phosphorus(III) compounds discussed in the earlier volume of this series¹; P—C bond cleavage is observed after adding one electron (1e) to the organophosphorus compound. By contrast, the P—O bond in phosphorus(V) compounds is remarkably stable and is useful in generating reactive species for initiating redox reactions. One example of this kind is the energy transduction in biochemical reactions occurring through the phosphate bond of adenosine triphosphate (ATP); the high-energy phosphate bond (ca 33 kJ mol⁻¹)² usefully converts the reduced or oxidized form of 1e transducing systems. Examples of transducing systems are pyruvate–acetate, CO₂; pyruvate CoA–acetyl CoA*, CO₂; α -ketoglutarate–succinate, CO₂; and acetaldehyde–acetate. The phosphate bond has the potential to increase the concentration of the unenergized form 10⁶-fold by changing the Nernstian voltage by 350 mV.

These results have led to the introduction of energy coupling schemes in biological chemistry³. An important transduction of the phosphate bond energy into redox energy is the ATP-dependent reduction by dihydronicotinamide adenine dinucleotide (DPNH) of 3-phosphoglycerate^{3,4} via 1,3-diphosphoglycerate to glyceraldehyde-3-phosphate. By this mechanism uphill reactions proceed at the expense of the high-energy phosphate bond of ATP. Consequently, there has been growing interest in the redox reactions of organophosphorus(V) compounds in the last two decades. This quest has led to the synthesis and characterization of phosphorus(V) liganded complexes using electrochemical techniques. Of greater importance is the chemistry of the geometrical isomerization of metal–phosphido complexes⁵.

The electrochemistry of diphosphonucleotides has evoked detailed investigations for more than a decade into understanding the reduction mechanisms of these compounds. Does the chemical or biochemical reduction occur through a hydride ion or an electron–proton–electron transfer scheme? This question led to analogues of phosphonucleotides being synthesized for electrochemical studies to obtain an answer.

The interfacial phenomena at the electrode/solution interface such as adsorption of organics, in general, and more specifically organophosphorus(V) compounds, has

generated an interest in understanding the geometry of these molecules in the adsorbed state in addition to the adsorption kinetics. Theoretical models proposed by Frumkin⁶, Langmuir⁷ and others⁸ have been tested by using the interfacial adsorption of phosphorus compounds.

This review discusses the mechanisms and reactivities of organophosphorus(V) compounds during and after the charge transfer at the electrode.

II. PHOSPHINE OXIDES

A. Triphenylphosphine Oxide: Ph_3PO

1. Polarographic characteristics

The electrochemistry of Ph_3PO is of interest in relation to Ph_3P for the mechanistic changes occurring in the valence transformation of phosphorus(III) to phosphorus(V)⁹⁻¹⁴. The polarographic characteristics have been examined in solvents such as *N,N*-dimethylformamide (DMF), acetonitrile (MeCN) and hexamethyl phosphoramide (HMPA); the two waves appearing for Ph_3PO in these solvents are identified as due to successive 1e additions occurring with $E_{1/2}^{\text{I}} = -2.51 \text{ V}$ and $E_{1/2}^{\text{II}} = -2.84 \text{ V}$ vs SCE. Figure 1 shows a typical polarogram of 1.32mM Ph_3PO . The wave nature defined by

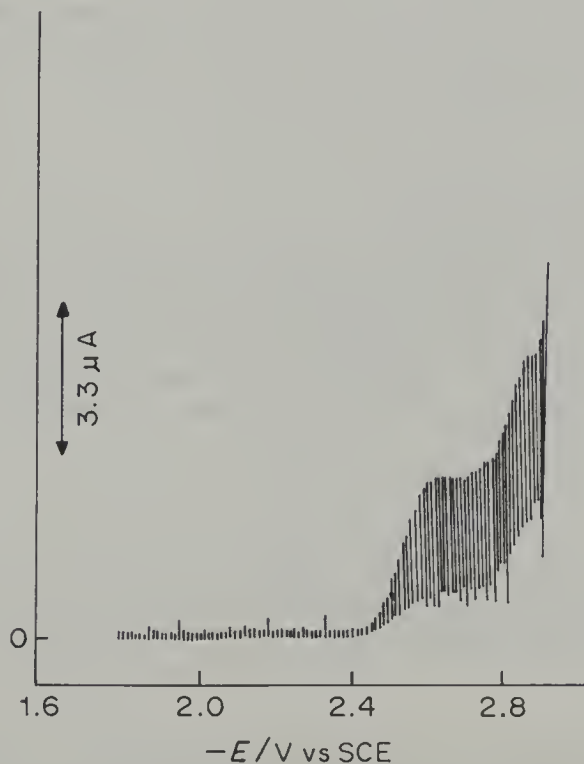


FIGURE 1. Polarogram of triphenylphosphine oxide from a solution containing 1.32 mM triphenylphosphine oxide and 0.1 M tetrabutylammonium iodide in DMF. Taken from ref. 11. Copyright (1968) American Chemical Society.

$E_{3/4} - E_{1/4}$ for the first wave has a value of 60 mV and for the second wave about 62 mV. The diffusion coefficient of $(\text{Ph}_3)_3\text{PO}$ is estimated to be $2.35 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in DMF. The polarographic wave of this compound is shifted in the positive direction with respect to Ph_3P , which shows $E_{1/2} = -2.70 \text{ V}$ vs SCE. Both the polarographic waves of Ph_3PO are diffusion controlled in the above solvents.

2. Cyclic voltammetric characteristics

Cyclic voltammetric experiments at a hanging mercury drop electrode (HMDE) also exhibit two cathodic peaks at $E_{\text{pc}}^{\text{I}} = -2.52 \text{ V}$ and $E_{\text{pc}}^{\text{II}} = -2.88 \text{ V}$, corresponding to two successive 1e transfers; the first peak is reversible, exhibiting a complementary anodic peak. The constancy of the current function of the first peak and the peak current ratio $i_{\text{pa}}/i_{\text{pc}} \approx 1.0$ suggests high stability of the radical anion and the absence of any prior reaction of Ph_3PO and DMF¹¹. However, at very low scan rates, below 0.067 V s^{-1} , the anion radical of Ph_3PO produced at -2.52 V undergoes a catalytic reaction¹³ in solvents such as MeCN and HMPA; the catalytic reaction is faster in MeCN. This catalytic reaction is attributed to the electrophilic attack by the solvent on the radical anion or impurities in the solvent. This interpretation is supported by the observation of the ESR spectrum of the free radical anion of Ph_3PO in DMF by Illyasov *et al.*¹⁴ with ^{31}P coupling to the protons of the ring. However, the radical anion decomposes during longer periods of storage.

The solvent-dependent feature of cyclic voltammetric behaviour was reported by Santhanam and Bard¹¹; in DMSO containing Bu_4NI two peaks at $E_{\text{pc}} = -2.44 \text{ V}$ and $E_{\text{pc}} = -2.51 \text{ V}$ were observed at a slower scan rate of 0.15 V s^{-1} . The two peaks merged into one broad peak at higher sweep rates. Both peaks are irreversible in nature. These peaks are shifted to negative potentials in DMF.

3. Controlled potential electrolysis

The long-term stability of the 1e reduction product of Ph_3PO has been investigated by controlled potential electrolysis^{11,13}. Exhaustive reduction in DMF at -2.60 V invariably resulted in a higher steady-state current than the background current electrolysis. The current-time decay features and cyclic voltammetric analysis after the electrolysis were indicative of a Ph_3PO radical anion reacting with the medium to regenerate Ph_3PO . Saveant and Binh¹³ proposed an electrophilic addition by the supporting electrolyte.

4. ESR features

The electrochemically generated Ph_3PO radical anion produces an ESR spectrum^{12,14} with fine structure arising from ^{31}P coupling with the ring protons. Chemical reduction using metallic potassium resulted in the radical anion spectrum of $\text{Ph}_3\text{PO}^- \text{K}^+$, with the spectrum containing potassium ion hyperfine splittings.

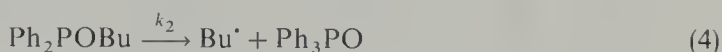
5. Redox reaction scheme

The first step in the electrochemical reduction of Ph_3PO produces the anion by reaction 1^{11,13}.



The radical anion reacts with the supporting electrolyte, Bu_4N^+ , as indicated by

reactions 2–4.



An alternative mechanism depicted by reactions 5–7 has also been proposed¹³.



The alkylation reactions in DMF and HMPA proceed with rate constants $k_1 = 0.14 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_1 = 0.05 \text{ mol}^{-1} \text{ s}^{-1}$ ¹³, suggesting that the alkylation reaction 3 is 20 times slower in HMPA. The cleavage of the P—C bond in reaction 3 is dependent on the dielectric constant; it appears to be facilitated by the alkylation reaction 2.

III. PHOSPHATES

A. Nitrophenyl Phosphates

1. Polarographic characteristics

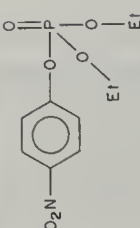
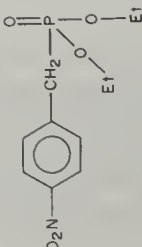
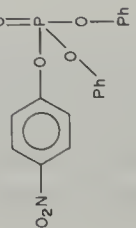
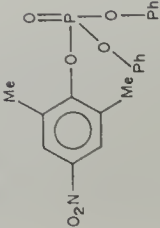
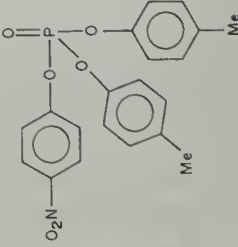
A large number of nitro-substituted phenyl phosphates have characteristic polarographic reductions^{15–17}. The characteristic constants are listed in Table 1. The diffusion current constant values indicate that these nitro compounds undergo 1e reductions with the exception of multi-nitro-substituted compounds. This class of compounds show multiple reductions as each nitro group is susceptible to reduction [see tris(*p*-nitrophenyl) phosphate], provided that geometrical considerations allow sufficient electron density for the electron transfer. The 1e reduction produces a stable radical anion of nitrophenyl phosphates; these behavioural patterns are comparable to those of the well studied nitrobenzenes^{18–24}.

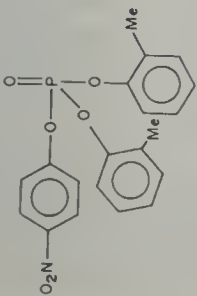
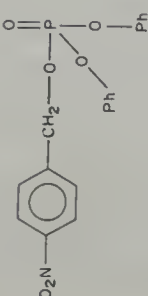
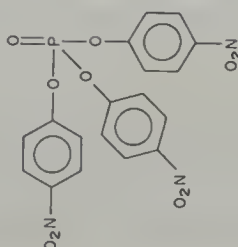
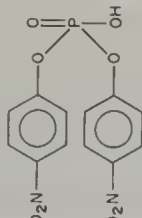
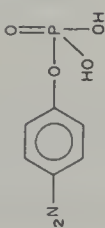
A general feature of nitro compounds is their affinity for adsorption on a mercury surface; this adsorption results in the appearance of polarographic pre-waves. In a few cases these waves have been identified and distinguished from the diffusion-limited waves. Thus *p*-nitrophenyl phosphate exhibits a well defined adsorption wave (see Table 2)^{25,26}. The $E_{1/2}$ of diphenyl-4-nitrobenzyl phosphate is shifted in the positive direction owing to its adsorption on mercury; this feature is also observed with tris(*p*-nitrophenyl) phosphate^{15,25}. The polarographic characteristics such as $E_{1/2}$ and $|E_{3/4} - E_{1/4}|$ are not significantly altered by the solvent; the values in MeCN and DMF are nearly the same¹⁵.

2. Cyclic voltammetric patterns

In-depth studies of nitro-substituted phosphates have been carried out using tris(*p*-nitrophenyl) phosphate, bis(*p*-nitrophenyl) phosphate and mono(*p*-nitrophenyl) phosphate as model compounds for the phosphates^{25,26}. Typical cyclic voltammetric curves of tris(*p*-nitrophenyl) phosphate and bis(*p*-nitrophenyl) phosphate are depicted in Figure 2. The five well defined peaks of tris(*p*-nitrophenyl) phosphate in the cyclic voltammogram are reduced to three for bis(*p*-nitrophenyl) phosphate. This difference

TABLE 1. Characteristic polarographic features of nitro-substituted phosphorus compounds in acetonitrile^a

Structure	Species	$-E_{1/2}$ (V)	$i_{d/c}$ ($\mu\text{A lmmol}^{-1}$)	$E_{3/4}-E_{1/4}$ (V)	I^b
	Diethyl-4-nitrophenyl phosphate	1.07	2.93	0.078	2.7
	Diethyl-4-nitrobenzyl phosphate	1.11	4.18	0.053	3.6
	Diphenyl-4-nitrophenyl phosphate	1.09	3.92	0.057	3.4
	Diphenyl-2,6-dimethyl-4-nitrophenyl phosphate	1.14	3.19	0.056	2.8
	Di(4-methylphenyl)-4-nitrophenyl phosphate	1.09	4.77	0.057	4.2

	Di(2-methylphenyl)-4-nitrophenyl phosphate	1.10	3.52	0.05	3.1
	Diphenyl-4-nitrobenzyl phosphate	0.086 1.211	4.64 3.81	0.071 0.068	4.0 3.3
	Tris(<i>p</i> -nitrophenyl) phosphate	0.83	—	0.080	3.5
	Bis(<i>p</i> -nitrophenyl) phosphate	0.94	0.80	—	—
	<i>p</i> -Nitrophenyl phosphate	1.28	0.080	—	—

^aTaken from refs 15–17. Potentials measured with respect to the saturated calomel electrode (SCE).

^b $I = \frac{i_d}{m^{2/3} t^{1/6} C}$, calculated from i_d/C values.

i_d = diffusion current, m = mass of mercury drop, t = seconds, C = concentration.

TABLE 2. Relative changes in the polarographic reduction of tris(*p*-nitrophenyl)phosphate^a

Height of mercury column (cm)	Wave I, $i_{d/h}$ ($\mu\text{A cm}^{-1}$)	Wave II, $i_{d/h}^{1/2}$ ($\mu\text{A cm}^{-1/2}$)
110.9	0.0139	0.86
100.9	0.0139	0.87
90.9	0.0137	0.83
70.9	0.0127	0.92

^aMedium: DMF containing 1.47 mM tris(*p*-nitrophenyl) phosphate and 0.1 M Bu₄Nl. $m = 1.70 \text{ mg s}^{-1}$; $t = 2.4 \text{ s}$. Reprinted with permission from ref. 25. Copyright (1967) American Chemical Society.

appears to arise from the complex chemical reactions that occur with the multiple charge-transfer schemes on attachment of more nitrophenyl groups to phosphate. Table 3 gives cyclic voltammetric data for the three nitro compounds; these features are indicative of chemical reactions accompanying the charge-transfer process²⁵. The peak current increases directly with increasing scan rate.

3. ESR features

The nitrophenyl phosphates produce ESR spectra on electrochemical reduction on the first wave. Mononitrophenyl phosphates of the type listed in Table 4 show ESR spectra with characteristic coupling constants arising from nitrogen, protons and phosphorus¹⁵. The anion radical of diphenyl-4-nitrobenzyl phosphate is unstable and hence produces no ESR signal. An interesting feature of the ESR of nitrophenyl phosphates is their close resemblance to those of the nitrophenyl group. The nitrogen coupling constants of nitrobenzene can be matched with those of nitrophenyl phosphates; $a_{\text{H(o)}}$ and $a_{\text{H(p)}}$ are identical for the two compounds. The conclusion one can draw from the data is that the introduction of the phosphate moiety into the nitrobenzene ring does not perturb the π -electron density distribution in the ring. Further, as the phosphorus coupling to the electron is observed, there is no steric hindrance offered by the phosphate. The characteristic ESR patterns of a variety of phosphates are shown in Figure 3.

The mechanism of the spin density transmission to phosphorus in anion radicals is fascinating from a geometrical point of view. If the geometry of the neutral molecule persists even after the 1e reduction, then the P—O bond length in PO₄³⁻ will be 1.54 Å (shorter by 0.19 Å from covalent radii) with a bond order of 1.70. It is altered in esters and phosphoryl oxygens to 1.63 and 1.43 Å. As the O—P—O and P—O—C angles were determined by Davies and Stanley²⁷ from crystallographic data as 117° and 122°, the nitrophenyl phosphates with the above parameters have tetrahedral geometry. The situation changes with diethyl-4-nitrobenzyl phosphonate; the P—CH₂—C angle is estimated to be 109°. The spin density transmission would depend on the position of the C—Y—P plane with respect to the plane of the nitrophenyl group (C and Y refer to the ring carbon atom and oxygen or carbon atom). When a group such as —CH₂PO(OEt)₂ is coupled to the nitrophenyl ring, the phosphorus atom is pushed out of the plane of the aromatic ring¹⁵. This understanding is supported by the value of methylene proton coupling constant (2.70 G), which is far from that of the 4-nitrotoluene anion radical (3.92 G). Further, this non-planarity has reduced a_p in comparison with

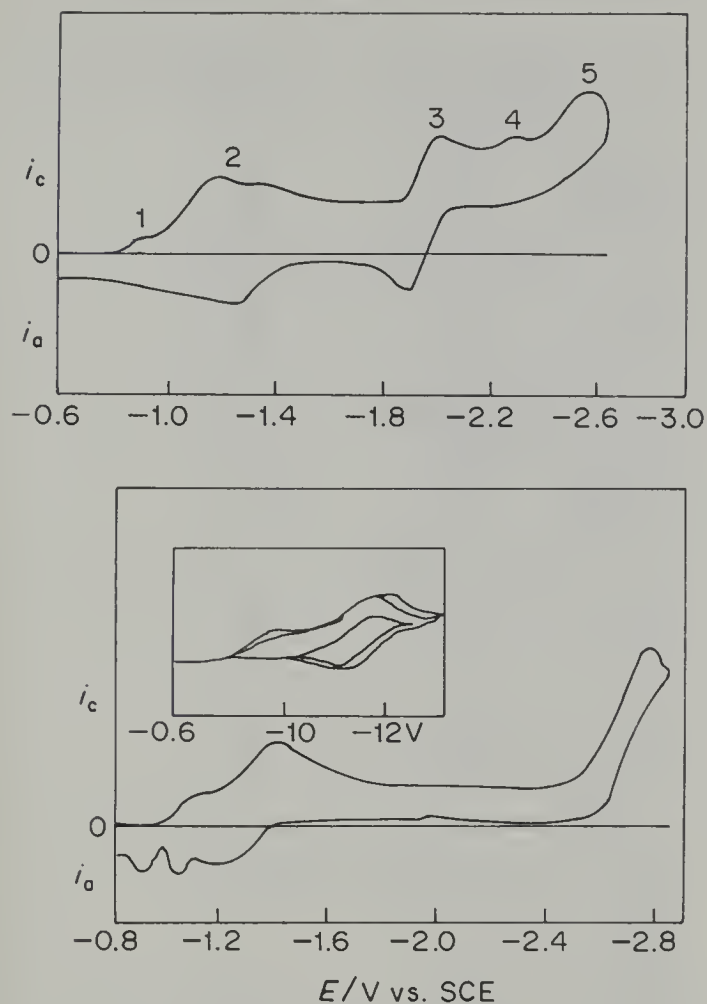


FIGURE 2. Top: cyclic voltammetric curve of tris(*p*-nitrophenyl) phosphate from a solution containing 0.1 M tetra-*n*-butylammonium iodide and 2.85 mM tris(*p*-nitrophenyl) phosphate in DMF. Numbers on the recording represent the number of peaks observed. Sweep rate, 153 mV s^{-1} ; working electrode, platinum (area = 0.031 cm^2). Taken from ref. 16. Bottom: cyclic voltammetric curve of bis(*p*-nitrophenyl) phosphate from a solution containing 0.1 M tetra-*n*-butylammonium iodide and 0.3 mM bis(*p*-nitrophenyl) phosphate. Sweep rate, 153 mV s^{-1} . Inset: repetitive cycling of the electrode potential between -0.83 and -1.25 V . Working electrode, hanging mercury drop electrode (area: 0.022 cm^2). The oscillations on the anodic scan are due to oscillation of the mercury drop due to the 'stirring phenomenon'. Reprinted with permission from ref. 17. Copyright (1969) American Chemical Society.

the planar structure that exists in the semiquinone phosphates²⁸ which have values in the range 17.2–20 G. Hence the mechanism of spin transmission appear to be based on C—P hyperconjugation.

The bis- and tris-(*p*-nitrophenyl) phosphates produce radical anions that can be

TABLE 3. Cyclic voltammetric characteristics of nitrophenyl phosphates^a

Compound	Peak 2		Peak 3		Peak 4		Peak 5	
	E_{pc} (V)	$i_p/v^{1/2}$ ($\mu A s^{1/2}$ $mV^{-1/2}$)	E_{pc} (V)	$i_p/v^{1/2}$ ($\mu A s^{1/2}$ $mV^{-1/2}$)	E_{pc} (V)	$i_p/v^{1/2}$ ($\mu A s^{1/2}$ $mV^{-1/2}$)	E_{pc} (V)	$i_p/v^{1/2}$ ($\mu A s^{1/2}$ $mV^{-1/2}$)
Tris(<i>p</i> -nitrophenyl) phosphate	-1.13 ^b	3.27	-1.96	3.12	-2.24	0.81	-2.51	6.11
	-1.14 ^c	2.96	-1.99	1.93	-2.34	2.47	-2.59	1.98
Bis(<i>p</i> -nitrophenyl) phosphate	-1.35 ^d	0.73	-2.54	2.40	-	-	-	-
	-1.37 ^e	0.65	-2.77	2.50	-	-	-	-
Nitro-phenyl phosphate	-1.28 ^f	-	-2.02	-	-	-	-	-

^aTaken from refs 25 and 26. Potentials are with respect to SCE.^bSweep rate for this set at 67.1 $mV s^{-1}$.^cSweep rate for this set at 222 $mV s^{-1}$.^dSweep rate for this set at 91.4 $mV s^{-1}$.^eSweep rate for this set at 943 $mV s^{-1}$.^fSweep rate of 67.1 $mV s^{-1}$.

TABLE 4. Electron spin resonance data for nitrophenyl phosphates^a

Compound ^b	Parameter	Acetonitrile	DMF
1	a_N	10.43 ± 0.06	9.93 ± 0.03
	$a_{H(o)}$	3.64 ± 0.04	3.44 ± 0.04
	$a_{H(m)}$	1.13 ± 0.02	1.13 ± 0.02
	a_p	7.05 ± 0.06	7.28 ± 0.02
2	a_N	10.27 ± 0.04	9.71 ± 0.03
	$a_{H(o)}$	3.47 ± 0.02	3.46 ± 0.02
	$a_{H(m)}$	1.13 ± 0.02	1.12 ± 0.01
	a_p	10.29 ± 0.04	10.84 ± 0.02
3	a_N	10.26 ± 0.26	9.61 ± 0.19
	$a_{H(o)}$	3.33 ± 0.05	3.38 ± 0.02
	$a_{H(m)}$	1.10 ± 0.02	1.08 ± 0.05
	$a_{H(CH_2)}$	2.70 ± 0.02	2.81 ± 0.02
	a_p	13.59 ± 0.23	17.51 ± 0.24
4	a_N	9.96 ± 0.03	9.50 ± 0.03
	$a_{H(o)}$	3.42 ± 0.02	3.47 ± 0.02
	$a_{H(m)}$	1.12 ± 0.01	1.12 ± 0.01
	a_p	7.92 ± 0.02	8.35 ± 0.02
5	a_N	10.50 ± 0.04	9.75 ± 0.19
	$a_{H(o)}$	3.39 ± 0.01	3.40 ± 0.01
	$a_{H(m)}$	1.03 ± 0.01	1.02 ± 0.01
	a_p	10.50 ± 0.04	11.06 ± 0.06
6	a_N	10.14 ± 0.04	9.89 ± 0.03
	$a_{H(o)}$	3.46 ± 0.02	3.45 ± 0.02
	$a_{H(m)}$	1.12 ± 0.01	1.12 ± 0.01
	a_p	7.90 ± 0.02	8.00 ± 0.03
7	a_N	10.15 ± 0.06	9.87 ± 0.03
	$a_{H(o)}$	3.46 ± 0.01	3.46 ± 0.04
	$a_{H(m)}$	1.12 ± 0.02	1.12 ± 0.02
	a_p	8.27 ± 0.06	8.39 ± 0.03
8	a_N	10.32	9.83
	$a_{H(o)}$	3.39	3.32
	$a_{(m)}$	1.09	1.09
	$a_{H(p)}$	3.97	3.97

^a Absolute values of coupling constants are given in gauss, and standard deviations from the mean are indicated. Proton positions are labelled with respect to the nitro group. All the radicals in both solvents had a g factor close 2. Reprinted with permission from ref. 15. Copyright (1966) American Chemical Society.

^b 1 = Diethyl-4-nitrophenyl phosphate; 2 = *O,O*-diethyl-*O*-4-nitro-phenyl thio-phosphate; 3 = diethyl-4-nitrobenzyl phosphonate; 4 = diphenyl-4-nitrophenyl phosphonate; 5 = diphenyl-2,6-dimethyl-4-nitrophenyl phosphate; 6 = di(4-methylphenyl)4-nitrophenyl phosphate; 7 = di(2-methylphenyl)-4-nitrophenyl phosphate; 8 = nitro-benzene.

explained as being due to secondary products such as 4,4'-dinitrobiphenyl anion radical with coupling constants $a_N = 2.96$ G, $a_H = 1.21$ G and $a_H = 0.21$ G. The ESR spectra of these radicals are shown in Figure 4. The 4-nitrophenyl phosphate group can be identified in the spectral recordings²⁶.

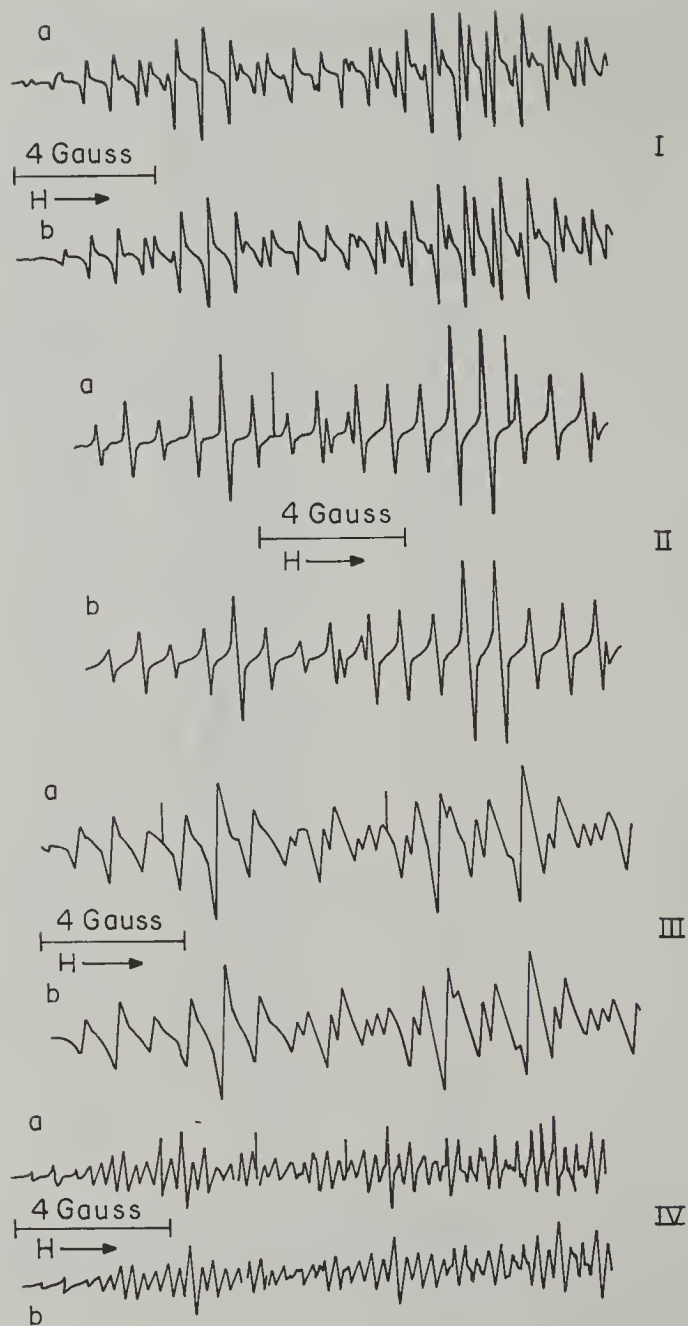


FIGURE 3. I. (a) First-derivative ESR spectrum of the anion radical of diphenyl-2,6-dimethyl-4-nitrophenyl phosphate in DMF. Low-field half of the spectrum. (b) Computed spectrum using $a_N = 9.71$ G, $a_H = 3.395$ G, $a_{H_1} = 1.02$ G and $a_P = 11.06$ G. Line width: 0.125 G. II. (a) ESR spectrum of diphenyl-4-nitrophenyl phosphate anion radical in DMF. Low-field half of the spectrum. (b) Computed spectrum using $a_N = 9.46$ G, $a_H = 3.46$ G, $a_{H_1} = 1.12$ G and $a_P = 8.31$ G. Line width, 0.125 G. III. (a) ESR spectrum of diethyl-4-nitrophenyl phosphate anion radical in DMF. Low-field half of the spectrum. (b) Computed spectrum using $a_N = 9.93$ G, $a_H = 3.47$ G and $a_P = 7.28$ G. Line width, 0.23 G. IV. (a) ESR spectrum of diethyl-4-nitrobenzyl phosphonate in DMF. Slightly more than the low-field half of the spectrum. (b) Computed spectrum using $a_N = 9.70$ G, $a_{H_1} = 3.34$ G, $a_{H_2} = 1.08$ G, $a_{H_3} = 2.79$ G and $a_P = 17.60$ G. Line width, 0.140 G. Reprinted with permission from ref. 15. Copyright (1986) American Chemical Society.

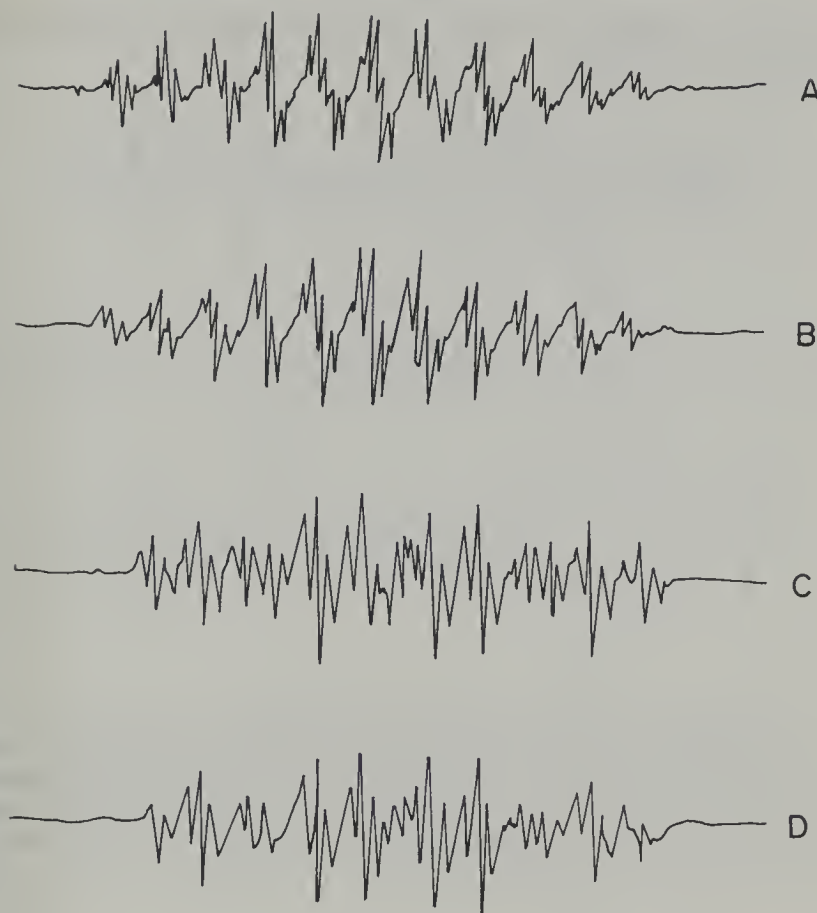


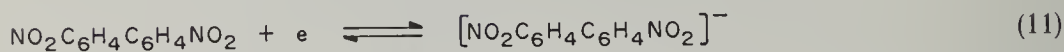
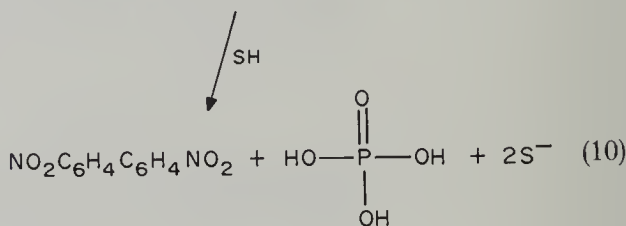
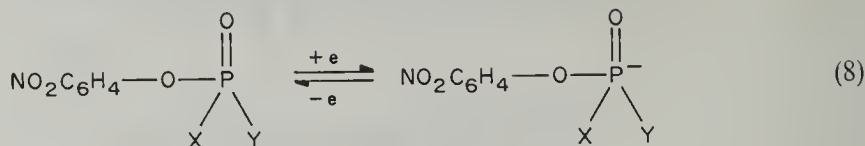
FIGURE 4. (A) Derivative ESR spectrum of 4,4'-dinitrobiphenyl anion radical obtained by electroreduction of 2.38 mM tris(*p*-nitrophenyl) phosphate in DMF. (B) Computed spectrum with $a_N = 2.62$ G, $a_H = 1.21$ G and $a_H = 0.21$ G. (C) Derivative ESR spectrum of nitrophenyl phosphate anion radical during reduction of tris(*p*-nitrophenyl) phosphate in DMF. (D) Computed spectrum with $a_N = 3.3$ G, $a_H = 0.83$ G and $a_P = 11.4$ G. Reprinted with permission from ref. 16. Copyright (1969) American Chemical Society.

4. Redox mechanisms

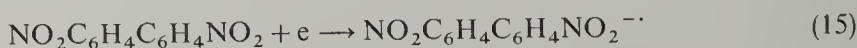
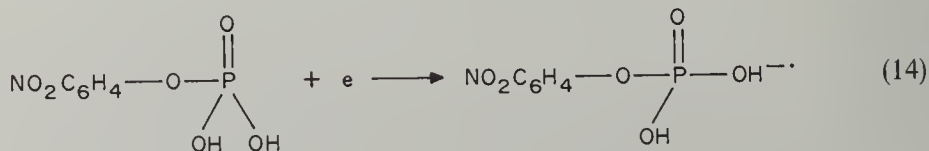
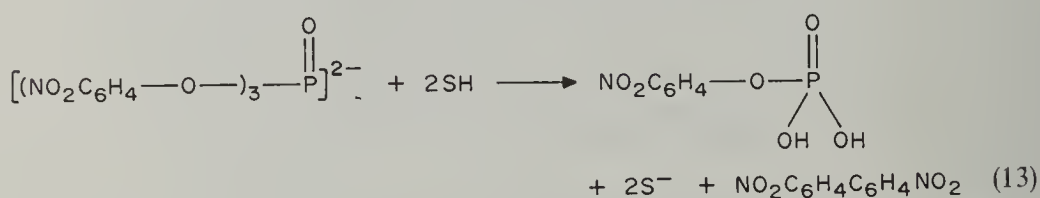
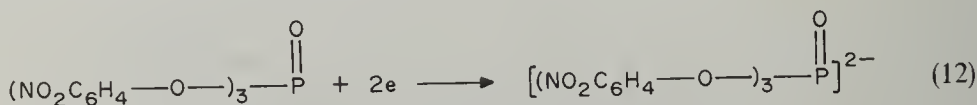
A strong resonance interaction between the nitro group and other substituents has been observed in the series of compounds listed in Table 1. The half-wave potentials for compounds with reference to nitrobenzene shift in the direction predicted by Hammett's constant, σ . This shift also correlates with the observed shift in the values of a_p ^{15,19}.

With only one *p*-nitrophenyl substituent attached to phosphate, the reduction proceeds as in equation 8, where X and Y represent the substituent groups listed in Table 1, such as phenyl, methyl, ethyl or benzyl. When two *p*-nitrophenyl substituents are attached to phosphate, the radical anion produced is unstable and decomposes by the pathway in reactions 9–11, where SH represents DMF. The 4,4'-dinitrobiphenyl is further reduced at -2.54 V and appears as the third peak in the cyclic voltammetric patterns. Cleavage of the C—O bond has been observed by Santhanam and Bard²⁶ followed by coupling of the radicals to produce 4,4'-dinitrobiphenyl. This molecule is easier to reduce than

bis(*p*-nitrophenyl) phosphate and hence the electron spin resonance spectrum of 4,4'-dinitrophenyl is observed.



The introduction of third nitrophenyl group into phosphate produces more complexity but nevertheless cleavage of the C—O bond is observed. The reaction scheme during reduction is depicted by equations 12–15. With this series of molecules the energy-rich P—O bond remains intact; cleavage of the C—O bond takes place with ease; a similar phenomenon is observed with diphenylphosphate on reduction.



B. Nitrophenyl Thiophosphate

O,O-Diethyl *O*-4-nitrophenyl thiophosphate generates a polarographic wave in MeCN with a half-wave potential at $E_{1/2} = -1.16$ V vs SCE, with a wave slope of $|E_{3/4} - E_{1/4}|$

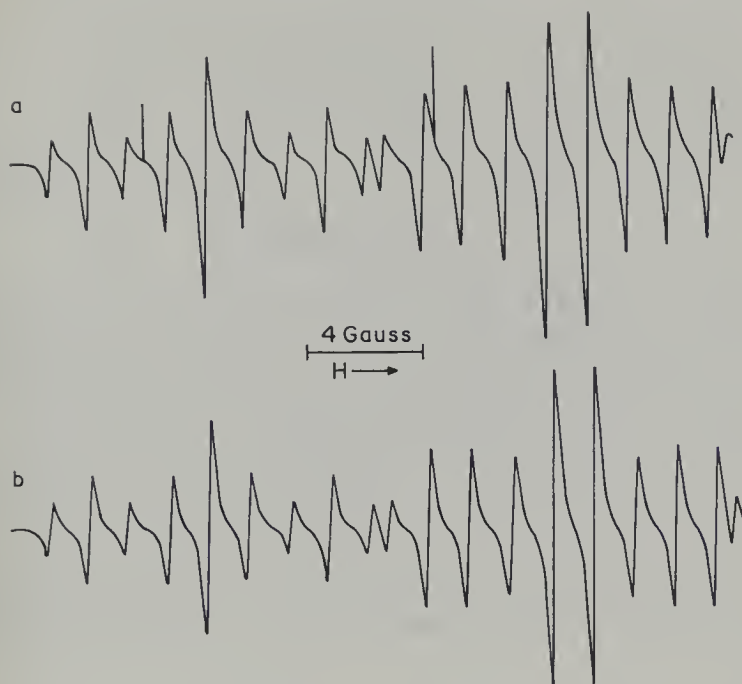


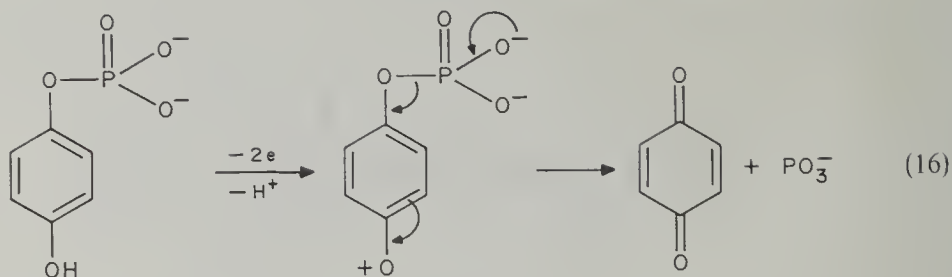
FIGURE 5. (a) Derivative ESR spectrum of the anion radical of 0,0-diethyl-0,4-nitrophenyl thiophosphate in DMF. (b) Computed spectrum using $a_N = 9.68$ G, $a_{H(O)} = 3.46$ G, $a_{H(m)} = 1.135$ G and $a_p = 10.82$ G. Line width, 0.185 G. Reprinted with permission from ref. 15. Copyright (1966) American Chemical Society.

≈ 53 mV. This wave is due to a 1e reduction of this molecule¹⁵ and the free radical anion produces an ESR spectrum as shown in Figure 5. The spectrum shows the following coupling constants in DMF: $a_N = 9.68$ G, $a_{H(O)} = 3.46$ G, $a_{H(m)} = 1.13$ G and $a_p = 10.82$ G. The coupling constants are slightly shifted in MeCN: $a_N = 10.27$ G, $a_{H(O)} = 3.47$ G, $a_{H(m)} = 1.13$ and $a_p = 10.29$ G. Replacement of the phosphoryl oxygen by sulphur (see Section 3.) produces a_N and ring proton coupling constants that are virtually unchanged, but results in an increase in a_p by about 45%. This feature of increasing a_p has also been observed for the radical produced by dehydrogenation of diphenyl(4-hydroxy-3,5-di-*tert*-butylphenyl)phosphine oxide; a change in a_p from 14.7 to 15.4 G is observed with the analogous phosphine sulphide³⁰. As oxygen is more electronegative than sulphur, it does not attract the electron towards itself.

C. Quinol Phosphates—Biological Significance

1. Oxidative phosphorylation

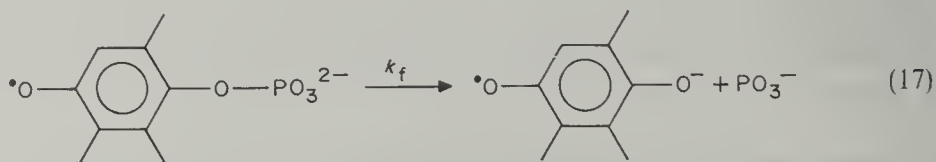
Oxidative phosphorylation plays a role in energy transfer schemes in biological processes. Quinol phosphates possesses the potential for understanding the energy transduction in biological mechanisms³¹. The pioneering work in understanding the phosphorylating agent stems from a series of publications by Todd and co-workers³²⁻³⁵. Phosphorylating agents such as phosphonic anhydrides on reaction with quinol phosphate expel an anion as in equation 16.



Several studies^{32,33} have been carried out on the initiation of the P—O and C—O bond fission processes. Lapidot and Samuel^{36,37} indicated that both fission processes operate in the oxidation schemes. The implication of this finding is that the P—O bond fission will produce a metaphosphate intermediate for the phosphorylation. Todd's group³² has demonstrated metaphosphate generation, but could not find support for phosphoryl cation formation during the oxidation of quinol diphosphates by a number of oxidizing agents. The product of these oxidations is quinone; a qualitative correlation between the redox potential of the quinone–quinol system and the efficiency of quinone formation has been observed³². Further support for the finding that P—O bond fission is susceptible to metaphosphate intermediate formation during phosphorylation has been arrived at through cyclic voltammetric studies on 2-methyl-1,4-naphthoquinol 1-phosphate³⁸.

2. Cyclic voltammetric pattern

Quinol phosphate (2-methyl-1,4-naphthoquinol 1-phosphate) oxidation at an electrode takes place over a wide pH range from 2.50 to 10.39³⁸. The 2e oxidation occurs in acidic solutions at $E_p = 0.60$ V vs SCE. The product undergoes fast hydrolysis to produce a semiquinone. The oxidation process occurring at different pH values is depicted in Figure 6. The anodic peak current decreases with increasing pH, which is attributed to the equilibrium that exists between the ionized and non-ionized forms. A complete reaction scheme is shown in Figure 7. The oxidized product is unstable and decomposes to form the quinone, which is easily identified by its characteristic cyclic voltammetric features. The cyclic voltammetric parameters are listed in Table 5. The $|E_p - E_{p/2}|$ value is close to the 2e irreversible peak having a transfer coefficient of 0.5³⁸; the increase in the $|E_p - E_{p/2}|$ value with increasing pH is consistent with the complexity of the mechanism and changes in the transfer coefficient. The current function also decreases with increasing pH and is a characteristic feature of this oxidation.



In basic media 1e oxidation of quinol phosphate followed by further oxidation and cleavage of the P—O bond is observed. The rate constant for the process in equation 17 is controlled by the prior equilibrium that exists which depends on the hydroxide ion concentration (pH of the medium and pK_a). It is considered to be composed of

$$k_f = k_1 + k_2[\text{OH}^-] \quad (18)$$

with $k_1 = 0.2 \pm 0.1 \text{ s}^{-1}$ and $k_2 = 700 \pm 400 \text{ l mol}^{-1} \text{ s}^{-1}$. Using equation 18, an estimate of k_f in any basic solution can be determined.

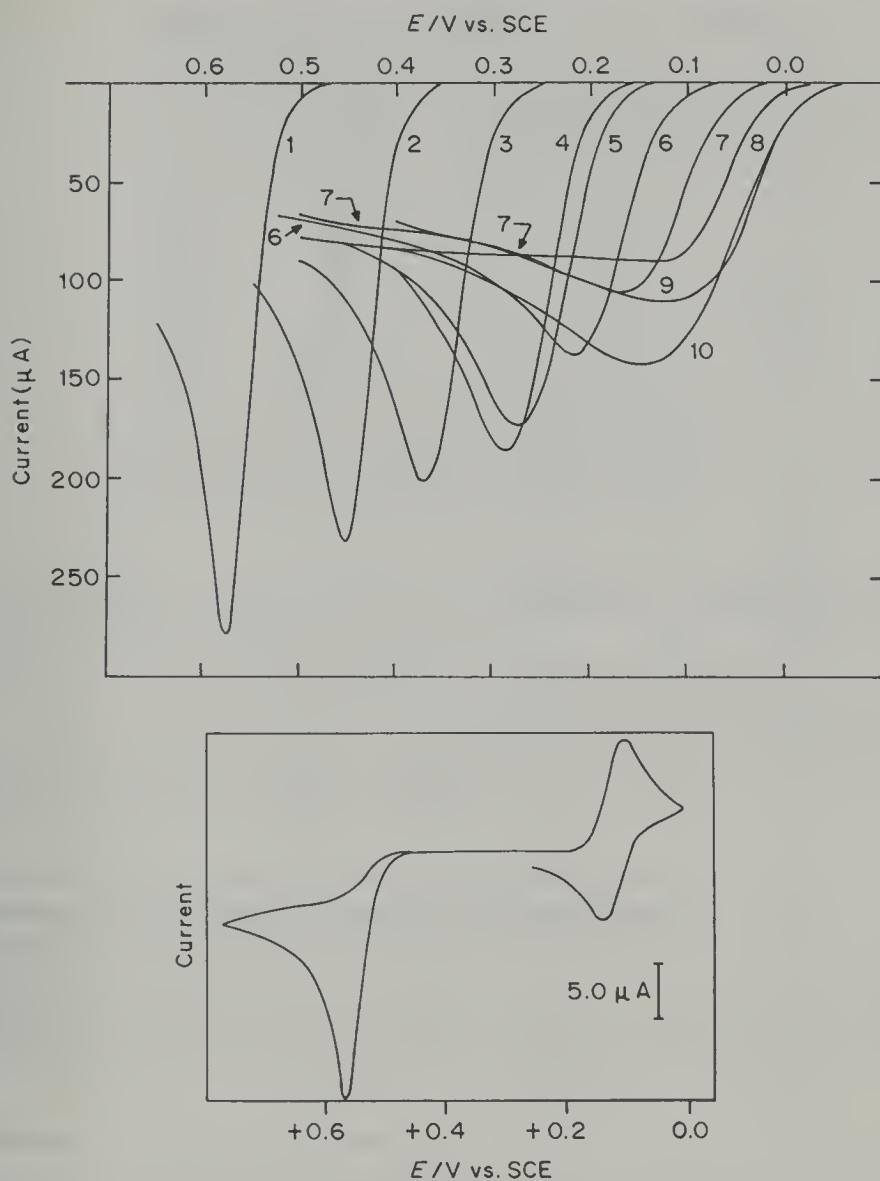


FIGURE 6. Top: current-voltage curves for 2-methyl-1,4-naphthoquinol 1-phosphate in acetate, phosphate and borate buffers. (1) 1 M H_2SO_4 ; (2) pH 2.50; (3) pH 4.04; (4) pH 5.63; (5) pH 6.32; (6) pH 7.44; (7) pH 8.38; (8) pH 9.27; (9) pH 11.18; (10) pH 11.87. Bottom: cyclic voltammetric curve for 0.53 mM 2-methyl-1,4-naphthoquinol 1-phosphate in 1 M H_2SO_4 . Sweep rate for both recordings, 60 mV s^{-1} . The reversible couple at 0.20 V is due to the quinone formed after the electrochemical oxidation of the electroactive species at +0.58 V. Working electrode, carbon paste (Nujol). Reprinted with permission from ref. 38. Copyright (1966) American Chemical Society.

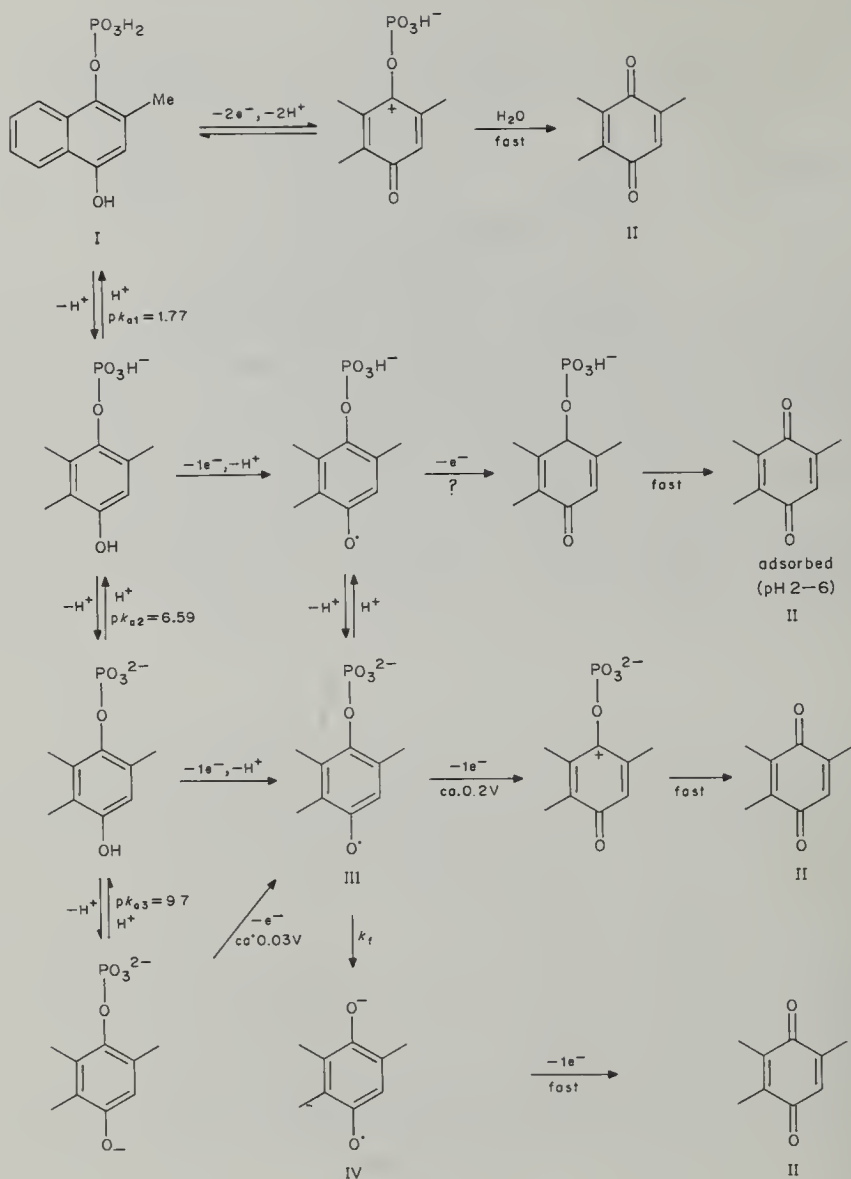


FIGURE 7. Reaction mechanism for quinol phosphate oxidation.

3. Electron spin resonance features

The ESR spectral features of the oxidized product of quinol phosphate (2-methyl-1,4-naphthaquinol 1-phosphate) are identified as arising from the substituted quinone (product II in Figure 7)³⁸. Allen and Bond³⁹, however, generated the following semiquinone phosphate radical:

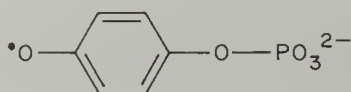


TABLE 5. Cyclic voltammetric parameters 2-methyl-1,4-naphthoquinol 1-phosphate^a

pH	$E_p - E_{p/2}$ (mV)	$i_p/ACv^{1/2}$ (A cm ⁻² l mol ⁻¹ V ^{-1/2} S ^{1/2})
0.59	26.5	2.18
1.44	30.5	1.89
2.50	30	1.84
3.48	36	1.86
4.04	40	1.55
4.48	46	1.38
5.63	49	1.41
6.32	55	1.35

^aSweep rate 0.10 V s⁻¹. Reprinted with permission from ref. 38. Copyright (1966) American Chemical Society.

by chemical oxidation using permanganate at high pH (11.7). The electrolytic oxidation of quinol phosphate at this pH value can only generate a weak, unresolved signal, indicating the instability of the radical.

The phosphorylation reaction in biological systems has been of importance in arriving at the bioenergetics. The nature of the phosphorylating agent is speculative^{31,40,41}; is there a reactive intermediate in phosphorylation reactions^{42,43}? The electrochemical data together with ESR results for quinol phosphate suggest that the semiquinone phosphate radical is the phosphorylating agent³⁸.

D. *S*-(1,2-Dicarbethoxyethyl)-*O,O*-dimethyl Dithiophosphate or *O,O*-Dimethyl *S*-(1,2-dicarbethoxyethyl Phosphorodithioate) (Malathion): (CH₃O)₂P(S)SCH(COO C₂H₅)CH₂COOC₂H₅

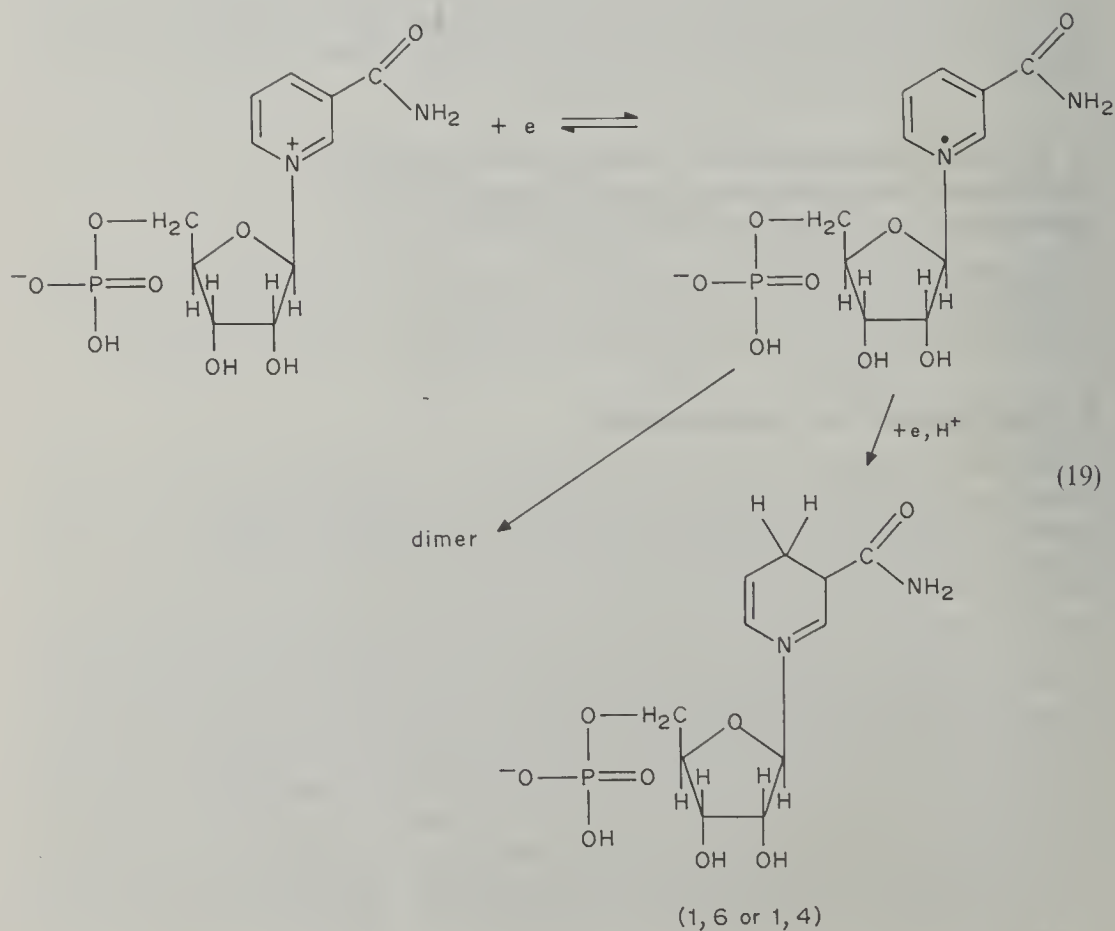
The electrochemical reduction of malathion occurs at $E_p = -0.21$ V vs SCE at a DME in ethanol-HCl medium. The second peak is observed at $E_p = -0.80$ V vs SCE. In alkaline medium (NaOH), only one reduction peak at $E_p = -0.80$ V is observed⁴⁴.

E. Nicotinamide Ribose Monophosphate

The redox chemistry of the most familiar form of β -nicotinamide ribose monophosphate (NMN) has been investigated extensively by Schmakiel *et al.*⁴⁵, using this as a model compound to understand several nucleotides, such as nicotinamide adenine dinucleotide (NAD⁺) and nicotinamide adenine dinucleotide phosphate (NADP⁺). NMN exhibits a half-wave potential which is independent of pH up to 5, becomes more negative between pH 5.0 and 7.5 and then remains constant up to pH 12. These shifts occur as a result of secondary phosphate dissociation. While the first well defined wave of NMN⁺ is observed at $E_{1/2} = -0.90$ V vs SCE, the second wave which appears at $E_{1/2} = -1.60$ V vs SCE is not visible in solutions of pH 5 owing to the background electrolysis setting in earlier. Both the waves are well defined in solutions of pH 9.6. A.c. polarographic measurements conclusively establish the first wave as being due to a reversible 1e process. The reversibility of the electron transfer reaction has been confirmed by fast-sweep cyclic voltammetric studies. Table 6 provides the data for NMN⁺ at pH 5–9. The first 1e reduction produces a neutral radical which dimerizes rapidly with a rate constant of 1.5×10^6 l mol⁻¹ s⁻¹. The dimer has been identified by spectral and

TABLE 6. Dimerization rates of the free radicals derived from NMN⁺, DPN⁺ and TPN⁺^a

Parent compound	Solvent	pH	k_d (l mol ⁻¹ s ⁻¹)	Temperature (°C)
NMN ⁺	H ₂ O	5-9	1.5×10^6	30
DPN ⁺	H ₂ O	5	2.2×10^6	30
		7	8.49×10^6	
		8	$> 10^b$	
		9	2.4×10^6	
TPN ⁺	DMSO		9.0×10^5	40
	H ₂ O	5	4.3×10^6	30
		7	$5.45 \times 10^{10}{}^b$	
		9	1.6×10^6	30
	DMSO		5×10^6	40

^aTaken from ref. 58. Measurements using peak current ratio.^bCyclic voltammetric peak potential method.

NMR studies as a mixture of isomers of 4,4'-, 4,2'- and 6,6'-dimers⁴⁵⁻⁴⁷. The activation energy for the dimerization process has been estimated at $3.6 \text{ kcal mol}^{-1}$. The oxidation of the dimer at -0.28 V produces the monomer^{45,46}.

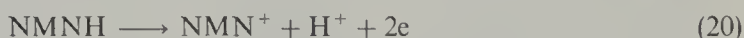
The second electron reduction process produces 1,6-dihydro-NMN (NMNH) as the major product; the other product is 1,4-dihydro-NMN (NMNH). The characteristic features of the absorption spectra are NMN^+ in unreduced form having a peak at 265 nm ; in the reduced form 1,2-species, i.e. 1,2-NMNH, has a maximum at 400 nm . 1,4-NMNH has maximum at 340 nm and 1,6-NMNH shows maxima at 270 and 350 nm . The features for the dimers of NMN are that the 4,4'-dimer absorbs at 340 nm and the 6,6'-dimer at 260 and 345 nm .

The electrochemical redox pattern in DMSO for NMN^+ provides strong support for the mechanism postulated in aqueous media. It is reduced at $E_{1/2} = -0.99 \text{ V}$ with a wave slope of 45 mV . By detailed analysis of the polarographic, cyclic voltammetric and a.c. polarographic data, the reduction is attributed to the nicotinamide moiety⁴⁸. NMN is strongly adsorbed on mercury and exhibits a pre-wave at -0.38 V . The diffusion-controlled process occurs at -0.99 V and a wave slope of 45 mV is indicative of a dimerization process accompanying the $1e$ reduction.

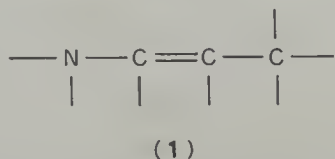
The controlled potential electrolysis of NMN^+ in both aqueous and non-aqueous media supports the $1e$ reduction process producing the dimer at the first polarographic wave. The electrolysis at the second polarographic wave results in the consumption of $2e$ per mole of NMN^+ . The dihydro product has been identified by several physical techniques^{45,48}. The reaction mechanism postulated for NMN^+ is as shown in equation 19.

1. Oxidation of NMNH

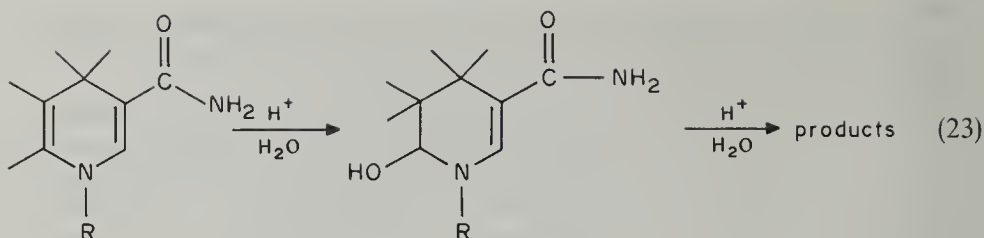
The electrochemical oxidation of NMNH in DMSO proceeds at $E_p = 0.84 \text{ V}$ vs SCE and based on the data obtained through cyclic voltammetry and chronoamperometry the process responsible for this wave is estimated to be $2e$. The $2e$ oxidation produces NMN^+ and has been identified by the characteristic cathodic peak at -0.97 V vs SCE. Interestingly, the exhaustive electrolysis of NMNH does not produce NMN^+ due to the following reaction scheme⁴⁹⁻⁵²:



The source of the proton in large-scale electrolysis is attributed to the first step (i.e. reaction 20) or impurities of H_2O in the solvent. The absorption arising at 280 nm is due to the chromophore **1**⁴⁹. The pseudo-first-order rate constant for this decomposition is $8.2 \times 10^{-4} \text{ s}^{-1}$ at pH 7.1. The decomposition reaction is given in equation 23.



The redox patterns of NMN^+ and NMNH discussed in this section are very similar to that of 1-methylnicotinamide; the $E_{1/2}$ of 1-methylnicotinamide is -1.03 V and that of NMN^+ is -0.99 V vs SCE. The charge-transfer schemes are identical with these molecules, as the nicotinamide ring is reduced during electrochemical reduction.



F. Diphosphopyridine Nucleotide (DPN^+)—Redox Scheme

The electrochemical reduction of DPN^+ at low pH (< 2) is hampered by catalytic evolution of hydrogen^{53,54}. If the medium provides a large potential window, such as -2.0 V vs SCE, then DPN^+ undergoes two successive 1e reductions. Under other conditions, it undergoes only one 1e reduction. For example, at pH 4–5, a 1e reduction is generally observed at a mercury electrode, whereas between pH 8 and 10 two successive

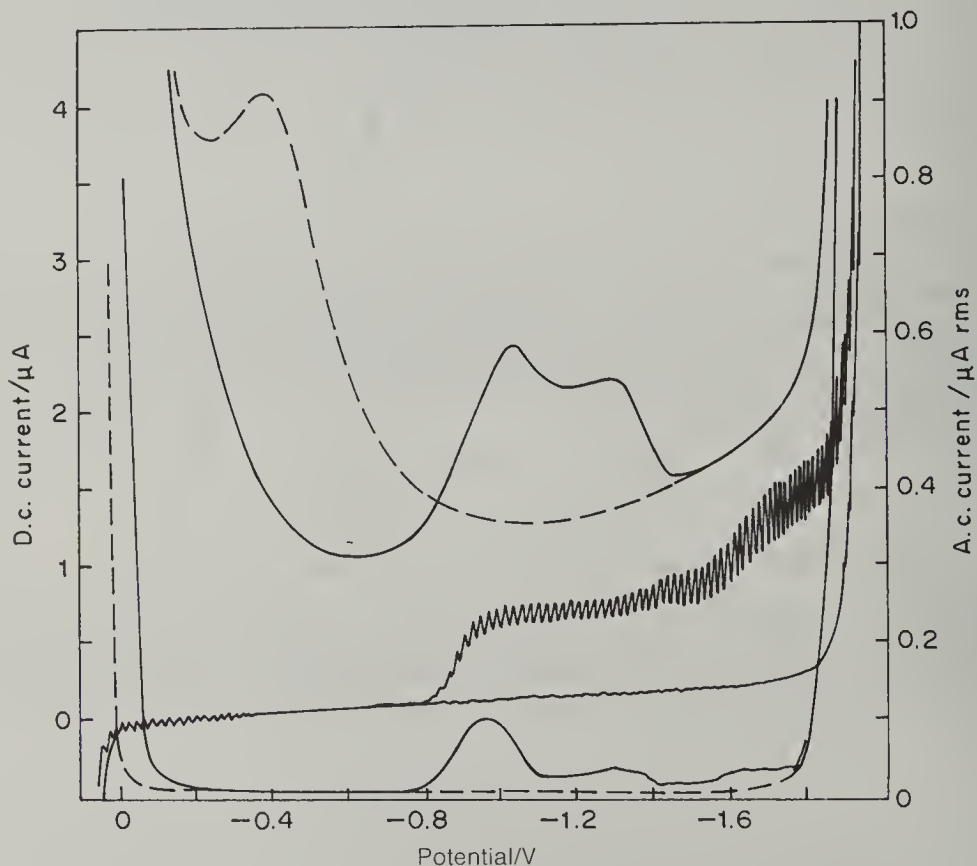


FIGURE 8. D.c. and a.c. polarograms of DPN^+ (0.31 mM) in pH 9.3 KCl-carbonate buffer. D.c. polarograms shown with and without the electroactive species (oscillatory curve and the one below it, respectively). A.c. polarograms: solid lines represent in-phase (lower set) and quadrature (upper set) components of total a.c. current. Dashed lines represent corresponding background current. Reprinted with permission from ref. 53. Copyright (1975) American Chemical Society.

1e reductions are observed. Above pH 10, DPN^+ undergoes hydrolysis to produce nicotinamide and a wave due to the reduction of this species is observed by both polarography and cyclic voltammetry. The decomposition rate is a function of pH; at pH 9.6 it is 1.9% decomposed and at pH 11.8 it is 88% decomposed during the same period of time⁵³. As a result of these investigations, an electrochemical redox pattern is evolved at pH 9.6 where it is less decomposed.

The characteristic d.c. and a.c. polarograms of DPN^+ are shown in Figure 8. Note that the d.c. polarogram, which exhibits a maximum, is of the first kind. This can be suppressed by 0.0008% Triton or 5 mM Et_4NCl . The a.c. polarogram shows a faradaic peak (in phase component) at -0.97 V (wave I process, quadrature component at -1.04 V) and a barely discernible peak at -1.65 V; this is due to the wave II process capturing $2e$ by DPN^+ at the electrode. The adsorption-desorption phenomena are well depicted in Figure 8. A significant depression of the differential double layer capacity is observed at -0.65 V due to the above process.

The first 1e reduction of DPN^+ produces a neutral radical which dimerizes to produce an a.c. polarogram as shown in Figure 9; the dimer surface activity shifts the tensammetric peak ($E_s = -1.27$ V) in the negative direction. The formation of a DPN free radical, its dimerization rate and the redox characteristics of the dimer have been investigated in detail^{48,53,54}. As it is coenzyme I in several biological reactions, the redox characteristics have been examined in the pH range 0–12. The lack of a potential window up to pH 2 restricts the study of DPN^+ above pH 2. From pH 2.0 to 9.3, it undergoes a well defined 1e reduction. Above this pH, DPN^+ undergoes two successive cyclic voltammetric 1e reductions at $E_p^I = -0.90$ V and $E_p^{II} = -1.16$ V. None of the peaks shows complementary

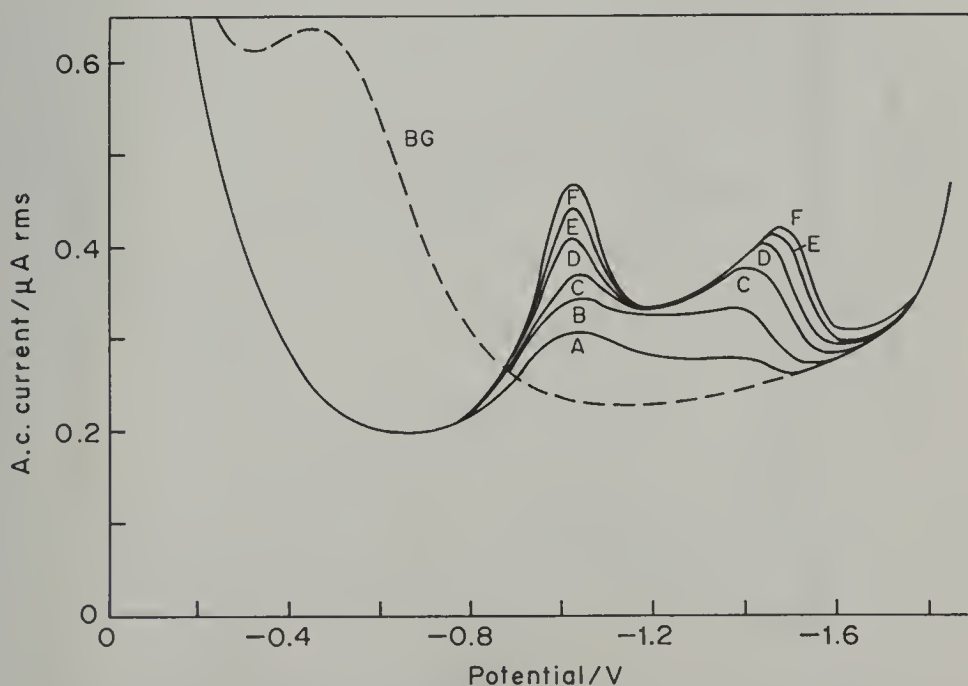


FIGURE 9. Effect of DPN^+ concentration on the adsorption-desorption behaviour of the DPN dimeric reduction product. Quadrature components of a.c. polarograms for solutions of 1.50 M in KCl and 0.25 M in carbonate buffer (pH 9.9). DPN concentration: (A) 0.04; (B) 0.12; (C) 0.34; (D) 0.88; (E) 1.26; (F) 1.76 mM.

anodic peaks at sweep rates of $< 10 \text{ V s}^{-1}$. This sweep rate dependence on the appearance of anodic peak ($> 10 \text{ V s}^{-1}$) has been used to obtain the dimerization rate constant for DPN^+ and the activation energy for this process. Table 6 summarizes the data for the dimerization reaction.

Controlled potential coulometry of DPN^+ at -1.20 V consumes $1e$ per mole, producing a dimer with $E_{1/2} = -0.25 \text{ V}$ (the process is due to oxidation of the dimer to DPN^+). The effect of pH on the stability of the DPN dimer is shown in Figure 10. The nature of the dimer has been identified^{46,55-57} by absorption spectroscopy to be a mixture of dimers linked in the 4,4'- and 6,6'-positions. As it was not possible to isolate the products⁵⁸, subsequent studies⁵⁷ using reversed-phase HPLC and gel filtration on Sephadex G-15 and NMR spectra identified the dimer as the 4,4'-isomer. Small amounts ($< 10\%$) of other isomers were also isolated. Electrolysis at -1.60 V produced a mixture of 1,4- and 1,6-dihydro isomers of DPN^+ . The 1,4-dihydro isomer is 54% enzymatically active^{57,58}; the 4,5-C=C bond of the 1,6-isomer has enamic nucleophilicity and exhibits a UV absorption maximum at 340 nm ; conjugation with the 3,4-double bond of the pyridinium ring is removed by protonation.

The electrochemical behaviour of diphosphopyridine nucleotide in non-aqueous media was first studied by Santhanam and Elving⁴⁸. This study established the need to have

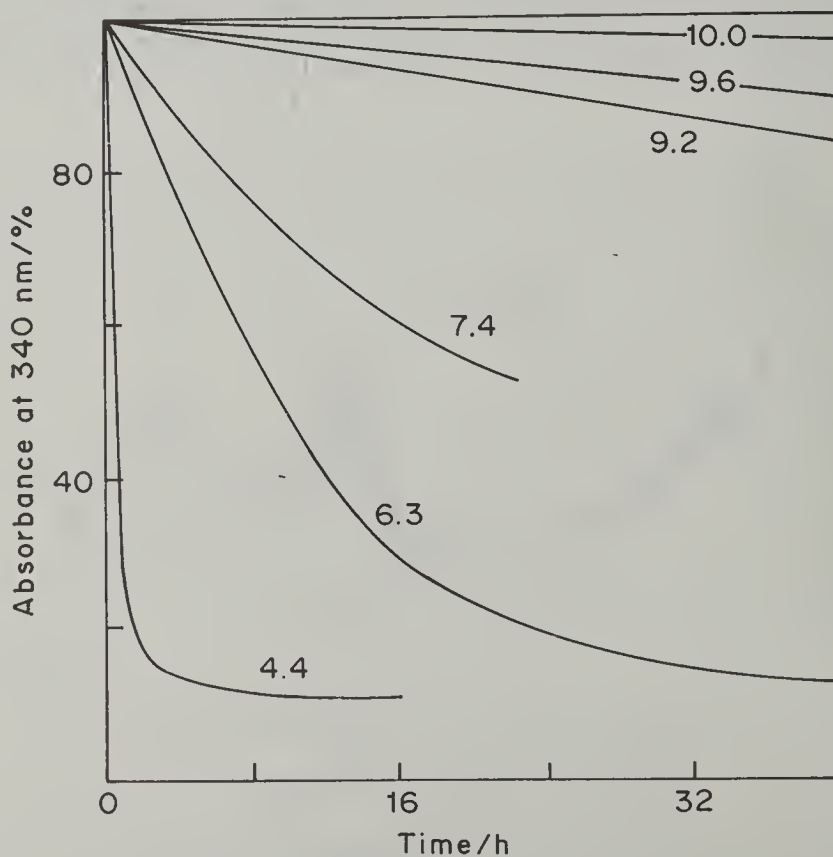
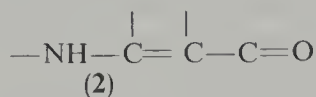
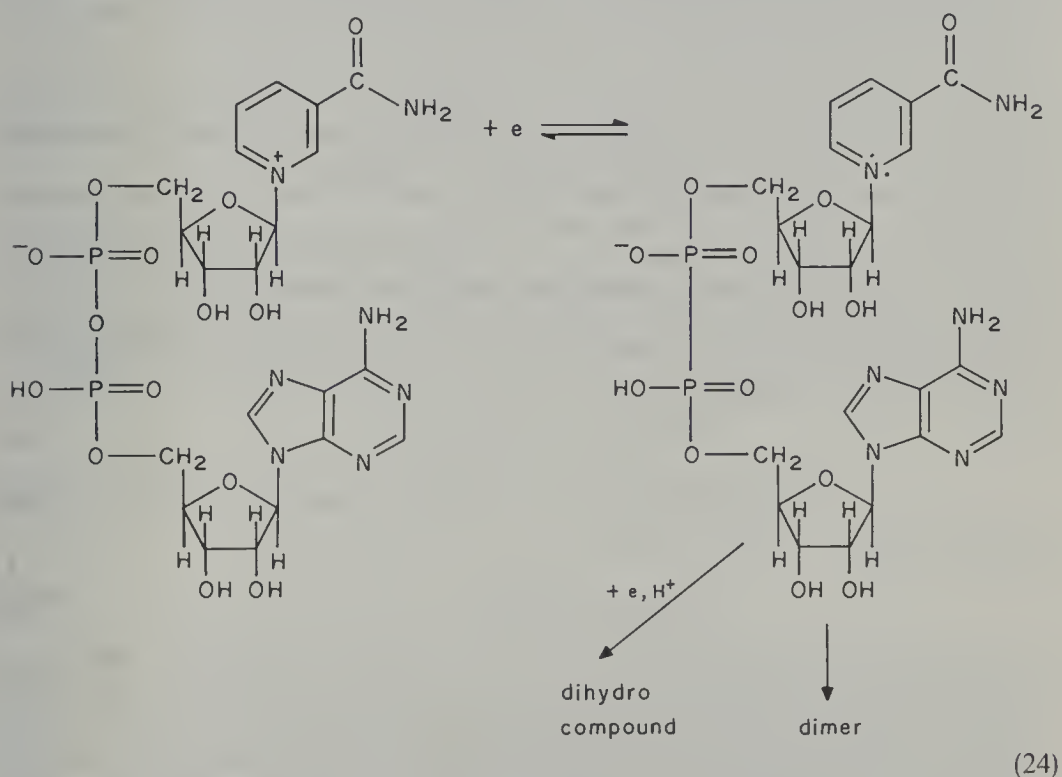


FIGURE 10. Effect of pH on stability of the DPN dimer. Buffer solutions and dimer concentrations above pH 9, carbonate buffer and $2.16 \times 10^{-5} \text{ M}$; below pH 9, McIlvaine buffer and $1.89 \times 10^{-5} \text{ M}$; all solutions stored under air at room temperature.

a proton environment for the reduction scheme. The reduction of DPN^+ in DMSO occurs at $E_{1/2} = -0.98 \text{ V}$, with the polarographic wave having a slope of 46 mV . The diffusion coefficient of DPN^+ in DMSO is evaluated as $0.28 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is considerably lower than in aqueous media. The cyclic voltammetric pattern is well defined with a peak at $E_{\text{pc}} = -1.03 \text{ V}$ vs SCE which is irreversible at slow sweep rates of $< 6.0 \text{ V s}^{-1}$, consuming $1e$; the neutral radical of DPN dimerizes with a rate constant of $9 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$. Based on quantum mechanical calculations, the site of dimerization is predicted to be either the 4,4'- or the 6,6'-position. A clear demonstration of the stability of the dimer in DMSO compared with aqueous media shows the proton involvement in its decomposition reaction. As the instability is due to the pyridine-derived species having a chromophore of the type 2:



the ring structure is removed by the proton addition. The low proton activity of DMSO explains the greater stability of the dimer. Based on the results obtained in aqueous^{42,57-59} and non-aqueous media^{48,60,61}, the redox scheme shown in equation 24 has been proposed for DPN^+ .



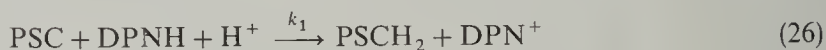
1. Oxidation of DPNH

The electrochemical oxidation of DPNH at solid electrodes such as a glassy carbon or platinum exhibits a cyclic voltammetric oxidation peak at $E_{\text{pa}} = 0.67 \text{ V}$ and a complementary cathodic peak at $E_{\text{pc}} = -1.13 \text{ V}$ in aqueous media^{49,50}. The cyclic voltammetric features are ratio of the peak currents = 0.25, $(E_{\text{pa}} - E_{\text{pa}/2}) = 80 \text{ mV}$ and

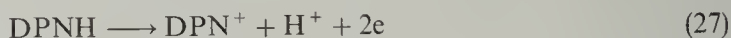
$(E_{pa} - E_{1/2}) = 7$ mV at pH 7.1. The value of αn_a (where α is the transfer coefficient and n_a is the number of electrons involved in the rate-determining steps) is 0.46. The above features in solvents such as DMSO are $E_{pa} = 0.89$ V, $E_{pc} = -0.95$ V, $i_{pc}/i_{pa} = 0.26$ and $n = 2$. The effect of added bases such as pyridine or tri-*n*-butylamine is to increase the peak current in acetonitrile⁵⁰, but no effect is observed in DMSO. This is probably caused by oxidation of the base taking place at the potential of DPNH. The presence of dissolved oxygen in the medium did not affect the anodic peak but it significantly shifted the cathodic process⁴⁹ as oxygen is reduced in this region. The chronoamperometric data of DPNH in the absence of a base gives an estimate of $n = 2$.

Controlled potential coulometric oxidation of DPNH yields a non-integral electron-transfer process ($n = 1.5$)⁴⁹. This lower value has been ascribed to protonation of DPNH by the protons generated during electrochemical oxidation; this process is similar to acid-catalysed decomposition of DPNH. The process rate constant is measured as $8.5 \times 10^{-4} \text{ s}^{-1}$. The decomposition product absorbs at 280–290 nm with no peak characteristic of DPNH being present. As this reaction is slow, Jaegfeldt *et al.*⁶² coupled a coulometric oxidation of DPNH to a continuous flow reactor system where the 2e product of DPNH is enzymatically reduced. By this method, the coulometric value of $n = 2$ was obtained. However, to achieve this n value, a special electrode treatment is necessary⁴⁷. At the glassy carbon electrode very little adsorption of the final product, DPN, has been observed^{48,63,64}; very significant adsorption and passivation of the electrode process have been observed on a clean platinum electrode⁶⁵.

The electrochemical oxidation of DPNH has also been carried out at chemically modified electrodes^{66,67}. The catechols 4-[2-(2-naphthyl) vinyl catechol](NSCH₂) and 4-[2(9,10-ethano-anthracene-9-yl)vinyl catechol (ASCH₂) are adsorbed on a graphite electrode. The catechol moiety was tailored to move in and out of the solution, whereas the naphthalene and ethane-anthracene ring systems were attached to the electrode. The catalytic oxidation of DPNH decreased from 410 to 185 mV vs SCE at the NSCH₂-covered electrode in aqueous medium of pH 7.0⁶⁷. The catalytic oxidation of the NSCH₂ and ASCH₂ electrodes between DPNH and the mediating group is much faster for the NSCH₂ electrode. A similar catalytic process has been observed with a 4-[2-(1-pyrenyl) vinyl catechol](PSCH₂) modified electrode. The reaction scheme is shown in equations 25–27.

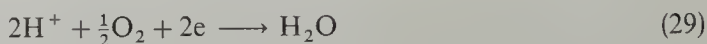
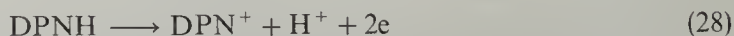


Overall reaction:



k_1 is estimated to be $1 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ ^{68–70}. The reaction pathway of DPNH was unravelled in several investigations^{71–73}. Of these the catalytic oxidation of DPNH through electrogenerated diimines is an interesting model system⁷².

An interesting experiment on phosphorylation coupled to DPNH oxidation was performed by combining two galvanic DPNH oxidation cells with a galvanic-electrolytic phosphorylation cell⁷⁴. This scheme is depicted in Figure 11. The four galvanic cells of DPNH oxidation are



and the overall reaction is



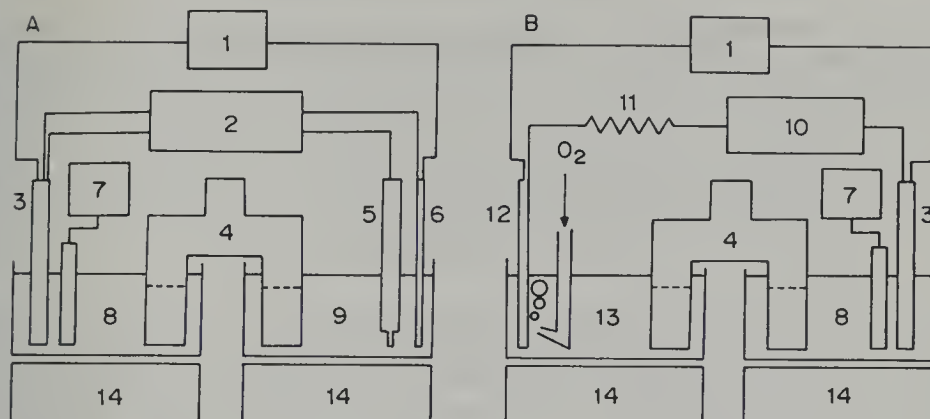
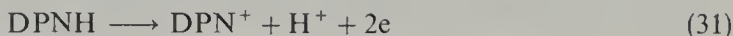
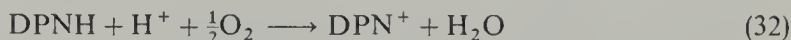


FIGURE 11. Phosphorylation set-up: Electrolytic cell (A) and galvanic cell (B). 1, Voltmeter; 2, potentiostat and coulometer; 3, anode of titanium nitrocarbide base ceramic; 4, salt bridge; 5, saturated calomel electrode; 6, cathode (iron wire); 7, pH meter; 8, KCl aqueous solution (40 ml) containing 1–3 mM ADP and 2–6 mM acetyl phosphate for ADP phosphorylation + 1.1 mM DPNH for DPNH oxidation; 9, 0.1 M HCl (40 ml); 10, coulometer; 11, resistance (1.0 Ω); 12, cathode (platinum plate); 13, 2.8 M HCl (40 ml); 14, magnetic stirrer. Copyright (1989) Electrochemical Society.

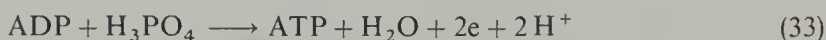
The electrolytic cell for DPNH oxidation occurs as



The overall reaction is represented by



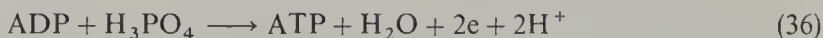
The galvanic cell for phosphorylation follows the reaction



and the overall reaction is represented by



The electrolytic phosphorylation cell is depicted as



A comparison of the electrochemical with a non-electrochemical method, such as DPNH oxidation by a titanium-nitroxide based ceramic board, shows that the velocity of phosphorylation in the former method is faster⁷⁴. The mechanism of oxidation of DPNH to DPN^+ and the reverse reduction reaction involving a one-step hydride transfer or a stepwise electron–proton–electron transfer has been investigated^{75,76} by using DPN analogues.

G. Other Diphosphonucleotides

Triphosphopyridine nucleotide (TPN^+ , coenzyme II) shows characteristic features with $E_{1/2} = -0.95$ V having a wave slope of 60 mV⁵³. It is strongly adsorbed at the electrode/solution interface; this feature is observed with DDPN^+ (deamino

diphosphopyridine nucleotide). An adsorption well or depression prior to the appearance of the first polarographic wave I is striking with DDPN^+ ⁵³. The general features of all these compounds are very similar with 1e reductions to form neutral radicals followed by their dimerization. The dimerization rate for TPN is $4.3 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ (pH 5.0) and $1.6 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ (pH 9.0) and for DDPN^+ $1.7 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ ⁵³. The activation energy for the dimerization process is estimated to be $9.0 \text{ kcal mol}^{-1}$ for TPN. The electrochemical behaviour of DDPN^+ and TPN^+ in a non-aqueous solvent indicates $E_{1/2} = -1.00 \text{ V}$ and -1.06 V vs SCE with diffusion coefficient values of 0.08×10^{-5} and $0.14 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ⁴⁸.

The synthesis of the DPN^+ analogue having ϵ -adenine (etheno bridge between exocyclic amine group and the N(6) atom of adenosine) instead of adenine and its electrochemical properties have been reported⁷⁷. It gives rise to two polarographic waves in the pH range 2–12, but the mechanisms involved in acidic and alkaline media are different. The acidic medium produces the first 1e reduction of the nicotinamide ring, which is subsequently followed by reduction of the E-adenine moiety of the β - DPN^+ molecule. This one-step successive 1e reduction is changed to two one-electron reduction steps in alkaline media as observed with DPN^+ .

One of the important questions that is addressed in DPN^+ redox chemistry concerns the mechanism by which it is converted into the reduced form, DPNH^{78} . There are two ways by which a chemical reductant can bring out this process. One is to transfer an electron, then a proton and finally another electron^{58,79}, and the other is to transfer a hydride directly⁷⁸. The discussion in the literature is oriented towards high-energy intermediates. A recent study⁷⁸ of measurements of 35 rate constants for hydride transfer in DPN^+ analogues, and application of Marcus theory by utilizing structure-sensitive solvent reorganisation parameter, λ , overwhelmingly supports the second way. The electrochemical reduction of DPN^+ follows a different route, however, as discussed earlier.

Pyridoxal-5'-phosphate and *n*-hexylamine form a Schiff's base, which has been investigated in detail in the pH range 2–13. Two waves were observed in d.c. polarography; the first is due to the reduction of the $-\text{CH}=\text{N}-$ bond and the second to the reduction of pyridoxal-5'-phosphate⁸⁰. Pyridoxal-5'-phosphate has been investigated polarographically⁸¹. The hydration and dehydration of pyridoxal-5'-phosphate over a wide pH range has been determined experimentally; the reaction is centred on the carbonyl group⁸¹. The polarographic and voltammetric data indicate that the currents are kinetically controlled.

Cytidine monophosphate exhibits a reduction at $E_{1/2} = -1.45 \text{ V}$ in acetate buffer (pH 4.1)⁸² and the reaction mechanism is kinetically controlled.

H. Flavin-5'-phosphoric acid

Flavin mononucleotide (riboflavin-5'-phosphoric acid) (FMN) and flavin adenine dinucleotide (FAD) are strongly adsorbed on electrodes, especially mercury electrodes⁸³. The molecular orientation in the adsorbed state has been probed; FAD occupies a geometrical area of 280 \AA^2 corresponding to the molecular model.

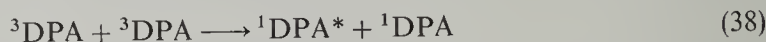
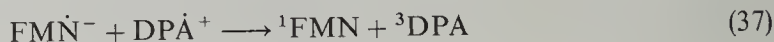
The electrochemistry of FMN is very similar to that of riboflavin in both aqueous^{84,85} and non-aqueous media⁸⁶; it exhibits a prewave. Riboflavin also has similar prewave. It undergoes 1e reduction to form the riboflavin anion with $E_{\text{pc}} = -0.78 \text{ V}$ vs SCE followed by its decomposition to give two products with one of the products undergoing reduction at -1.07 V . In aqueous media FMN reduction to an $\text{FMNH}:\text{FMNH}_2$ complex which is not further reduced is suggested⁸³. The reversible reduction of FAD and FMN has been conclusively shown by impulse polarization; the maximum height is proportional to the concentration of prosthetic group⁸⁷.

TABLE 7. Product yields from β -dicarbonyl enol phosphate electrolysis^a

Compound	Product	Yield (%)
		58
		55
		38
		63
		53
		51 R ₁ = H, R ₂ = Me 10 R ₁ = Me, R ₂ = H
		41 R ₁ = H, R ₂ = Me 18 R ₁ = Me, R ₂ = H
		26 R ₁ = CO ₂ Et R ₂ = H 22 R ₁ = H, R ₂ = CO ₂ Et

^aReprinted with permission from ref. 88a. Copyright (1990) American Chemical Society.

The electrochemluminescence of the FMN anion and the 9,10-diphenylanthracene (DPA) cation has been investigated⁸⁸. The reaction mechanism for the production of the excited state has been proposed as in equations 37 and 38. This conclusion is supported by the effect of a magnetic field on the electroluminescence intensity. This reaction is an example of an intermolecular electron transfer between FMN^- and an acceptor to produce the triplet state.

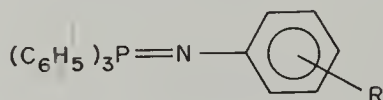


The electrolysis of β -dicarbonyl enol phosphates in DMF produces α,β -unsaturated carbonyl compounds via the attack of vinyl radical produced during the electrolysis^{88a}. Table 7 gives the yields obtained with various β -dicarbonyl enol phosphates. The results are indication of a double intramolecular cyclization of initially formed vinyl radicals.

IV. PHOSPHAENZES

A. Phospha- λ^5 -azenes: $p\pi$ - $d\pi$ double bonded systems

Phospha- λ^5 -azene systems of type 3, where $R = p\text{-NO}_2$, $p\text{-CN}$, $m\text{-NO}_2$, $p\text{-CF}_3$, $p\text{-Cl}$, $p\text{-F}$, H , $p\text{-Me}$, $p\text{-OMe}$ and $p\text{-NMe}_2$ are unique in that they have the resonance forms



(3)

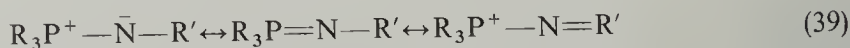


TABLE 8. Polarographic and cyclic voltammetric characteristics of phosphonitriles^a

Compound	Structure	$E_{1/2}$ (V)	Lifetime of radical (s) ^c
I. Hexaphenyl cyclotriphosphazene	$[\text{NPPh}_2]_3$	-2.65	< 1
II. Octaphenyl cyclotetraphosphazene	$[\text{NPPh}_2]_4$	-2.67	< 1
III. Tris(2,3-dioxy- naphthyl)cyclo- triphosphazene	$[\text{NP}(2,3\text{-O}_2\text{C}_{10}\text{H}_6)]_3$	-1.24	> 10
IV. Tris(1,8-dioxy- naphthyl)cyclo- triphosphazene	$[\text{NP}(1,8\text{-O}_2\text{C}_{10}\text{H}_6)]_3$	-1.83	> 10
V. Tris(2,2'-dioxy- biphenyl)cyclotri- phosphazene	$[\text{NP}(2,2'\text{-O}_2\text{C}_{12}\text{H}_8)]_3$	-2.33	—
VI. Tris(1,3,5-triphenyl)- tris(1,3,5-trifluoroethoxy)- cyclotriphosphazene	$[\text{NPPh}(\text{OCH}_2\text{CF}_3)]_3$	-2.45	< 1

^aPotentials are referred to SCE. Reprinted with permission from ref. 100. Copyright (1969) American Chemical Society.

^bFrom polarographic data.

^cCyclic voltammetric method.

TABLE 9. Cyclic voltammetric data for reduction of azenes^a

Compound	Scan rate (V S ⁻¹)	E _{pc} (V)	E _p (V)	i _{pa} /i _{pc}	D × 10 ⁻⁵ (cm ² s ⁻¹)
Ph ₃ P=NC ₆ H ₄ NO ₂ - <i>p</i>	0.02	-1.728	-1.660	0.95	1.34
	0.05	-1.730	-1.658	0.96	
	0.10	-1.732	-1.655	0.97	
	0.20	-1.734	-1.652	0.99	
Ph ₃ P=NC ₆ H ₄ NO ₂ - <i>m</i>	0.02	-1.601	-1.535	0.99	1.50
	0.05	-1.603	-1.532	0.99	
	0.10	-1.606	-1.529	0.98	
	0.20	-1.610	-1.528	0.97	

^a Medium, acetonitrile; carbon working electrode. Potentials are referred to Ag/AgNO₃. Reprinted with permission from ref. 103. Copyright (1986) American Chemical Society.

which involve $p\pi$ - $d\pi$ double bonds. The resonance forms and the electronic structures of the above systems have been probed^{89,90} by electrochemistry and spectroscopy to gain an insight into the phosphorus-nitrogen coupling⁹¹⁻⁹⁹. Phosphazines of the type [NP(OPh)₂]₃, [NP(OPh)₂]_n, [NP(NHPh)₂]₃, [NP(OCH₂CF₃)₂]₃ and [NP(O₂C₆H₄)]₃, where $n = 15\ 000$, have been investigated by electrochemical and ESR methods¹⁰⁰ to obtain structural parameters. The cyclic voltammetric characteristics are given in Table 8.

Controlled potential electrolysis of the compounds listed in Table 8 have generated ESR spectra indicating that the reduction is a simple 1e process. The ESR spectra of radical anions of I and II produced an unresolved spectrum with $g = 2$, with a total spectral line width of 20–30 G. The ESR spectra of III, IV and V showed 13–15, 5 and 15–20 lines, respectively. The delocalization of the unpaired electron in Ph₂P is indicated in the above radicals.

N-Phenyltriphenylphospha- λ^5 -azene has been examined polarographically in DMF¹⁰¹ and acetonitrile¹⁰². The anion radical formed by 1e reduction is accompanied by protonation and further reduction. In-depth studies by Pomerantz *et al.*¹⁰³ led to the characterization of electrochemical process. Tables 9–11 summarize the cyclic voltammetric characteristics for the above compounds and *m*-NO₂-substituted azene. The mechanism for the reversible cyclic voltammetric peak is represented by equation 40. The anion radical undergoes hydrogen abstraction and a further electron transfer resulting in the formation of aniline derivatives. The characteristic diffusion coefficients of azenes are given in Table 9.



1. Oxidative patterns

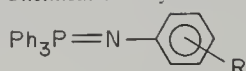
The azenes exhibit irreversible peaks in cyclic voltammetric experiments, the location of the peak potential being dependent on the nature of the substituent R¹⁰³. Table 10 gives the characteristic peak potentials for a large number of azenes. With *p*-OMe and *p*-NMe₂ as substituents, the anodic peaks are partially reversible at a slow rate of 0.10 V s⁻¹ and tend towards complete reversibility at 10 V s⁻¹. The cyclic voltammetric patterns suggest an initial electron transfer followed by a chemical reaction. The stability of the one-electron oxidation product can be correlated with the lowering of the charge density on the substituted aryl ring by the substituent.

TABLE 10. Oxidative peak potentials of azenes^a

R ^b	E _{pa} (V)	R ^b	E _{pa} (V)
<i>p</i> -NO ₂	0.844	<i>p</i> -F	0.480
<i>p</i> -CN	0.741	H	0.465
<i>m</i> -NO ₂	0.752	<i>p</i> -CH ₃	0.371
<i>p</i> -CF ₃	0.740	<i>p</i> -OCH ₃	0.210
<i>p</i> -Cl	0.512	<i>p</i> -N(CH ₃) ₂	-0.195

^aPotentials are with respect to Ag/AgNO₃. Medium, acetonitrile; working electrode platinum. Reprinted with permission from ref. 103. Copyright (1986) American Chemical Society.

^bBasic structure



The effect of the substituent on the primary oxidation wave for phosphazenes has also been successfully correlated with the ionization potential (energy of the highest occupied molecular orbital, E_{HOMO}). The observed trend is an indication of the site of electron abstraction in the azenes as the lone pair on nitrogen which is delocalized into the aromatic ring¹⁰³; the plot of $E_{1/2}$ of anilines with the same substituents and E_{pa} of phosphazenes yields a straight line.

The electronic properties of phosphazenes are of importance in understanding the electron-withdrawing power^{91,93,100-105} of these molecules. The redox potentials of phosphazenes bonded to ferrocene have been measured; the *trans* annular linked

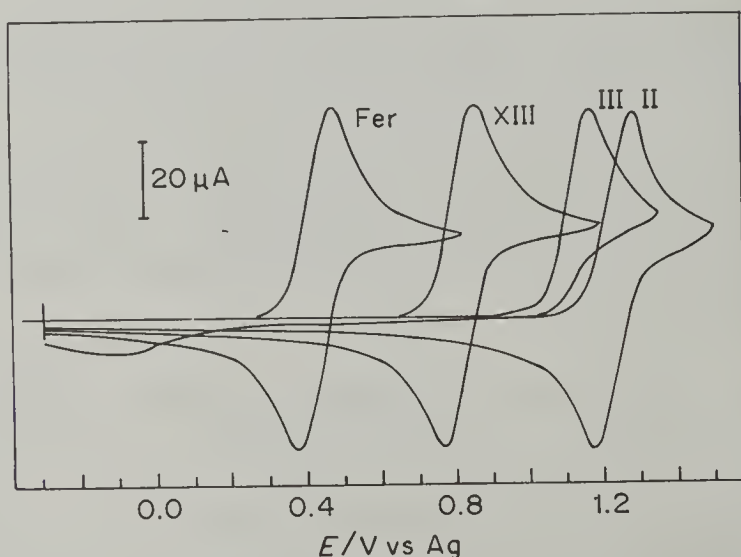
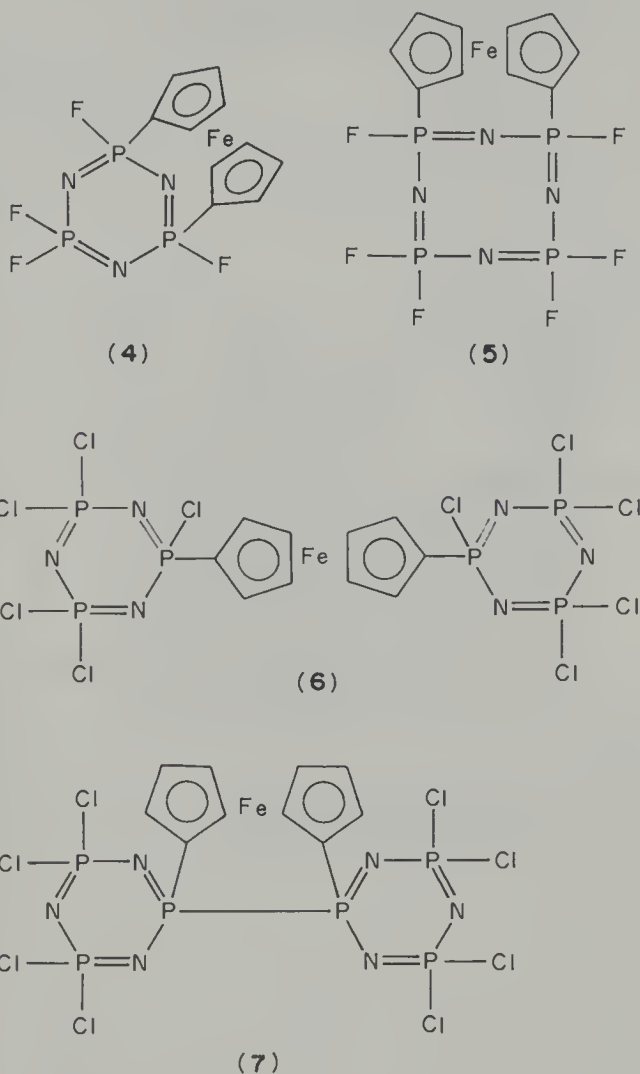


FIGURE 12. Cyclic voltammetry of 1 mM solutions of ferrocene (Fer) and XIII = $[\text{N}_3\text{P}_3\text{F}_5(\eta\text{-C}_5\text{H}_4)\text{Fe}(\eta\text{-C}_5\text{H}_5)]$, III = $[\text{N}_3\text{P}_3\text{F}_4(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]$ and II = $[1,5\text{-N}_4\text{P}_4\text{F}_6(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]$ in acetonitrile containing 0.1 M tetraethylammonium perchlorate. Sweep rate, 0.10 V s^{-1} . Reprinted with permission from ref. 106. Copyright (1988) American Chemical Society.

ferrocenyl phosphazenes have potentials shifted twice as much as those of the pendent analogues. The structures of a few ferrocene-substituted phosphazenes (4–7) are shown.



The oxidation potentials are dependent on the non-geminal site substituent. The cyclic voltammetric reversibility of phosphazenes is well defined in Figure 12.

The electronic properties and redox conduction of ferrocene-substituted high polymeric phosphazenes¹⁰⁷ are markedly different from the solution behaviour of the monomers. Surface-immobilized films of $[N_3P_3F_4(\eta-C_5H_4)_2Fe]_n$ in CH_2Cl_2 exhibit a large difference in their oxidation and reduction peak potentials ($\Delta E_p = 0.26$ V). For $[N_3P_3(OCH_2CF_3)_5(\eta-C_5H_4)Fe(\eta-C_5H_5)]_n$ the separation is negligible, showing a symmetric pattern. A similar pattern was noticed for $[N_3P_3(OCH_2CF_3)_4(\eta-C_5H_4)_2Fe]_n$. The mechanism of charge transport in these polymeric films has been probed and the charge transport rates are given in Table 12. The structure of polyphosphazene (shown in Figure 13) together with the data in Table 12 suggests that the charge transport rate depends on the mobility of the ferrocene. The greater rate of charge transport observed with the rigid bridged ferrocene polymer $[N_3P_3(OCH_2CF_3)_4(\eta-C_5H_4)_2Fe]_n$ suggests a metal-like conduction occurring in the partially oxidized form¹⁰⁷.

TABLE 11. Cyclic voltammetric oxidation peak potentials of phosphazenes^a

Aryl- <i>P,P,P</i> -triphenylphosphazene ^b	E_{pa} (V)	Ferrocene-substituted phosphazenes ^c	E_{pa} (V)
$\text{Ph}_3\text{P}=\text{NC}_6\text{H}_4\text{NO}_2\text{-}p$	0.844	$[\text{N}_6\text{P}_6\text{Cl}_{10}(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]$	1.25
$\text{Ph}_3\text{P}=\text{NC}_6\text{H}_4\text{CN-}p$	0.741	$[\text{1,5-}\text{N}_4\text{P}_4\text{F}_6(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]$	1.21
$\text{Ph}_3\text{P}=\text{NC}_6\text{H}_4\text{NO}_2\text{-}m$	0.752	$[\text{N}_3\text{P}_3\text{F}_4(\eta\text{-C}_5\text{H}_5)_2\text{Fe}]$	1.18
$\text{Ph}_3\text{P}=\text{NC}_6\text{H}_4\text{CF}_3\text{-}p$	0.740	$[\text{N}_6\text{P}_6\text{Cl}_8(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]$	1.18
$\text{Ph}_3\text{P}=\text{NC}_6\text{H}_4\text{Cl-}p$	0.512	$[\text{N}_3\text{P}_3\text{F}_3(\text{OCH}_2\text{CH}_3)_3(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]$	1.14
$\text{Ph}_3\text{P}=\text{NC}_6\text{H}_4\text{F-}p$	0.480	$[\text{N}_6\text{P}_6(\text{OCH}_2\text{CF}_3)_{10}(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]$	1.13
$\text{Ph}_3\text{P}=\text{NPh}$	0.465	$[\text{N}_3\text{P}_3\text{F}_3(\text{OC}_6\text{H}_5)_3(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]$	1.12
$\text{Ph}_3\text{P}=\text{NC}_6\text{H}_4\text{Me-}p$	0.371	$[\text{1,3-}\text{N}_4\text{P}_4(\text{OCH}_2\text{CF}_3)_6(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]$	1.06
$\text{Ph}_3\text{P}=\text{NC}_6\text{H}_4\text{OMe-}p$	0.210	$[\text{1,3-}\text{N}_4\text{P}_4(\text{OCH}_2\text{CF}_3)_6(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]$	0.98
$\text{Ph}_3\text{P}=\text{NC}_6\text{H}_4\text{NMe}_2\text{-}p$	-0.195	$[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_4(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]$	0.94
		$[\text{N}_3\text{P}_3\text{F}_5(\eta\text{-C}_5\text{H}_4)\text{Fe}(\eta\text{-C}_5\text{H}_5)]$	0.86
		$[\text{N}_4\text{P}_4\text{F}_7(\eta\text{-C}_5\text{H}_4)\text{Fe}(\eta\text{-C}_5\text{H}_5)]$	0.85
		$[\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_5(\eta\text{-C}_5\text{H}_4)\text{Fe}(\eta\text{-C}_5\text{H}_5)]$	0.75

^aPt working electrode. Medium: acetonitrile.^bPotentials referred to Ag/AgNO₃. Taken from ref. 103.^cPotentials referred to Ag. Reprinted with permission from ref. 107. Copyright (1988) American Chemical Society.

TABLE 12. Charge transport rates of ferrocene-substituted polyphosphazenes^a

Polymer	$(D_{\text{ct}}^{1/2}C)_{\text{anod.}}$ ($10^{-8} \text{ mol cm}^{-2}$)	$(D_{\text{ct}}^{1/2}C)_{\text{cath.}}$ ($10^{-8} \text{ mol cm}^{-2}$)
$[\text{N}_3\text{P}_3\text{F}_4(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]_n$	1.41 ± 0.15	1.52 ± 0.24
$[\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_5(\eta\text{-C}_5\text{H}_4)\text{Fe}(\eta\text{-C}_5\text{H}_5)]_n$	1.96 ± 0.18	1.81 ± 0.44
$[\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_4(\eta\text{-C}_5\text{H}_4)_2\text{Fe}]_n$	3.20 ± 0.20	6.19 ± 1.65

^aMeasurements were made on potential step transients. Reprinted with permission from ref. 107. Copyright (1988) American Chemical Society.

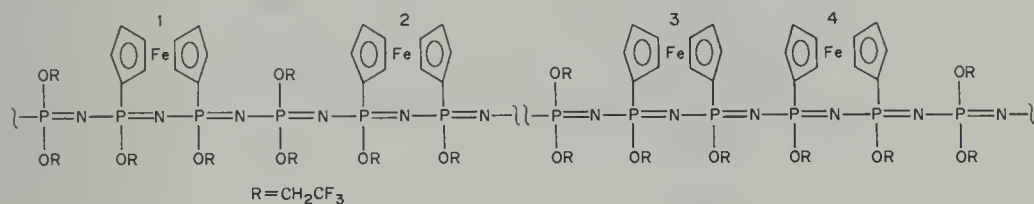


FIGURE 13. Structure of polyphosphazene. The numbers represent the number of anchored units.

V. PHOSPHORUS-BRIDGED METALLICS

A. Rhodium Phosphido-bridged Complexes

The electronic effects in phosphido-bridged complexes of transition metals have evoked a number of studies^{108–113}. The electrochemistry of the Rh—Rh double bond and the isomerization of the rhodium(I) system on electrochemical reduction and reoxidation have been of interest in determining the electronic effects. A series of metal carbonyl complexes (phosphido-bridged complexes) were investigated by Winner *et al.*¹¹⁴ and Dessy and coworkers^{115–117}. The carbonyl complexes of rhodium provide a case for reversible geometrical isomerization¹¹⁸. Figure 14 depicts such an isomerization for a di-*tert*-butyl phosphido-bridged complex on reduction. This scheme is a typical case of electron transfer followed by chemical reaction followed by further chemical reaction (ECE), where the chemical reaction is a geometrical isomerization producing an isomer which is more easily reduced than the parent compound. The rate constant for this isomerization is estimated to be about 600 s^{-1} ¹¹⁸. Interestingly, the reoxidation at an electrode produces the parent species through the steps shown in Figure 15; the original geometry of the metal is restored. The cyclic voltammetric features interestingly provide a model for understanding this isomerization (see Figure 16) a typical cathodic peak followed by two anodic peaks representing an ECE process. The X-ray crystallographic structure of the dianion shows an imposed inversion centre at the middle of the Rh—Rh vector. The structure of $[\text{Rh}(\mu\text{-}t\text{-Bu}_2\text{P})(\text{CO})_2]_2$ shown in Figure 17 indicates the possibility of three isomers with metal bonds of order 0, 1 and 2 extremely close in energy¹¹⁹; the square-planar–tetrahedral and square-planar–square-planar isomers are the only ones actually observed.

The electrochemical reduction of rhodium phosphido-bridged complexes places the added electron on a π^* -antibonding orbital of the metal–metal doubly bonded isomer. Further reduction of this system requires 2e to be accommodated, which forces the tetrahedral–tetrahedral configuration.

The cyclic voltammetric pattern of $[\text{Rh}(\text{PPh}_3)_3]_3(\text{DME})(\text{ClO}_4)$ correlates well with the rhodium phosphido-bridged complexes^{119–122}; it is reduced in two 1e reversible

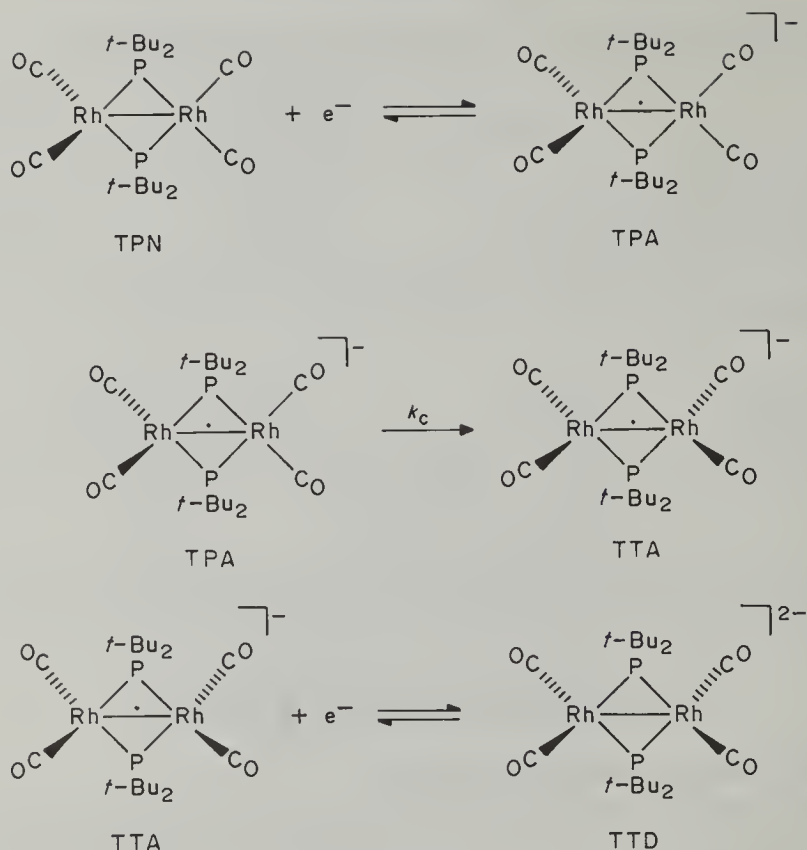
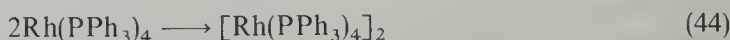
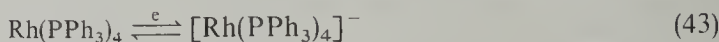
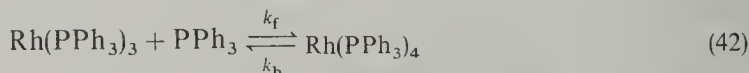
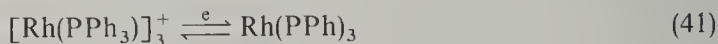


FIGURE 14. Reaction mechanism. Geometrical isomerization following the reduction of rhodium phosphido-bridged complexes. Representation of ECE mechanism is indicated. The abbreviations for each species describe the approximate geometry of the metals (T = tetrahedral, P = planar) and the charge on the complex (N = neutral, A = anion, D = dianion). Reprinted with permission from ref. 118. Copyright (1985) American Chemical Society.

steps (equations 41–44). The first reduction has $E^\circ = -1.20$ V and the second $E_2^\circ = -1.73$ V¹¹⁹. The above reaction scheme is sensitive to the excess PPh_3 concentration. The kinetic parameter for reaction⁴² has been evaluated from the dependence of the scan rate on the half-wave potential; it is given in Table 13.



The effect of PPh_3 concentration on the kinetic parameter is also revealed by the data in Table 13. The ESR spectrum of $[\text{Rh}(\text{PPh}_3)_4]$ obtained by controlled potential 1e reduction of $[\text{Rh}(\text{PPh}_3)_3]^+$ shows anisotropy (Figure 18) with $g_1 = 2.22$, $g_2 = 2.10$ and $g_3 = 1.99$. The interaction of the metal with one phosphorus ligand is revealed by the

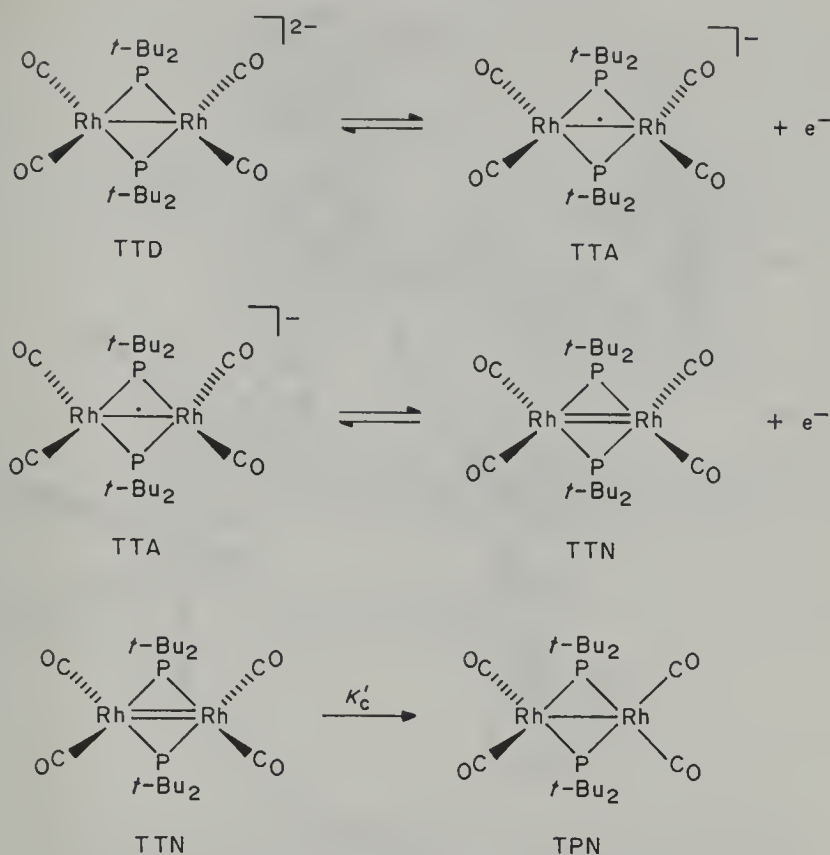


FIGURE 15. Reaction mechanism of geometrical isomerisation (reverse of that shown in Figure 14) on oxidation of the final product. The last step is a chemical step. Abbreviations as in Figure 14. Reprinted with permission from ref. 118. Copyright (1985) American Chemical Society.

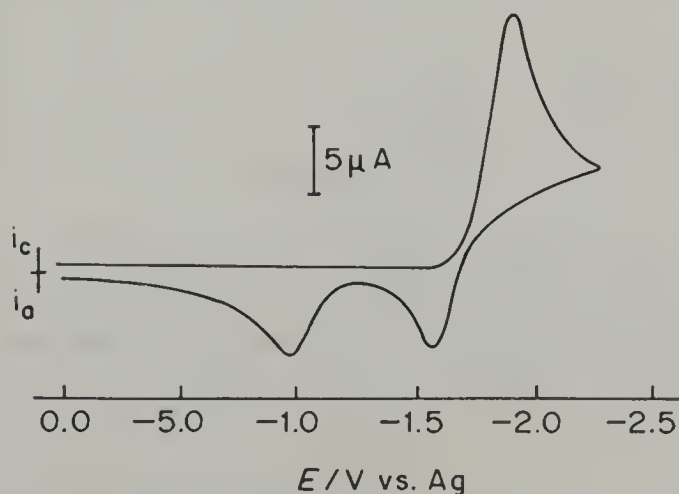


FIGURE 16. Cyclic voltammogram of $[\text{Rh}(\mu\text{-Bu}_2\text{P})(\text{CO})_2]_2$ in THF. Sweep rate, 0.20 V s^{-1} ; working electrode, platinum disc; reference electrode, Ag wire (potential with respect to SCE, -0.36 V). Copyright (1985) American Chemical Society.

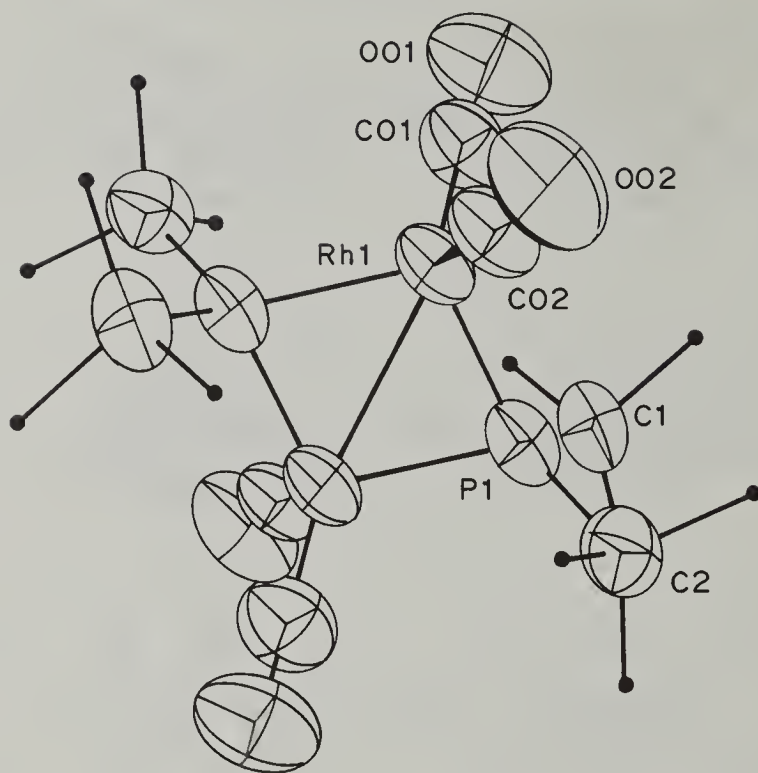


FIGURE 17. Structural view of $[\text{Rh}(\mu\text{-}t\text{-Bu}_2\text{P})(\text{CO}_2)]_2^{2-}$. Methyl groups on the *tert*-butyls are represented by sticks. Reprinted with permission from ref. 118. Copyright (1985) American Chemical Society.

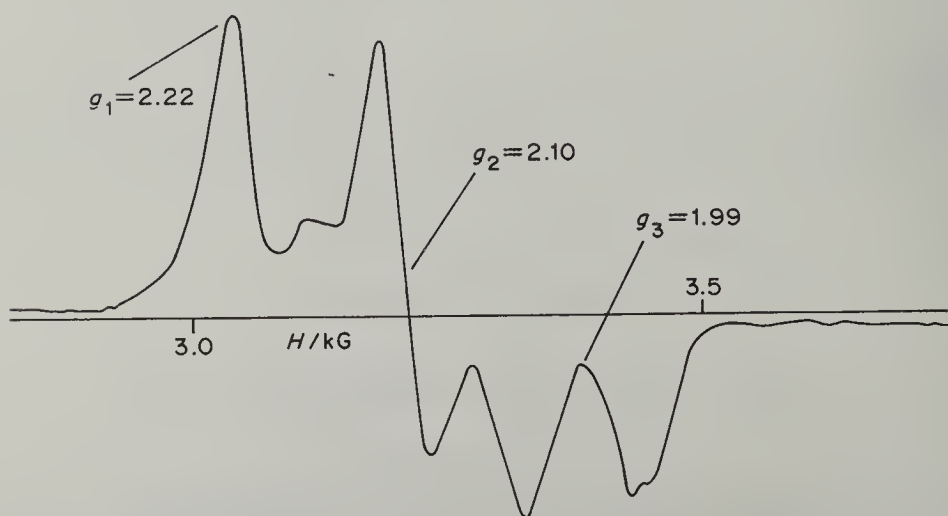


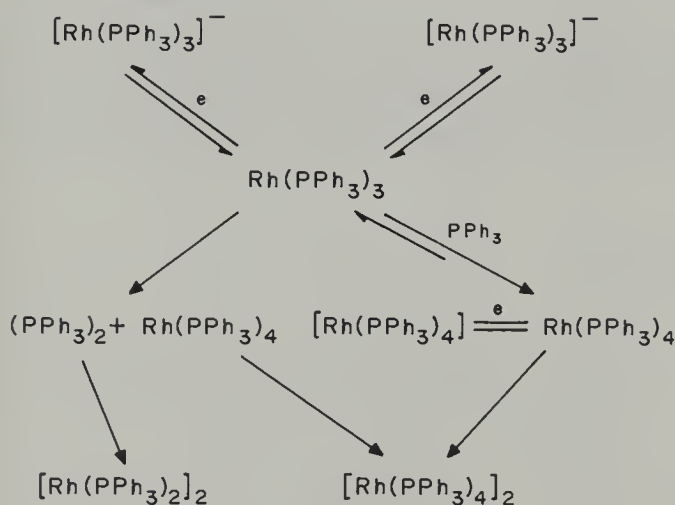
FIGURE 18. ESR spectrum of $[\text{Rh}(\text{PPh}_3)_4]$ in DME at 120 K. Reproduced by permission of Elsevier Publishers from ref. 120.

TABLE 13. Kinetics of triphenylphosphine addition to $\text{Rh}(\text{PPh}_3)_3^a$

PPh_3 concentration (M)	Sweep rate (V s^{-1})	$E_{\text{p}/2}$ (V)	$E_{\text{p}/2} - E_{\text{p}/2}^\circ$ (V)	$K(k_f + k_b)^{-1/2}$ ($\text{s}^{-1/2}$)
0.01	0.02	-1.233	0	—
	0.20	-1.239	0.006	—
	0.50	-1.245	0.013	0.23
	1.00	-1.253	0.020	0.27
	2.00	-1.258	0.023	0.24
	5.00	-1.270	0.035	0.30
0.016				0.078
0.030				0.15
0.100				0.26

^aConcentration of $[\text{Rh}(\text{PPh}_3)_3]^+ = 1 \text{ mM}$ in DME; supporting electrolyte, 0.2 M tetra-*n*-butylammonium perchlorate; temperature of the experiment, 25°C. Potentials are with respect to Ag/AgClO_4 .

spectrum. It appears to have a distorted tetrahedral geometry. The electrochemical redox pattern of $[\text{Rh}(\text{PPh}_3)_3]^+$ is shown in Scheme 1.



SCHEME 1

The second-order rate constant for the formation of $[\text{Rh}(\text{PPh}_3)_4]$ is estimated to be $1.4 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$; ligand redistribution competes with this with a rate constant of $300 \text{ l mol}^{-1} \text{ s}^{-1}$, which forces us to conclude that the former process of forming $[\text{Rh}(\text{PPh}_3)_4]$ is complete on the time scale of typical cyclic voltammetric experiments (ms to s). The second wave is well developed as the ligand addition is faster; this is depicted in Figure 19. It is possible to prepare the d^9 complex $[\text{Rh}(\text{PPh}_3)_4]$ by the electrochemical method¹²⁰.

B. Nickel Complexes with Triphenylphosphine and Ethylene

Nickel exhibits a pattern similar to rhodium in its reaction with PPh_3 ¹²². The redox reactions may be represented as equations 45 and 46, where $\text{X} = \text{Cl}^-$, Br^- or I^- and

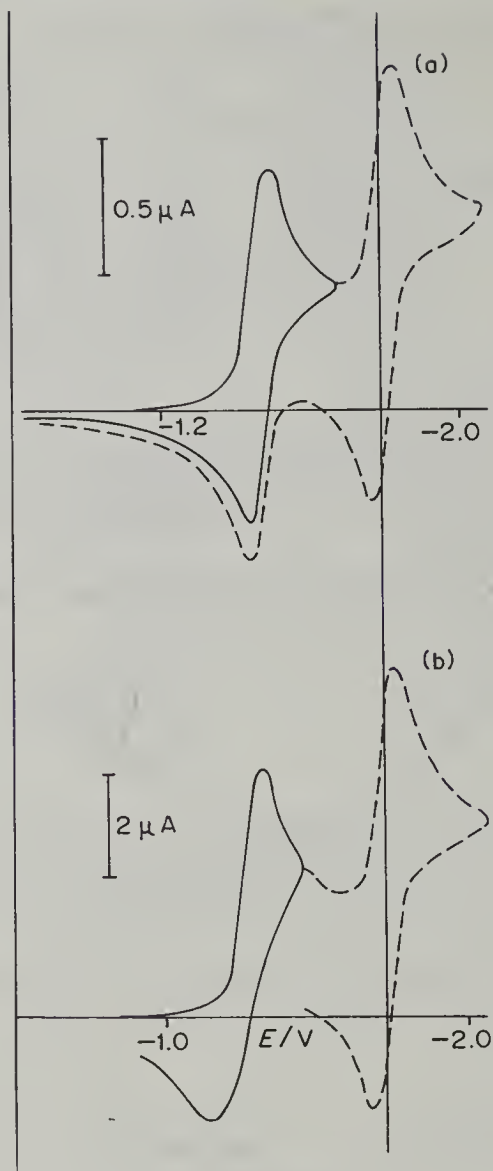
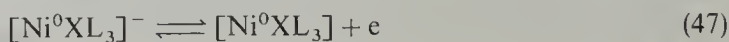
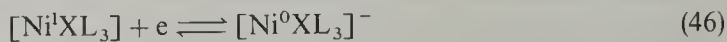
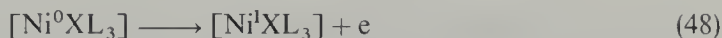


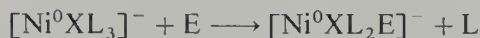
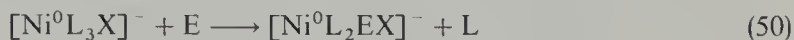
FIGURE 19. Cyclic voltammograms of 1 mM $[\text{Rh}(\text{PPh}_3)_3]^+$ in DME containing 0.2 M tetra-*n*-butylammonium perchlorate. (a) $\text{PPh}_3 = 10^{-2}$ M; sweep rate, 5.0 Vs.^{-1} (b) in the presence of $\text{PPh}_3 = 10^{-1}$ M. Reproduced by permission of Elsevier Publishers.

$\text{L} = \text{PPh}_3$; $[\text{Ni}^{\text{I}}\text{XL}_3]$ is yellow and $[\text{Ni}^0\text{XL}_3]^-$ is red. These nickel(0) and Nickel(I) complexes can be oxidized as equations 47–49.





These redox processes have been confirmed using *N*-methylpyrrolidinone as the solvent. When ethylene is introduced into the medium before initiating the electrochemical step, the reaction scheme is modified as in equations 50 or 51, where E represents ethylene. $[\text{Ni}^0\text{L}_2\text{E}]$ is oxidized at 0.16 V. Now,



Steps 52 and 53 occur at -0.40 and 0 V, respectively. The current–voltage curves depicting the above processes are shown in Figure 20.

1. Nickel bis-1,2-diphenylphosphinoethane

The existence of the complexes $[\text{NiD}_2]^{2+}$, $[\text{NiD}_2\text{X}]^+$ and $[\text{NiX}_2\text{D}]$, where X is Cl^- or Br^- and D = bis-1,2-diphenylphosphinoethane, were established by electrochemical work^{123,124}. Using *N*-methylpyrrolidine as solvent, the electrochemical reduction produces nickel(I) or nickel(0) complexes. At a mole ratio of 1D per Ni the zerovalent

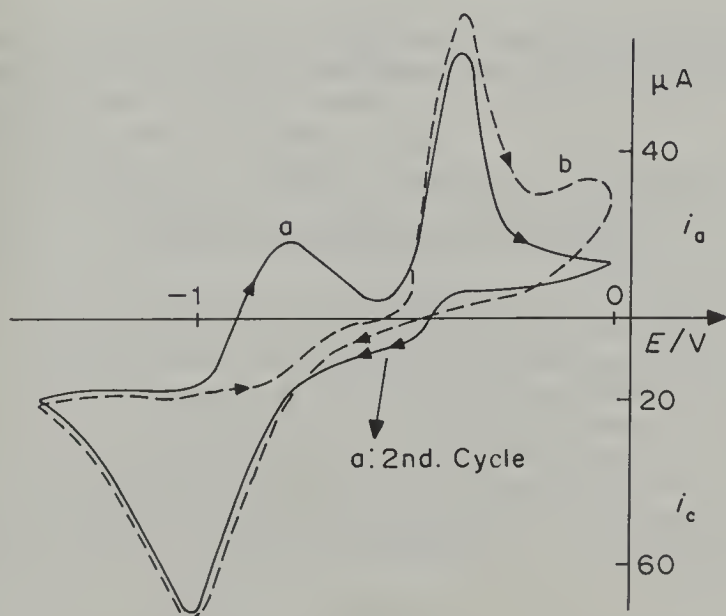


FIGURE 20. Cyclic voltammetric curves of NiX_2L_2 ($\text{X} = \text{Br}^-$) in *N*-methylpyrrolidinone solutions at a gold micro electrode. The dashed line shows the curve in the presence of ethylene. Sweep rate, 0.1 V s^{-1} . Note the absence of an anodic peak in the presence of ethylene. Reproduced by permission of Elsevier Publishers from ref. 122.

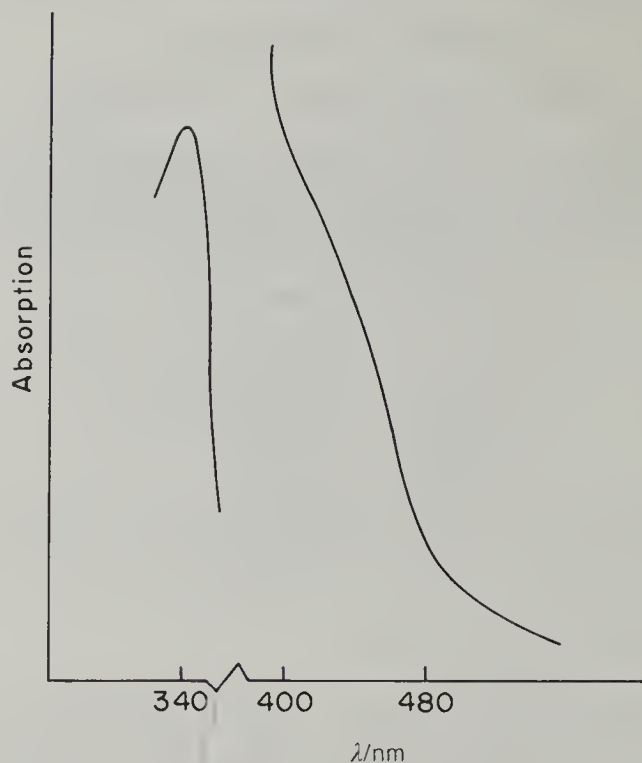
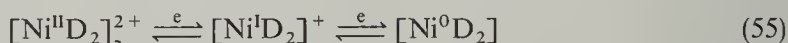
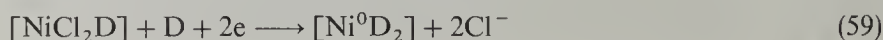
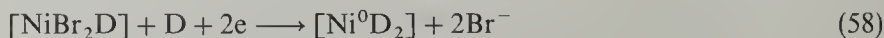


FIGURE 21. UV absorption spectrum of 2 mM $[\text{NiClO}_4\text{D}_2]$ in *N*-methylpyrrolidone.

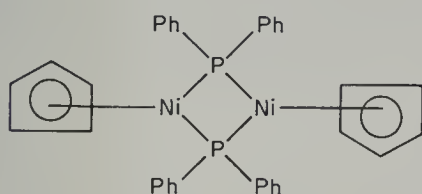
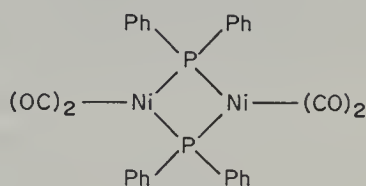
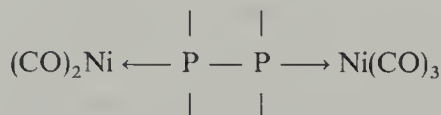
complex reacts rapidly with organic halides (RX). The electrocatalytic reduction of halide is proposed which has a hypothetical intermediate $[\text{RNiXD}]^{119,120}$. The establishment of an equilibrium for D:Ni ratios of ≥ 2 is to produce $[\text{NiD}_2]^{2+}$ through the equations 54 and 55.



The species $[\text{Ni}^{\text{II}}\text{D}_2]^{2+}$ is yellow and shows the absorption spectrum as shown in Figure 21. Nickel(II) species disproportionate more in acetonitrile than in *N*-methylpyrrolidinone. The disproportionation reaction leads to nickel(0) species via reaction 56. The $\text{p}K$ of disproportionation $= \Delta E_{1/2}/0.06 \approx 2$. The reactivity of $[\text{Ni}^{\text{II}}\text{D}_2]^{2+}$ towards halides has been examined¹²⁵; when the ratio $\text{Br}^-:[\text{Ni}^{\text{II}}\text{D}_2]^{2+} = 1.0$, a 2e reversible reduction is observed (equation 57). As this ratio increases and reaches an excess in Br^- , an irreversible 2e reduction process is observed due to reaction 58. Notice that the end products of reactions 57 and 58 are the same except for the higher numbered moles of Br^- generated in reaction 61. The corresponding reaction for Cl^- (in place of Br^-) is shown in equation 59.

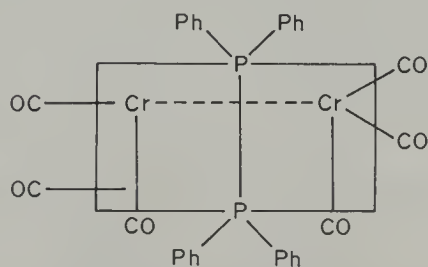


Dessy and coworkers^{115,117} arrived at an interesting generalization based on the electrochemical patterns of nickel carbonyl complexes, namely that a reversible electron transfer requires a metal—metal bond to exist in the complex to obtain a stable radical anion. For example, $[(\pi\text{-C}_5\text{H}_5)\text{NiPPh}_2]_2$ (**8**) produces a stable radical anion on electrochemical reduction at -2.30 V vs a Ag/AgClO_4 electrode, giving an ESR spectrum of 10 G wide with a g value of 2.060. The nickel carbonyl species **9** also produces a reversible cyclic voltammetric wave at -1.75 V; an exhaustive electrochemical reduction at this potential generates an ESR spectrum of a purple anion radical with a total width of 6 G having a characteristic $g = 1.979$ ¹¹⁶. On the other hand, a species without a metal—metal bond having structure **10**, where the nickel atoms are separated by phosphorus, produces an irreversible wave at -2.40 V; in this case the anion could not be generated¹¹⁶ for this compound. Popdoko *et al.*'s¹²⁶ results on nickel(II) complexes with diphenylphosphine are in parallel with those for the above-mentioned carbonyl complexes.

**(8)****(9)****(10)**

C. Chromium Carbonyls Bound to Phosphorus

Dessy *et al.*¹¹⁶ suggested the formation of a metal—metal bond in chromium complexes of the type $[\text{Cr}(\text{CO})_4\text{PMe}_2]_2$. The structure is visualized as **11**, where the metal—metal bond is shown by the dashed line. The electrochemical reduction of **11**

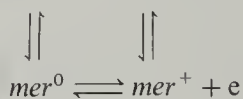
**(11)**

occurs at $E_{1/2} = -1.85$ V; the wave is reversible owing to the presence of the metal—metal bond. The $2e$ reduction product gives an ESR spectrum having a 1:2:1 triplet arising from the interaction of the odd electron with both phosphorus nuclei; a phosphorus splitting constant of 13 G and a proton splitting constant of 12 G are observed in the spectrum.

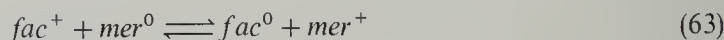
This spectrum is attributed to reactions 60 and 61, where X represents **11**. The radical anion shows an infrared stretching frequency which is shifted by 100 cm^{-1} relative to the neutral species¹¹⁶. This arises from the interaction of $d\pi$ orbitals of the metal with the carbonyl antibonding $2\pi^*$ orbitals. The chromium carbonyl complex containing phosphorus ligands has an octahedral configuration about each chromium with the two octahedra sharing an edge which is occupied by PMe_2 bridges. Metal—metal bond formation is indicated by the diamagnetism studies¹¹⁶.



The redox chemistry of tricarbonyl derivatives of chromium complexed with polycyclic tridentates shows¹²⁷⁻¹³² two reversible 1e oxidation processes. Bond *et al.*¹³² observed isomerization, cross-redox and self-exchange reactions in $[\text{Cr}(\text{CO})_3\text{P}_3]^{10+}$, where P represents monodentate phosphorus ligands $\text{P}(\text{OMe})_3$, $\text{P}(\text{OPh})_3$, $\text{P}(\text{OMe})_2\text{Ph}$ and PMe_2Ph . The electrochemical data are summarized in Table 14 and indicate quasi-reversible electron transfer processes. The stereochemistry in the facial (*fac*) and meridional (*mer*) forms forces the following redox equilibria in $[\text{Cr}(\text{CO})_3\text{P}_3]^{10+}$:



The electrochemical characteristics indicate a cross-redox reaction (63).



The controlled potential oxidation of fac^0 generates *mer*- $[\text{Cr}(\text{CO})_3\text{P}_3]$. It is represented by the above reaction⁶³. A cyclic voltammetric study shows (see Table 15) that at -57°C , the isomerization of fac^+ to mer^0 is inhibited. The isomerization of fac^+ to mer^0 is extremely slow in dichloromethane, but the conversion of mer^+ to fac^+ is very fast. The ESR spectra of *mer*- $[\text{Cr}(\text{CO})_3(\text{PMe}_2\text{Ph})_3]^+$ at 273 and 213 K and of *mer*- $[\text{Cr}(\text{CO})_3(\text{P}(\text{OMe})_2\text{Ph})_3]^+$ at 298, 273 and 213 K are depicted in Figure 22. The spectral features include a doublet of triplets due to ^{31}P hyperfine coupling, which is consistent with meridional form of the chromium(I) cation. These spectra show no hyperfine splitting due to ^{53}Cr ($I = 3/2$). The spectrum of *mer*- $[\text{Cr}(\text{CO})_3(\text{P}(\text{OMe})_2\text{Ph})_3]^+$ is broad at room temperature owing to fast exchange between the cation and the neutral species. In both 18- and

TABLE 14. Electrochemical data for the oxidation of $[\text{Cr}(\text{CO})_3\text{P}_3]$ complexes^a

Compound	$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (V)	E_p^{ox} (V)	E_p^{red} (V)
<i>mer</i> - $[\text{Cr}(\text{CO})_3(\text{P}(\text{OMe})_3)_3]$	0.356	0.056	0.400	0.322
<i>mer</i> - $[\text{Cr}(\text{CO})_3(\text{P}(\text{OPh})_3)_3]$	0.732	0.0555	0.784	0.674
<i>mer</i> - $[\text{Cr}(\text{CO})_3(\text{P}(\text{OMe})_2\text{Ph})_3]$	0.287	0.070	0.347	0.237
<i>fac</i> - $[\text{Cr}(\text{CO})_3(\text{P}(\text{OMe})_3)_3]$	0.456	0.057	0.561	0.475
<i>fac</i> - $[\text{Cr}(\text{CO})_3(\text{PMe}_2\text{Ph})_3]$	0.219	0.062	0.290	0.205
<i>mer</i> - $[\text{Cr}(\text{CO})_3(\text{PMe}_2\text{Ph})_3]$	-0.067	0.060	-0.005	-0.100

^a Solvent, CH_2Cl_2 ; working electrode, Hg electrode; E_p values recorded at 500 mV s^{-1} ; reference electrode, Ag/AgCl . Taken from ref. 132. Copyright American Chemical Society.

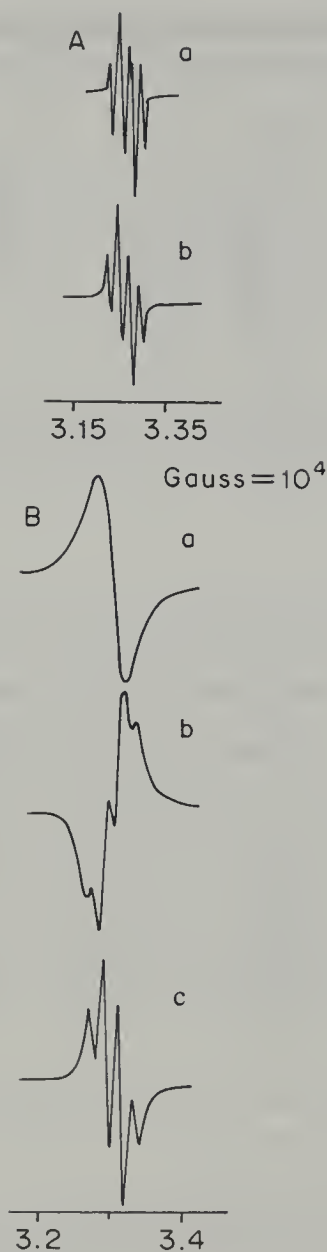
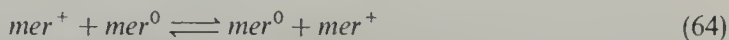


FIGURE 22. ESR spectra of (A) *mer*-[Cr(CO)₃(PMe₂Ph₃)⁺ at (a) 273 K and (b) 213 K and (B) *mer*-[Cr(CO)₃(POMe)₂Ph₃]⁺ at (a) 298 K, (b) 273 K and (c) 213 K. Abscissa in gauss; 1 = unit = 10³ G. Solvent CH₂Cl₂. Reprinted with permission from ref. 132. Copyright (1984) American Chemical Society.

17-electron complexes, the *mer*-isomer is favoured and the line broadening occurs due to reaction 64.



Chromium tricarbonyl bis[bis(diphenylphosphino)] methane and bis[1,2-bis(diphenylphosphino)]ethane complexes are susceptible to 1e redox reactions. The electrochemical characteristics of meridional and facial forms are given in Table 16. The stepwise conversion processes are shown in reaction 65. The second electron step occurring at positive potentials, close to the solvent (CH₂Cl₂) limit, results in the generation of chromium (reaction 66), where dppm = Ph₂PCH₂PPh₂ and dppe = Ph₂PCH₂CH₂PPh₂.

TABLE 15. Cyclic voltammetric oxidation of *fac*-[Cr(CO)₃(PMe₂Ph)₃]^a

Temperature (°C)	Sweep rate (mV s ⁻¹)	E_p^{oxb} (V)	E_p^{redb} (V)	E_p^{oxc} (V)	E_p^{redc} (V)
18	500	0.34	0.18	0.00	-0.13
	50	0.26	d	-0.03	-0.10
-15	500	0.36	0.15	0.01	-0.15
	50	0.30	0.17	-0.03	-0.09
-43	500	0.40	0.13	0.03	-0.17
	50	0.30	0.17	d	d
-57	500	0.46	0.09	d	d
	50	0.31	0.15	d	d

^a Working electrode, Pt electrode; medium, CH₂Cl₂ containing 0.1 M Bu₄NClO₄. Potentials are vs Ag/AgCl. Reprinted with permission from ref. 132. Copyright (1984) American Chemical Society.

^b For process $fac \rightleftharpoons fac^+ + e$



^c For process $mer \rightleftharpoons mer^+ + e$.

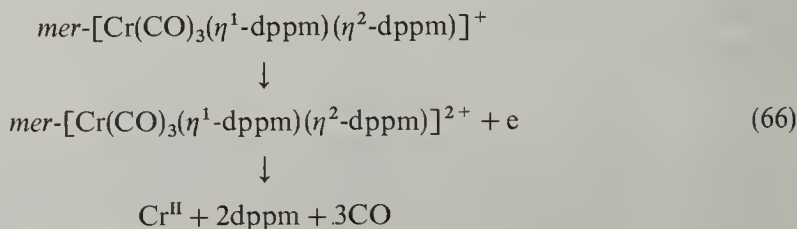
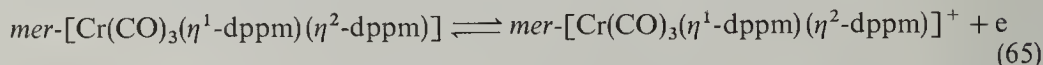
^d No peak observed.

TABLE 16. Electrochemical data for the [Cr(CO)₃(η¹-PP)(η²-PP)] complexes^a

Compound	Solvent	E_p^{ox} (V)	E_p^{red} (V)	E^0 (V)	T (V)
<i>mer</i> -[Cr(CO) ₃ (η ¹ -dppm)(η ² -dppm)]	CH ₂ Cl ₂	0.15	0.02	0.09	20
	Acetone	0.08	-0.00	0.04	20
<i>mer</i> -[Cr(CO) ₃ (η ¹ -dppm)(η ² -dppm)] ⁺	CH ₂ Cl ₂	1.27			20
	Acetone	1.00			
<i>fac</i> -[Cr(CO) ₃ (η ¹ -dppe)(η ² -dppe)]	CH ₂ Cl ₂	0.47	0.38	0.43	-78
	CH ₂ Cl ₂	0.43	-	-	20
<i>mer</i> -[Cr(CO) ₃ (η ¹ -dppe)(η ² -dppe)]	CH ₂ Cl ₂	0.22	0.13	0.18	20
<i>mer</i> -[Cr(CO) ₃ (η ¹ -dppe)(η ² -dppe)] ⁺	CH ₂ Cl ₂	1.24	-	-	20

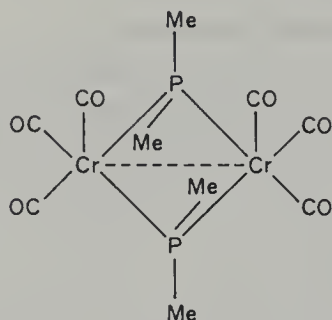
^a Potentials are referred to Ag/AgCl. Reprinted with permission from ref. 131. Copyright (1986) American Chemical Society.

The facial form of [Cr(CO)₃(η¹-dppe)(η²-dppe)] shows a similar 1e oxidation wave but the product decomposes to chromium(II). The cation is more stable at -78 °C.



Bis-(μ-phosphido)dichromium species exhibit reversible voltammetric waves with $n = 2^{134}$. The resulting dianion disproportionates to give a monoanion and the ESR

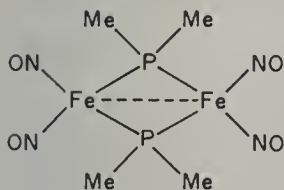
spectrum of the anion radical shows hyperfine couplings with two identical phosphorus atoms and the triplet split into a 13-fold multiplet due to Me groups of the compound (12).



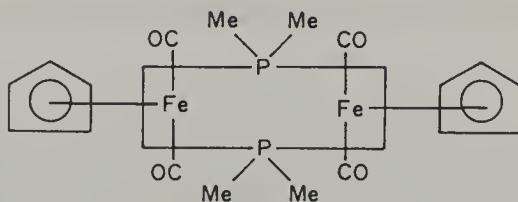
(12)

D. Iron Carbonyls and Nitrosyl Complexed to Diphenylphosphine

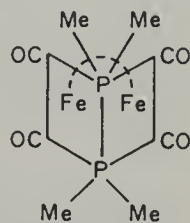
Iron derivatives are useful in understanding metal—metal bond interactions¹¹⁶ in compounds such as 13–15. The octahedral configuration around the metal in $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{PPh}_2]_2$ shows essentially two octahedra sharing an edge; this compound exhibits a polarographic wave at -0.20 V vs Ag/AgClO_4 , oxidizing to a deep-blue radical cation. The wave is reversible and on exhaustive electrolysis the product shows a featureless ESR spectrum which is 12.5 G wide. The second polarographic wave is located at -0.50 V; this wave is attributed to dication formation¹¹⁶. When an Fe—Fe bond exists in the complex, such as in $[(\text{CO})_3\text{FePMe}_2]_2$, the structure is octahedral around each iron, with the octahedra sharing a face; the metal—metal bond occupies one of the ligand positions. It undergoes a 2e reduction with $E_{1/2} = -2.10$ V. The dianion shows no ESR signal but on addition of the parent produces a radical anion exhibiting a line width of 75 G, which is difficult to resolve further. The radical anion has $g = 1.977$ ¹¹⁶.



(13)



(14)



(15)

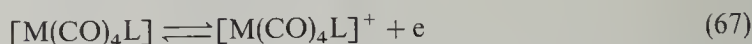
The tetrahedral configuration that exists in the nitroso compound $[(\text{NO})_2\text{FePPh}_2]_2$ has $E_{1/2}^I = -1.70$ V Ag/AgClO_4 and $E_{1/2}^{II} = -2.19$ V vs Ag/AgClO_4 . The formation of a radical anion and dianion is confirmed by ESR studies. The anion gives a phosphorus triplet (1:2:1) with $\Delta H_p = 20$ G with $g = 1.937$.

Several dialkylamino phosphorus iron carbonyls have been synthesized from bis(diisopropylamino)phosphine with iron carbonyls by King and Fu¹³¹. These carbonyl complexes have an unusual property of rapid and selective cleavage of one diiso-

propylamino group on reaction with hydrogen halides; this selective cleavage might be caused by radical cation formation.

E. Molybdenum Carbonyl Bond to Phosphorus

The molybdenum cluster system $[\text{PhMoPPh}_2(\text{CO})]_3$ produces an ill-defined irreversible polarographic wave. It does not produce a radical species on exhaustive reduction in DME¹¹⁶, at the first polarographic wave. Complexes of the type $[\text{Mo}(\text{CO})_4\text{R}_2\text{P}(\text{CH}_2)_3\text{PR}_2]$, where R = F, Cl, C_6F_5 , MeO, Ph, Me or C_6H_{11} show characteristic quasi-reversible oxidations as in reaction 67.



The effectiveness of the phosphorus ligands to remove a charge from the metal follows qualitatively the order of electronegativity of the substituent on the donor phosphorus atom, i.e. $\text{F} > \text{Cl} > \text{C}_6\text{F}_5$; $\text{C}_6\text{FH}_5 > \text{Me} > \text{C}_6\text{H}_{11}$ ¹³³. The cyclic voltammetric data for the above complexes are given in Table 17. For comparison, data for the corresponding chromium complexes are also included. The $E_{1/2}$ of the two series correlate very well, as shown by Figure 23.

The complexes of $[\text{Mo}(\text{CO})_3\text{P}_3]$, where P is a monodentate phosphorus ligand, undergo oxidation by the scheme in equation 68. The *fac*-form undergoes oxidation in CH_2Cl_2 with $E_p^{\text{ox}} = 0.68 \text{ V}$ and the *mer*-form at $E_{\text{pa}} = 0.42 \text{ V}$.

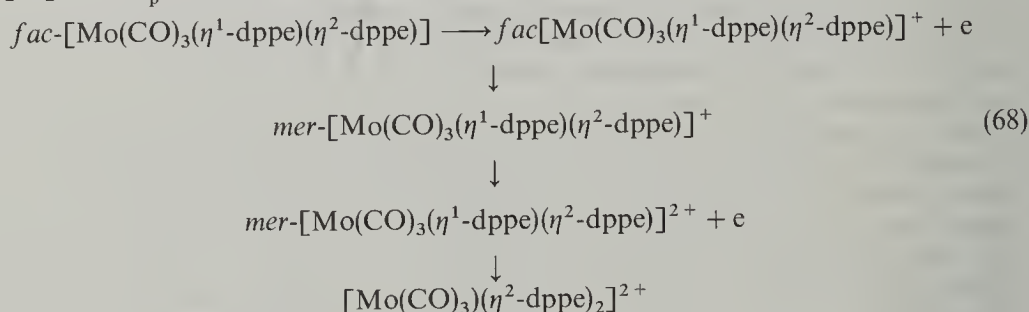


TABLE 17. Electrochemical data for $[\text{M}(\text{CO})_6]$ and $[\text{M}(\text{CO})_4\text{R}_2\text{P}]\text{CH}_2\text{PR}_2$ complexes in CH_2Cl_2 and acetonitrile^a

Solvent	R	M = Mo			M = Cr		
		(V)	(V)	(V)	(V)	(V)	(V)
CH_2Cl_2	C_6F_5	1.46	1.10	1.28	1.235	0.860	1.05
	MeO	1.38	1.04	1.21	1.15	0.840	0.995
	Ph	1.24	0.86	1.05	1.025	0.690	0.860
	Me	0.710	0.470	0.530	0.560	0.260	0.410
	$\text{M}(\text{CO})_6$	1.65			1.49	1.320	1.410
MeCN	F	1.37			1.32	1.18	1.250
	C_6F_5	1.23			1.01	0.87	0.940
	MeO	1.18			0.96	0.82	0.890
	Me	0.46			0.35	0.19	0.270
	$\text{M}(\text{CO})_6$						

^aVoltages are vs SCE. Working electrode, glassy carbon; supporting electrolyte, Bu_4NClO_4 ; $E_{1/2} = (E_a + E_c)/2$. Reprinted with permission from ref. 133. Copyright (1984) American Chemical Society.

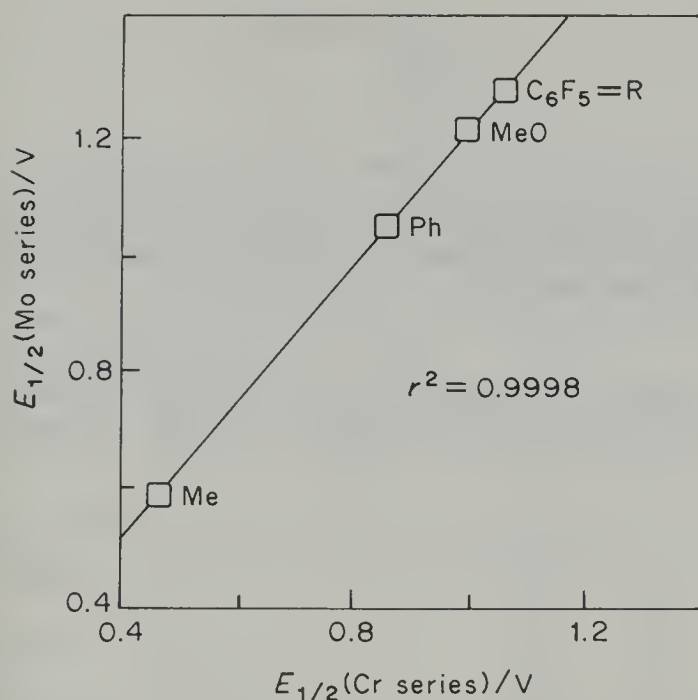
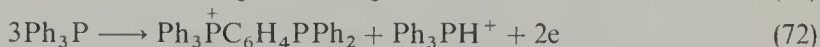


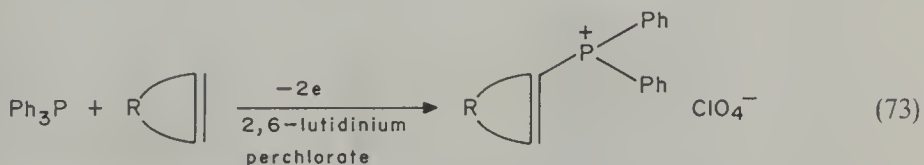
FIGURE 23. Correlation of half-wave potentials for $[\text{M}(\text{CO})_4\text{-R}_2\text{PCH}_2\text{PR}_2]$ complexes in CH_2Cl_2 . Reprinted with permission from ref. 133. Copyright (1984) American Chemical Society.

VI. PHOSPHONIUM SALTS

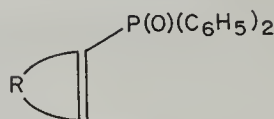
By oxidation of Ph_3P using ferricinium ion in a nitrogen atmosphere, a phosphonium salt, Ph_4P^+ , has been prepared¹³⁵. This oxidation produces ferrocene in 100% yield. Schiavon *et al.*¹³⁶ proposed the oxidation scheme shown in equations 69–71 and the overall reaction 72. The reduction of Ph_3P^+ is observed at -2.20 V.



Cycloalk-1-enyl phosphonium salts are prepared in reasonable yields by a constant-current electrolysis of Ph_3P in dichloromethane at a graphite anode in the presence of cycloalkenes by reaction 73¹³⁷. The phosphonium salts are converted to the

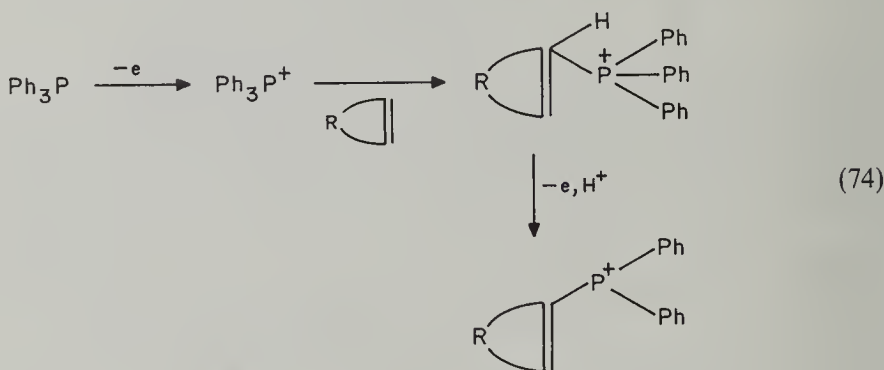


corresponding phosphine oxide by treatment with NaOH dissolved in aqueous ethanol¹³⁸. The oxides have structure 16. The yields and the melting point of



(16)

phosphonium salts are given in Table 18. The oxidation of triphenylphosphine at a controlled potential at 1.40 V vs silver wire results in the formation of cycloalk-1-enyl phosphonium salts (equation 74).



The charge-transfer salt formed by reaction of tetracyanoquinodimethane (TCNQ) and diphosphonium iodide undergoes a 2e oxidation at a carbon paste electrode¹³⁹; reactions 75 and 76 occur in acetonitrile. Similar schemes can be generated for $D'P^{2+}$, where $D'P^{2+} = PhMeP^+CH=CHP^+MePh_2$ ¹³⁹.



The phosphonium salts are electrochemically reduced to phosphines¹⁴⁰ through reactions 77 and 78, but the neutral radical R^\bullet is electrochemically active and undergoes reactions 79–81.

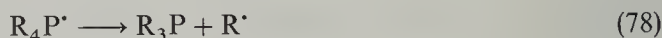


TABLE 18. Electrochemical preparation of cycloalk-1-enyl phosphonium salts^a

Cycloalkene	Yield (%)	M.p. (°C)
Cyclopentene	53	277–279
Cyclohexene	53	290–291
Cycloheptene	56	214–216
Cyclooctene	53	197–199
Norbornene	66	192–104

^a3 mmol of Ph_3P and 15 mmol of cycloalkene in CH_2Cl_2 containing 0.2 M 2,6-lutidinium perchlorate at 1.07 mA cm^{-2} . Electrolysis is carried out for 8 h.



Table 19 gives the half-wave potentials, diffusion currents and the number of electrons consumed in the reaction for different substituents. The half-wave potentials for $[\text{Ph}_3\text{P}(\text{CH}_2)_n\text{PPh}_3]\text{Br}_2$ for $n = 1-12$ show the trend represented in Figure 24. Cleavage of the phosphorus—carbon bond occurs in all the phosphonium salts¹⁴⁰. This can be used successfully in the analytical determination of phosphonium salts (phenyltrimethylphosphonium iodide and tetra-*O*-tolylphosphonium iodide) in the range 0.001–0.005 M¹⁴¹; the reductions consist of two successive 1 e steps.

The electrolytic reductive cleavage of cyanoalkyl phosphonium compounds of the type $\text{Ph}_3\text{P}^{+}(\text{CH}_2)_n\text{CNX}^{-}$, where $n = 1-4$, has been demonstrated by Wagenknecht and Baizer¹⁴² through polarographic and controlled potential electrolysis. The anion X

TABLE 19. Electrochemical characteristics of phosphonium compounds^a

Phosphonium bromide	$-E_1$ (V)	i_d (μA)	n_1	n_2
Methyltriphenyl-	1.862	2.60	2.7	1.1
Cyclohexyltriphenyl-	1.859	2.94	1.6	
	2.092	0.28	1.2	
Ethyltriphenyl-	1.837	1.79	3.1	1.2
	1.970	0.80	1.7	
Isopropyltriphenyl-	1.833	1.56	9.1	
	2.092	2.14	0.7	1.2
<i>n</i> -Propyltriphenyl-	1.822	1.36	2.3	
	1.962	0.72	1.4	
	2.075	0.14	2.2	1.2
<i>n</i> -Butyltriphenyl-	1.802	1.16	2.1	
	1.984	1.22	1.2	
2-Butyltriphenyl-	1.709	1.38	6.3	1.0
	2.686	1.20	1.0	
Isobutyltriphenyl-	1.720	1.26	2.4	
	2.039	1.28	0.6	2.0
<i>tert</i> -Butyltriphenyl-	1.657	0.86	2.0	
	2.041	0.54	2.2	
Allyltriphenyl-	1.626	2.10	1.4	0.9
	1.775	0.20	0.9	
	2.065	0.45	2.2	
	2.468	1.35	2.1	1.3
Benzyltriphenyl- ^b	1.552	2.80	1.3	
Cyanomethyltriphenyl- ^b	1.301	1.62	0.9	
	2.051	0.84	0.9	1.3
Benzhydryltriphenyl-	1.271	0.58	1.3	
	2.067	0.13	2.2	
Dimethyldiphenyl-	2.087	4.38	1.3	0.9
Trimethylphenyl-	2.271	5.10	0.9	
Diethyldiphenyl-	2.031	2.58	2.1	
4-Bromo- <i>n</i> -butyltriphenyl-	1.160	0.46	0.4	0.7
	1.766	2.25	3.4	
	2.151	1.25	0.6	
Methylenebistriphenyl-	1.195	2.50	0.8	1.7
	1.817	0.95	1.7	

(continued)

TABLE 19. (continued)

Phosphonium bromide	$-E_1$ (V)	i_d (μ A)	n_1	n_2
	1.932	1.19	2.7	
Dimethylbistriphenyl-	1.475	2.50	1.9	
	2.064	2.70	2.2	
Trimethylbistriphenyl-	1.307	0.40	2.7	
	1.712	5.40	2.1	
	2.054	1.00	2.0	
Tetramethylenebistriphenyl-	1.798	8.80	1.8	
	2.058	0.90	2.1	
Pentamethylenebistriphenyl-	1.807	5.04	3.6	
Hexmethylenebistriphenyl-	1.822	4.75	1.8	
	2.000	1.10	0.8	
Octamethylenebistriphenyl-	1.732	3.70	2.3	
	1.971	1.50	1.2	
Decamethylenebistriphenyl-	1.715	1.25	10.9	
	1.916	0.65	2.2	
	2.073	0.45	—	
Dodecamethylenebistriphenyl-	1.664	1.50	2.7	
	1.944	2.50	0.9	
<i>n</i> -Propyltri- <i>p</i> -anisyl-	1.934	0.68	0.7	
	2.109	1.12	0.9	
	2.364	0.90	0.7	
Methyltrisdimethylamino-	1.642	0.31	0.3	
	2.098	0.64	0.7	
Benzyltrisdimethylamino-	1.637	0.17	0.5	
	2.230	2.65	6.3	
Benzyltris- <i>N</i> -trimorpholino-	1.627	0.31	—	
	2.206	6.40	0.4	
Methyltris- <i>p</i> -dimethylaminophenyl-	1.697	0.17	—	
Benzyltris- <i>p</i> -dimethylaminophenyl-	1.279	0.36	0.8	
	1.886	0.21	—	
<i>p</i> -Hydroxyphenyltriphenyl- ^b	1.000	2.40	0.7	
	2.046	0.50	3.0	
<i>p</i> -Anisyltriphenyl-	1.835	1.26	1.4	
	1.988	0.26	1.8	
	2.128	0.56	1.9	
<i>p</i> -Aminophenyltriphenyl-	1.801	0.88	2.0	
	1.916	0.34	1.3	
	2.144	0.30	2.3	
	2.473	1.56	1.2	
<i>p</i> -Dimethylaminophenyltriphenyl-	1.777	2.60	2.1	0.7
	2.091	0.41	1.1	
<i>p</i> -Tolyltriphenyl-	1.692	2.50	2.0	0.8
	2.073	0.26	1.7	
<i>m</i> -Tolyltriphenyl-	1.684	2.28	2.0	0.7
	2.066	0.46	1.9	
Tetraphenyl-	1.680	2.80	2.1	0.6
	2.068	0.15	1.5	
<i>o</i> -Tolyltriphenyl-	1.678	2.12	2.0	0.3
	2.061	0.21	1.8	
<i>p</i> -Benzhydrylphenyltriphenyl-	1.668	0.60	1.0	0.6
<i>p</i> -Cumyltriphenyl-	1.654	2.78	1.7	0.7
	2.056	0.40	1.3	

(continued)

TABLE 19. (continued)

Phosphonium bromide	$-E_1$ (V)	i_d (μ A)	n_1	n_2
<i>p</i> -Carbohydroxyphenyltriphenyl-	1.630	1.10	0.6	0.2
	2.346	2.70	0.6	
1-Naphthyltriphenyl-	1.439	0.88	3.5	1.1
	1.781	0.50	0.9	
	2.054	0.45	1.9	
	2.326	1.70	0.8	
2-Naphthyltriphenyl-	2.488	1.30	2.0	
	1.554	1.80	2.0	
	1.653	0.75	1.4	
	2.049	0.44	1.4	
	2.207	1.00	1.1	
	2.325	2.20	1.0	
<i>p</i> -Biphenyltriphenyl-	2.494	1.65	1.4	
	1.527	1.70	2.4	0.9
	1.655	0.35	1.1	
	2.076	0.29	1.6	
	2.279	1.30	1.0	
	2.490	4.70	1.2	
<i>p</i> -Nitrophenyltriphenyl-	0.454	2.90	3.1	1.5
	1.502	1.35	1.1	
	1.831	0.65	2.0	
	2.118	0.50	1.8	
<i>p</i> -Phenylenebistriphenyl-	1.155	0.40	1.6	
	1.269	0.08	1.5	
	1.477	1.24	1.2	
	1.667	2.48	1.6	
	2.069	0.24	1.5	
	2.435	4.70	3.1	
<i>p</i> -Trifluoromethylphenyltriphenyl-	1.410	7.85	1.1	
	2.077	0.35	2.2	
	2.323	7.90	0.7	
	2.482	1.20	3.3	
<i>p</i> -Phenylsulphophenyltriphenyl-	1.227	2.06	1.8	
	1.677	0.65	3.1	
	1.954	1.15	1.3	
	2.083	0.17	1.3	
	2.350	1.65	1.4	
	2.490	1.05	2.0	
Di- <i>p</i> -tolyl-diphenyl-	1.695	2.48	1.5	0.9
	2.092	1.18	0.9	
Tri- <i>p</i> -tolylphenyl-	1.727	2.60	2.1	1.2
	2.071	0.32	3.0	
Di- <i>p</i> -anisyl-diphenyl-	1.790	0.908	1.3	
	1.954	3.12	—	
Tri- <i>p</i> -anisylphenyl-	1.848	1.30	1.2	
	2.006	0.22	2.1	
	2.128	0.74	2.9	
Tri- <i>p</i> -tolyl- <i>p</i> -cumyl-	1.713	2.50	2.2	0.6
	2.004	0.46	2.5	
	2.455	0.28	1.6	

^aConcentration of phosphonium salt: 10^{-3} M. Potentials are vs SCE. Reproduced by permission of Elsevier Publishers from ref. 140.

^bPhosphonium chloride.

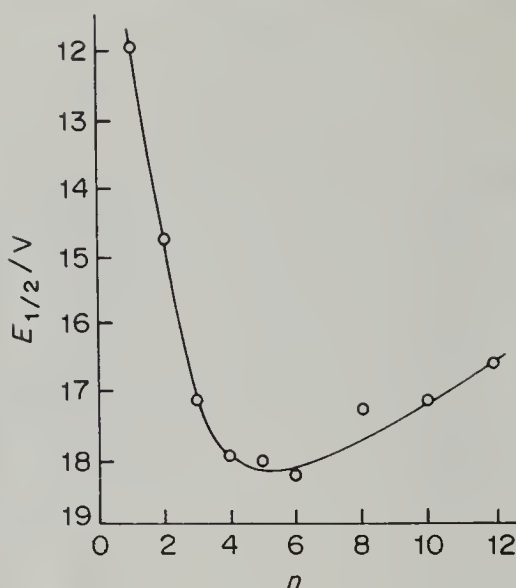


FIGURE 24. Half-wave potentials of $\text{Ph}_3\text{P}(\text{CH}_2)_n\text{PPh}_3\text{Br}_2$ vs the number of CH_2 groups. Reproduced by permission of Elsevier Publishers from ref. 140.

generally represents a halide or *p*-toluenesulphonate. The compounds produce three or four polarographic waves depending on the value of *n*. The first wave is attributed to reactions 82–84. The second wave appears to be due to the reduction of **19**, represented by reaction 85. Species **18** decomposes by reaction 86. The third wave is observed due to the reduction of Ph_3P formed in reaction 86¹. The electrolytic reductive coupling has been demonstrated by the isolation of the products. Table 20 gives the yields of the products obtained in electroreduction of $[\text{Ph}_3\text{P}^+(\text{CH}_2)_n\text{CN}]\text{X}^-$ in the presence of styrene; styrene captures the carbonion formed in the reductive cleavage. Ph_3PO is formed due

TABLE 20. Yields of products in the reduction of $[\text{Ph}_3\text{P}^+(\text{CH}_2)_n\text{CN}]\text{X}^-$ in the presence of styrene^a

Product	Yield (%)			
	<i>n</i> = 1, X = Br	<i>n</i> = 2, X = T ^c	<i>n</i> = 3, X = Br	<i>n</i> = 4, X = Br
Ph_3P	26.4	58–74	82.5	57
Ph_3PO	23.6	—	—	—
$\text{Me}(\text{CH}_2)_n\text{CN}$	^b	^b	^b	^b
C_6H_6	—	14	—	10
$[\text{CN}(\text{CH}_2)_n]_2\text{Hg}$	—	^b	^b	^b
$\text{CH}_2=\text{CHCN}$	—	^b	—	—
$\text{CN}(\text{CH}_2)_n\text{CN}$	—	^b 6	—	—
$\text{CN}(\text{CH}_2)_n\text{CHPh}$				
$\text{CN}(\text{CH}_2)_n\text{CHPh}$				

^aThe data are for the passage of 1 faraday per mole. Reprinted with permission from ref. 142. Copyright (1966) American Chemical Society.

^bProduct isolated, but yield not determined.

^cT = Toly.

to reaction of $\text{Ph}_3\text{P}=\text{CHCN}$ with water during the isolation of the products. Pardini *et al.*¹⁴³ have investigated benzyl cinnamyl polyenylphosphonium salts in a similar way.

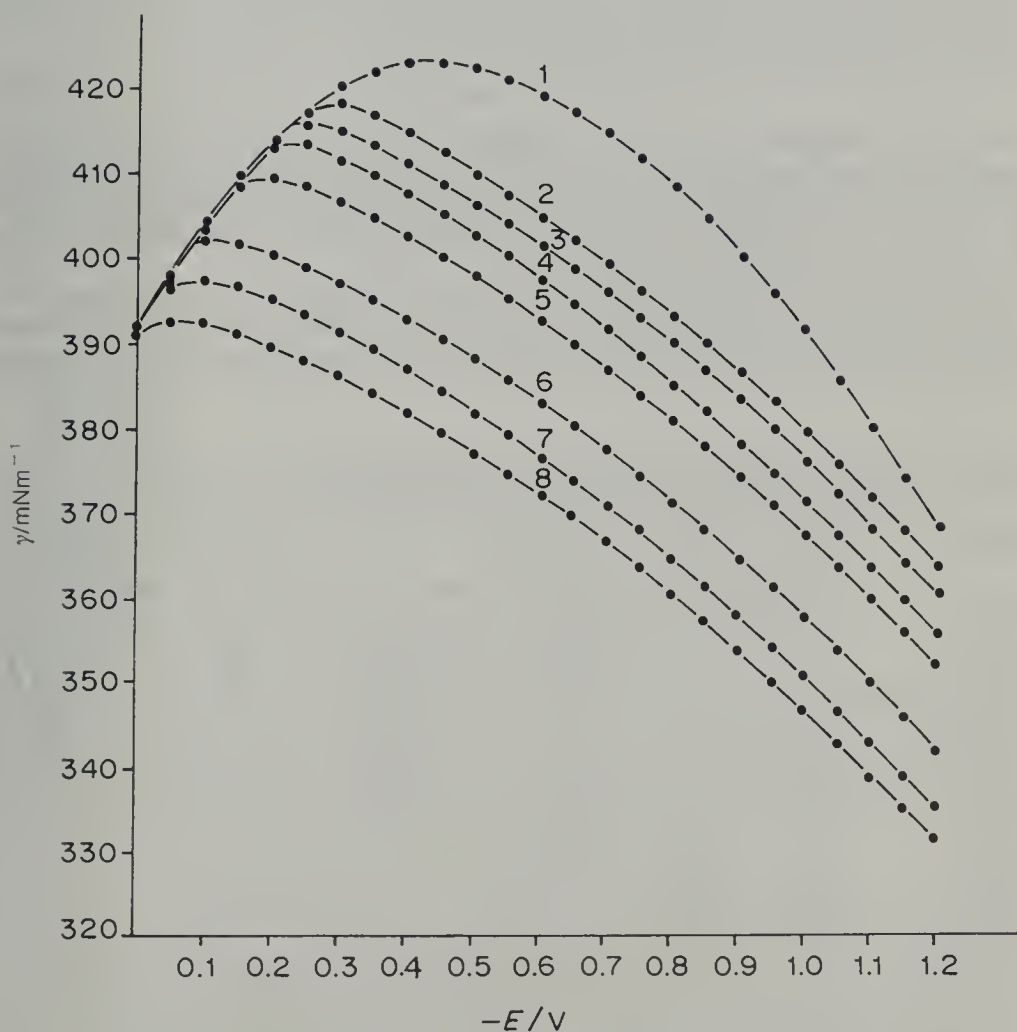
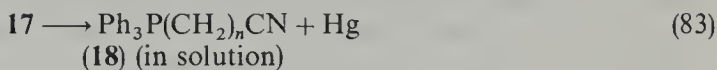
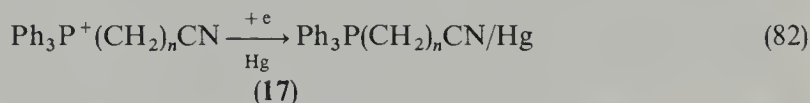


FIGURE 25. Electrocapillary curves of phosphine oxides at various concentrations in 0.1 M H_2SO_4 : (1) 0; (2) 2×10^{-4} ; (3) 4.98×10^{-4} ; (4) 9.9×10^{-4} ; (5) 1.96×10^{-3} ; (6) 1×10^{-2} ; (7) 2×10^{-2} ; (8) 5×10^{-2} M. Reproduced by permission of Elsevier Publishers.

VII. INTERFACIAL ADSORPTION BEHAVIOUR OF PHOSPHORUS(V) COMPOUNDS

The adsorption of phosphine oxides of the type dialkyl-, phenyl-, alkyl dimethyl- and alkyl diethyl-phosphine oxides at the mercury/electrolyte solution interface is a common feature¹⁴⁴ with the extent of adsorption controlled by the composition of the medium and the structure of phosphine oxides. The interaction constant of the oxide is also dependent on its nature. The electrocapillary curves of phosphine oxides are shown in Figure 25. The surface tension, γ , values in the presence of $C_5H_{11}(C_2H_5)_2PO$ systematically decrease as the bulk concentration of the oxide increases. An increase in chain length by one CH_2 group causes a decrease in γ by about 7 mNm^{-1} . This effect is observed for the homologous dialkylphenylphosphine oxides. The adsorption of the phosphine oxides is analysed through the Frumkin isotherm defined by equation 87, where b is the adsorption coefficient and a is the lateral interaction constant; θ is the degree of coverage, defined by $(C_0 - C)/(C_0 - C_s)$, where C_0 is the differential capacity of the supporting electrolyte, C is the differential capacity for the phosphine oxide at any concentration and C_s is the saturation differential capacity. Table 21 gives estimates of the adsorption parameters of phosphine oxides. The parameters a and b increase by an order of magnitude on increasing the chain length.

$$bc(1 - \theta) = \theta \exp(-2a\theta) \quad (87)$$

The areas occupied by adsorbed phosphine oxides in aqueous solutions were experimentally evaluated at 0.63, 0.57 and 0.52 nm^2 for Ph_3PO , $EtPh_2PO$ and $MePh_2PO$, respectively. The calculated area values based on structural considerations for these three molecules are 0.71, 0.63 and 0.57 nm^2 , respectively. The lower experimental values are attributed to multi-layer adsorption^{145,146}.

Adsorption of phosphine oxides influences the rate of electrochemical reductions^{147,148}. The three homologous dialkylphenylphosphine oxides PhR_2PO , where $R = Et, Pr$ and Bu , influences the reduction of Cu^{2+} with the rate being proportional to the adsorbed

TABLE 21. Interfacial adsorption characteristics of phosphine oxides^a

Molecule ^b	E_{\max} (V)	$\sigma_{\max}^{M^d}$ ($\mu\text{C.cm}^{-2}$)	$\Gamma_s \times 10^{10}$ (mol cm^{-2})	a	b ($10^3 \text{ dm}^3 \text{ mol}^{-1}$)	$-\Delta G_A^{\circ e}$ (kJ.mol^{-1})
Et_2PhPO	-0.80	—	2.7	1.3 ± 0.2	4.00	30
Pr_2PhPO	-0.75	—	2.6	1.5 ± 0.3	38.66	36
Bu_2PhPO	—	—	2.5	1.7 ± 0.5	43.0	43
$BuPh_2PO$	—	—	—	1.3 ± 0.1	4.31	30
$PeMe_2PO$	-0.75	—	2.9	1.0 ± 0.1	0.92	26
$HxMe_2PO$	-0.75	—	2.8	1.4 ± 0.2	4.16	30
$HxEt_2PO$	-0.73	—	2.4	1.2 ± 0.3	120.4	38
Ph_3PO	-0.72	-5.85	2.65	—	—	—
$EtPh_2PO$	-0.75	-5.95	2.93	—	—	—
$MePh_2PO$	-0.76	-6.00	3.22	—	—	—
Ph_3PO^c	-0.90	-6.40	2.36	—	—	—
$EtPh_2PO^c$	-0.95	-6.90	2.66	—	—	—
$MePh_2PO^c$	-1.02	-7.50	2.91	—	—	—

^aAqueous solution. Adsorption on Hg surface.

^bPe = pentyl; Hx = hexyl.

^cMethanolic solution.

^d σ_M^M = Electrode charge.

^e ΔG_A^0 = Adsorption free energy change.

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film pressure. There appears to be a surface reaction between adsorbed reactant and the electroactive species. Electrosorption of tri-*n*-octylphosphine oxide in methanol and methanol–water solutions has been examined at a polarized mercury electrode^{148–151}.

Several dithiophosphates and bis(diphenyldithiophosphine) disulphides exhibit catalytic currents due to their adsorption on mercury^{151–153}. Trialkyl phosphine oxides, on the other hand, inhibit non-metallic reactions at the electrode¹⁵⁴.

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CHAPTER 4

Photochemistry of phosphine chalcogenides

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I. INTRODUCTION

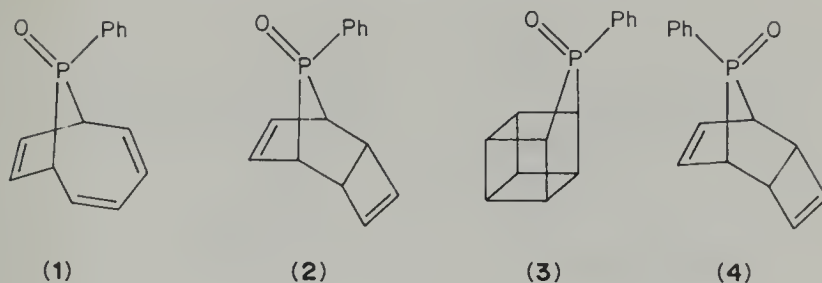
The number of publications in the field of preparative photochemistry has increased continuously. In 1958 Schönberg wrote one of the first systematic reviews on this topic, which was revised in 1968¹. The most important publications since then have been reviewed². The photochemistry of phosphine chalcogenides³ had its beginnings with the investigations of Niebergall⁴ concerning the addition of phosphine sulphides and allylsilanes. Selected results are published annually⁵. A recent review dealing with irradiation of organophosphorus(III) compounds by Dankowski appeared in Volume 1 of this series⁶. This chapter covers the photochemical reactions of phosphine chalcogenides, mainly the preparative aspects. Reactions concerning stabilizers, polymers and complexes are excluded.

II. PHOSPHINE DERIVATIVES

A. Molecular Reactions

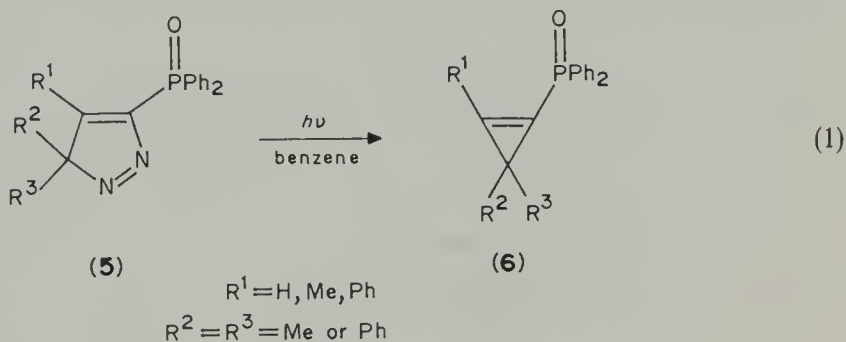
1. Oxides

Photolysis of bridged phosphine oxide **1** in benzene through Pyrex glass yields, presumably by an intermediate **2**, the phosphine oxide **3** and some cyclooctatetraene. A similar result has been achieved by irradiation in acetone. Irradiation of a mixture of

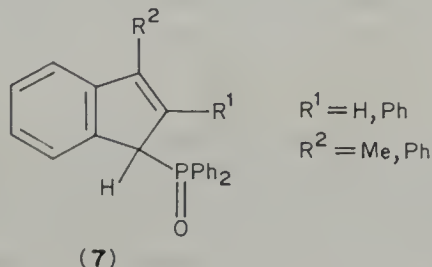


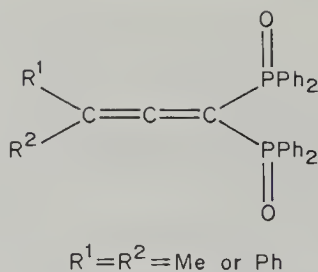
1, **2** and **4** in benzene–acetone through Corex glass also gives the oxide **3**⁷. The difference in mechanism between this reaction and that of the corresponding phosphines lies in the singlet character of the former⁸ and the triplet character of the latter⁹, and naturally leads to different products.

Irradiation of 5-diphenylphosphoryl-3*H*-pyrazoles (**5**) generates the phosphorylated cyclopropenes **6** via ring fissure and N₂ loss, yielding as an intermediate the corresponding (diphenylphosphorylvinyl)carbene. The use of the 4,5-isomer results in a similar product¹⁰ (equation 1).

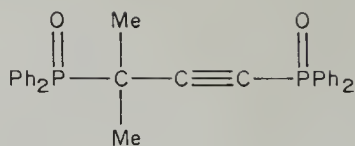


Photolysis of a 3*H*-pyrazole with a phenyl group in the C₃ position leads to the indene derivative **7**¹⁰. 4,5-Bis(diphenylphosphoryl)-3*H*-pyrazoles [$\text{R}^1 = \text{P}(\text{O})\text{Ph}_2$] not only give the cyclopropene derivative but also a corresponding allene with geminal PO substituents (**8**). When $\text{R}^1 = \text{Me}$ and $\text{R}^2 = \text{Ph}$, the acetylene **9** is available by a 1,3-sigmatropic shift¹⁰. The fact that the allene **8** is equally produced by irradiation of the cyclopropene **6** proves that the mechanism involves ring fissure and a 1,2-shift of the diphenylphosphoryl group¹⁰.



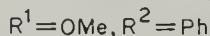
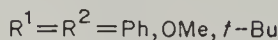
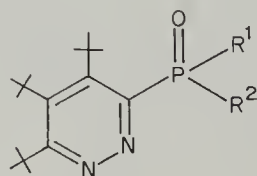


(8)

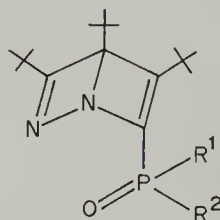


(9)

On irradiation of various pyridazines **10** in benzene or pentane, the extremely thermostable 1,2-dewar pyridazines **11** are formed by an electrocyclic ring closure between N_1 and C_4 ¹¹ (equation 2). In the presence of Hg and UV light dimerization of phosphine oxide is observed¹². Measurements of the kinetics and quantum yield of the photoisomerization reaction have been performed with 4-diphenylphosphorylstilbenes using different substituents at the second aromatic ring¹³. UV irradiation of tris(trifluoromethyl)phosphine oxide for 200 h yields a mixture of carbonyl fluoride, hexafluoroethane and phosphorus trifluoride in addition to tris(trifluoromethyl)phosphine and some uncondensable material and the educt¹⁴.



(10)

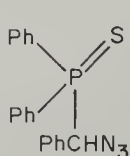


(11)

(2)

2. Sulphides

Investigations of the photochemical degradation of phenyl(diphenylthiophosphoryl)methyl azide (**12**) showed that the formation of N_2 followed by benzyldeneamino-diphenylthiophosphorane (**13**) and aminodiphenylthiophosphorane (**14**) takes place, analogous to the thermally induced reaction (equation 3). This reaction is the first example of a thiophosphorus group migration¹⁵. Photolysis of 5-diphenylthiophosphoryl-3H-pyrazoles leads, like the oxophosphoranes, to the corresponding thiophosphoryl cyclopropenes (**15**) via ring fissure, N_2 elimination and ring closure of the resulting carbene¹⁰.



(12)

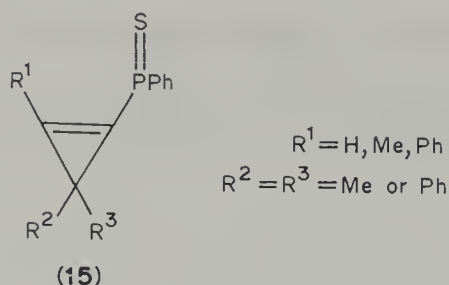


(13)



(14)

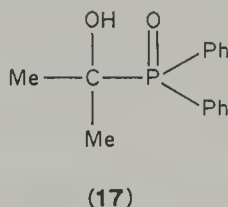
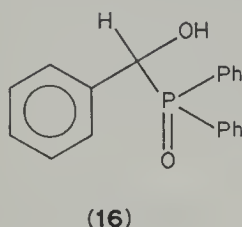
(3)



B. Reactions with Carbonyl Compounds

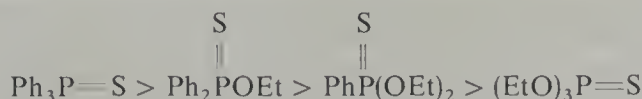
1. Oxides

Diphenylphosphine oxide, formed by photolysis of benzoyldiphenylphosphines, generates the corresponding alcohols **16** and **17** by addition of a carbonyl^{16,17}. The reaction with phenanthrene quinone takes place analogously¹⁸. Formation of the reactive OPR_2 radicals is realized by H-abstraction from the corresponding phosphine oxides¹⁹. Irradiation of the entirely substituted phosphine oxide, however, leads to the phosphino radical PPh_2 ²⁰. These intermediates may be trapped by reactions with carbonyl compounds, e.g. quinones^{20,21}.

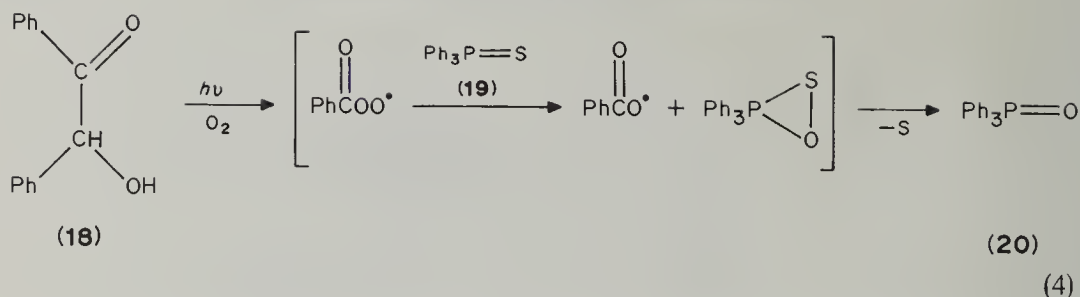


2. Sulphides

1,2-Dicarbonyl compounds, e.g. quinones and benzoin, sensitize the photooxidation of pentavalent phosphine sulphides. Hence, photooxidative desulphurization of triphenylphosphine sulphide in the presence of benzil, biacetyl, acenaphthaquinone, pyruvic acid, methyl pyruvate, butyl pyruvate, benzoin, 2,3-dichloro-5,6-dicyano benzoquinone or 2,3,5,6-tetrachlorobenzoquinone results in conversion of the $\text{P}=\text{S}$ group to a $\text{P}=\text{O}$ group²². Whereas irradiation of phosphine sulphides in oxygenated solution in the presence of singlet oxygen sensitizers such as Rose Bengal and Methylene Blue does not lead to a reaction, the 1,2-dicarbonyl compounds do give the expected result²². 1,4-Quinone react with oxygen to form 1,4-biradicals which can be trapped by olefins^{22,23}. The reactivity of some phosphorus compounds with regard to this reaction increases in the following series²²:



UV irradiation of benzoin (**18**) in the presence of oxygen leads via a Norrish type I fission process to give the corresponding peroxy radical. The latter reacts with triphenyl-

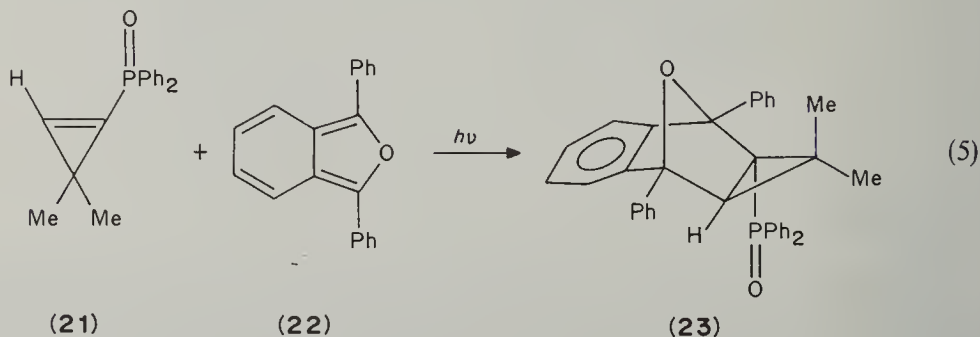


phosphine sulphide (19) with desulphurization to generate triphenylphosphine oxide (20) and sulphur^{22,24,25} (equation 4). Further investigations have led to similar results concerning the irradiation of acylphosphine oxides and acylphosphonates in the presence of triphenylphosphine sulphide as a photoinitiator²⁶.

C. Reactions with Unsaturated Compounds

1. Oxides

Phosphine oxides are easily and quantitatively added to vinyl- or allyl-silanes in a photochemical reaction. Polyvinylsiloxanes may be employed in the same way. For example, dibutylphosphine oxide reacts with divinylchlorosiloxane in its hydrolysed and polycondensed form to give poly{bis-[2-(dibutylphosphonyl)ethyl]siloxane}⁴. Irradiation of the phosphorylated cyclopropene **21** in the presence of diphenylisobenzofuran (**22**) as a 1,3-diene leads to a Diels–Alder reaction forming the exo-configured adduct **23**¹⁰ (equation 5).

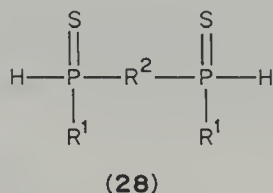
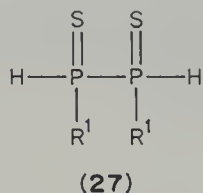
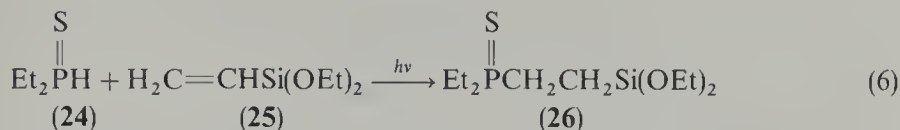


Whereas the reaction of tris(trifluoromethyl)phosphine oxide with ethylene does not result in a well characterized product, the use of tetrafluoroethylene yields a mixture of carbonyl fluoride, phosphorus trifluoride and hexafluoroethane in addition to recovered educt and polytetrafluoroethylene¹⁴.

2. Sulphides

On irradiation, diethylphosphine sulphide (**24**) easily adds to the olefinic bond of triethoxyvinylsilane (**25**), generating 1-diethylthiophosphoryl-2-triethoxysilyl ethane (**26**)⁴ (equation 6). Photoreaction of diethylphosphine sulphide with acrylonitrile results quantitatively in the formation of cyanoethyldiphenylphosphine sulphide²⁷. Diphosphine sulphides of the general formulae **27** and **28** react in the same way. While experiments trying to add *sec*-phosphine sulphides to isocyanates or activated olefins under alkaline

conditions failed, this reaction proceeds well under UV irradiation²⁸.



R^1 = alkyl or alkenyl, cycloalkyl or cycloalkenyl or aryl group

R^2 = alkylene or arylene group

D. Reactions with Other Compounds

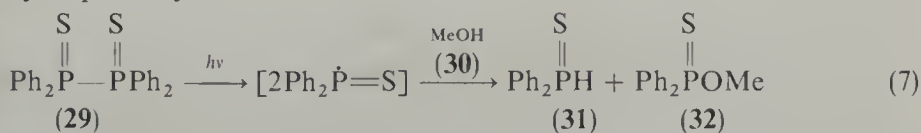
1. Oxides

Using chlorine as a radical initiator, cyclohexane reacts with phosphorus compounds having a coordination number of four and a H-substituent to yield the corresponding phosphoryl compounds²⁹. In a similar manner this reaction proceeds using phosphonic acid and phosphinic acid derivatives. Chlorohexane is formed as a by-product in all cases. An explanation is to be found on the one hand in the low selectivity of the chlorine atom and on the other in the similarity of the bond energies of the cyclohexyl C—H bond³⁰ and the P—H bond³¹.

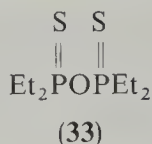
<i>sec</i> -Phosphine oxide	Phosphine oxide	Yield (%)
$\text{Et}_2\text{P}(\text{O})\text{H}$	$\text{Et}_2(\text{C}_6\text{H}_{11})\text{PO}$	84
$(\text{C}_6\text{H}_{11})_2\text{P}(\text{O})\text{H}$	$(\text{C}_6\text{H}_{11})_3\text{PO}$	80
$\text{Ph}_2\text{P}(\text{O})\text{H}$	$\text{Ph}_2(\text{C}_6\text{H}_{11})\text{PO}$	30

2. Sulphides

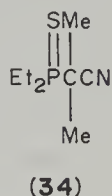
UV-irradiation of tetraphenyldiphosphine disulphide (29) in the presence of methanol (30) under a nitrogen atmosphere using a mercury lamp leads to diphenylphosphine sulphide (31) and *O*-methyl diphenylphosphinothioate (32). The reaction mechanism is explained by a homolytic fission of the P(S)—P(S) bond³² (equation 7). A similar reaction of tetraphenyldiphosphine in alcohols is reported to occur both photolytically and thermolytically respectively⁽³³⁾.



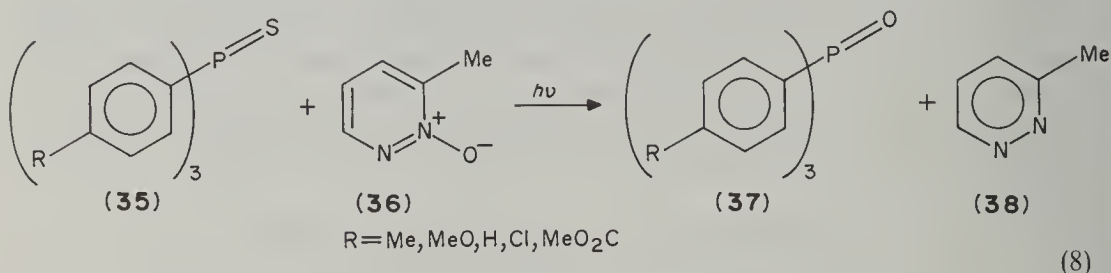
While the irradiation of tetraethyldisphosphine disulphide in carbon disulphide or methanol in the presence of Rosc Bengal as a sensitizer and oxygen does not lead to the insertion product 33, reaction in benzene does produce this product, sulphur and



diethylphosphinic acid. The last is generated by oxidative desulphurization of the P=S group³². Photoreaction of tetraethyldiphosphine disulphide with α,α' -azobisisobutyronitrile in benzene solution only yields IR and mass spectroscopically determined amounts of diethyl-1-cyano-1-methylethylphosphine sulphides (34)³².



Investigations of the photochemically induced transfer of oxygen atoms of heterocyclic *N*-oxides to phosphine sulphides have primarily been undertaken with *P*-substituted phosphine sulphides (35) and 3-methylpyridazine-2-oxides (36) yielding the corresponding *P*-oxides (37) and the pyridazine 38³⁴ (equation 8).

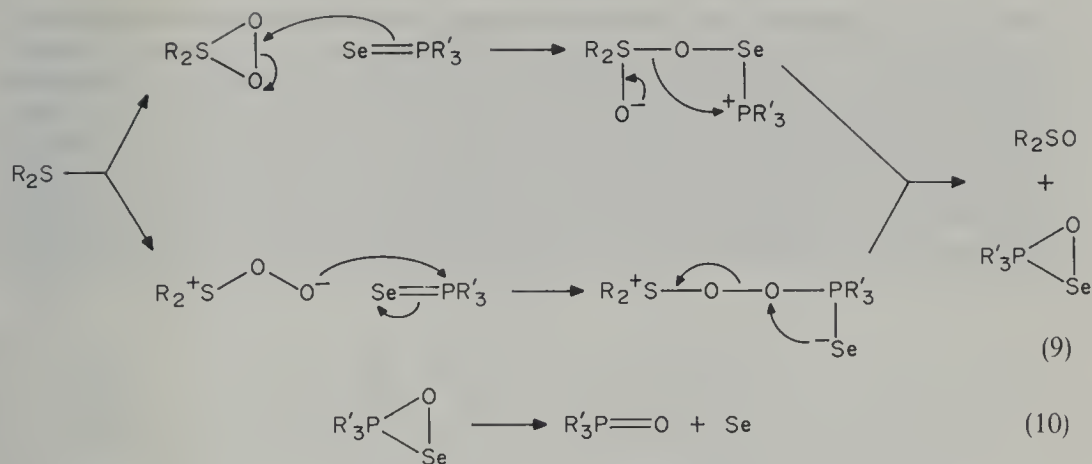


On photolysis of pyridazine oxides in the presence of *para*-substituted triarylphosphine sulphides, no significant dependence on substitution is shown in the formation of the resulting phosphine oxides³⁵. The lack of a substitution effect implies either that the oxygenating species is not a strong electrophile or, being an electrophile, that the reactivity towards thiophosphoryl species is very high and, therefore, the selectivity is low. A similar effect is known in carbene chemistry³⁶. Such oxidation reactions are presumably of high ecological importance for the use of organophosphorus insecticides in agriculture^{37,38}.

Photooxidation of dialkyl sulphides leads to the corresponding sulphur peroxidic species, which react with phosphine sulphides to give dialkyl sulfoxides³⁹.

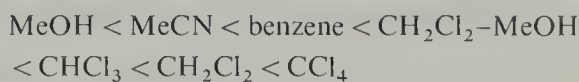
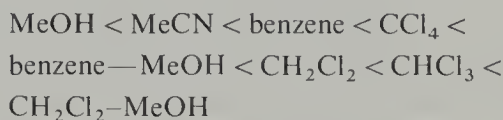
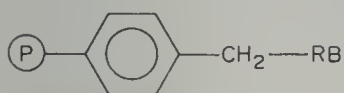
3. Selenides

The oxidation desulphurization at pentavalent phosphorus by photogenerated peroxidic species also proceeds as a deselenation, similar to the reaction of sulphides already described. The reaction mechanisms in equations 9 and 10 have been proposed³⁹. The reaction is not restricted to dialkyl sulphides but also finds applications in the photooxidation of diphenyldiazomethane with benzophenone as product instead of sulfoxides³⁹.



Photooxidation of triphenylphosphine selenide in the presence of Rose Bengal or polystyrene- and silica gel-supported Rose Bengal exhibits different reactivities in the formation of triphenylphosphine oxide in different solutes⁴⁰:

RB



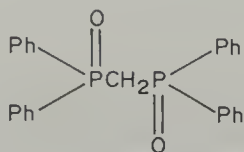
RB = Rose Bengal; Ⓟ = polystyrene copolymer; Ⓢ = silica gel

The formation of phosphine oxides is inhibited by the addition of a typical singlet oxygen quencher, 1,4-diazobicyclo[2.2.2]octane (dabco), especially in non-polar solvents⁴⁰.

E. Radiolysis

1. Oxides

Tetraphenylmethylenediphosphine dioxide (**39**) in CHCl₃ shows high stability to γ -radiation⁴¹.



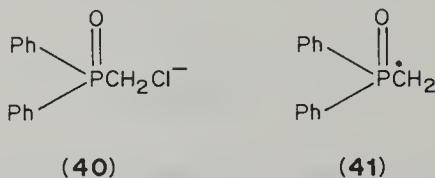
(39)

F. Miscellaneous

1. Oxides

Numerous EPR-investigations have been performed concerning the formation of radicals, e.g. photochemical reactions of quinonoid compounds¹⁹, carbenes and ketones²¹,

3-methyl-3-nitrosobutan-2-one, nitroso-*tert*-butane, nitrosobenzene and α -phenyl-*N*-*tert*-butylnitron⁴² with phosphine oxides. These have involved kinetic and spectroscopic characterization of the diarylphosphonyl radical⁴³. X-irradiation of phosphine oxides leads to phosphino radicals⁴⁴ or to phosphonyl radicals²⁰, whereas on using (chloromethyl)diphenylphosphine oxide at 3 K the chloro-anion **40** is formed, although the C-radical **41** is formed at 70 K⁴⁴. Formation of the corresponding radicals on γ -irradiation has been investigated using the following substrates: triamylphosphine oxide⁴⁵, tri-*n*-butylphosphine oxide⁴⁶, trimethylphosphine oxide⁴⁷ and triphenylphosphine oxide⁴⁸.



2. Sulphides

Numerous EPR investigations provide proof of radical formation, e.g. diphenylphosphino radicals are generated on X-irradiation of single crystals of triphenylphosphine sulphide^{20,44}. Diphenylphosphine sulphide gives the thiophosphonyl radical⁴⁹ and *tert*-phosphine sulphides yield thiophosphonyl radicals instead of the corresponding phosphoranyl radicals⁵⁰. Quantum chemical computations have been performed for the dialkylphosphine sulphide⁵¹ and the trialkylphosphine sulphide⁵² systems. Investigations have been published describing the generation of radicals by γ -irradiation of triphenylphosphine sulphide^{48,53} and tetramethyldiphosphine disulphide⁵⁴.

3. Selenides

Radical formation has been identified by single crystal EPR measurement, e.g. methylphenylpropylphosphine selenide gives a σ^* radical anion⁵⁰. The measurements provide detailed information about its geometric and electronic structure. After X-irradiation of trimethylphosphine selenide, two different phosphorus-centred radicals are observed in the EPR experiment⁵², similarly to the photolysis of tricyclohexylphosphine selenide⁵².

III. ACYLPHOSPHINE DERIVATIVES

A. Molecular Reactions

1. Oxides

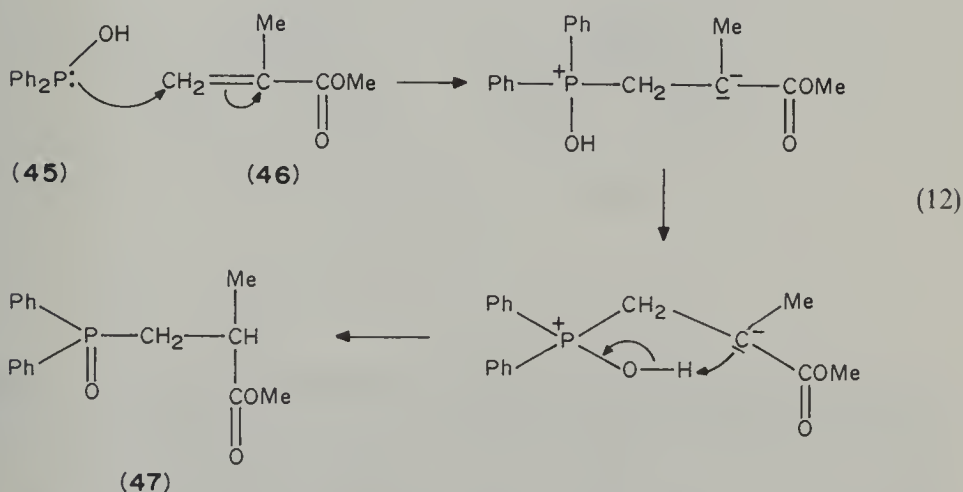
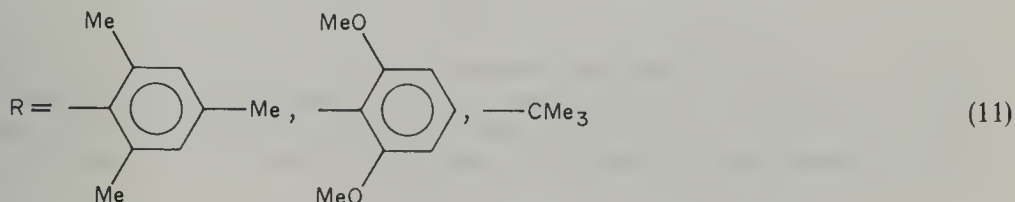
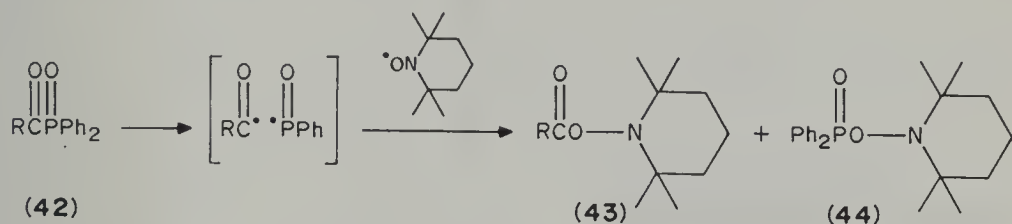
Photolysis of acylphosphine oxides yields radicals via type I fission of their triplet states⁵⁵.

B. Reactions with Other Compounds

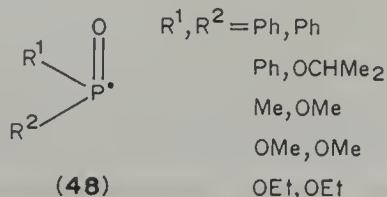
1. Oxides

Photoinduced α -fission of acylphosphine oxide **42** leads to the adducts **43** and **44** by radical intermediates which can be scavenged using 2,2,6,6-tetramethylpiperidine-1-oxyl

(tmpo)⁵⁶ (equation 11). Chemical trapping experiments using tmpo have proved to be a valuable means for the elucidation of reaction mechanisms⁵⁷⁻⁵⁹. Irradiation of trimethylbenzoyldiphenylphosphine oxide leads, in the presence of *N*-methyl-diethanolamine, to the corresponding ester and diphenylphosphinous acid⁶⁰. This can be explained by attack of the amino alcohol on the electron-deficient carbonyl group. The pentavalent form of the tautomeric pair diphenylphosphine oxide–diphenylphosphinous acid prevails because of the possibility of $d\pi-p\pi$ bond formation. Nevertheless, the nucleophilic character of the phosphinous acid **45** is revealed by the Michael addition of methyl methacrylate (**46**) yielding **47**⁶⁰ (equation 12).



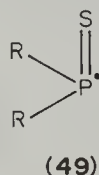
The phosphonyl radicals **48** show high reactivity towards olefins such as methacrylonitrile, styrene, methyl methacrylate, acrylonitrile, methyl acrylate, butyl vinyl ether and vinyl acetate⁶¹. This can be ascribed to their tetrahedral structure. In the presence of



oxygen the radicals formed by a Norrish type I cleavage process cause oxidative desulphurization at pentacovalent phosphorus.

2. Sulphides

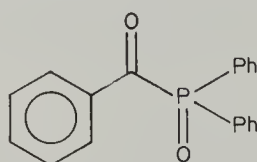
Acylphosphine sulphides react in a similar manner to their oxygen analogues. Compared with the phosphine oxides their reactivity towards olefins is about one order of magnitude lower⁶². Here, the reactive agent is the thiophosphonyl radical **49**.



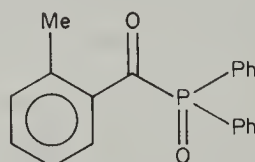
C. Use as Polymerization Initiators

1. Oxides

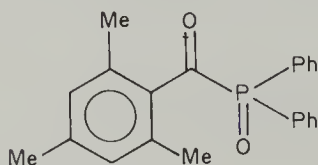
The results of the investigations described in the last section point to the most important application of acylphosphine oxides as photoinitiators⁶³. Compared with acetophenones they show a red shift of the UV absorption maximum of about 50 nm⁶⁴. The first species to be investigated which were stable against solvolysis were phosphine oxides (**50–53**) prepared by Arbuzov synthesis^{64–66}.



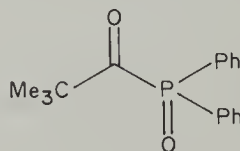
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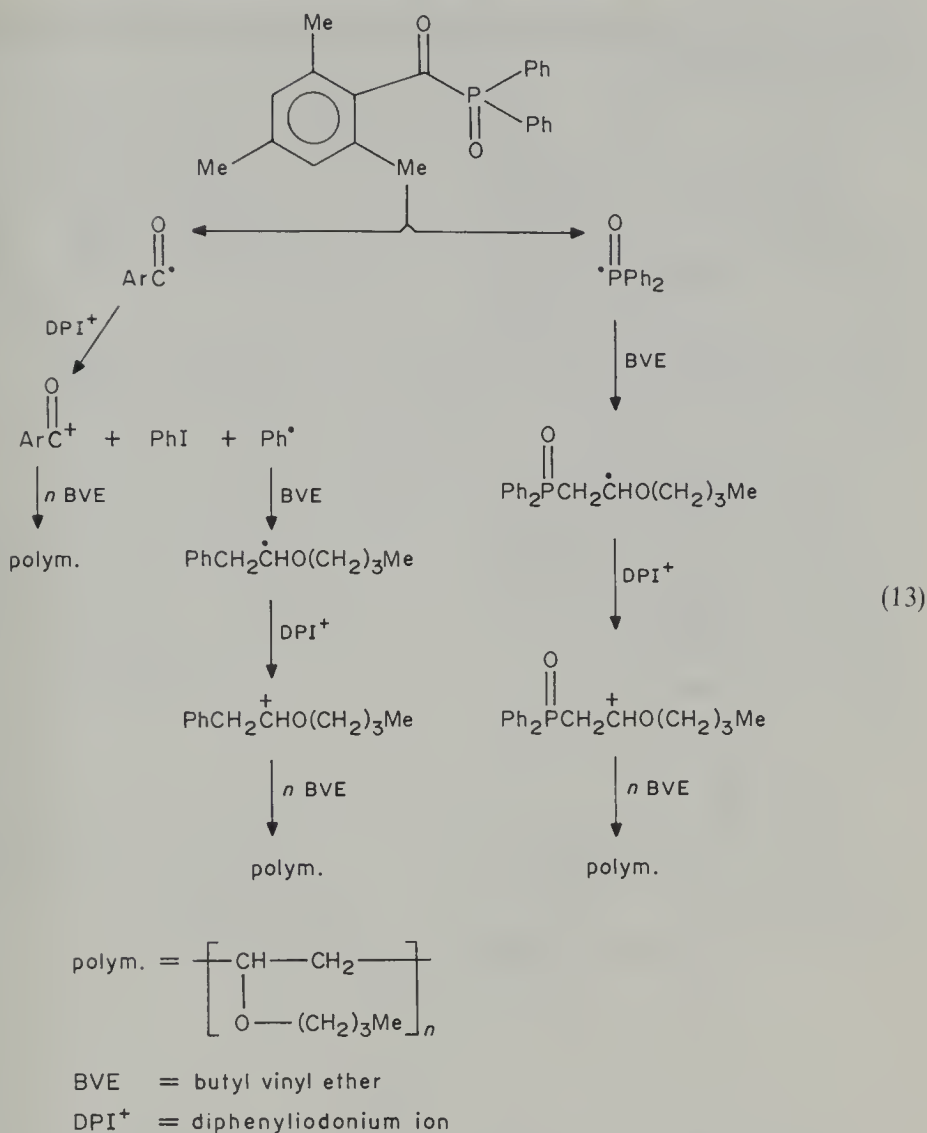
(52)



(53)

Reactions of acylphosphine oxides and also other photoinitiators are described phenomenologically⁶⁷. Trimethylbenzoyldiphenylphosphine oxide promotes the cationic polymerization of butyl vinyl ether in the presence of diphenyliodonium ions. The reaction mechanism shown in equation 13 is proposed⁶⁸.

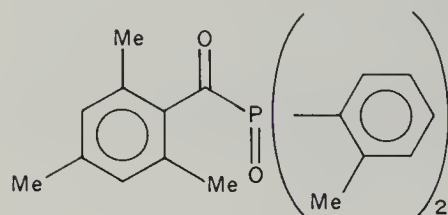
Although stable onium salts have been shown to be good photoinitiators for cationic polymerization⁶⁹, it has to be admitted that in the absence of acylphosphine oxide the reaction described above does not yield the polymer. Investigations of the mechanism have been performed similarly using tetrahydrofuran^{68,70} and (3,4-epoxycyclohexylmethyl)-3', 4' -epoxycyclohexane carboxylate⁷¹. The reactivity of several acylphosphine oxides is comparable to that of the corresponding acetophenone derivatives⁶⁵.



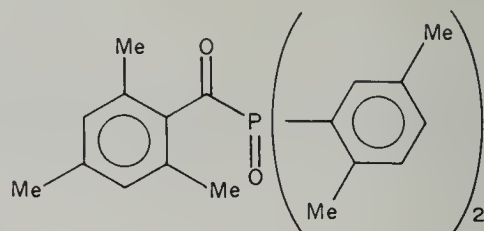
Photochemical polymerization yielding copolymers containing isocyanate groups can be achieved with acylphosphine oxides. For example, reaction of vinyl isocyanate, 2-ethylhexyl acrylate, methyl acrylate, methyl acetate and *tert*-butyl chloride in the presence of 2,4,6-trimethylbenzoyldiphenylphosphine oxide all lead to the corresponding polymers⁶³. Photopolymerization of acrylates is enhanced by the addition of a leuco dyestuff such as triphenylmethane rosaniline⁷². Photoinitiators are used in the production of acrylic resins in both non-pigmented⁷³ and TiO₂-pigmented systems⁷⁴. Different P=O and C=O units containing initiators have been compared by the method of thin-film polymerization of acrylates⁶⁶ and unsaturated polyesters⁷⁵ using laser nephelometry.

Acylphosphine oxides can be used as photoinitiators for unsaturated polyesters with^{73,76,77} and without^{76,78} using solvents. For example, a hardened film is developed by irradiation of a TiO₂ containing styrene solution of the unsaturated polyesters derived from tetrahydrophthalic anhydride, maleic anhydride and diethylene glycol⁷⁹. Various useful phosphine oxides (54–70) have been synthesized and characterized^{76,79,80}. The sunlight-induced photohardening of some polymer systems can be achieved by using

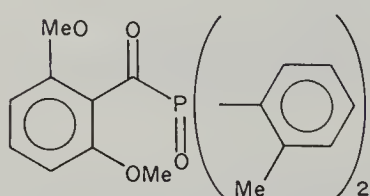
additional initiators such as benzil dialkyl ketals and/or methylthioxanthone together with phosphine oxides⁸¹.



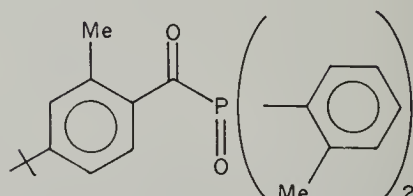
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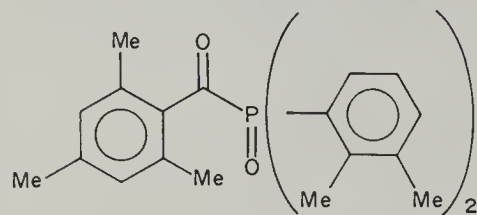
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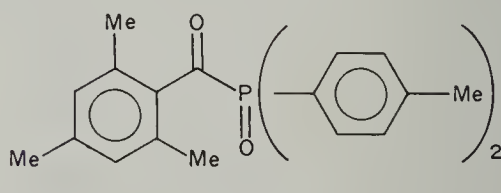
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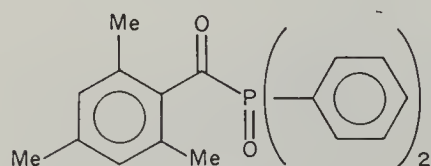
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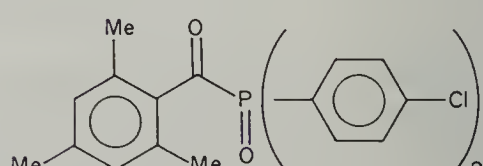
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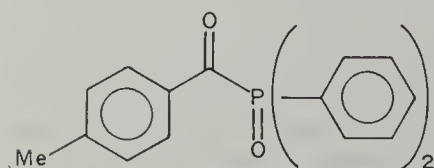
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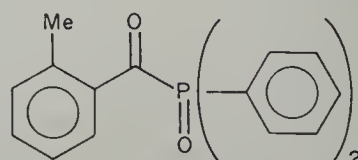
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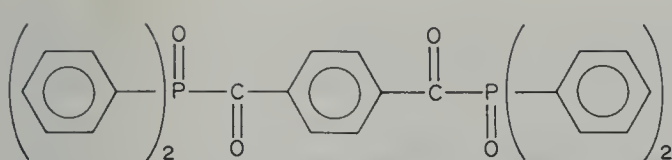
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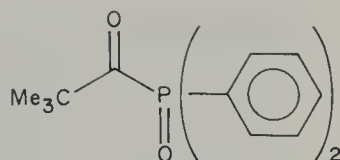
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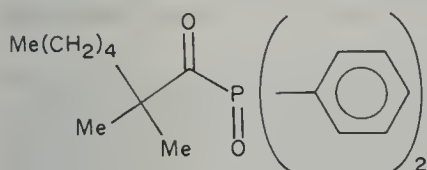
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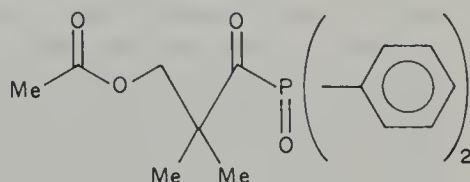
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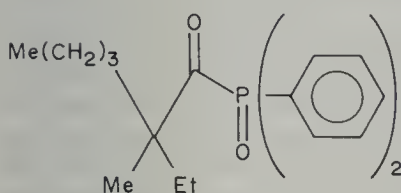
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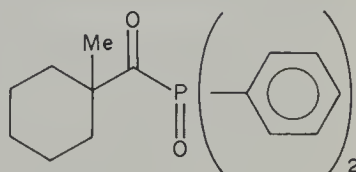
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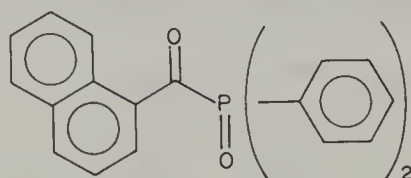
(67)



(68)



(69)



(70)

2. Sulphides

In the presence of acylphosphine oxides or sulphides, photopolymerization can be induced of oligomeric epoxyacrylates such as bisphenol A diglycidyl ether, trimethylpropane triacrylate, Michler's ketone (tetramethyl-*p,p*-diaminobenzophenone) and Victoria Blue⁷². The exposure times are as follows:

Initiator	Irradiation cycle
2,4,6-Trimethylbenzoyldiphenylphosphine oxide	5
2,4,6-Trimethylbenzoyldiphenylphosphine sulphide	5
2,4,6-Trimethylbenzoylditolylphosphine oxide	5
2,4,6-Trimethylbenzoylditolylphosphine sulphide	7

The time of exposure required to obtain a sufficient degree of polymerization is extended in the absence of a sensitizer, e.g. Michler's ketone⁷². Acylphosphine sulphides can also be used as initiators in the polymerization of unsaturated polyesters⁷⁷.

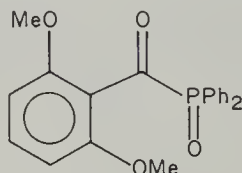
D. Miscellaneous

1. Oxides

Kinetic and mechanistic aspects concerning the initiation of free radical polymerization by acylphosphine oxides have been reported^{82,83}. These compounds show relatively strong absorptions at 350–400 nm⁸⁴. Flash photolysis of *o*-methylbenzoyldiphenylphosphine oxide indicates that α -fission competes with enolization (triplet state). A high quantum yield is found for the formation of the diphenylphosphonyl radical^{82,83}. The bimolecular rate constants for the reaction of phosphonyl radicals with several monomers in cyclohexane have been reported⁸³.

Absorption measurements of 2,4,6-trimethylbenzoyldiphenylphosphine oxide in dilute solutions of benzene, methanol and dichloromethane using 20-ns flashes of 347 nm radiation indicate the formation of phosphonyl radicals. The singlet and triplet lifetimes were estimated as $\tau < 1$ -ns, the singlet energy being around 288 kJ mol⁻¹. Rate constants for the reaction with olefinic compounds are 6.0×10^7 (styrene and methyl methacrylate), 2.7×10^7 (methylacrylate), 1.8×10^7 (acrylonitrile), 5.0×10^6 (*tert*-butyl vinyl ether) and 2.0×10^6 (vinyl acetate). The quantum yield of radical formation lies in the range $\phi = 0.5$ – 0.7 ⁸⁵.

The influence of methyl substitution in benzoyldiphenylphosphine oxides has been investigated under flash photolytic conditions⁸⁶ in addition to reactions of pivaloyldiphenylphosphine oxide⁸⁷. The use of Fourier transform infrared (FTIR) spectroscopy gave helpful hints in the determination of the photoinitiative efficiencies of acylphosphine oxides, e.g. 2,4,6-trimethylbenzoyldiphenylphosphine oxide⁸⁸. The flash photolysis ESR method together with chemically induced dynamic electron polarization (CIDEP) allowed the mechanism of photochemical reactions leading to the formation of radicals to be explained^{89,90}. After photolysis of 2,6-dimethoxybenzoylphosphine oxide (71) with a 308-nm laser, the ESR signals have been evaluated by time integration spectroscopy (TIS)⁹¹.

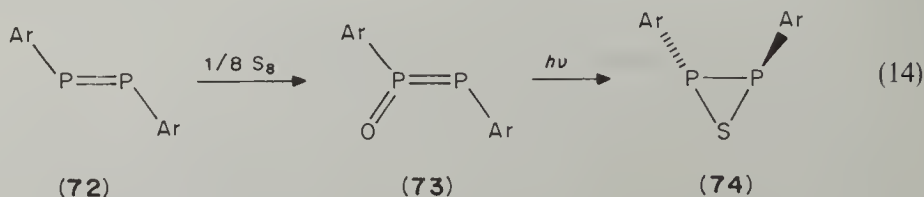


(71)

IV. PHOSPHENE DERIVATIVES

A. Sulphides

Reactions of phosphorus (III) compounds with $p\pi$ – $p\pi$ double bonds have occasionally been investigated^{92,93}. The sterically stable educt (*E*)-bis(2,4,6-tri-*tert*-butylphenyl)-diphosphene (72) readily reacts with elemental sulphur to give the monosulphide 73.



Ar = 2,4,6-tri-*t*-BuC₆H₂

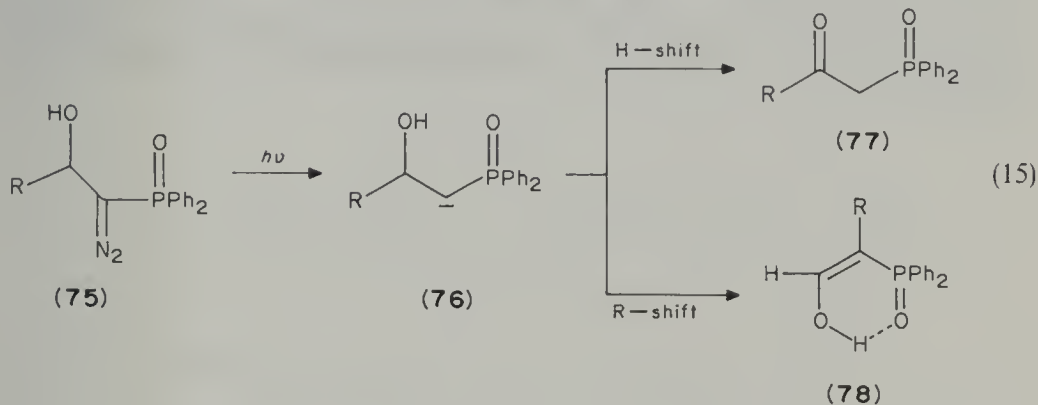
After UV irradiation in toluene solution, (*E*)-2,3-bis(2,4,6-tri-*tert*-butylphenyl)-1,2,3-thiadiphosphirane (**74**) is formed quickly⁹⁴ (equation 14). Even in the solid state the sulphide **73** after irradiation gives the isomeric diphosphirane **74**.

V. DIAZOPHOSPHINE DERIVATIVES

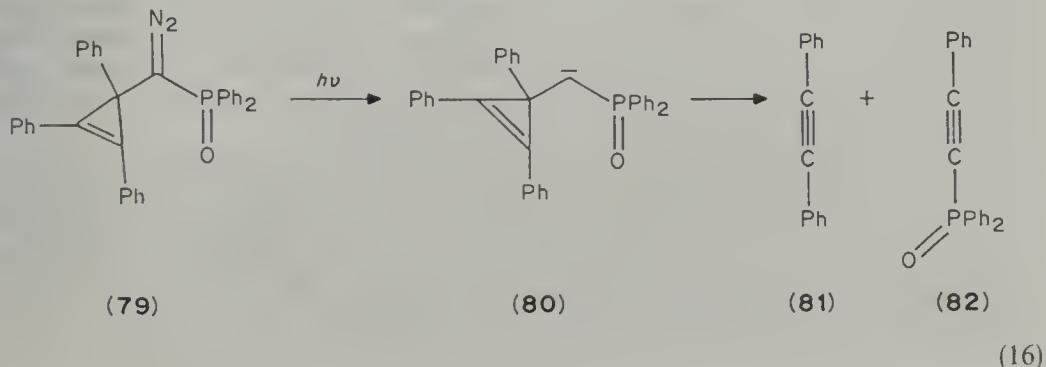
A. Molecular Reactions

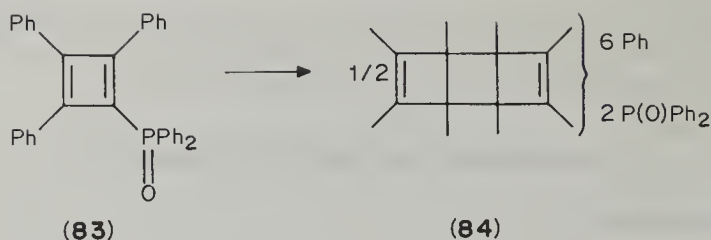
1. Oxides

Diazo compounds produced in an aldol-like reaction of (diazomethyl)diphenylphosphine oxide with aldehydes show two competing reaction pathways after UV irradiation: H- and R-migration. For example, photolysis of (1-diazo-2-hydroxypropyl)diphenylphosphine oxide (**75**) yields the carbene **76** which undergoes H-shift predominantly to form (2-oxopropyl)diphenylphosphine oxide (**77**). In other cases the carbenes are less reactive and undergo R-migration to form (2-hydroxyvinyl)diphenylphosphine oxide (**78**)⁹⁵ (equation 15). This reaction occurs similarly to the copper(I) acetylacetonate-catalysed thermolysis⁹⁵.



After irradiation of (diazomethyl)cyclopropene (**79**), the carbene **80** is obtained, which decays to give the acetylenes **81** and **82** in a sort of chelotropic reaction, whereas by widening of the ring the phosphorylated cyclobutadiene **83** is formed, which in turn dimerizes to give **84**⁹⁶ (equation 16).

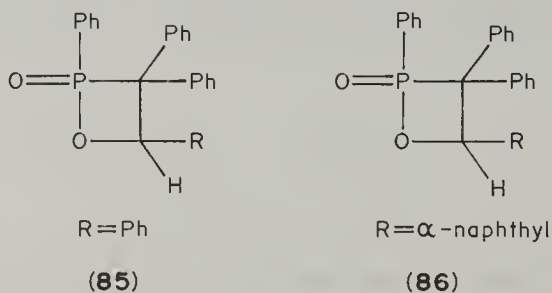




B. Reactions with Carbonyl Compounds

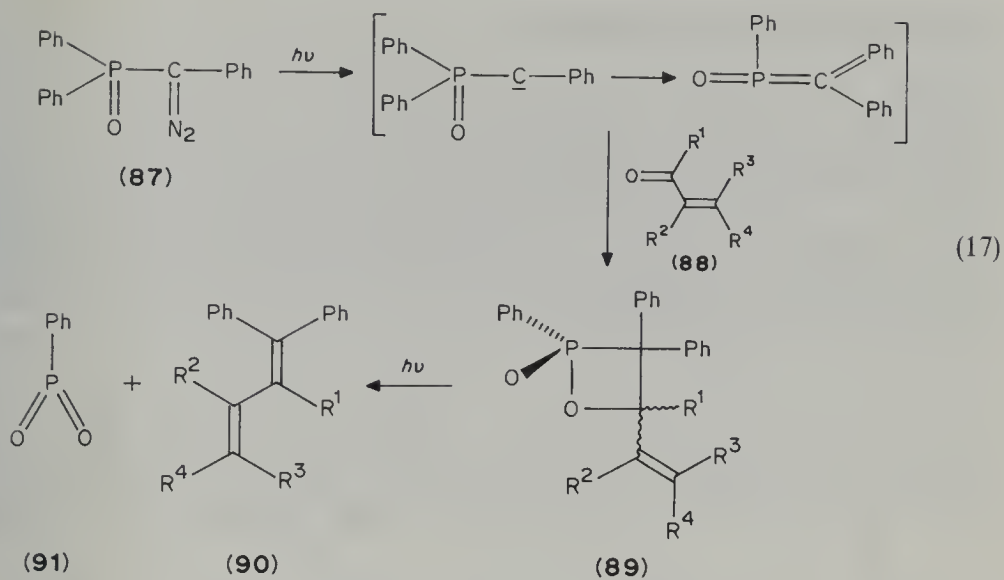
1. Oxides

After irradiation with UV light (diazobenzyl)diphenylphosphine oxide yields the phosphorylcarbene with N_2 loss, showing a 1,2-phenyl shift from phosphorus to the carbene carbon atom^{97,98}. A short-lived intermediate is (diphenylmethylene)phenylphosphine oxide with the rare coordination number of 3. Isolation of the reactive 'phosphene' species has not been achieved in this system⁹⁹. With carbonyl compounds trapping of these phosphines is possible. For example, irradiation of (diazobenzyl)diphenylphosphine oxide in the presence of benzaldehyde or 1-naphthaldehyde in benzene yields the corresponding 1,2-oxaphosphetanes **85** and **86** in addition to the cyclopropanated solvent by [2 + 2]-cycloaddition of the carbene with the aldehydes¹⁰⁰.



Irradiation of the (diazo)phosphine oxide **87** in the presence of α,β -unsaturated carbonyl compounds **88** yields 2-oxo-2,3,3-triphenyl-4-vinyl-1,2-oxaphosphetanes (**89**) via the intermediates described above. A subsequent cycloreversible reaction, such as an olefination, leads to butadienes or hexatrienes (**90**), respectively and dioxophenylphosphorane (**91**)¹⁰¹⁻¹⁰³ (equation 17). The carbene $PhP(O)\dot{C}PhBz$, produced photochemically from the corresponding diazo compound, undergoes [4 + 2]-cycloaddition with aldehydes and ketons, e.g. $BzPh$, $p-RPhBz$ ($R = OMe, Me, Cl$), $AcMe$, $AcPh$, cyclohexanone, $AcCMe_3$, AcH , BzH , Cl_3CCHO , crotonaldehyde and cinnamaldehyde. In the case of $BzPh$ the heterocyclic **91-94** are obtained¹⁰⁴.

Triphenylphosphene **95**, produced in a photoreaction, reacts with tropone⁹⁶ in an [8 + 2]-cycloaddition reaction to give 3,3 α -dihydro-2,3,3-triphenyl-2H-cyclohept[d]-1,2-oxaphosphole-2-oxide (**97**) (equation 18). The [2 + 2]-adduct is not obtained¹⁰⁵. Comparisons with the C-analogue diphenyl ketene have been published¹⁰⁶. The reaction of the carbene with tetracyclone yields the [6 + 2]-adduct **98** and the [12 + 2]-adduct **99**¹⁰⁵; the structure of **98** is known from X-ray analysis.

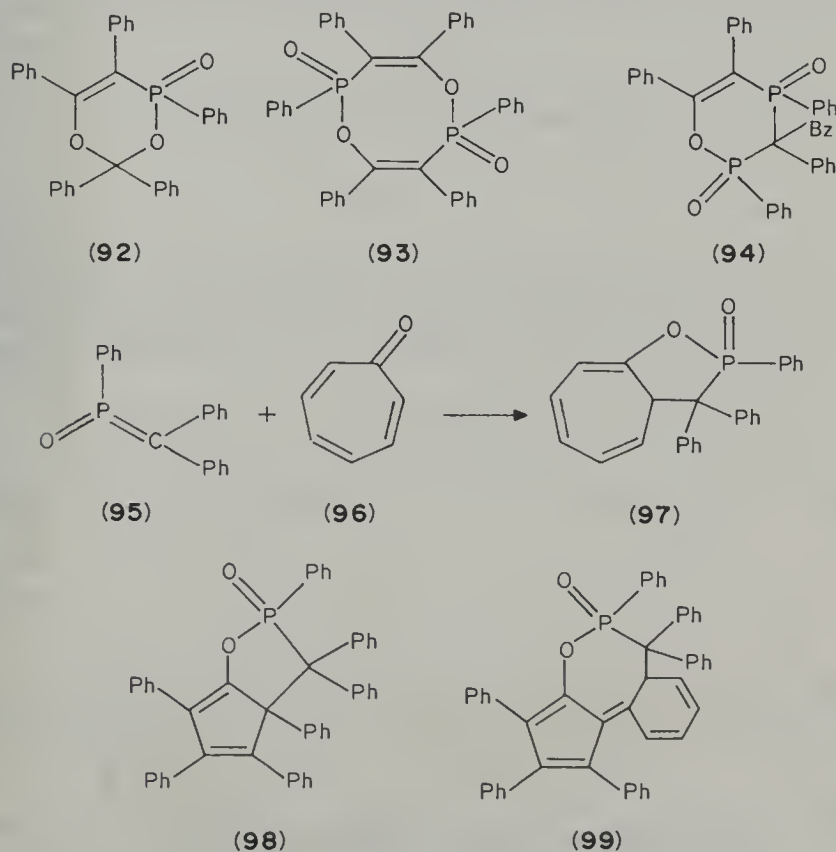


$\text{R}^1 = \text{Ph}, p\text{-MePh}, \text{H}, \text{Me}, p\text{-CH}=\text{CHPhOMe}, \text{CH}=\text{CMe}_3$

$\text{R}^2 = \text{H}, \text{Me}$

$\text{R}^3 = \text{H}, \text{Ph}, \text{Me}$

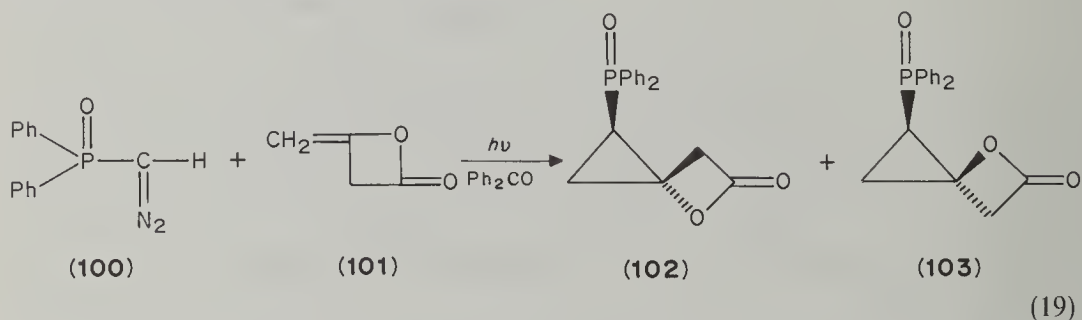
$\text{R}^4 = p\text{-MeOPh}, p\text{-MePh}, \text{H}, \text{Ph}, \text{Me}$



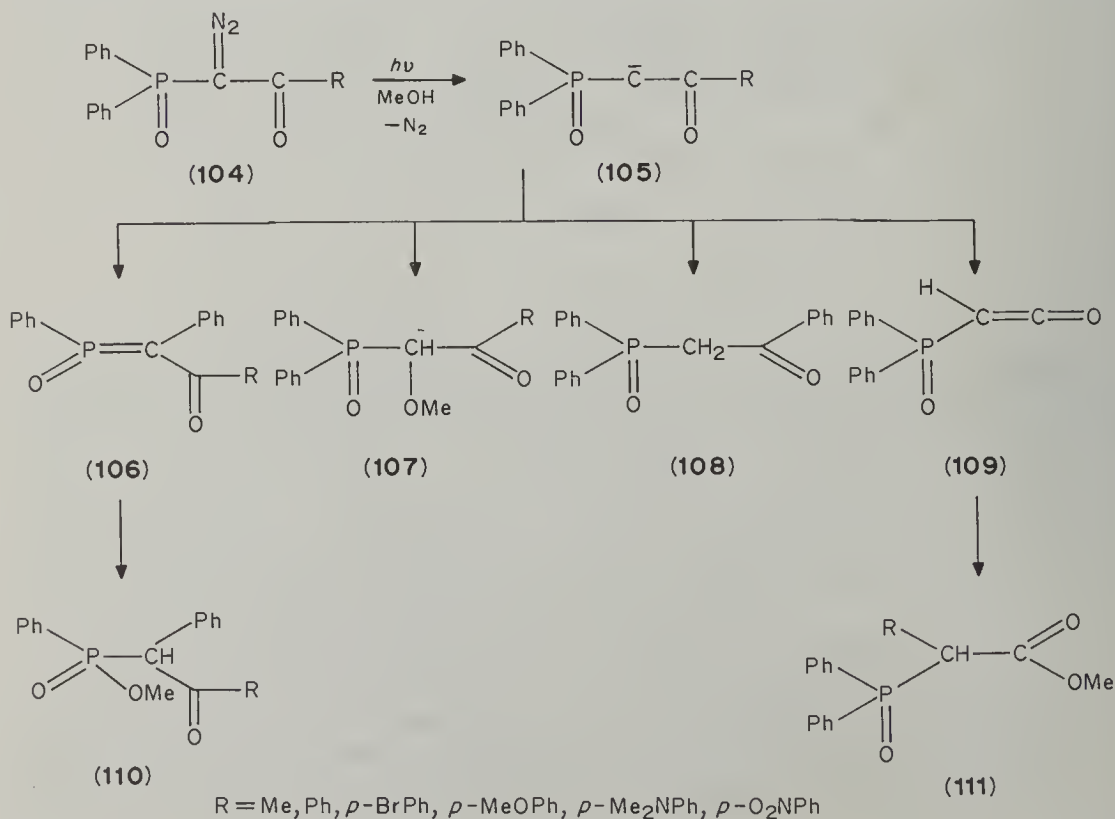
C. Reactions with Other Compounds

1. Oxides

Photolysis of (diazobenzyl)diphenylphosphine oxide in benzene yields 7-(*exo*-diphenylphosphoryl)-7-*endo*-phenylnorcaradiene as the adduct of the carbene with the solvent^{100,101}. After reaction of (diazomethyl)diphenylphosphine oxide (**100**) with ketene **101** in the presence of benzophenone in CH₂Cl₂ under nitrogen, two products showing a spiro structure are obtained, i.e. (*E*)-1-(diphenylphosphinyl)-5-oxo-4-oxaspiro[2.3]-hexane (**102**) and the corresponding *Z*-isomer **103**¹⁰⁷ (equation 19). In a similar manner diketene reacts with α -diazoketones¹⁰⁸⁻¹¹⁰.



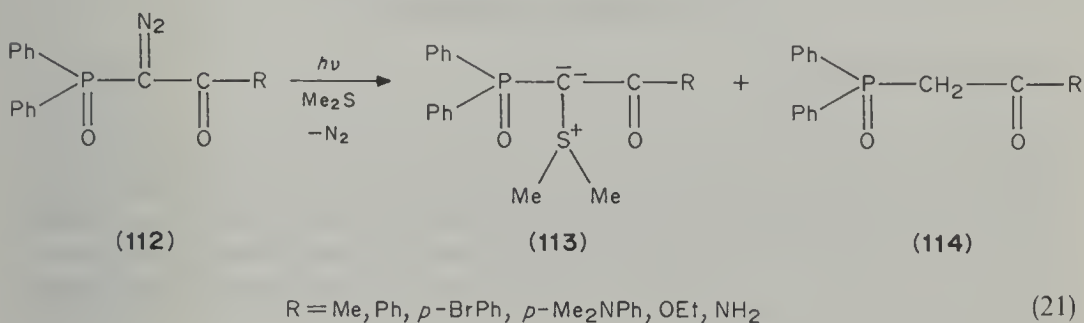
The carbene reactions of substituted (diazomethyl)diphenylphosphine oxide **104** in methanol proceed in a complex sequence. At the carbene stage (**105**), P/C—Ph shift competes with formation of the phosphinic ester **110** via the intermediate **106** and with



(20)

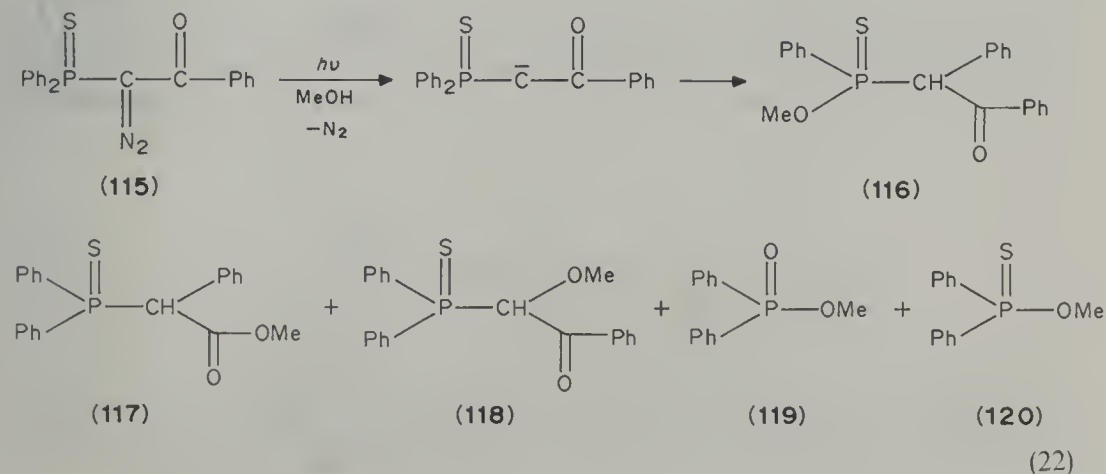
formation of the carboxylic ester **111** via C/C—R shift and the ketenes **109**. OH-insertion yields the methoxy compound **107** and the acyl methane **109** is formed via reductive N₂ elimination¹¹¹ (equation 20). The methoxy compound **107** may undergo cyclomerization to the corresponding oxetanes by intramolecular reduction of the carbonyl group¹¹¹. This reaction should proceed via the diradical similarly to the formation of cyclobutanol^{112,113}. Presumably for steric reasons, only the *trans* isomers (P—acyl group) of the resultant oxetanes could be detected¹¹¹.

(Diazobenzyl)diphenylphosphine oxide reacts with H₂O with OH insertion and via a Wolff rearrangement with H₂O addition to give the α -hydroxyphosphine oxide and the diphenylmethyl phenylphosphinic acid¹¹⁴. Using (diazomethyl)diphenylphosphine oxide it could be shown that the P/C—Ph shift product also reacts with other protic nucleophiles than H₂O and methanol, e.g. with isopropanol, morpholine and aniline¹¹¹. Photolysis of the (diazophosphine) oxides **112** in dimethyl sulphide leads to a reaction similar to a radical trap reaction to form dimethylsulphonio methanides **113** and, sometimes, the methylene compounds **114**¹¹⁵ (equation 21). The first ylide syntheses were performed using bis(phenylsulphono)diazomethane¹¹⁶, tetraphenyldiazocyclopentadiene¹¹⁷ and diazomalonic esters¹¹⁸.

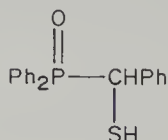


2. Sulphides

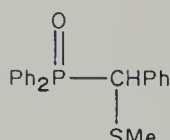
UV irradiation of benzoyldiphenylthiophosphoranyldiazomethane (**115**) in methanol yields the thiophosphinate **116** and the sulphides **117** and **118**. In methanol–benzene mixtures also the phosphinate **119** and the thiophosphinate **120** are formed¹¹⁹ (equation 22).



Sulphur migration is observed in the photolysis of (diazobenzyl)diphenylphosphine sulphide in alcoholic solution¹²⁰. The mechanism can be explained by the formation of a three-membered ring intermediate. These thiirenes are found to be very reactive^{121,122}. The last step can be viewed as an intramolecular Arbuzov-type reaction. Analogously, *N*-methylanilinophosphonium iodide reacts with alkoxide and thiol¹²³. Consequently, in dioxane–water α -mercaptobenzylidiphenylphosphine oxide (**121**) is obtained whereas in methanol–xylene α -methylthiobenzylidiphenylphosphine oxide (**122**) is formed¹²⁰. Irradiation in pure xylene leads only to the carbene dimer¹²⁰. Analogously to the phosphine oxides, a 1,2-phenyl migration occurs, and phosphine sulphides yield the corresponding products to the oxides¹²⁰.



(121)



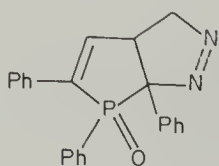
(122)

VI. PHOSPHOLE DERIVATIVES

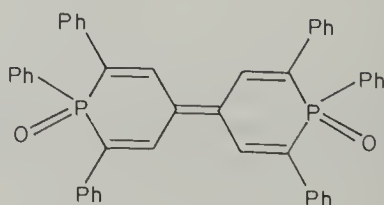
A. Molecular Reactions

1. Oxides

When a solution of 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide in dry peroxide-free tetrahydrofuran is photolysed under a nitrogen atmosphere, orange crystals of 3,3',4,4',5,5'-hexaphenyl-4,4'-diphosphabi(cyclohexyl-2,5-dienylidene)-4,4'-dioxide are obtained in good yield¹²⁴. Irradiation of the structurally similar pyrazoline **123** leads to the same reaction product **124**¹²⁴. Analytical data for the product **124** are similar to those of Märkl's compound¹²⁵.

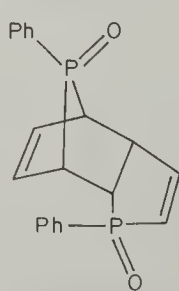


(123)

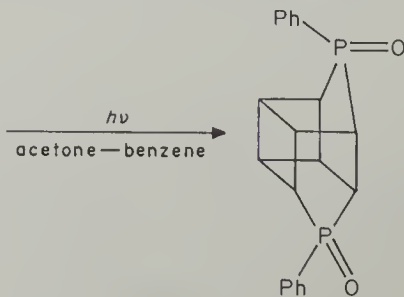


(124)

Sensitized irradiation of 1-phenyl-3-phospholene oxide dimer (**125**) led to the cage product **126** in nearly quantitative yield¹²⁶ (equation 23). Analytical investigation of this



(125)

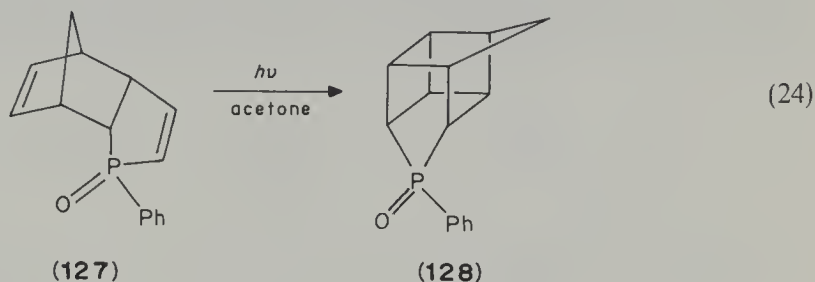


(126)

(23)

structure indicates a cage structure obtained by intramolecular $[2 + 2]$ -cycloaddition of the *endo*-Diels–Alder product **125**¹²⁷.

Photolysis of 3-phospholene-1-oxides yields stereoisomeric dienes depending on the substituents used only if the phenylphosphinidene oxide that is formed simultaneously is trapped^{128,129}. Reaction of buta-1,3-diene with phenyldibromophosphine followed by bromination, debromination with triethylamine and $[2 + 4]$ -addition with cyclopentadiene leads to the Diels–Alder adduct **127**. Reacting as a dienophile, the cage product **128** is formed with photochemical initiation in acetone¹³⁰ (equation 24).



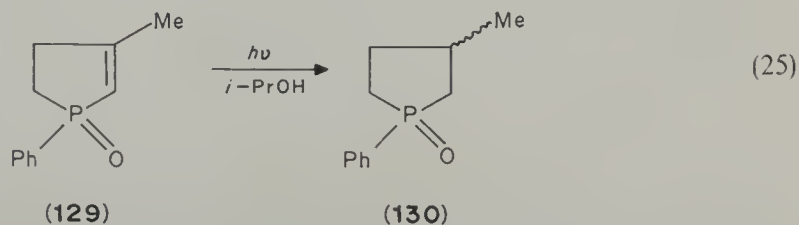
2. Sulphides

Irradiation of 3,4-dimethyl-1-phenyl-3-phospholene-1-sulphide in solutions of acetonitrile, diethyl ether, tetrahydrofuran or dioxane yields a polymer and the basic material. If, however, precautions are taken to ensure that the reactive phenylphosphinothiolidene intermediate is fully consumed, the corresponding dienes are obtained¹²⁸.

B. Reactions with Alcohols

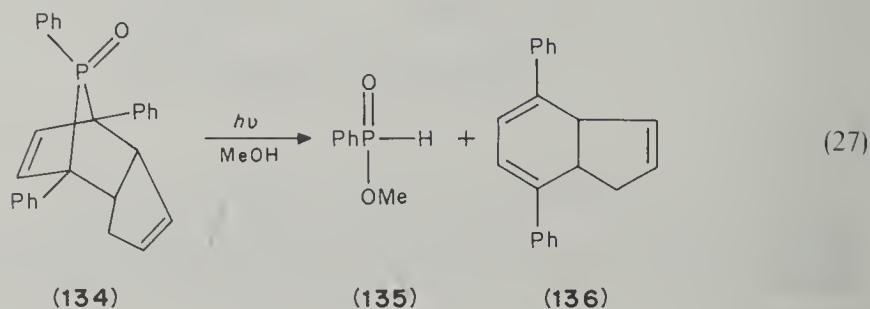
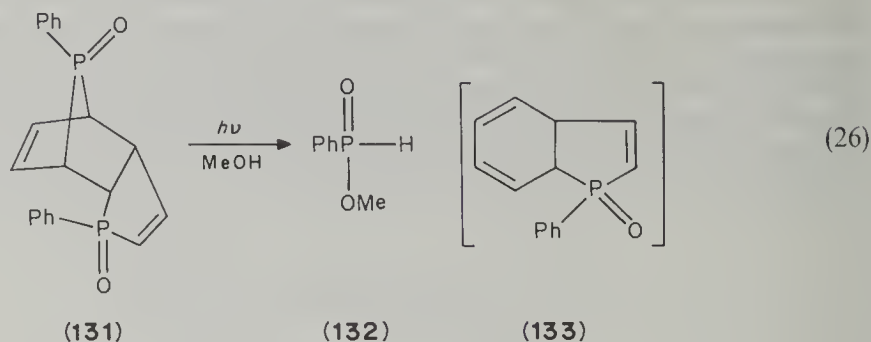
1. Oxides

2-Phospholene oxide (**129**) is photochemically reduced in the presence of isopropyl alcohol to yield a mixture of isomeric phospholanes (**130**)^{131,132} (equation 25). After irradiation of **129** in methanol–xylene, the possible ROH adducts are not obtained^{131,132}. Photolysis of 1-phenyl-3-methyl-3-phospholene oxide in methanol yields methyl phenylphosphinate as the only isolable products, whereas some isoprene is detected in the reaction mixture¹³³. The existence of the presumed intermediate phosphinidene oxide is proved by the following method: photolysis of phospholene oxide in benzene, addition of methanol as a trapping agent in the dark and detection of 10% methyl phenylphosphinate¹³³. The reaction is assumed to proceed via a poly(phosphinidene oxide) intermediate¹³⁴.

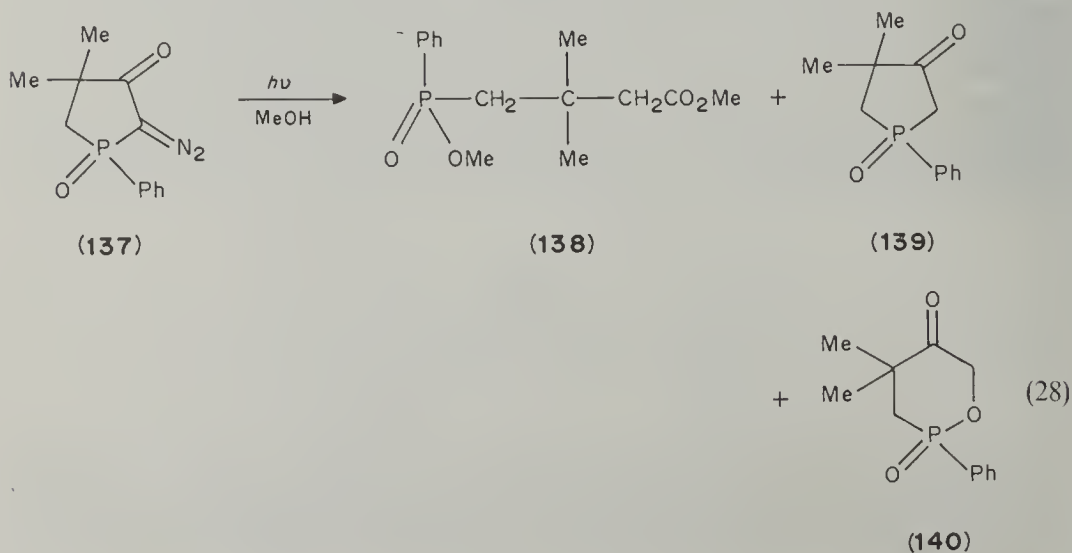


Photolysis of 1-phenyl-3-phosphole oxide dimer (**131**) in methanol yields methyl phenylphosphinate (**132**); the expected dihydroposphindole product **133** could not be isolated¹²⁶ (equation 26). However, after irradiation in methanol solution, the

adduct **134** from triphenylphosphole oxide¹³⁵ and cyclopentadiene leads to the phosphinate **135** and the dihydroindene derivative **136**¹³⁰ (equation 27).



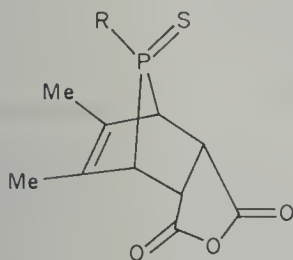
Photolysis of 2-diazo-4,4-dimethyl-1-phenyl- λ^5 -phospholane-1,3-diene (**137**) in methanol does not show a phosphorylcarbene–methyleneoxophosphorane rearrangement⁹⁹ but formation of the carboxylic ester **138**, presumably by solvolysis and Wolff rearrangement. Further, the cyclic α -oxophosphine oxide **139** is formed by reductive nitrogen elimination¹³⁶ and the 1,2, λ^5 -oxaphosphorinane **140** by O/H insertion, ether cleavage and isomerization¹³⁷ (equation 28). This isomerization to **140** corresponds to the ‘diphenyl reduction’ of 2,3-dihydroxy-1,3-diphenylprop-2-en-1-one¹³⁸.



2. Sulphides

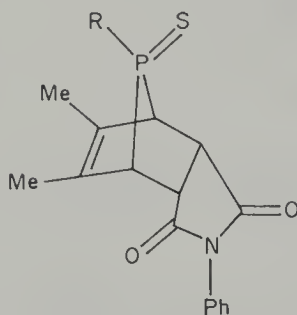
UV irradiation of 3,4-dimethyl-1-phenyl-3-phospholene-1-sulphide in methanol yields 2,3-dimethylbuta-1,3-diene, *O*-methyl phenylphosphinothioate and *O,O*-dimethyl phenylphosphonothioate. The product ratio depends on the length of irradiation¹²⁸. Several methyl-substituted 3-phospholene sulphides have been investigated to determine their ability to generate dienes¹²⁸.

Different species **141**–**143** have been probed in relation to photofission of 7-phosphanorbornene in methanol¹³⁹. Likewise, investigation were undertaken to determine whether the very high strain existing in the 3-phospholene ring would improve the yield of the photoreaction. Thermolysis, however, shows loss to the $RP=S$ bridge^{140–142}.



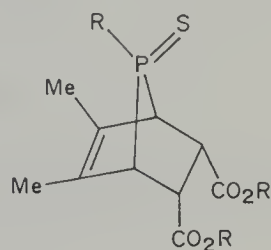
$R = \text{Ph}, n\text{-Bu}$

(141)



$R = \text{Ph}, n\text{-Bu}$

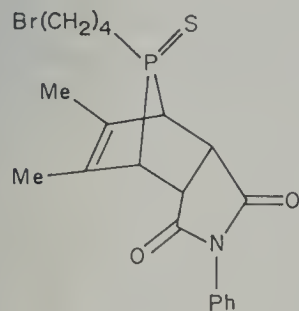
(142)



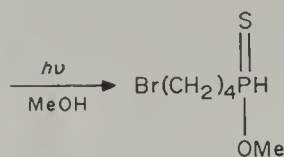
$R = \text{Me}, \text{H}$

(143)

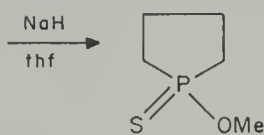
For example, photolysis of 7-(4-bromobutyl)-7-phosphanorbornene (**144**) leads to *O*-methyl (4-bromobutyl)phosphinothioate (**145**) in good yield, reacting after treatment with NaH – thf to give an interesting carbon phosphorus heterocyclic 1-methoxyphospholane sulphide (**146**)¹³⁹ (equation 29). This reaction sequence is also applicable to the production of ring systems such as phosphorinanes and phosphepanes¹³⁹. After irradiation in methanol, the adduct from triphenylphosphole sulphide and cyclopentadiene generates the corresponding thiophosphinate and diphenyldihydroindene¹³⁰.



(144)



(145)



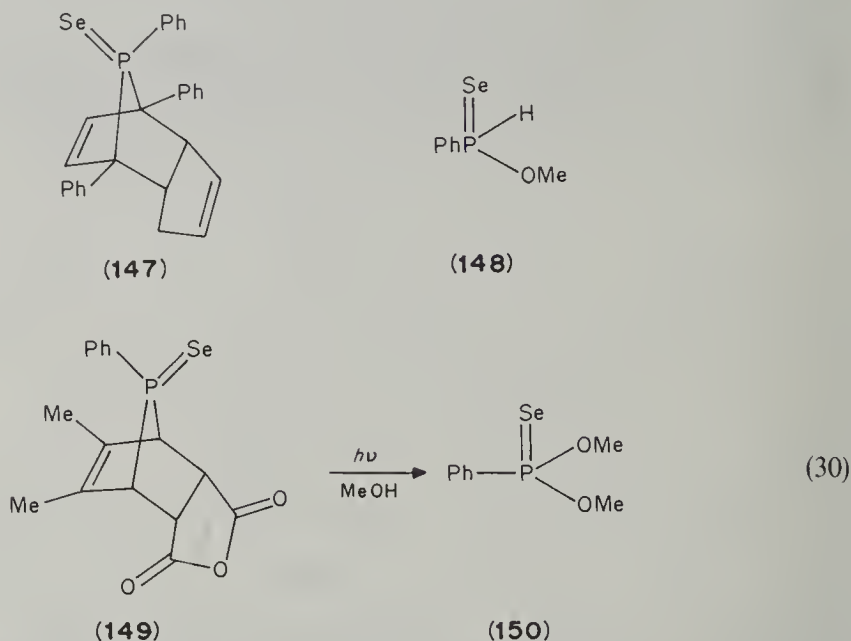
(146)

(29)

3. Selenides

After UV irradiation in methanol, the phosphine selenide **147** reacts to give the selenophosphinate **148** via the intermediate phenyl selenoxophosphine $\text{PhP}=\text{Se}$ ¹³⁰. Photolysis of 5,6-dimethyl-8-*anti*-phenyl-3a,4,7a-tetrahydro-4,7-phosphinideneisobenzofuran-1,3-dione-8-selenide (**149**) in the presence of methanol leads, after a sufficient irradiation time, to the product *O,O*-dimethylphenylselenophosphinate (**150**) via the cor-

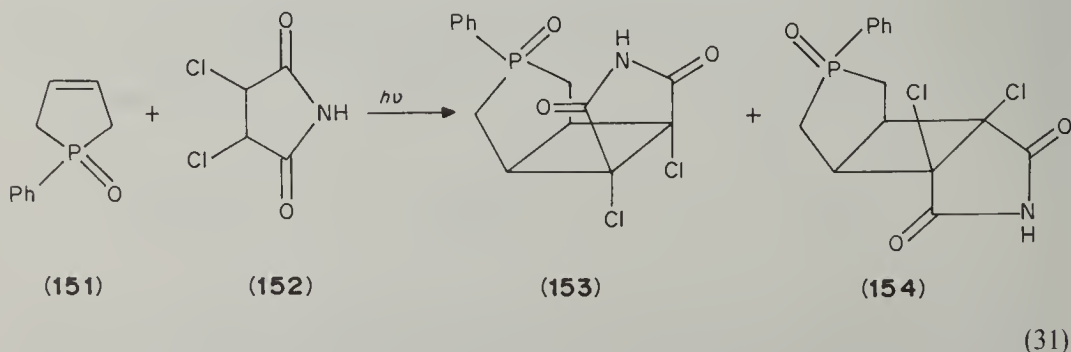
responding phosphinate^{143,144} (equation 30). A similar mechanism is shown by 5,6-dimethyl-2, 8-*anti*-diphenyl-3a, 4, 7, 7a-tetrahydro-4, 7-phosphinideneisindole-1, 3-dione-8-selenide¹⁴⁴. The central point of the reactions described above is the intermediate $\text{PhP}=\text{X}$ ($\text{X} = \text{Se}, \text{S}, \text{O}$) as a typical example of the very interesting compounds with $\lambda^3\sigma^2$ -phosphorus¹⁴⁵⁻¹⁴⁹.



C. Reactions with Other Compounds

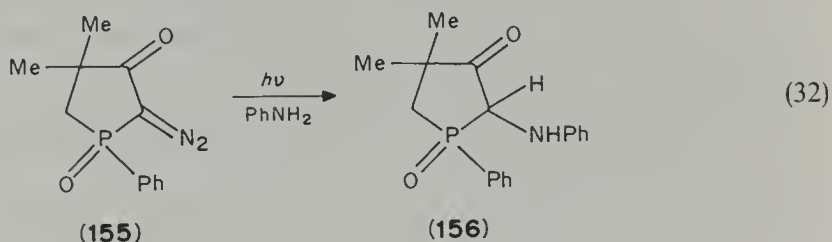
1. Oxides

Photochemical initiation of a cycloaddition between 1-phenyl-3-phospholene-1-oxide (151) and dichloromaleimide (152) yields the two isomeric forms 153 and 154. Their structure follows from their chemistry and the stereochemistry of their fission products¹⁵⁰ (equation 31). Using these compounds, the synthesis of 1-phenyldihydrophosphepin-1-oxide and some other dihydrophosphepins can be realized¹⁵⁰.



In a similar manner, 1-methyl-3-phospholene-1-oxide, 1-ethoxy-3-phospholene-1-oxide and 1-chloro-3-phospholene-1-oxide react with dichlorovinylene carbonate. In the presence of acetophenone this addition is stereoselective. The adducts may be used as

educts for the synthesis of 3-phospha[3.1.0]bicyclohexanes¹⁵¹. The cyclic α -diazo- β -oxophospholane oxide **155** undergoes photolysis in aniline via N/H insertion to give the secondary amine **156**. The difference to the reaction in basic methanol (methanolate ion) is due to the weaker nucleophilic character of the aniline¹³⁷ (equation 32).



D. Miscellaneous

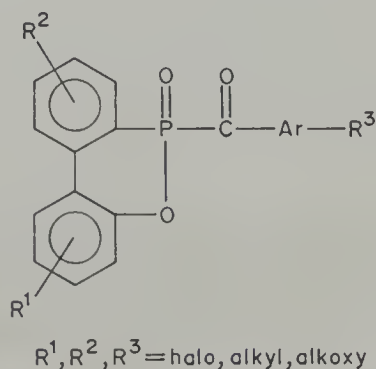
The reaction rate and the stereospecificity of the photochemical extrusion of phosphinidene oxide from the excited singlet states of 3-phospholene oxides are dependent on the configuration of the asymmetric leaving group. Consequently a steric influence on the transition state exists¹²⁹.

An effect of the elements in the phospholene chalcogenide group during the photofragmentation of 3,4-dimethyl-1-phenyl-3-phospholene derivatives has been reported, as has a methyl substitution effect in the 3-phospholene-1-sulphide species¹²⁸. The rate of photochemical diene generation from 3-phospholene-1-sulphide is comparable to that from the corresponding oxides¹²⁸.

VII. PHOSPHORIN DERIVATIVES

A. Oxides

Although, strictly, the oxaphosphorin oxides are not phosphorus chalcogenides, they may be compared with the acylphosphine oxides because of the similarity of the reactive molecular site and the homologous reaction mechanisms. For example, the 6-acyl-(6*H*)-dibenz[*c,e*][1,2]oxaphosphine-6-oxides **157** are used as photoinitiators in polymerization¹⁵². Investigations performed on the effect of γ - and α -rays in the extraction of americium(III) and curium(III) with tetraphenylmethylenediphosphorin dioxide in chloroform from aqueous nitric acid solution showed an unusually high resistance to radiation. Up to 15 kJ ml⁻¹ could be observed¹⁵³.



(157)

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Spectroscopy of phosphine chalcogenides

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I. INTRODUCTION

This chapter is concerned with UV-visible, vibrational and magnetic resonance spectroscopic results available for $\text{RR}'\text{R}''\text{PX}$, where R, R' and R'' are hydrogen atoms or substituents bonded to phosphorus via a carbon atom and $\text{X} = \text{O}, \text{S}, \text{Se}$ or Te . We shall consider the spectroscopic techniques in descending order of energies for the transitions involved, which also corresponds to increasing numbers of published papers.

II. ULTRAVIOLET AND VISIBLE (ELECTRONIC) SPECTROSCOPY

Following early reports on UV absorptions of Ph_3PO by Jaffé and Freedman^{1,2} and Horner and Ödiger³, a more detailed listing of UV absorptions for Ph_3PO and related molecules was reported by Schindlbauer⁴. These are summarized in Table 1; the band

TABLE 1. UV absorptions of some phosphine oxides (band positions in nm with log ϵ values in parentheses)^a

Compound	UV absorptions			
Ph ₃ PO	225(4.30)	259(3.13)	264(3.22)	271(3.13)
(PhCH ₂) ₃ PO	219(4.26)	255(2.67)	261(2.78)	267(2.60)
Ph ₂ MePO	223(4.22)	259(2.96)	264.5(3.10)	271(3.13)
PhP(O)(CH ₂ CH ₂ CN) ₂	218(4.13)	259(2.81)	265(2.93)	272(2.86)
PhP(O)(CH ₂ CH ₂ COOH) ₂	218(4.51)	258(2.49)	264(2.63)	271(2.56)

^aAll data refer to solutions in ethanol.

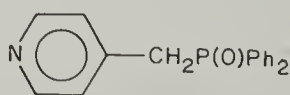
intensities were found to increase with the number of PhP units, but the band positions depended on other substituents.

UV spectra of Ph₃PO, 1,4-phenylenebis(diphenylphosphine oxide), α -naphthylidiphenylphosphine oxide and several naphthylenebis(diphenylphosphine oxides) show that the PO group effectively 'insulates' the ligands from one another, and there is little conjugation in the molecules⁵.

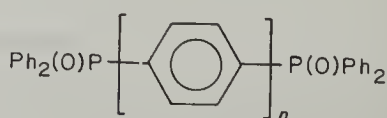
A Russian paper⁶ states that curve-fitting techniques can resolve the UV absorptions of Ph₃PO into no less than ten components, but no explanation was given as to the assignment of these.

The lack of change in λ_{\max} for $(p\text{-XC}_6\text{H}_4)_3\text{PE}$, where X = H, Me or MeO and E = O, or X = Me or MeO and E = S, with changing solvent was ascribed to a dominant role for the ArP^+E^- form, rather than $\text{ArP}=\text{E}$ ⁷.

UV spectra of arylphosphine oxides containing electron-donating *para* substituents show progressive shifts to longer wavelength with increasing substituent electron-donor ability. This is consistent with $d\pi\text{-}p\pi$ bonding between the PO group and the aromatic ring⁸. The UV absorption band of aniline is shifted to longer wavelength by *para* substituents containing phosphorus in a way typical of -M substituents, e.g. for $p\text{-H}_2\text{NC}_6\text{H}_4\text{P(O)Ph}_2$, λ_{\max} is at 267.5 nm, with log $\epsilon = 4.32$ ⁹. UV spectra of $\text{Ph}_n\text{P(Z)(C}_6\text{H}_4\text{OMe-}p\text{)}_{3-n}$, where Z = O or S and $n = 0\text{--}2$, show no dependence of the electronic effect of P on the nature of the second substituent¹⁰. The UV spectra of 2-, 3- and 4-picolyldiphenylphosphine oxides, such as **1**, show that they exist in that form, with no evidence for the tautomeric 4-ylidene forms¹¹.



(1)



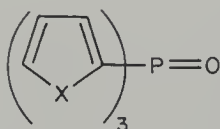
(2)

Small bathochromic shifts were found, due to the Ph₂P(O) groups, in the UV bands of the oligophenyls in **2**, where $n = 1\text{--}4$ ¹². Substitution of an NMe₂ group into the phenyl ring of bis(*p*-nitrophenylethynyl)phenylphosphine oxide gave rise to extra UV absorptions assigned to electronic transitions involving electrons delocalised through phosphorus¹³.

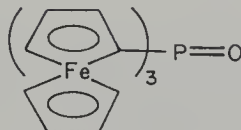
Other phosphine oxides and sulphides for which UV data have been reported are tris(*n*-methylphenyl)phosphine oxides, $n = 2, 3$ or 4 ¹⁴; $(p\text{-XC}_6\text{H}_4)_3\text{PE}$, X = H, Cl, OMe or NMe₂, E = O or S¹⁵; Ph₂EtPO¹⁶; $(p\text{-XC}_6\text{H}_4)_2\text{PE}$, X = H, Cl or OMe, E = O or S¹⁷; *cis*-4-Ph₂P(O)C₆H₄CH=CHC₆H₄R, R = 4-Me₂N, 3-Me₂N, 4-MeO-, 3-MeO or 2-MeO¹⁸; R₂P(O)Ph, RP(O)Ph₂, R₂P(O)C₆H₄NMe₂-*p*, R₂P(O)Et, R₃PO, R = PhC \equiv C-¹⁹; (*o*-, *m*- and *p*-MeOC₆H₄)PhP(O)Me²⁰; (*p*-CNC₆H₄)P(O)R₂, R = Me or Ph²¹; (2,3,5,6-Me₄C₆H)₃P(O) and (2,3,5,6-Me₄C₆H)₂P(O)Ph²²; and Bu₂P(O)CH=CH₂²³.

Changes in the luminescence properties of substituted triarylphosphine oxides with the nature of the substituent have been reported²⁴. The fluorescence properties of 14 tertiary phosphine oxides showed that significant fluorescence only occurred if the substituent on phosphorus was itself fluorescent, e.g. ArPhP(O)Me, where Ar = isomeric naphthyl derivatives²⁵. UV data on RPh₂PO, where R = 1 = naphthyl, 9-anthryl or 1-pyrenyl, all showed intense fluorescence in the blue region²⁶.

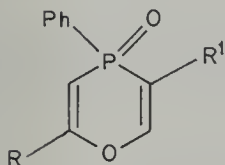
The UV spectra of **3**, where X = NR (R = H or Me), O or S, are indicative of strong d π -p π bonding between PO and the ring^{27,28}. The UV spectra of **4** and its diferrocenyl analogue show very little π -electron donation from the ferrocenyl fragment to the phosphorus²⁹. λ_{max} values have been listed for **5**, where R, R' = Me or Ph³⁰.



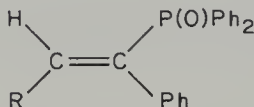
(3)



(4)



(5)



(6)



(7)

I₂, IBr and ICl complexation with phosphine oxides, sulphides and selenides was followed by shifts in characteristic UV bands of the latter compounds³¹. The UV spectra of **6**, where R = **7**, with a range of substituents X, show that the P(O)Ph₂ group induces a bathochromic shift in the ¹L_a and ¹L_b bands of the styrene fragment³². The λ_{max} (and log ϵ) values for a range of P=Se compounds have been given, including the following data for Bu₃P=Se: $\pi \rightarrow \pi^*$ 195 nm (4.18); $n \rightarrow \sigma^*$ 208 nm (4.06); $n \rightarrow \pi^*$ 238 nm (3.53)³³.

III VIBRATIONAL SPECTROSCOPY

A. Phosphine Oxides

Values of $\nu\text{P}=\text{O}$ in a wide range of phosphine oxides have been tabulated by Thomas³⁴. The parent oxide PH₃O was prepared by red-visible photolysis of PH₃-O₃ mixtures in matrices. All its vibrational modes were seen for H₃P¹⁶O and most of its other isotopomers (Table 2). Normal coordinate analysis gave the following force constant values: P=O stretch, $(9.53 \pm 0.16) \times 10^2 \text{ N m}^{-1}$; P-H stretch, $(3.25 \pm 0.01) \times 10^2 \text{ N m}^{-1}$. ³⁵*Ab initio* SCF calculations gave calculated IR spectra of H₃PO, D₃PO and H₃P¹⁸O which were in good agreement with the above figures³⁶.

IR and Raman spectra of Me₂P(H)=O were assignable under C_s symmetry, with νPH at 2333 cm⁻¹ (IR) and 2348 cm⁻¹ (Raman), and $\nu\text{P}=\text{O}$ 1169 cm⁻¹ (IR) and 1155 cm⁻¹ (Raman). A normal coordinate analysis suggested that there was extensive mixing of all modes except for these two³⁷. Ranges of νPH wavenumbers were listed for RR'P(H)O (2294–2380 cm⁻¹) and R₂P(H)S (2288–2299 cm⁻¹)³⁸. IR data were listed for CH₃(CF₃)P(H)=O and Me₂(CF₃)P=X, where X = O or S³⁹. νPH for (cyclo-C₈H₁₇)₂P(H)O showed that the P-H bond could take part in weak hydrogen bonding⁴⁰.

TABLE 2. Vibrational assignments for PH_3O (cm^{-1})

	$\text{H}_3\text{P}^{16}\text{O}$	$\text{H}_3\text{P}^{18}\text{O}$	$\text{D}_3\text{P}^{16}\text{O}$	$\text{D}_3\text{P}^{18}\text{O}$
$\nu_{as}\text{PH}$	2371.5	2371.6	—	—
$\nu_s\text{PH}$	2359.0	2367.0	1721.1	1720.0
$\nu\text{P}=\text{O}$	1240.2	1213.7	1217.3	1174.1
$\delta_s\text{PH}_3$	1143.5	—	843.6	840.5
$\delta_{as}\text{PH}_3$	1114.3	1114.3	—	—
δHPO	853.0	849.4	655.9	651.3

The intensity of νPH in $\text{R}_2\text{P}(\text{H})=\text{O}$, where $\text{R} = n\text{-C}_6\text{H}_{13}$, cyclo- C_6H_{11} , Ph or PhCH_2 , correlates with the electronegativity of the phosphorus substituents⁴¹.

A very thorough assignment of the vibrational modes of Me_3PO , Me_3PS and Me_3PSe and their perdeuterated analogues has been made (Table 3)⁴²; values of the Me torsional modes had been proposed earlier⁴³, and there had been several other, incomplete, studies⁴⁴⁻⁴⁷. There have also been a number of approximate or partial normal coordinate analyses of Me_3PO ⁴⁸⁻⁵⁴.

IR data have been collected for $\text{Me}_2\text{P}(\text{O})\text{CH}_2\text{X}$, where $\text{X} = \text{Cl}$, Br or I. These show that there are equilibria between *trans* (C_s symmetry) and *gauche* (C_1) conformers in CCl_4 solution⁵⁵. $(\text{ClCH}_2)_3\text{PO}$ has δCH_2 modes at 1391 and 1410cm^{-1} ⁵⁶. νPO (1327cm^{-1})

TABLE 3. Vibrational assignments (cm^{-1}) for Me_3PE , where $\text{E} = \text{O}$, S or Se (data for perdeuterated analogues in parentheses)

	E		
	O	S	Se
A_1			
$\nu_1 \nu\text{CH}_3$	2974(2226)	2967(2219)	2958(2218)
$\nu_2 \nu\text{CH}_3$	2906(2126)	2895(2116)	2892(2117)
$\nu_3 \delta\text{CH}_3$	1408(1028)	1408(1020)	1400(1016)
$\nu_4 \delta\text{CH}_3$	1300(1021)	1306(1015)	1301(1016)
$\nu_5 \rho\text{CH}_3$	946(781)	951(782)	952(782)
$\nu_6 \nu\text{PC}_3$	667(597)	714(648)	689(619)
$\nu_7 \nu\text{P}=\text{E}$	1161(1165)	565(533)	441(414)
$\nu_8 \delta\text{PC}_3$	320(271)	282(270)	260(232)
E			
$\nu_{13} \nu\text{CH}_3$	2974(2226)	2976(2225)	2975(2230)
$\nu_{14} \nu\text{CH}_3$	2974(2226)	2967(2210)	2967(2224)
$\nu_{15} \nu\text{CH}_3$	2906(2126)	2895(2116)	2892(2117)
$\nu_{16} \delta\text{CH}_3$	1438(1040)	1429(1043)	1425(1027)
$\nu_{17} \delta\text{CH}_3$	1430(1028)	1424(1020)	1417(1023)
$\nu_{18} \delta\text{CH}_3$	1282(1021)	1287(1015)	1290(1016)
$\nu_{19} \rho\text{CH}_3$	962(701)	982(647)	978(695)
$\nu_{20} \rho\text{CH}_3$	867(797)	865(822)	862(805)
$\nu_{21} \nu\text{PC}_3$	741(625)	744(628)	748(627)
$\nu_{22} \delta\text{PC}_3$	250(224)	282(247)	271(232)
$\nu_{23} \rho\text{PC}_3$	360(226)	229(202)	202(180)

and other modes were assigned for $(\text{CF}_3)_3\text{PO}$ ⁵⁷. Detailed vibrational assignments have been proposed for $\text{Me}_2(\text{R})\text{P}=\text{O}$, where R = decyl or dodecyl, which suggest that in the crystals the P=O bond is perpendicular to the plane of the hydrocarbon skeletal plane⁵⁸.

Solutions of $\text{Ph}_3\text{P}^{16}\text{O}$ and $\text{Ph}_3\text{P}^{18}\text{O}$ in CCl_4 show νPO at 1202 and 1123 cm^{-1} respectively⁵⁹. Several other papers have discussed the vibrational spectrum of triphenylphosphine oxide, mostly relating to phenyl modes, however⁶⁰⁻⁶³.

$[\text{Me}_3\text{CC}\equiv\text{C}]_3\text{P}=\text{O}$ has $\nu\text{P}=\text{O}$ at 1235 and νPC_3 at 576 and 610 cm^{-1} , together with ligand modes in the expected ranges. The P=S analogue has $\nu\text{P}=\text{S}$ at 689 and νPC_3 at 556 and 588 cm^{-1} ⁶⁴. $\nu\text{P}=\text{O}$ assignments are summarized for $\text{R}_n(\text{C}_6\text{F}_5)_{3-n}\text{P}=\text{O}$, where R = Me, Et or Ph and $n=0,1$ or 2, in Table 4⁶⁵.

The $\nu\text{P}=\text{O}$ wavenumbers in the IR spectra of $\text{R}^1\text{R}^2\text{R}^3\text{P}=\text{O}$, where R^1, R^2 and R^3 are Ph or alkyl groups, are related by quadratic equations to the P-substituent bond energies and to the $\text{P}(\text{O})-\text{M}$ bond energies in their uranyl complexes⁶⁶. The $\nu\text{P}=\text{O}$ wavenumbers of $\text{R}_3\text{P}=\text{O}$, where R = *n*-butyl, 2-ethylhexyl, *n*-octyl or phenyl, suggest that there is no fundamental theoretical justification for equations relating $\nu\text{P}=\text{O}$ to π -parameters of substituents at the phosphorus⁶⁷. Two other reports have been made of νPO for tri-*n*-octylphosphine oxide^{68,69}.

A linear dependence was found between $\nu\text{P}=\text{X}$ in $\text{R}_3\text{P}=\text{E}$, where R = alkyl and X = O, S, Se or Te, and the function $(\Sigma M/m_{\text{P}}m_{\text{X}})^{1/2}E_{\text{P}}E_{\text{X}}$, where M = total mass of the molecule, $m_{\text{P}}, m_{\text{X}}$ = masses of P and X and $E_{\text{P}}, E_{\text{X}}$ = Pauling electronegativities of P and X⁷⁰.

The IR spectra of Ph_3PX , where X = O, S or Se, suggest the following values for $\nu\text{P}=\text{X}$; 1191 (O), 637 (S) and 561 (Se) cm^{-1} . In each case $\nu_{\text{as}}\text{PPh}_3$ lay in the range 511–540 cm^{-1} ⁷¹. νPO of R_3PO , where R = phenyl, *p*-tolyl, *o*-tolyl, 2,4-xylyl, 2,6-xylyl, mesityl or duryl, were assigned. In the *o*-tolyl and xylyl species the wavenumbers were lowered owing to interaction between the *ortho*-Me proton and the oxygen atom. Additional lowering in the last three compounds was due to further steric crowding⁷². There has been an extensive series of papers on the IR spectra of substituted triarylphosphine oxides or sulphides, in many cases proposing empirical relationships between $\nu\text{P}=\text{E}$ and the electronic parameters of the substituents⁷³⁻⁷⁹.

The IR intensity of νPO for Ph_3PO (1205 cm^{-1}) and other phosphoryl compounds shows no correlation with the band positions. The inductive effect of the substituents has the main influence on the intensity⁸⁰. There has been a further report of the absolute IR intensities for the νPO band of many phosphoryl compounds, including Ph_3PO ⁸¹.

The P—Me rocking modes in (*o*-, *m*- or *p*- MeOC_6H_4) PhMePO were all in the range 863–902 cm^{-1} ⁸².

IR intensities for the ν_8 ring stretching mode (near 1600 cm^{-1}) for (*p*- YC_6H_4) $_3\text{PO}$, where Y = OMe, Cl, Et, Me or MeCO, and (*p*- YC_6H_4) $_3\text{PS}$, where Y = NMe₂, OMe, Cl, Et, Me or MeCO, suggest σ_{R}^0 values for PPh_2O and PPh_2S of +0.07 and +0.06, respectively⁸³. The intensity of νCC in the IR spectra of $\text{Ph}_2\text{P}(=\text{O})\text{C}\equiv\text{CX}$, where X = H, Me, Ph or $\text{C}(\text{OH})\text{Me}_2$, is greater than for the corresponding band in $\text{Ph}_2\text{PC}\equiv\text{CX}$. There was an almost linear correlation between this intensity and the Taft coefficient $\sigma^*\text{X}$ for X⁸⁴.

TABLE 4. $\nu\text{P}=\text{O}$ assignments for $\text{R}_n(\text{C}_6\text{F}_5)_{3-n}\text{P}=\text{O}$

n	$\nu\text{P}=\text{O}$ (cm^{-1})		
0	1242		
1	1222 (R = Ph)	1223 (Me)	1221 (Et)
2	1201 (R = Ph)	1193 (Me)	1205 (Et)

The IR spectra of $\text{Ph}_2\text{P}(=\text{O})\text{CH}=\text{C}=\text{CR}^1\text{R}^2$, where R^1 and $\text{R}^2 = \text{H}$ or Me , show the presence of two conformational isomers. There is therefore restricted rotation about the $\text{P}-\text{C}(\text{allene})$ bond. The influence of the allenic group on the $\text{P}=\text{O}$ bond suggests that the phosphorus is conjugated with the allene system⁸⁵. The value of $\nu\text{CO}(\text{aromatic})$ of $(p\text{-MeOC}_6\text{H}_4)\text{P}(\text{X})\text{Ph}_2$, where $\text{X} = \text{O}$ or S , shows that the phosphorus is acting as a proton acceptor⁸⁶.

The IR spectra of $\text{R}_3\text{P}=\text{O}$, where $\text{R} = \text{C}_1\text{--C}_{16}$ *n*-alkyl, show that there is a dynamic equilibrium between conformers in solution. In the crystalline state only one conformer was present each time⁸⁷. The IR spectrum of $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{Ph}$ shows that only the *gauche* conformation is present in the crystal. The liquid also contains a small amount of the *trans* conformer⁸⁸. There is IR evidence for the presence of two conformers of $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NHNH}_2$ in solution, in the crystal and in vitreous forms⁸⁹.

$\text{Ph}_2\text{P}(=\text{E})\text{P}(=\text{E})\text{Ph}_2$, where $\text{E} = \text{O}$ or S , have $\nu\text{P}=\text{E}$ at 1180 cm^{-1} (O) or 635 cm^{-1} (S)⁹⁰. IR assignments have been made of $\nu\text{P}=\text{O}$ modes for $[\text{Ph}_2\text{P}(=\text{O})]_2\text{CH}_2$ (1211 , 1194 cm^{-1}) and $[\text{Ph}_2\text{P}(=\text{O})\text{CH}_2]_2\text{P}(=\text{O})\text{Ph}$ (1215 , 1192 , 1163 cm^{-1})⁹¹. νCC wave-numbers for $\text{Ph}_2\text{P}(\text{X})\text{C}\equiv\text{CP}(\text{X})\text{Ph}_2$, where $\text{X} = \text{O}$ (2143 cm^{-1}) or S (2150 cm^{-1}) are consistent with significant $\text{X} \rightarrow \text{P}$ $p\pi\text{--}d\pi$ back bonding, thereby raising the $\text{C}\equiv\text{C}$ bond order by $\text{P} \rightarrow \text{C}$ $d\pi\text{--}p\pi$ interaction⁹². $\nu\text{P}=\text{X}$ modes were assigned for $\text{C}[\text{CH}_2\text{P}(\text{X})\text{Ph}_2]_4$, where $\text{X} = \text{O}$ (1187 cm^{-1}), S ($625/613\text{ cm}^{-1}$) or Se ($588/540\text{ cm}^{-1}$)⁹³.

Shifts of νPO for a range of phosphine oxides in the presence of I_2 , IBr , ICl or Br_2 show the coordination of halogen to the oxygen atom, e.g. for Bu_3PO , νPO decreases from 1169 to 1118 cm^{-1} in the presence of I_2 ⁹⁴. Solvent effects on the IR spectrum of $(n\text{-C}_8\text{H}_{17})_3\text{PO}$ (νPO band) show that the PO bond behaves similarly to the $\text{C}=\text{O}$ bond in the same solvents⁹⁵. There have been many reports on the effects of hydrogen bonding on the $\text{P}=\text{O}$ stretching mode of phosphine oxides^{96–104}. There is a linear correlation between $\nu_{\text{max}}(\text{P}=\text{O})$ and $\Delta\delta^{31}\text{P}$ for Ph_3PO in a wide range of solvents. It is therefore possible to predict NMR chemical shifts from IR results¹⁰⁵.

B. Phosphine Sulphides

Values of $\nu\text{P}=\text{S}$ have been tabulated for a wide range of phosphine sulphides¹⁰⁶. Some earlier assignments from the IR and Raman spectra of $\text{Me}_2\text{P}(\text{H})\text{S}$ ¹⁰⁷ have been superseded by fuller data on the compound¹⁰⁸ and $\text{Me}_2\text{P}(\text{D})\text{S}$ ¹⁰⁹. The IR and Raman data were assigned in terms of C_s symmetry, with νPH and νPD at 2350 and 1714 cm^{-1} , respectively. A normal coordinate analysis showed that, apart from νPH and νCH , all of the modes were extensively mixed. Earlier references has been made to νPH assignments for $\text{R}_2\text{P}(\text{H})\text{S}$, where $\text{R} = \text{alkyl}$ ³⁸.

A detailed study has been made of the IR and Raman spectra of $(\text{CH}_3)_n(\text{CD}_3)_{3-n}\text{PS}$, where $n = 0\text{--}3$ ¹¹⁰. Assignments for the d_0 and d_9 molecules were consistent with C_{3v} symmetry and those for the d_3 and d_6 analogues with C_s symmetry. These assignments, together with a normal coordinate analysis, complement the data referred to above^{42–43}. Some approximate force constant calculations on Me_3PS were also mentioned previously^{51–54}. Some partial resolution of gas-phase IR bands of Me_3PS has been achieved, with P, Q and R branches of the νPC_3 band at 575 , 582 and 591 cm^{-1} , respectively¹¹¹. Some vibrational assignments were also given for R_3PS , where $\text{R} = \text{Me}$ or Et ^{112,113} or Pr^i or Ph ¹¹³. There has been a study of the dependence of νPS in R_3PS on the electronegativity of R ⁷⁰.

The IR and Raman spectra of $\text{EtP}(\text{S})\text{Me}_2$ in the liquid phase could only be assigned on the assumption that both *gauche* and *trans* conformers were present. Only the *gauche* form persists in the solid. The vibrational spectrum of the latter was assigned completely, including a value of 110 cm^{-1} for the antisymmetric torsional mode¹¹⁴. Earlier reference was made to νCH and νCF assignments for $\text{Me}_2(\text{CF}_3)\text{P}=\text{S}$ ³⁹.

Durig *et al.*¹¹⁵ have also carried out a thorough investigation of the vibrational spectra of Et_3PE , where $\text{E} = \text{S}$ or Se . In each case 60 of the 63 fundamentals were assigned, assuming C_3 symmetry. When $\text{E} = \text{S}$, but not when $\text{E} = \text{Se}$, there was strong coupling between νPE and νPC_3 ¹¹⁵. $\nu\text{P}=\text{S}$ or $\nu\text{P}=\text{Se}$ modes were assigned for R_3PE , $\text{R} = \text{Me}$, Pr^n , Pr^i , cyclopropyl, cyclohexyl or Ph and $\text{E} = \text{S}$ or Se . The values for $\text{R} = \text{Pr}^i$ and cyclopropyl were unusually high, presumably for steric reasons¹¹⁶. An early report listed νPS or νPSe for 15 phosphine sulphides and 13 phosphine selenides¹¹⁷. νPS values were also tabulated for $\text{R}_{3-n}(\text{C}_6\text{F}_5)_n\text{PS}$, where $\text{R} = \text{Me}$, Et or Ph and $n = 1$ or 2 ¹¹⁸.

νPS in Ph_3PS has been assigned by a number of workers to a value of 637 cm^{-1} ^{71,119,120}, with νPSe at 562 cm^{-1} in Ph_3PSe ¹²⁰. Other reports gave νPS in a wide range of substituted triaryl phosphine sulphides^{73,74,79,83,86}. It has been suggested that νPS in R_3PS , where $\text{R} = \text{Ph}$ or Et , shows the presence of several rotamers¹²¹.

$\nu\text{C}\equiv\text{C}$ in $\text{Me}_2\text{P}(\text{S})\text{C}\equiv\text{CEt}$ was assigned to 2212 cm^{-1} ¹²². There has been disagreement about the assignment of skeletal stretches in $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$ ^{123,124}. The more recent work suggests that $\nu_s\text{PS}$ is at 610 cm^{-1} , $\nu_{as}\text{PS}$ at 550 cm^{-1} and νPP at 510 cm^{-1} ¹²⁴. $\nu\text{C}\equiv\text{C}$ in $\text{Ph}_2\text{P}(\text{S})\text{C}\equiv\text{CP}(\text{S})\text{Ph}_2$ is at 2150 cm^{-1} ¹²⁵.

C. Phosphine Selenides and Tellurides

A detailed assignment for Me_3PSe has already been given (Table 3)⁴²⁻⁴³. νPSe was also assigned for R_3PSe , where $\text{R} = \text{alkyl}$ ⁷⁰, or $\text{R} = \text{Me}$, Pr^n , Pr^i , cyclopropyl, cyclohexyl or Ph ¹¹⁶. In Ph_3PSe , νPSe is at 561 cm^{-1} ^{71,120}. The equivalent mode is at 544 or 574 cm^{-1} in R_3PSe , where $\text{R} = p\text{- or } m\text{-MeC}_6\text{H}_4$, respectively¹²⁵.

A full assignment has been proposed for Me_3PTe and $(\text{CD}_3)_3\text{PTe}$, based on C_{3v} symmetry. A normal coordinate analysis suggested that there was extensive mixing of modes, with νPTe contributing significantly to bands at 226 , 378 and (to a lesser extent) 674 cm^{-1} . The $\text{P}-\text{Te}$ force constant was, as expected, smaller than that for the other PE systems¹²⁶. The results of this work throw into considerable doubt earlier reports of νPTe modes, e.g. of values between 400 and 518 cm^{-1} , for R_3PTe , where $\text{R} = \text{Pr}^n$, Bu^n , $n\text{-C}_5\text{H}_{11}$, $\text{cyclo-C}_6\text{H}_{11}$ or $n\text{-C}_8\text{H}_{17}$ ¹²⁷.

IV. MAGNETIC RESONANCE SPECTROSCOPY

The nuclei will be dealt with separately, in the following sequence: ^{31}P , ^1H , ^{13}C , ^{19}F , ^{17}O , ^{77}Se and ^{125}Te . Each paper will be referred to only once, dealing with all of the nuclei mentioned in that paper, and referring back, wherever necessary, for nuclei later in the order given above.

A. ^{31}P

An extensive list of ^{31}P chemical shifts in R_3PE , where $\text{E} = \text{O}$, S or Se , has been published¹²⁸. These were referred to an 85% aqueous solution of H_3PO_4 as standard, as will all subsequent references, unless mentioned otherwise. The ^{31}P spectrum of $\text{Me}_2\text{P}(\text{H})=\text{O}$ consists of a doublet of septets, centred at -18.6 ppm , with $J_{\text{PH}} = 456\text{ Hz}$ and $J_{\text{PCH}} = 14\text{ Hz}$. The ^1H spectrum contained a doublet of septuplets ($\tau 2.5$; $J_{\text{PH}} 490\text{ Hz}$, $J_{\text{PHCH}} 3.5\text{ Hz}$), due to the unique proton, and a doublet of doublets ($\tau 7.89$, $J_{\text{PCH}} 14\text{ Hz}$, $J_{\text{PHCH}} 3.5\text{ Hz}$)¹²⁹.

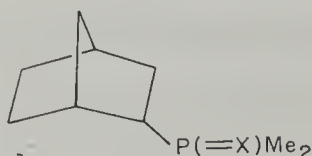
The ^{31}P spectrum of $\text{Ph}_2\text{P}(\text{O})\text{H}$ shows a 1:1 doublet, $\delta^{31}\text{P} - 25.9\text{ ppm}$, $^1J_{\text{PH}} 513\text{ Hz}$, while for $\text{Ph}_2\text{P}(\text{O})\text{D}$ a 1:1:1 triplet is seen, with $\delta^{31}\text{P} - 25.7\text{ ppm}$, $^1J_{\text{PD}} 78\text{ Hz}$ ¹³⁰. A different report gives $^1J_{\text{PH}}$ as 493.3 Hz in $\text{Ph}_2\text{P}(\text{O})\text{H}$ ¹³¹. CNDO/2 calculations of $^{31}\text{P}-^{13}\text{C}$ and $^{31}\text{P}-^1\text{H}$ couplings in a number of phosphine oxides and sulphides gave reasonable agreement with experiment. The results were consistent with a direct relationship between

$^1J_{\text{PC}}$ and the percentage σ -character of the phosphorus hybrid orbitals¹³². ^{31}P and ^{13}C NMR spectra of triply labelled ^{13}C forms of Me_3PO , Me_3PS and Me_3PSe oriented in a nematic phase have been recorded. The ^{31}P chemical shift tensor has a large anisotropy in all cases, but decreases in the order $\text{O} > \text{S} > \text{Se}$, consistent with decreased π -bonding in that series¹³³.

Ab initio M.O. calculations have been related to experimental values of $\delta^{31}\text{P}$ chemical shifts for a large number of trialkyl- and triaryl-phosphine oxides, sulphides and selenides¹³⁴⁻¹³⁶. Principal components of the ^{31}P chemical shift tensor were determined by ^{31}P solid-state NMR for R_3PX , where $\text{X} = \text{O}, \text{S}$ or Se and $\text{R} = \text{Me}, \text{C}_6\text{H}_{11}$ or Ph , $\text{X} = \text{O}$ or S and $\text{R} = \text{Et}$ or *p*-tolyl and $\text{X} = \text{S}$ and $\text{R} = o$ - or *m*-tolyl. The chemical shift anisotropy is greater for $\text{X} = \text{O}$ than for $\text{X} = \text{S}$ or Se ¹³⁷. The ^{31}P magnetic shielding anisotropies ($\sigma_{\parallel} - \sigma_{\perp}$) were found to $+210$ and $+127$ ppm for Me_3PO and Me_3PS respectively.¹³⁸ The calculated value for this anisotropy agrees very badly with this, however ($+69$ ppm)¹³⁹. The anisotropy of the ^{31}P screening constant of Me_3PO was calculated by CNDO/2 M.O. methods. The contribution of the π -P—O bond order gave stronger shielding in the direction of the P=O bond¹⁴⁰. The ^{31}P magnetic shielding anisotropies were also found for Me_3PX , where $\text{X} = \text{O}$ or S , in oriented liquid crystal media¹⁴¹.

The ^{31}P spectra of Me_3PX , where $\text{X} = \text{O}, \text{S}$ or Se , in liquid crystal phases gave values for the CPC angles which compared very well with those found from gas-phase electron diffraction¹⁴². The ^{31}P and ^1H lanthanide shifts in the NMR of MeR_2PO , where $\text{R} = \text{Et}$ or Ph , suggest that they are mainly due to a contact interaction¹⁴³. The upfield shift of the ^{31}P NMR signal of $\text{Me}_2\text{PhP}=\text{O}$ in the presence of cyclodextrins in water was interpreted in terms of inclusion complex formation between cyclodextrins and the phosphine oxide. The P=O group is closer to the solvent medium than to the interior of the hydrophobic cavity of the cyclodextrins¹⁴⁴.

$\delta^{31}\text{P}$ values were listed for $\text{Me}_n(\text{ClCH}_2)_{3-n}\text{PO}$, i.e. $n=0$, $+39.5$ ppm; $n=1$, $+42.9$ ppm; and $n=3$, $+42.6$ ppm¹⁴⁵. For the species with $n=2$, ^1H chemical shifts are $\delta(\text{PCH}_2) + 3.60$ and $\delta(\text{PCH}_3) + 1.57$ ppm. The respective $^2J_{\text{PCH}}$ coupling constants are 8.6 and 14.0 Hz¹⁴⁶. ^{31}P and ^1H NMR data were listed for $(\text{ClCH}_2)_2\text{P}(\text{Y})\text{R}$, where $\text{Y} = \text{O}$ and $\text{R} = \text{Et}$ or $\text{Y} = \text{S}$ and $\text{R} = \text{Me}, \text{Et}$ or Ph ¹⁴⁷.



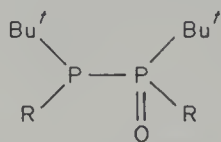
(8)

The ^{31}P chemical shifts for **8**, where $\text{X} = \text{O}$ or S , show that the *exo* species come to resonance at lower fields than the *endo* species¹⁴⁸. A list has been published of ^{31}P chemical shifts for $\text{R}_2\text{R}'\text{P}(\text{O})$, $\text{R}_2\text{R}'\text{P}(\text{S})$ and $\text{RR}'\text{P}(\text{S})\text{H}$, where $\text{R}, \text{R}' = \text{Me}, \text{Et}, \text{Pr}^i$ or Ph ¹⁴⁹. The $\delta^{31}\text{P}$ values for $\text{Ph}_2\text{P}(\text{X})\text{C}_n\text{H}_{2n+1}$, where $\text{X} = \text{O}$ or S and $n = 1-20$, show significant changes for $n = 1-3$, but then remain constant for the rest of the series. ^1H data were given on $n = 1-4$ only¹⁵⁰. $\delta^{31}\text{P}$ values were listed for $(\text{C}_6\text{F}_5)_n\text{R}_{3-n}\text{PO}$, where $\text{R} = \text{Me}, \text{Et}$ or Ph and $n = 1-3$ ¹⁵¹.

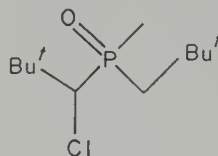
$\text{Me}_2\text{PhP}=\text{O}$ was found to be a useful standard for setting the magic angle in ^{31}P cross-polarization magic-angle spinning (CP-MAS) NMR of solid samples¹⁵². Early results gave $\delta^{31}\text{P}$ for Et_3PO , Bu_3PO , Et_3PS and Et_3PSe ¹⁵³. Lanthanide-induced ^{31}P , ^1H and ^{13}C NMR shifts for Et_3PO are dominated by the pseudo-contact effect¹⁵⁴.

$\delta^{31}\text{P}^{\text{V}}$, $\delta^{31}\text{P}^{\text{III}}$ and $^1J_{\text{P}^{\text{V}}\text{P}^{\text{III}}}$ have been reported for **9**, where $\text{R} = \text{Pr}^i, \text{Bu}^n, \text{Bu}^i, \text{Bu}^t$ and Ph , e.g. for $\text{R} = \text{Bu}^t$ $\delta^{31}\text{P}^{\text{V}}$ is -86.2 ppm, $\delta^{31}\text{P}^{\text{III}}$ is -49.7 ppm and $^1J_{\text{PP}}$ is 392 Hz¹⁵⁵. Acceptor numbers of a wide range of alcohols were estimated from ^{31}P chemical shift

changes of Bu^n_3PO in the presence of the alcohols¹⁵⁶. ^{31}P chemical shifts were reported for the $R,R/S,S$ and $R,S/S,R$ forms of **10** and also for related systems¹⁵⁷. A linear correlation was found between shifts in $\delta^{31}\text{P}$ of R_3PO , where $\text{R} = \text{C}_4\text{H}_9\text{--C}_8\text{H}_{17}$, on protonation and the sum of substituent constants ($\Sigma\sigma^\Phi$) on the phosphorus atom, and on the enthalpies of complex formation with phenol¹⁵⁸.



(9)



(10)

The solid-state CP-MAS ^{31}P NMR for OPPh_3 shows that δP is +29.2 ppm (cf. 23–27 ppm in a variety of solvents), whereas for $\text{OP}(\text{C}_{14}\text{H}_{29})_3$ δP is +51.5 ppm (48.5 ppm in CDCl_3 solution)¹⁵⁹. ^{31}P , ^1H and ^{19}F chemical shifts and coupling constants were reported for $(\text{CHF}_2)_3\text{PO}$. The results show that δF is shifted upfield and δP downfield compared with the phosphine analogue, whereas J_{FCH} is about 2 Hz lower¹⁶⁰. $(\text{CF}_3)_3\text{PO}$ has $\delta^{31}\text{P}$ at –2.3 ppm and $\delta^{19}\text{F}$ at +66.2 ppm (the latter with respect to CCl_3F)¹⁶¹.

^{31}P chemical shifts were listed as follows: Ph_3PO –25, $(\text{PhC}\equiv\text{C})_3\text{PO}$ +55.8, Ph_3PS –42.6, $(\text{PhC}\equiv\text{C})_3\text{PS}$ +44.6, $(\text{PhC}\equiv\text{C})_2\text{PhPS}$ +10.0 and $(\text{PhC}\equiv\text{C})\text{Ph}_2\text{PS}$ –18.8 ppm¹⁶². $\delta^{31}\text{P}$ and $\delta^{13}\text{C}$ values were listed for triphenylphosphine oxide, sulphide and selenide, together with a range of alkyl-substituted diphenylphosphine oxides. The values were consistent with the theory of competitive $d\pi\text{--}p\pi$ overlap with the $\text{P}=\text{O}$ bond¹⁶³. ^{31}P chemical shift anisotropies were measured for Ph_3PX , where $\text{X} = \text{O}, \text{S}$ or Se , oriented in liquid crystals. There was some evidence for delocalization of phosphorus electron density on to the phenyl ring¹⁶⁴.

$\delta^{31}\text{P}$ of Ph_3PX in liquid HCl shows that for $\text{X} = \text{O}$, protonation occurs at the oxygen, but for $\text{X} = \text{S}$ no protonation occurs¹⁶⁵. $\text{Ph}_3\text{P}=\text{O}$ has δP at +28.8 ppm and δO at +43.3 ppm (relative to H_2^{17}O), with $J(^{31}\text{P}\text{--}^{17}\text{O})$ at 160 ± 2.4 Hz¹⁶⁶. Relaxation times (T_1) and nuclear Overhauser effect (NOE) factors (η) were measured for Ph_3PO at 29 and 63 °C¹⁶⁷. ^{31}P chemical shifts and $^1J_{\text{PH}}$ were reported for $\text{Ph}(\text{R})\text{P}(=\text{O})\text{H}$, where $\text{R} = \text{Ph}, \text{Et}, \text{Pr}^i, \text{Bu}^n$ or Bu^s (Table 5)¹⁶⁸.

^{31}P , ^1H and ^{13}C NMR data were listed for $\text{Me}_3\text{CCH}_2(\text{Ph})\text{P}(\text{O})\text{Me}$ and related species and it was suggested that the changes could be related to conformational changes¹⁶⁹. It has been suggested subsequently, however, that such conclusions were erroneous¹⁷⁰.

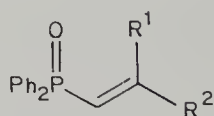
$\text{Ph}_3\text{P}^a=\text{CHP}^b(\text{O})\text{Ph}_2$ has $\delta^{31}\text{P}$ values of +18.4 ppm (a) and +23.4 ppm (b), with $^2J_{\text{P}^a\text{P}^b}$ of 19.0 Hz¹⁷¹. ^{31}P and ^1H NMR data were given for $\text{Ph}_2\text{P}(\text{O})\text{CHRPPh}_2$, where $\text{R} = \text{H}, \text{Me}$ or Pr^n , for which $\delta_{\text{P}=\text{O}}$ were –27.7, –33.6 and –32.7 ppm, respectively (each

TABLE 5. ^{31}P chemical shifts and $^1J_{\text{PH}}$ coupling constants for $\text{Ph}(\text{R})\text{P}(=\text{O})\text{H}$

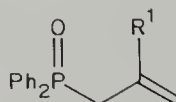
R	$\delta^{31}\text{P}$ (ppm)	$^1J_{\text{PH}}$ (Hz)
Ph	–23.1	487
Et	–32.3	458
Pr^i	–36.1	458
Bu^n	–29.0	467
Bu^s ^a	–34.3/–32.2	457.5/458.2

^aA mixture of diastereoisomers.

one a doublet), and for $\text{Ph}_2\text{P}(\text{O})\text{CHRP}(\text{O})\text{PhR}'$, where $\text{R} = \text{H}$, $\text{R}' = \text{Et}$ or $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$ ¹⁷². ^{31}P , ^1H and ^{13}C NMR data were also given for $\text{Ph}_2\text{P}(\text{X})\text{CH}=\text{CHR}$, where $\text{X} = \text{O}$ or S and $\text{R} = \text{Me}$, Ph or $\text{P}(\text{X})\text{Ph}_2$. The ^{31}P results show that the *E*-isomer comes to resonance at higher field than the *Z*-isomer¹⁷³. Analysis of high-resolution ^{31}P and ^1H NMR spectra for $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CHAr}$, where $\text{Ar} = \text{phenyl}$, 2- or 4-pyridyl or 2- or 4-quinolyl, was able to differentiate between isomers with the *P* and *Ar* *cis* or *trans*¹⁷⁴. Other diphenylphosphine oxides, sulphides or selenides for which NMR data have been given are $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}=\text{CH}_2$ and $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_2\text{CH}=\text{CH}_2$ (^{31}P and ^1H)¹⁷⁵, $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{H}$ and $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{X}$ (where $\text{X} = \text{H}$ or CO_2H) (^{31}P and ^1H)¹⁷⁶, $\text{Ph}_2\text{P}(\text{X})\text{CH}_2\text{P}(\text{Y})\text{Ph}_2$, where $\text{X}, \text{Y} = \text{O}, \text{S}, \text{Se}$ or electron pair (^{31}P , ^1H and ^{13}C)¹⁷⁷, $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CHCH}_2\text{R}$ ($\text{R} = \text{Pr}$ or Bu) (^{31}P , ^1H and ^{13}C)¹⁷⁸ and $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{-CHRP}(\text{O})\text{Ph}_2$ ($\text{R} = \text{Pr}$ or Bu) (^{31}P) (11 and 12), where $\text{R}^1, \text{R}^2 = \text{Me}, \text{Ph}, \text{H}$, etc. (^{31}P , ^1H and ^{13}C)¹⁷⁹.



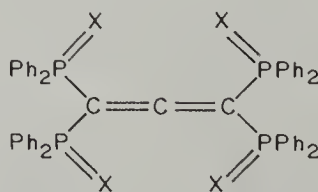
(11)



(12)

P-P nuclear spin-spin coupling was measured in $\text{Ph}_2\text{P}(\text{Y})\text{XP}(\text{Z})\text{Ph}_2$, where X is $=\text{CH}_2$, $=\text{C}=\text{CH}_2$, $-\text{CH}_2\text{CH}_2-$, *trans*- $\text{CH}=\text{CH}-$, *cis*- $\text{CH}=\text{CH}-$, $-\text{C}\equiv\text{C}-$ or $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $\text{Y} = \text{Se}$ or lone pair and $\text{Z} = \text{Se}$. $^{13}\text{C}\{-^1\text{H}, ^{31}\text{P}\}$ and $^{31}\text{P}\{-^1\text{H}, ^{77}\text{Se}\}$ magnetic triple resonance experiments gave the signs of these coupling constants¹⁸⁰. δ_{P} (ppm) and $^3J_{\text{PP}}$ (Hz) were reported for $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{PhR}$, where $\text{R} = \text{Me}$ (-31.2 , -36.9 ; 51), Et (-30.9 , -40.9 ; 50) or Pr^i (-31.4 , -46.0 ; 49)¹⁸¹. Phosphorus-31 and proton chemical shifts were found for $\text{Ph}_2\text{P}(\text{X})\text{CH}_2\text{C}(\text{OH})\text{Ph}_2$, where $\text{X} = \text{O}$ or S . The J_{PH} coupling constants were 10.2 Hz ($\text{X} = \text{O}$) and 9.6 Hz (S)¹⁸². $\delta^{31}\text{P}$ values (ppm) were also given for $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$, $n = 1$ (27.2) or 2 (36.7), $\text{P}(\text{O})\text{Ph}(\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$ [33.4 (terminal), 42.9 (non-terminal)], $\text{P}(\text{S})\text{Ph}(\text{CH}_2\text{CH}_2\text{P}(\text{S})\text{Ph}_2)_2$ [42.9 (terminal), 49.9 (non-terminal)] and Ph_3PSe (33.1), and $\text{Ph}_2\text{P}(\text{Se})(\text{CH}_2)_n\text{P}(\text{Se})\text{Ph}_2$, where $n = 1$ (22.6), 2 (34.6) or 3 (32.5). The measured $^1J_{\text{PSe}}$ coupling constants were all in the range 646–694 Hz¹⁸³. $\delta^{31}\text{P}$ values (ppm) for 13 were O 23.5, S 45.6 and Se 37.2¹⁸⁴.

The ^{31}P chemical shifts for $(\text{C}_6\text{F}_5)_3\text{PE}$, where $\text{E} = \text{O}$ or S , show that there is much greater shielding of phosphorus by C_6F_5 than by C_6H_5 ¹⁸⁵. Spin-spin coupling constants have been measured for a large number of R_3PX species, where $\text{X} = \text{O}, \text{S}$ or Se and $\text{R} =$ five- or six-membered heterocyclic aromatic group^{186–188}. Changes in ^{31}P chemical shifts have been used to study protonation in $\text{P}=\text{O}$ and $\text{P}=\text{S}$ compounds.^{189–190} ^{31}P and ^{13}C chemical shifts and coupling constants have been tabulated for Me_3PS and Me_3PSe (Table 6)¹⁹¹. $\delta^{31}\text{P}$ were reported for Me_3PS (-59.1 ppm), Me_2EtPS (-57.0) and Et_2PhPS (-52.0)¹⁹².



(13)

^{31}P NMR data for *syn* and *anti* isomers of norbornene with $\text{Me}_2\text{P}(\text{S})$ at the 7-position show deshielding of phosphorus on moving from the crowded *anti* to the less crowded

TABLE 6. ^{31}P and ^{13}C NMR data for Me_3PS and Me_3PSe

	Me_3PS	Me_3PSe
$\delta^{31}\text{P}(\text{H}_3\text{PO}_4 \text{ ref.})(\text{ppm})$	-28.9	-87
$\delta^{13}\text{C}(\text{CH}_3\text{COOH ref.})(\text{ppm})$	+150.4	+150.0
$^1J_{\text{PC}}(\text{Hz})$	+56.1	+48.5
$^2J_{\text{PH}}(\text{Hz})$	-13.0	-13.0
$^1J_{\text{CH}}(\text{Hz})$	+129.3	+130.5

TABLE 7. ^{31}P chemical shifts for $\text{Me}(\text{R})\text{-P}(=\text{S})\text{P}(=\text{S})(\text{R})\text{Me}$ (ppm from 85% aqueous H_3PO_4)

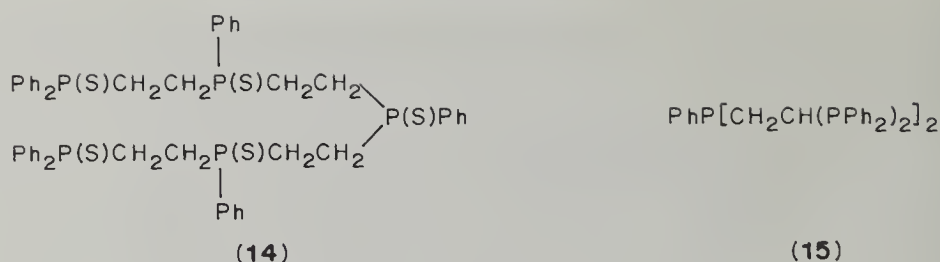
R	$\delta^{31}\text{P}$ (ppm)
Me	-34.7
Et	-42.1
Pr^n	-40.3
Ph	-37.0

syn position¹⁹³. Proton-decoupled ^{31}P NMR spectra of cyclohexyl, *cis*- and *trans*-4-methyl- and *cis*- and *trans*-4-*tert*-butyl-cyclohexyl derivatives of $\text{P}(\text{S})\text{Me}_2$ have been measured. The *tert*-butyl compounds are conformationally rigid, with greater shielding for the phosphorus group in the equatorial than the axial position¹⁹⁴.

The ^{31}P chemical shifts were measured for $\text{RR}'\text{R}''\text{PS}$, where $\text{R} = \text{Me}$, $\text{R}' = \text{Et}$ or Ph ; $\text{R}'' = \text{Ph}$; $\text{R} = \text{R}' = \text{R}'' = \text{Ph}$, *p*- MeC_6H_4 , *o*- or *p*- ClC_6H_4 ¹⁹⁵; and for $\text{RR}'\text{PP}(\text{S})\text{RR}'$, where $\text{R} = \text{R}' = \text{Me}$ or Et ; $\text{R} = \text{Me}$, $\text{R}' = \text{Et}$ or Ph ¹⁹⁶. The ^{31}P chemical shift of Et_3PS has been variously reported as -67.6¹⁹⁷ or -54.5 ppm¹⁹⁸. For Ph_3PS the corresponding value is -42.6 ppm¹⁹⁹. The ^{31}P chemical shifts for $\text{Me}(\text{R})\text{P}(=\text{S})\text{P}(=\text{S})(\text{R})\text{Me}$ are listed in Table 7²⁰⁰. Similar data were given for $\text{Et}_2\text{P}(=\text{S})(\text{CH}_2)_n\text{P}(=\text{S})\text{Et}_2$, where $n = 1, 3$ or 4 ²⁰¹. ^{31}P and ^1H chemical shifts have been measured for $\text{Ph}_2\text{P}(\text{X})\text{CH}_2\text{P}(\text{Y})\text{R}_2$, where $\text{X}, \text{Y} = \text{S}$ or lone pair and $\text{R} = \text{Me}$, Pr^i or Bu^t ²⁰².

The ^{31}P , ^1H and ^{13}C NMR data for $\text{Ph}(\text{H})\text{P}(\text{E})(\text{CH}_2)_n(\text{E})\text{P}(\text{H})\text{Ph}$, where $\text{E} = \text{S}$, $n = 2-4$ or 6 ; $\text{E} = \text{Se}$, $n = 2$, indicate that the ^{31}P chemical shifts show increasing differences between the *meso* and racemic forms for $\text{E} = \text{O} < \text{S} < \text{Se}$, for $n = 2$. There is little change in $\delta^{13}\text{C}$ between diastereoisomers, however. For all of the compounds the $^1\text{H}\{-^{31}\text{P}\}$ spectra are very different for the *meso* and racemic forms²⁰³.

Spin-lattice relaxation processes for ^{31}P in Ph_3PS and $\text{Ph}_2\text{P}(\text{S})(\text{CH}_2)_n(\text{S})\text{PPh}_2$, where $n = 1$ and 2 , all operate by the chemical shift anisotropy mechanism²⁰⁴. ^{31}P NMR data for $(\text{Ph}_2\text{P})_n[\text{Ph}_2\text{P}(\text{S})]_{2-n}\text{CH}$, $n = 0, 1$ or 2 , show that for $n = 2$ there is unhindered rotation about the P-methine C bond, but hindered rotation for $n = 0$ or 1 ²⁰⁵. ^{31}P and ^1H NMR data were listed for $[\text{R}_2\text{P}(\text{X})][\text{R}_2\text{P}(\text{Y})][\text{R}_2\text{P}(\text{Z})]\text{CH}$, where $\text{X} = \text{S}$ or Se , $\text{Y}, \text{Z} = \text{lone pair}$; $\text{X} = \text{Y} = \text{O}$, S or Se , $\text{Z} = \text{lone pair}$; $\text{X} = \text{S}$, $\text{Y} = \text{Se}$, $\text{Z} = \text{lone pair}$; $\text{X} = \text{Y} = \text{Z} = \text{S}$. $\text{R} = \text{Me}$ or Ph ²⁰⁶; and for $[\text{Ph}_2\text{P}(\text{X})][\text{R}'_2\text{P}(\text{Y})][\text{R}''_2\text{P}(\text{Z})]\text{CH}$, where $\text{R}' = \text{R}'' = \text{Ph}$, $\text{X} = \text{S}$, $\text{Y} = \text{Z} = \text{lone pair}$; $\text{X} = \text{Y} = \text{S}$, $\text{Z} = \text{lone pair}$; $\text{X} = \text{Y} = \text{Z} = \text{S}$; $\text{R}' = \text{R}'' = \text{Me}$, $\text{X} = \text{Y} = \text{Z} = \text{S}$, $\text{X} = \text{Y} = \text{S}$, $\text{Z} = \text{O}$ or lone pair; $\text{R}' = \text{Ph}$, $\text{R}'' = \text{Me}$, $\text{X} = \text{Z} = \text{S}$, $\text{Y} = \text{lone pair}$ ²⁰⁷. ^{31}P and ^1H chemical shifts were reported for **14**²⁰⁸, and one- and two-dimensional ^{31}P NMR spectra were used to disentangle the complex spectra due to a variety of sulphide derivative of the pentaphosphorus species **15**²⁰⁹.



A heteronuclear magnetic selective triple resonance technique was applied to a range of organophosphorus selenides. The results suggested that both P^+Se^- and $\text{P}=\text{Se}$ forms contributed significantly to the bonding. The ^{31}P - ^{77}Se coupling constants were shown to be negative, and they could be interpreted in terms of the inductive effects of the substituents on the phosphorus²¹⁰. The $^nJ_{\text{PSe}}$ coupling constants, where $n = 1-4$, were measured from proton-decoupled ^{31}P spectra of several diphosphorus selenides and diselenides²¹¹. The ^{31}P NMR spectrum of $\text{Me}_3\text{P}=\text{Se}$ oriented in liquid crystal media show that the $^1J_{\text{PSe}}$ spin-spin coupling is highly anisotropic²¹². Table 8 summarizes the ^{31}P chemical shifts and $^1J_{\text{PSe}}$ coupling constants for several alkyl- and aryl-phosphine selenides²¹³.

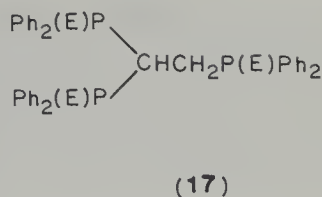
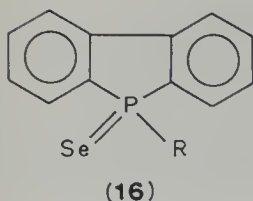
^{31}P , ^1H , ^{13}C and ^{77}Se chemical shifts and coupling constants were recorded for Bu_3^tPE , where $\text{E} = \text{Se}$ or Te . The $^1J_{\text{PE}}$ coupling constants were found to be 711.6 Hz (Se) and 1600 Hz (Te). The $\delta^{77}\text{Se}$ value, with respect to di-*p*-tolyl diselenide, for $\text{E} = \text{Se}$ is -890.5 ppm²¹⁴. $\delta^{31}\text{P}$ ($+36$ ppm), $\delta^{77}\text{Se}$ (-278 ppm, with respect to Me_2Se) and $^1J_{\text{PSe}}$ (-759 Hz) have been measured for Ph_3PSe ²¹⁵. The values of $\delta^{31}\text{P}$, $\delta^{77}\text{Se}$ and $^1J_{\text{PSe}}$ for several phosphorus(V) selenides shift in SO_2 solution in such a way as to suggest the formation of donor-acceptor complexes with the SO_2 ²¹⁶.

The ^{31}P - ^{77}Se coupling constants in $(\text{RC}_6\text{H}_4)_3\text{P}=\text{Se}$, where $\text{R} = p\text{-Cl}$, H , $p\text{-Me}$, $p\text{-OMe}$, $o\text{-Me}$ or $m\text{-Me}$, show a linear correlation with substituent constants, in the range 752.8 Hz ($p\text{-Cl}$) to 726.3 Hz ($m\text{-Me}$)²¹⁷. $\delta^{31}\text{P}$ and $\delta^{77}\text{Se}$ data were listed for $\text{R}_2\text{R}'\text{PSe}$, where R and $\text{R}' = \text{phenyl}$, 2- or 3-furyl, 2- or 3-thienyl or substituted aryl. Deshielding of selenium occurs on the introduction of *ortho* substituents into arylphosphine selenides, as it does on introducing 2-thienyl. The presence of 2-furyl, however, leads to increased shielding of the selenium²¹⁸.

^{31}P and ^{77}Se NMR data were tabulated for **16**, where $\text{R} = \text{Me}$, Et , Pr^i , Ph , etc.²¹⁹⁻²²⁰, as were ^{31}P , ^1H , ^{13}C and ^{77}Se data for $\text{Ph}_2\text{P}(\text{Se})(\text{CH}_2)_n\text{PPh}_2$ and $\text{Ph}_2\text{P}(\text{Se})(\text{CH}_2)_n(\text{Se})\text{PPh}_2$, where $n = 1$ or 2 ²²¹. Two-dimensional ^{31}P NMR spectra of mixtures of selenides **17**, where $\text{E} = \text{lone pair}$ or Se , led to assignments of resonances for a range of possible species²²².

TABLE 8. ^{31}P chemical shifts and $^1J_{\text{PSe}}$ coupling constants for phosphine selenides

Compound	$\delta^{31}\text{P}$ (ppm)	$^1J_{\text{PSe}}$ (Hz)
Et_3PSe	-44.2	705
Ph_3PSe	-36.1	738
EtPh_2PSe	-37.4	722
Et_2PhPSe	-44.6	705
MeEtPhPSe	-29.8	693
$\text{MePr}^i\text{PhPSe}$	-26.1	704
$\text{MeBu}^t\text{PhPSe}$	-47.7	702
Bu_3^iPSe	-36.4	693
$\text{H}(\text{Bu}^t)\text{PhPSe}$	-37.9	656



B. ^1H

Earlier reference has been made to a large number of papers containing ^1H NMR data on phosphorus chalcogenides: $\text{Me}_2\text{P}(\text{H})=\text{O}$, $\text{Et}_2\text{P}(\text{H})=\text{O}$ ¹²⁹; $\text{Me}_n(\text{ClCH}_2)_3-n\text{PO}$, $n=1$ ¹⁴⁶ or $n=0$, 2¹⁴⁴; $(\text{ClCH}_2)_2\text{P}(\text{Y})\text{R}$, where $\text{Y}=\text{O}$, $\text{R}=\text{Et}$, $\text{Y}=\text{S}$, $\text{R}=\text{Me}$, Et or Ph ¹⁴⁷; $\text{Ph}_2\text{P}(\text{X})\text{C}_n\text{H}_{2n+1}$, where $\text{X}=\text{O}$ or S , $n=1-4$ ¹⁵⁰; $\text{Et}_3\text{P}=\text{O}$ [154]; $(\text{CHF}_2)_3\text{PO}$ ¹⁶⁰; $\text{Me}_3\text{CCH}_2\text{P}(\text{O})\text{Ph}(\text{Me})$ ¹⁶⁹; $\text{Ph}_2\text{P}(\text{O})\text{CHRPPh}_2$, where $\text{R}=\text{H}$, Me or Pr^n ; $\text{Ph}_2\text{P}(\text{O})\text{CHRP}(\text{O})\text{PhR}'$, where $\text{R}=\text{H}$, $\text{R}'=\text{Et}$ or $\text{R}=\text{Me}$, $\text{R}'=\text{Ph}$ ¹⁷²; $\text{Ph}_2\text{P}(\text{X})\text{CH}=\text{CHR}$, where $\text{X}=\text{O}$ or S , $\text{R}=\text{Me}$, Ph or $\text{P}(\text{X})\text{Ph}_2$ ¹⁷³; $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CHAr}$, where $\text{Ar}=\text{Ph}$, 2- or 4-pyridyl, 2- or 4-quinolyl¹⁷⁴; $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}=\text{CH}_2$, $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_2\text{CH}=\text{CH}_2$, $\text{O}=\text{P}[(\text{CH}_2)_2\text{CH}=\text{CH}_2]_3$ ¹⁷⁵; $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{H}$, $(n-\text{C}_6\text{H}_{13})_2\text{P}(\text{O})\text{CH}_2\text{X}$, where $\text{X}=\text{H}$ or CO_2Me , $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{X}$, where $\text{X}=\text{H}$ or CO_2H , $\text{PhP}(\text{S})\text{Me}_2$, $\text{PhMeP}(\text{S})\text{CH}_2\text{CO}_2\text{H}$, $(n-\text{C}_6\text{H}_{13})_2\text{P}(\text{S})\text{CH}_2\text{X}$, where $\text{X}=\text{H}$ or CO_2Me ¹⁷⁶; $\text{Ph}_2\text{P}(\text{X})\text{CH}_2\text{P}(\text{Y})\text{Ph}_2$, where $\text{X}, \text{Y}=\text{O}, \text{S}, \text{Se}$ or electron pair¹⁷⁷; $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CHCH}_2\text{R}$, where $\text{R}=\text{Pr}$ or Bu , $\text{Bu}_2\text{P}(\text{O})\text{CH}=\text{CHCH}_2\text{R}$, where $\text{R}=\text{Pr}$, Bu or C_5H_{11} ¹⁷⁸; vinyl- and allyldiphenylphosphine oxides¹⁷⁹; $\text{Ph}_2\text{P}(\text{X})\text{CH}_2\text{C}(\text{OH})\text{Ph}_2$ ¹⁸²; $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{S})\text{R}_2$, where $\text{R}=\text{Me}$ or Pr ²⁰²; $\text{Ph}(\text{H})\text{P}(\text{E})(\text{CH}_2)_n\text{P}(\text{H})\text{Ph}$, where $\text{E}=\text{S}$, $n=2-4$, 6 or $\text{E}=\text{Se}$, $n=2$ ²⁰³; $[\text{R}_2\text{P}(\text{X})][\text{R}_2\text{P}(\text{Y})][\text{R}_2\text{P}(\text{Z})]\text{CH}$, where $\text{X}=\text{S}$ or Se , $\text{Y}, \text{Z}=\text{lone pair}$, or $\text{X}=\text{Y}=\text{O}$, S or Se , $\text{Z}=\text{lone pair}$, $\text{X}=\text{S}$, $\text{Y}=\text{Se}$, $\text{Z}=\text{lone pair}$, $\text{X}=\text{Y}=\text{Z}=\text{S}$, $\text{R}=\text{Me}$ or Ph ²⁰⁶; $[\text{Ph}_2\text{P}(\text{X})][\text{R}'_2\text{P}(\text{Y})][\text{R}''_2\text{P}(\text{Z})]\text{CH}$, where $\text{R}'=\text{R}''=\text{Ph}$, $\text{X}=\text{S}$, $\text{Y}, \text{Z}=\text{lone pair}$, $\text{X}=\text{Y}=\text{S}$, $\text{Z}=\text{lone pair}$, $\text{X}=\text{Y}=\text{Z}=\text{S}$; $\text{R}'=\text{R}''=\text{Me}$, $\text{X}=\text{Y}=\text{Z}=\text{S}$, $\text{X}=\text{Y}=\text{S}$, $\text{Z}=\text{O}$ or lone pair; $\text{R}'=\text{Ph}$, $\text{R}''=\text{Me}$, $\text{X}=\text{Z}=\text{S}$, $\text{Y}=\text{lone pair}$ ²⁰⁷; polytertiary phosphine sulphides²⁰⁸; $\text{Me}_n\text{Ph}_{3-n}\text{PSe}$, $n=0-3$ ²¹⁰; Bu^iPE , where $\text{E}=\text{Se}$ or Te ²¹⁴; and $\text{Ph}_2\text{P}(\text{Se})(\text{CH}_2)_n\text{PPh}_2$ and $\text{Ph}_2\text{P}(\text{Se})(\text{CH}_2)_n(\text{Se})\text{PPh}_2$, where $n=1$ or 2²²¹.

^1H NMR studies, including double resonance, show that for $\text{Ph}(\text{Me})\text{P}(\text{H})\text{O}$, $^1J_{\text{PH}}$ has a value of +467.8 Hz, whereas $^2J_{\text{PCH}}$ is -13.6 Hz²²³. $^1J_{\text{PH}}$ coupling constants were also measured for $\text{Bu}^i\text{P}(\text{X})\text{H}$, where $\text{X}=\text{O}$ (460 Hz) or S (431 Hz)²²⁴. The INDOR technique gave the following NMR parameters for $\text{Me}(\text{Bu}^i)\text{P}(\text{S})\text{H}$: $\delta(\text{PCH}_3)$ 1.70, $\delta(\text{PCCH}_3)$ 1.21, $\delta(\text{PH})$ 6.35, $\delta(\text{P})$ -36.2 ppm; $^1J_{\text{PH}}$ 434.5, $^2J_{\text{PH}}$ 13.4, $^3J_{\text{PH}}$ 18.9, $^3J_{\text{HH}}$ 4.5-4.8 Hz²²⁵.

Proton chemical shifts and coupling constants have been reported several times for Me_3PX and Et_3PX , where $\text{X}=\text{O}$ or S ²²⁶⁻²²⁹. For Me_3PO , δH was at 1.56 ppm and $^2J_{\text{PH}}$ 12.8 Hz. Laskorin *et al.*²³⁰ have developed empirical relationships between ^1H NMR parameters and substituent constants for a range of $\text{P}=\text{O}$ -containing compounds, including Me_3PO . M.O. calculations on Me_3PO and Me_3PS suggest that the dominant contribution to the proton shielding is made by the $\text{C}-\text{H}$ bonds²³¹.

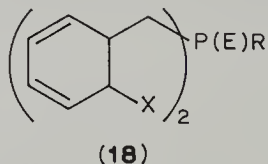
Methyl proton resonances for Me_2PhPO and Me_2PhPS are at 1.76 and 2.00 ppm, respectively. The corresponding $^2J_{\text{PH}}$ coupling constants are 13.0 and 13.2 Hz respectively.²³² $\text{p}K_{\text{BH}^+}$ values for $\text{Ph}_n\text{Me}_{3-n}\text{P}(\text{E})$, where $n=1$ or 2 and $\text{E}=\text{O}$ or S , were deduced from changes in the CH_3 ^1H chemical shift as a function of sulphuric acid concentration²³³. ^1H and ^{13}C NMR data were listed for $\text{RR}'\text{P}(\text{O})\text{CH}_2\text{Cl}$, where $\text{R}=\text{R}'=\text{Me}$ or Ph ; $\text{R}=\text{Me}$, $\text{R}'=\text{Ph}$, 4-Cl-, 4- MeOC_6H_4 or CH_2Ph , and related systems²³⁴. ^1H chemical shifts and $^2J_{\text{PH}}$ coupling constants were given for $(\text{RC}_6\text{H}_4)_2\text{P}(\text{E})\text{Me}_2$, where $\text{R}=4\text{-MeO}$, 4-Me or H, 4-Cl and $\text{E}=\text{O}$ or S , and $(\text{RC}_6\text{H}_4)_2\text{P}(\text{E})\text{Me}$, where $\text{R}=4\text{-Me}$, H or 4-Cl and $\text{E}=\text{O}$ or S ²³⁵.

Methylene proton chemical shifts and $^2J_{\text{PH}}$ coupling constants are listed in Table 9

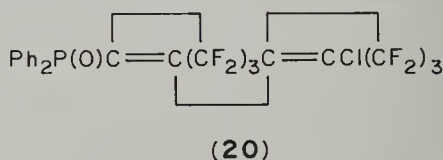
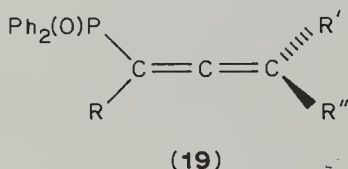
TABLE 9. ^1H NMR parameters for $(\text{XCH}_2)_3\text{PO}$

X	δCH_2 (ppm)	$^2J_{\text{PCH}}$ (Hz)
Cl	3.99	6.75
Br	3.76	6.25
I	3.58	6.87

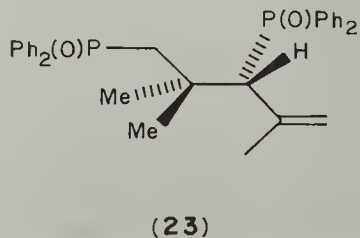
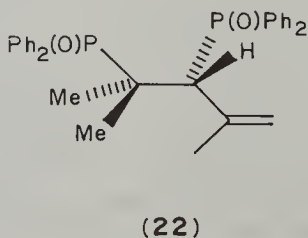
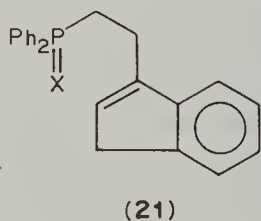
for $(\text{XCH}_2)_3\text{PO}$, where $\text{X} = \text{Cl}, \text{Br}$ or I . The methylene proton shielding increases with decreased electronegativity of X ²³⁶. A more recent paper on these compounds reveals that they possess three different conformers, with characteristic $^2J_{\text{PH}}$ coupling constants²³⁷. ^1H shifts were found for a range of enantiomeric monophosphine oxides using $(R)-(-)-N-(3,5\text{-dinitrobenzoyl})-\alpha\text{-phenylethylamine}$ as a chiral shift reagent²³⁸. Proton NMR data were listed for **18**, where $\text{X} = \text{H}, \text{R} = \text{Bu}^t, \text{E} = \text{O}$; $\text{X} = \text{H}$ or $\text{Br}, \text{R} = \text{Me}, \text{E} = \text{S}$ ²³⁹.



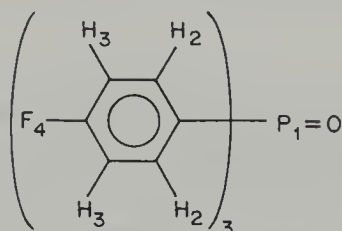
$\delta^1\text{H}$ and other NMR parameters were given for acetylenic phosphine oxides, $\text{R}_2\text{P}(\text{O})\text{C}\equiv\text{CH}$, where $\text{R} = \text{Et}, \text{Bu}^n, \text{Bu}^t, \text{Ph}$ or $\text{C}\equiv\text{CH}$ ²⁴⁰⁻²⁴¹ and $\text{Ph}_2\text{P}(\text{O})\text{C}\equiv\text{CR}$, where $\text{R} = \text{H}$ or Me ²⁴²⁻²⁴³. ^1H chemical shifts and coupling constants were given for the allenic fragment in $\text{R}_2\text{P}(\text{O})\text{CH}=\text{C}=\text{CH}_2$, where $\text{R} = \text{Et}$ or Ph ²⁴⁴. The ^1H data for the allenic phosphine oxides **19**, where $\text{R} = \text{H}$ or Me ; $\text{R}', \text{R}'' = \text{H}, \text{Me}$ or Et , reveal that the coupling constants $^2J_{\text{PH}}$ and $^2J_{\text{PH}}$ have the same sign, opposite to that of $^4J_{\text{PH}}$ ²⁴⁵. The phenyl proton chemical shifts for **20** are at 7.68 and 7.72 ppm (multiplets)²⁴⁶.



$\delta^1\text{H}(\text{aliphatic})$ and $^2J_{\text{PCH}}$ were reported for $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{X}$, where $\text{X} = \text{H}, \text{OH}, \text{Cl}, \text{NMe}_2, \text{OMe}, \text{SMe}, \text{Ph}, \text{CH}=\text{CH}_2$ or $\text{CH}=\text{C}=\text{CH}_2$, $\text{Ph}_2\text{P}(\text{O})\text{CH}(\text{X})\text{Ph}$, where $\text{X} = \text{OH}$ or Ph , and some related molecules. There was no simple explanation of the observed trends in $^2J_{\text{PCH}}$ values²⁴⁷. ^1H NMR data were listed and assigned for $\text{Ph}_2\text{P}(\text{O})\text{R}$, where $\text{R} = \text{CH}_2\text{Ph}, \text{CH}_2\text{CH}_2\text{Ph}, \text{CH}_2\text{C}_6\text{F}_5, \text{CH}_2\text{CF}_3$ and $\text{CH}_2\text{C}_6\text{H}_4\text{Cl}-p$ ²⁴⁸, and for **21**²⁴⁹. ^1H NMR spectra of **22** and **23** both show that there is severely restricted rotation about the $\text{C}-\text{C}$ single bond²⁵⁰.



Para-substituted triarylphosphine oxides and sulphides have been the subject of very extensive ^1H NMR investigations²⁵¹⁻²⁵⁶. For example, $(p\text{-FC}_6\text{H}_4)_3\text{P}=\text{O}$ (**24**) has $J_{12}(\text{PH})$ 10.87, $J_{13}(\text{PH})$ 2.54, $J_{23}(\text{HH})$ 8.97, $J_{24}(\text{HF})$ 5.83, $J_{34}(\text{HF})$ 9.03 and $J_{14}(\text{PF})$ 1.95 Hz and $\delta_2(\text{H})$ 7.70, $\delta_3(\text{H})$ 7.35 and $\delta_4(\text{F})$ 101.16 ppm. $\delta^1\text{H}$ values were listed for (*o*-, *m*- and *p*-tolyl)diphenylphosphine oxides. The *ortho* isomer gave evidence for $^4J(\text{PCH}_3)$ (ca 1 Hz). There was no evidence for analogous five- or six-bond coupling in the others²⁵⁷.



(24)

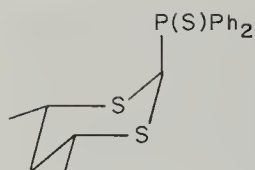
The temperature dependence of the ^1H NMR of $\text{R}_3\text{P}=\text{X}$, where $\text{X} = \text{O}$ or S and $\text{R} = 2,3,5\text{-Me}_3\text{C}_6\text{H}_2$ or $2,3,5,6\text{-Me}_4\text{C}_6\text{H}$, as used to determine free energies of activation for rotation of the rings²⁵⁸. ^1H NMR data were assigned for R_3PX , where $\text{X} = \text{O}$ or S and $\text{R} = \text{furyl}$, *thienyl* or ring-substituted derivatives of these²⁵⁹⁻²⁶³. Double resonance experiments on the ^1H NMR spectrum of tris-2-pyridylphosphine oxide and sulphide gave the relative signs of $^{31}\text{P}-^1\text{H}$ coupling constants. Thus the two four-bond couplings have opposite signs, whereas the three- and five-bond couplings have the same sign, implying a negative sign for $^4J_{\text{HP}}$ through the nitrogen²⁶⁴.

Table 10 summarizes the proton chemical shift values found for $\text{Ph}_2\text{P}(=\text{X})(\text{CH}_2)_n(\text{X}=\text{O})\text{PPh}_2$, where $n = 1$ or 2 , $\text{X} = \text{O}$, S or Se ²⁶⁵. ^1H NMR data were also given for $\text{Ph}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{PPh}_2$, $\text{Ph}_2\text{P}(\text{X})\text{CH}_2\text{CH}_2(\text{X})\text{PPh}_2$ and *cis*- and *trans*- $\text{Ph}_2\text{P}(\text{X})\text{CH}=\text{CH}(\text{X})\text{PPh}_2$, where $\text{X} = \text{O}$ or S ²⁶⁶, and for $\text{Ph}(\text{R})\text{P}(=\text{O})(\text{CH}_2)_3(\text{O}=\text{O})\text{R}'\text{Ph}$, where $\text{R} = \text{Ph}$, $\text{R}' = \text{Et}$ or Bu ; $\text{R} = \text{Bu}$, $\text{R}' = \text{Et}$, Pr^n , Pr^i , $n\text{-C}_5\text{H}_{11}$, $n\text{-C}_6\text{H}_{13}$; $\text{R} = \text{Me}$, $\text{R}' = \text{Et}$; and $\text{Ph}_2\text{P}(=\text{O})(\text{CH}_2)_4(\text{O}=\text{O})\text{P}(\text{Et})\text{Ph}$ ²⁶⁷. The ethylenic proton chemical shift in $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$ is at 7.30 ppm, with $^2J_{\text{PH}}$ 46 Hz²⁶⁸.

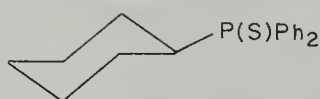
The methyl proton chemical shift in Me_3PS is at 1.78 ppm ($^2J_{\text{PH}}$ 13.10 Hz), whereas that in $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$ is at 1.96 ppm²⁶⁹. The methylene proton chemical shift in $\text{Bu}_3\text{P}=\text{S}$ is a doublet at 1.48 ppm (J_{PH} 14 Hz)²⁷⁰. ^1H NMR data were also given for $\text{Ph}_2\text{P}(\text{S})\text{CH}(\text{CO}_2\text{H})\text{C}_6\text{H}_{12-n}$ ²⁷¹. There is ^1H NMR evidence for the predominantly axial conformation of the $\text{P}(=\text{S})\text{Ph}_2$ in **25**²⁷². In **26**, however, the $\text{Ph}_2\text{P}(\text{S})$ group was shown to have a strong equatorial preference²⁷³. The olefinic proton in **27** gives a triplet at 8.2 ppm, with $^2J_{\text{PH}}$ 24 Hz²⁷⁴.

TABLE 10. Proton chemical shifts for $\text{Ph}_2\text{P}(=\text{X})(\text{CH}_2)_n(\text{X}=\text{O})\text{PPh}_2$ (ppm)

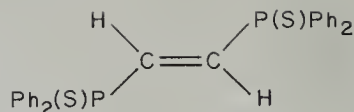
X	$n = 1$	$n = 2$
O	4.08	2.54
S	4.42	2.71
Se	4.83	2.87



(25)



(26)

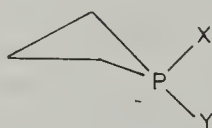


(27)

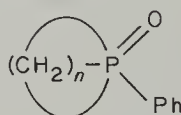
C. ^{13}C

The following earlier references have been made to ^{13}C NMR data: $(^{13}\text{CH}_3)_3\text{PE}$, where $\text{E} = \text{O}, \text{S}$ or Se ¹³³; Et_3PO ¹⁵⁴; Ph_3PE , where $\text{E} = \text{O}, \text{S}$ or Se ; $\text{Ph}_2(\text{R})\text{PO}$, where $\text{R} = \text{Me}, \text{Et}, \text{Pr}^i, \text{Bu}^i, \text{CH}=\text{CH}_2, \text{C}\equiv\text{CH}$; PhMe_2PO , Bu_3PE , where $\text{E} = \text{O}$ or S ¹⁶³; $\text{Me}_3\text{CCH}_2\text{P}(=\text{O})\text{Ph}(\text{Me})$ ¹⁶⁹; $\text{Ph}_2\text{P}(\text{X})\text{CH}=\text{CHR}$, where $\text{X} = \text{O}$ or S , $\text{R} = \text{Me}, \text{Ph}$ or $\text{P}(\text{X})\text{Ph}_2$ ¹⁷³; $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CHCH}_2\text{R}$, where $\text{R} = \text{Pr}$ or Bu ; $\text{Bu}_2\text{P}(\text{O})\text{CH}=\text{CHCH}_2\text{R}$, where $\text{R} = \text{Pr}, \text{Bu}$ or C_5H_{11} ¹⁷⁷; vinyl- and allyl-diphenylphosphine oxides¹⁷⁹; Me_3PS , Me_3PSe ¹⁹¹; $\text{Ph}(\text{H})\text{P}(\text{E})(\text{CH}_2)_n(\text{E})\text{P}(\text{H})\text{Ph}$, where $\text{E} = \text{S}$, $n = 2-4, 6$; $\text{E} = \text{Se}$, $n = 2^{203}$; Bu_3PSe ²¹⁴; $\text{Ph}_2\text{P}(\text{Se})(\text{CH}_2)_n\text{PPh}_2$, $\text{Ph}_2\text{P}(\text{Se})(\text{CH}_2)_n(\text{S})\text{PPh}_2$, where $n = 1$ or 2^{221} ; $\text{RR}'\text{P}(\text{O})\text{CH}_2\text{Cl}$, where $\text{R} = \text{R}' = \text{Me}, \text{Ph}$; $\text{R} = \text{Me}, \text{R}' = \text{Ph}$ or $4\text{-Cl-C}_6\text{H}_4$, $4\text{-MeOC}_6\text{H}_4$ or CH_2Ph ²³⁴; $\text{HC}\equiv\text{CP}(\text{O})\text{Ph}_2$ ²⁴²; and $\text{RC}\equiv\text{CP}(\text{O})\text{Ph}_2$, where $\text{R} = \text{H}$ or Me ²⁴³. ^{13}C chemical shifts and J_{PC} coupling constants were listed for $\text{R}_3\text{P}=\text{X}$, where $\text{R} = \text{Me}$ or Ph , $\text{X} = \text{O}$ or S , $\text{R} = \text{Me}$, $\text{X} = \text{Se}$. Thus, for $\text{R} = \text{Me}$, $\text{X} = \text{O}$, $\delta^{13}\text{C}$ is -17.4 ppm and $J_{\text{CP}} + 68$ Hz²⁷⁵.

The ^{13}C NMR spectrum of $\text{HC}_1\equiv\text{C}_2\text{P}(\text{O})\text{Bu}_2$ shows that $\delta^{13}\text{C}_1$ is 100.4 ppm and $\delta^{13}\text{C}_2$ 111.6 ppm (CS_2 as standard), with $^1J(\text{HC}_1)$ 266 Hz²⁷⁶. $\delta^{13}\text{C}$ and various coupling constants were reported for $(\text{C}_8\text{H}_{17})_2\text{P}(=\text{O})\text{R}$, where $\text{R} = \text{Ph}, \text{C}_8\text{H}_{17}$ or Bu^i , and $(\text{C}_8\text{H}_{17})_2\text{P}(=\text{O})\text{R}'\text{P}(=\text{O})(\text{C}_8\text{H}_{17})_2$, where $\text{R}' = -(\text{CH}_2)_n-$, $n = 1-6$ ²⁷⁷. ^{13}C chemical shifts and J_{CP} coupling constants were recorded for a wide range of phosphorus heterocyclic oxides and sulphides, e.g. **28**, where $\text{X}, \text{Y} = \text{O}$ or S ; $\text{Me}, \text{CH}_2\text{Ph}, \text{Bu}^i$, etc. The data are consistent with puckered conformations, which are mostly stereorigid on the NMR time scale²⁷⁸. ^{13}C chemical shifts and $^{13}\text{C}-^{31}\text{P}$ spin-spin coupling constants were given for **29**, where $n = 3-7$, and for $\text{Bu}_2\text{P}(=\text{O})\text{Ph}$ ²⁷⁹.

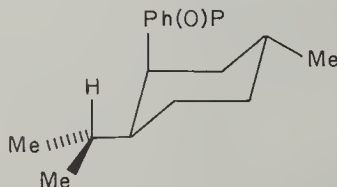


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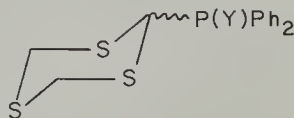


(29)

^{13}C NMR data were reported for **30**²⁸⁰. Axial preference is revealed by ^{13}C NMR to be $\text{Ph}_2\text{P}(\text{S}) > \text{Ph}_2\text{P}(\text{O})$ in **31** and related heterocyclic derivatives²⁸¹. $(\text{CF}_3)_3\text{P}=\text{O}$ has $\delta^{13}\text{C}$ at 119.50 ppm (SiMe_4 standard), with J_{CP} 163.3 Hz, J_{CF} 316.9 Hz and J_{CPCF} 3 Hz²⁸². ^{13}C NMR data for $\text{phP}(\text{O})\text{Z}_2$ and $\text{PhP}(\text{S})\text{Z}_2$, where $\text{Z} = \text{Me}$ or Ph , were used to estimate substituent parameters for $\text{P}(\text{E})\text{Z}_2$. The electron-attracting abilities are $\text{P}(\text{E})\text{Me}_2 > \text{P}(\text{E})\text{Ph}_2$ for both O and S compounds²⁸³.



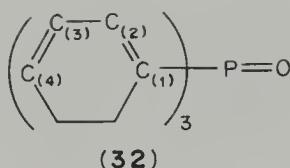
(30)



(31)

TABLE 11. ^{13}C NMR data for $\text{Ph}_3\text{P}=\text{O}$

	Carbon No.			
	1	2	3	4
Chemical shift (ppm)	135.56	132.28	128.76	132.25
$^{13}\text{C}-^{31}\text{P}$ coupling constant (Hz)	104.4	9.8	12.1	2.8



^{13}C chemical shifts and $^{13}\text{C}-^{31}\text{P}$ nuclear spin coupling constants were obtained for $\text{Ph}_3\text{P}=\text{O}$ (32) (Table 11)²⁸⁴. The ^{13}C NMR spectra of $\text{Ph}_3\text{P}=\text{X}$, where $\text{X} = \text{O}, \text{S}$ or Se , are all consistent with delocalization of π -charge from the phenyl groups to the $3d_\pi$ orbitals of the phosphorus²⁸⁵. $\delta^{13}\text{C}$ and J_{PC} were reported for unsymmetrical triarylphosphine oxides $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{P}(\text{O})(4\text{-XC}_6\text{H}_4)$, where $\text{X} = \text{Me}, \text{MeO}$ or PhCOO . The results were consistent with a propeller-like arrangement of the aromatic rings and non-equivalence of the two mesityl groups²⁸⁶.

^{13}C NMR data were listed for an extensive series of phosphine sulphides²⁸⁷. ^{13}C MAS NMR of solid Me_3PS shows a doublet due to $^1J_{\text{PC}}$ coupling, with a coupling constant of 54 Hz, close to the solution-state value of 56.1 Hz²⁸⁸. $\delta^{13}\text{C}$ and $^1J_{\text{PC}}$ were measured for $\text{Bu}^n\text{P}(\text{S})\text{RR}'$, where $\text{R} = \text{R}' = \text{Me}$ or Bu^n ; $\text{R} = \text{Me}, \text{R}' = \text{Bu}^n$ ²⁸⁹. ^{13}C NMR data for the *cis* and *trans* isomers of *tert*-butylcyclohexane with $\text{P}(\text{S})\text{Me}_2$ at the 4-position show that the $\text{P}(\text{S})\text{Me}_2$ group causes considerable ring distortion in the *cis* isomer²⁹⁰.

D. ^{19}F

Earlier reference was made to ^{19}F NMR data for $(\text{CHF}_2)_3\text{PO}$ ¹⁶⁰ and $(\text{CF}_3)_3\text{PO}$ ¹⁶¹. The ^{19}F chemical shift of $(\text{CF}_3)_2\text{P}(\text{O})\text{C}(\text{CH}_3)_3$ is 64.7 ppm, with CCl_3F as standard. The $^2J_{\text{FP}}$ coupling constant is 84.7 Hz²⁹¹. ^{19}F NMR data for $(\text{XC}_6\text{H}_4)(\text{C}_3\text{F}_7)_2\text{P}=\text{O}$, where $\text{X} = \text{H}, m\text{-F}$ or $p\text{-F}$, are shown in Table 12 ($\delta^{19}\text{F}$ with respect to CF_3COOH as standard)²⁹².

The ^{19}F NMR spectrum of **33** shows that it adopts a chiral, propeller equilibrium conformation in solution²⁹³. ^{19}F chemical shifts were given for several phosphine oxides and sulphides containing 3- or 4- FC_6H_4 substituents²⁹⁴⁻²⁹⁸. J_{PF} coupling constants were derived for $(\text{C}_6\text{F}_5)_n\text{Ph}_{3-n}\text{P}=\text{O}$, where $n = 1-3$ ²⁹⁹. Table 13 gives the ^{19}F chemical shifts for $(\text{C}_6\text{F}_5)_3\text{P}=\text{X}$, where $\text{X} = \text{O}$ or S .³⁰⁰

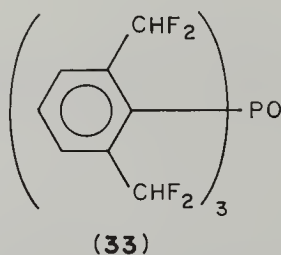
TABLE 12. ^{19}F chemical shifts for $(\text{XC}_6\text{H}_4)(\text{C}_3\text{F}_7)_2\text{P}=\text{O}$ (ppm)

X	$\text{CF}_2(\alpha)^a$	$\text{CF}_2(\beta)^a$	CF_3	F_{arom}
H	-39.9	-45.0	-2.4	—
<i>m</i> -F	-39.8	-45.1	-2.8	-30.0
<i>p</i> -F	-40.0	-45.2	-2.8	-20.8

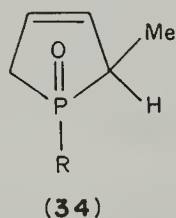
^a $\text{PCF}_2(\alpha)\text{CF}_2(\beta)\text{CF}_3$.

TABLE 13. ^{19}F chemical shifts for $(\text{C}_6\text{F}_5)_3\text{P}=\text{X}$ (ppm with respect to CFCl_3)

X	<i>o</i> -F	<i>m</i> -F	<i>p</i> -F
O	132.6	142.4	158.5
S	132.2	144.3	159.0

E. ^{17}O

Earlier reference was made to ^{17}O NMR data for $\text{Ph}_3\text{P}=\text{O}$ ¹⁶⁶. $^1J_{\text{PO}}$ was found to be 120 ± 15 Hz from the natural abundance ^{17}O NMR spectrum of $\text{Me}_3\text{P}=\text{O}$. CNDO/2 FPT calculations of the analogous coupling constant in $\text{H}_3\text{P}=\text{O}$ gave a value of 98.5 Hz³⁰¹. ^{17}O chemical shifts were found for a range of cyclic phosphine oxides, such as **34**, where $\text{R} = \text{Me}, \text{Ph}$, etc. The values were found to be very sensitive to the ring size and to the presence of γ -interactions³⁰². ^{17}O NQR data were obtained for Ph_3PO : $\nu_{5/2-3/2}$ 1403 kHz, $\nu_{3/2-1/2}$ 708 KHz, e^2Qq_{zz}/h 4.683(2) MHz and η 0.085³⁰³. There was also evidence for substantial π -bond order in Ph_3PO and related species, in the sequence $(\text{PhO})_3\text{PO} > \text{Ph}_2\text{SO}_2 \approx \text{Ph}_3\text{PO} > \text{Ph}_2\text{SO}$ ³⁰⁴.

F. ^{77}Se and ^{125}Te

Data on ^{77}Se NMR have been given for $\text{Me}_n\text{Ph}_{3-n}\text{PSe}$, where $n = 0-3$ ²¹⁰; Bu^t_3PSe ²¹⁴, Ph_3PSe ²¹⁵; Ph_3PSe , $(p\text{-MeC}_6\text{H}_4)_3\text{PSe}$, Et_3PSe , $[\text{Ph}_2\text{P}(\text{Se})]_2\text{CH}_2$, etc.²¹⁶; $\text{R}_2\text{R}'\text{PSe}$, where $\text{R}, \text{R}' = \text{Ph}$, 2-furyl or substituted analogues,²¹⁸; RPh_2PSe , where $\text{R} = \text{Me}, \text{Et}, \text{Pr}^i, \text{Ph}$, etc., and related heterocyclic compounds²²⁰; and $\text{Ph}_2\text{P}(\text{Se})(\text{CH}_2)_n\text{PPh}_2$ and $\text{Ph}_2\text{P}(\text{Se})(\text{CH}_2)_n(\text{S})\text{PPh}_2$, where $n = 1$ or 2²²¹. Heteronuclear triple resonance techniques were used to obtain $\delta^{77}\text{Se}$ for Me_3PSe (-235 ppm) and Ph_2HPSe (-349 ppm), both with respect to Me_2Se as standard. The results were consistent with contributions from both $\equiv\text{P}^+-\text{Se}^-$ and $\equiv\text{P}=\text{Se}$ to the bonding³⁰⁵.

The $^1J_{\text{TeP}}$ coupling constant for Bu^t_3PTe is 1720 Hz³⁰⁶. In Bu^t_3PTe this coupling constant is 1600 Hz, with $\delta^{125}\text{Te} -480$ ppm with respect to ditolyl telluride as standard³⁰⁷.

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CHAPTER 6

Methods of preparation of phosphine chalcogenides

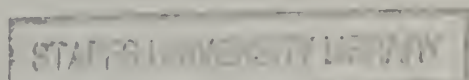
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I. INTRODUCTION

Phosphine oxides are the most stable organophosphorus compounds and belong to an important class. The oxides and sulphides find extensive use as flame retardants¹, fire-proofing agents in polyurethane foams², as intermediates in catalytic reactions including carbon dioxide and nitrogen fixation³, as polydentate chelating legands⁴, as catalysts^{5,6}, in the chlorination of carbohydrates^{7,8}, in surface coatings⁹, as adhesives¹⁰, as fire retardants¹¹, as biologically active compounds^{12,13}, in inhibiting the precipitation of scale-forming salts¹⁴, as powerful sequestering agents^{15,16}, in the preparation of polyesters with improved properties¹⁷, as flotation reagents for minerals¹⁸, in the solvent extraction of precious metals^{16,19} and many more. Allylic phosphine oxides have also been used as precursors²⁰ of dienes of defined geometry, as in the synthesis of 3-deoxy-vitamin D₂.

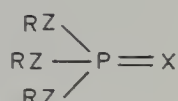
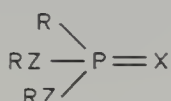
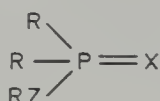
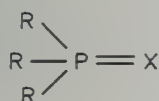
Good reviews on the subject have been published by Hays and Peterson²¹, Maier²², several by Miller²³ and others^{24,25}. Older reviews include those by Maier²⁶, Berlin and Butler²⁷ and Sasse²⁸. Generally these reviews are more than a decade old and the list of new organophosphorus compounds has grown tremendously in the meantime. This review attempts to cover the literature for the last 20 years or so up to June 1990. The reader is recommended to refer to the older literature and texts for the earlier references.

II. SCOPE AND LIMITATIONS

Phosphine oxides, as their name implies, are derivatives of phosphine and hence their methods of preparation necessarily include the methods of preparation of phosphines. In some cases the reactants interact to give the oxides directly, whereas in other cases they have to be synthesized through the phosphines.

The phosphines have been dealt with in detail in the first volume of this series, including their methods of preparation. There is bound to be some overlap with the corresponding chapter of the previous volume, but the emphasis in this chapter is on the methods of preparation of the oxides and sulphides.

Organophosphorus chemistry has grown at a phenomenal rate in the last two decades or so, and a wide variety of analogous compounds are known. Thus:



R = alkyl, aryl, etc. X = O, S, Se, Te

Z = O, S, N

Phosphine

oxide

(1)

Phosphinite

(2)

Phosphonite

(3)

Phosphate

(4)

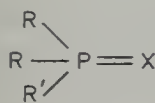
For the purpose of this Chapter, the scope will be limited to the compounds as described in 1 above, i.e. with no P—alkoxy, S—alkyl or N—alkyl linkage. This automatically excludes the compounds represented by 2, 3 and 4 as they are discussed elsewhere in the series. However, the oxides of polyphosphines, which could have one or more P—P linkages instead of the usual P—C linkages, are included here.

III. METHODS OF PREPARATION OF PHOSPHINE OXIDES

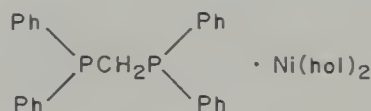
A. Reactions Involving Conversion of P^{III} to P^V

1. Through oxidation of phosphines

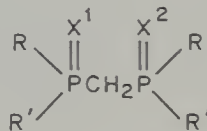
a. *By air oxidation.* Tertiary phosphine oxides are prepared²⁹ by refluxing the phosphine, 5 (R = octyl, hexyl, decyl, Ph; R' = Ph; X = nil or O), in air. Compounds 5 in turn were prepared by treating R'PCl₂ with sodium powder and then Rhal (hal = halogen) in an oxygenated atmosphere. Thus 35.8 g of PhPCl₂ were refluxed for 6 h in xylene with sodium powder and the resulting disodium derivative was further refluxed with 1-bromooctane in air to give the oxide 5 (X = O). Nickel(II) halides form complexes 6 with diphosphines, which are stable in the solid state but decompose slowly if heated above 220°C, undergoing air oxidation³⁰ to yield the diphosphine dioxide 7 (X¹ = X² = O; R = R' = Ph).



(5)



(6)

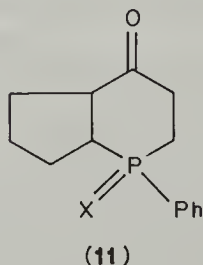
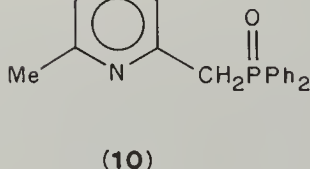
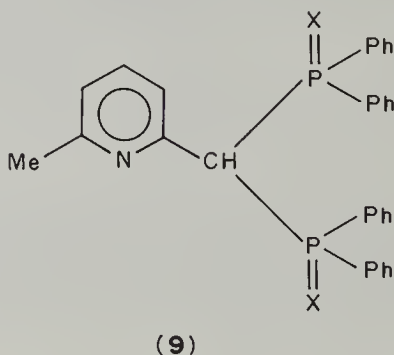
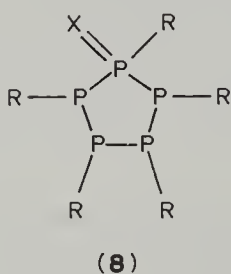


(7)

Phosphines on oxidation with air or oxygen in the presence of π -cyclopentadienyl- or π -indenyl-nickel catalysts give phosphine oxides in excellent yields³¹, e.g. Ph₃P on stirring with nickelocene in benzene in the presence of oxygen gives Ph₃PO in 90% yield. Catalytic oxidation of phosphines using molecular oxygen has been reported³² in the presence of (R₂NCS₂)·MoO₂ (R = Pr, Et). Thus R₃P=O (R = Ph, Bu) is prepared by stirring a

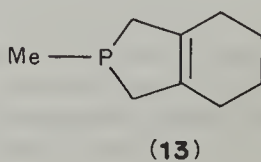
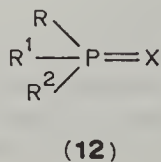
benzene solution of R_3P ($R = Ph$) containing $(Pr_2NCS_2)_2 \cdot MoO_2$ under 1 kg cm^{-2} of oxygen.

Ph_3P is reported to be converted³³ quantitatively into its oxide by treatment with oxygen in the presence of $Ph_4P^+Cl^-$, whereas in the absence of the catalyst the reaction failed. Mono-oxidation of methyl or ethyl derivatives of cyclopentaphosphine **8** is reported to occur³⁴ by treatment with dry atmospheric oxygen ($R = Me, Et$; $X = \text{nil}, O$). 2-Bis(diphenylphosphino)methylpyridine and its 6-methyl derivative **9** ($X = \text{nil}$), on aerial oxidation³⁵ followed by quaternization with Br_2 or warming with acetic acid, gave the monophosphine oxide **10** in 82% yield by the loss of one phosphine group, whereas oxidation with MnO_2 yielded the bisphosphine oxide **9** ($X = O$). Formation of **10** is unusual as $RCH(PPh_2)_2$ do not undergo similar loss of a phosphine group.



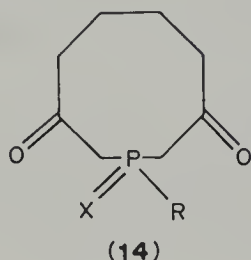
Catalytic oxidation of phosphines, e.g. Bu_3P , in the presence of $[Pd\{Ph_2P(CH_2)PPh_2\}_2]$ at $25-45^\circ C$ with dry air is found to give the oxide³⁶. Il'yasov *et al.*³⁷ reported the oxidation of the phosphabicyclononane system **11** ($X = \text{nil}$) into its oxide ($X = O$) by reaction with oxygen. Compound **11** is prepared by reaction of β -diethylaminoethyl cyclopentenyl ketone with phenylphosphine.

Chloromethyldimethylphosphine **5** ($R = Me$; $R' = CH_2Cl$; $X = \text{nil}$) is oxidized³⁸ by oxygen to give the phosphine oxide **5** ($X = O$). Likewise, acylphosphine **12** ($R = Ph$; $R^1 = Me$; $R^2 = COMe$; $X = \text{nil}$) is oxidized to **12** ($X = O$) on treatment³⁹ with dry oxygen. Halogenated acylphosphines **12** ($R = R^1 = Ph$; $R^2 = COCH_2Cl, COCH_2F, COC_2F_5, COC_3F_7, COC_6F_5$) are also similarly oxidized⁴⁰, as are the diorganyltrifluoroacetyl-

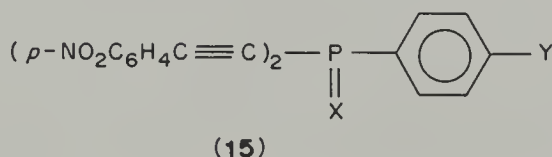


phosphines⁴¹ **12** ($R = \text{Ph}$; $R^1 = \text{PhCH}_2$, cyclohexyl, Me_3C ; $R^2 = \text{COCF}_3$). Aryldiphenylphosphines **5** [$R = \text{Ph}$; $R' = \text{COMe}$, COCF_3 , COOMe , $\text{CO}-(3,5\text{-dinitrophenyl})$] are known to react^{42,43} with oxygen if the latter is slowly introduced into a diethyl ether solution of the phosphine, to give the oxides **5** ($X = \text{O}$).

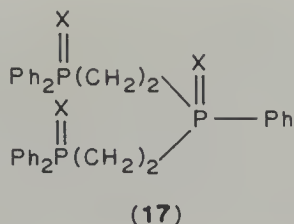
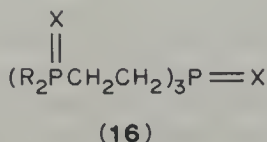
Ozone and *m*-chloroperbenzoic acid are also known⁴⁴ to oxidize phosphines and the oxidation proceeds with retention of configuration. 3-Phospholene derivatives **13** with cyclohexane or substituted cyclohexanes fused at the double bond, on ozonolysis at -78°C , are reported⁴⁵ to offer a useful route for the synthesis of 3,8-phosphonanedione-1-oxide systems **14** ($R = \text{Me}$; $X = \text{O}$).

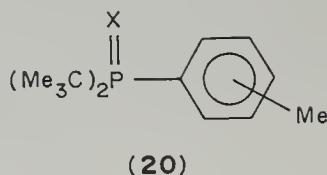
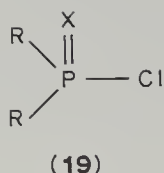
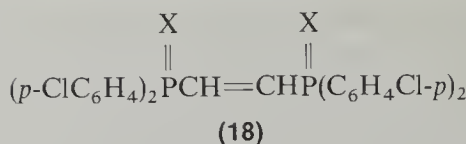


b. By peroxy compounds. Dimethylphosphine on oxidation⁴⁶ with 7% H_2O_2 at $20\text{--}30^\circ\text{C}$ in the presence of 4% HCl gives the oxide in 96% yield. The dioxide **7** is prepared⁴⁷ by oxidation of the phosphine with 100% H_2O_2 in acetone. H_2O_2 oxidation has also been used to oxidize⁴⁸ the phosphine **5** ($R = n\text{-octyl}$; $R' = \text{sec-butyl}$). Acetylenic phosphine⁴⁹ **15** ($X = \text{nil}$; $Y = \text{H}$, Cl , OMe , etc.) and trivinylphosphine⁵⁰ are also prepared by oxidation with dilute aqueous hydrogen peroxide at less than 100°C .

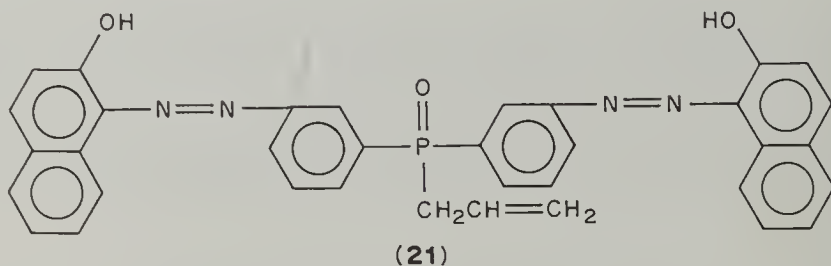


King and Heckley⁵¹ have reported the H_2O_2 oxidation of the poly(tertiary phosphines) **16** ($R = \text{Ph}$; $X = \text{O}$) and **17** ($X = \text{nil}$), resulting in the oxidation of all the P^{III} present in the molecule. The preparation of poly(tertiary phosphines) is described in the literature (see Sections III.A and IV.B.1). Phosphines of the type **5** [$R = \text{CH}_2\text{OAc}$, $\text{CH}_2\text{CH}(\text{Me})\text{OH}$] are also known^{52,53} to give, on H_2O_2 oxidation, the corresponding oxides ($X = \text{O}$) in 84–95% yield. Tetraaryl(alkyl)vinylidenephosphines **18** ($X = \text{nil}$) have been oxidized with H_2O_2 to give the *trans* isomer in 84% yield⁵⁴. Compound **18** was, in turn, prepared in 55% yield of the *trans* isomer, by treatment of bis-*p*-chlorophenylphosphine chloride **19** ($R = p\text{-ClC}_6\text{H}_4$; $X = \text{nil}$) with lithium in thf, followed by reaction with $\text{ClHC}=\text{CHCl}$ for 1.5 h at -20°C .

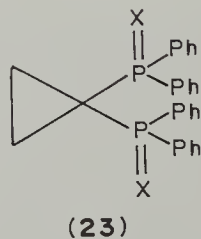
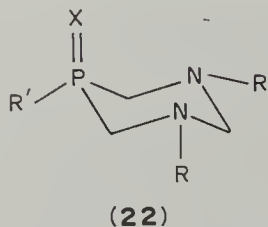




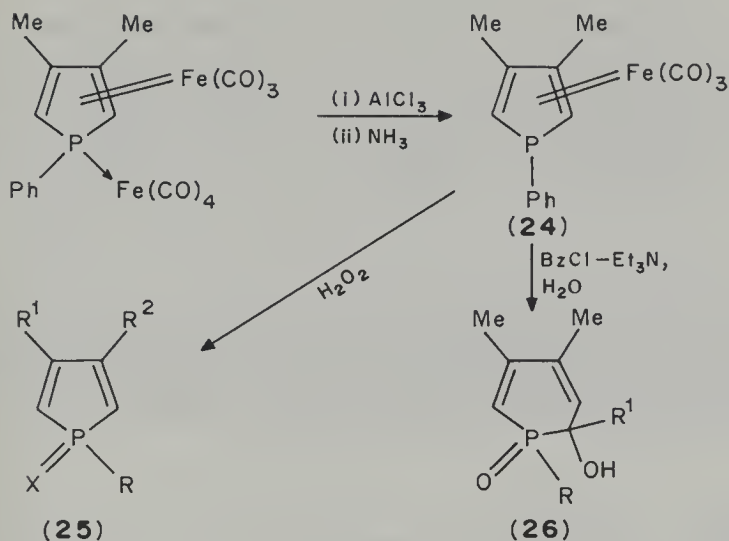
H_2O_2 oxidation of **20** (*m*-Me or *p*-Me) and **5** ($\text{R} = \text{Ph}$; $\text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$) is reported⁵⁵ to give the corresponding oxides ($\text{X} = \text{O}$) in 91% and 82% yields, respectively. The oxide **5** ($\text{R} = \text{Ph}$; $\text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$; $\text{X} = \text{O}$), obtained above, on nitration and reduction with Sn-HCl followed by diazotization and coupling with 2-naphthol, gives a phosphine oxide dye⁵⁶ (**21**).



The stereochemistry of the oxidation of phosphines with H_2O_2 has been described by Leuchenbach⁵⁷.



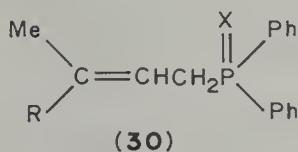
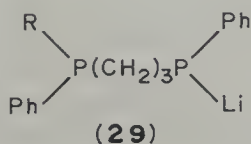
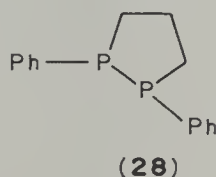
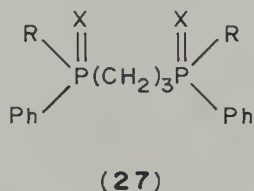
Diazaphosphorinanes **22** ($\text{R} = \text{Ph}$, *p*-MeC₆H₄, *p*-BrC₆H₄, H₂CPh; $\text{R}' = \text{Ph}$; $\text{X} = \text{nil}$) are known to be oxidized⁵⁸ to 5-oxo derivatives **22** ($\text{X} = \text{O}$) by H_2O_2 . Similarly, cyclopropylidenebis(diphenylphosphine) **23** ($\text{X} = \text{nil}$) is reported⁵⁹ to be prepared in 91% yield by H_2O_2 oxidation. The phosphine **23** is prepared in 26% yield by cyclopropanation of $(\text{Ph}_2\text{P})_2\text{C}=\text{CH}_2$ with $\text{Me}_2\text{SO}(=\text{CH}_2)$ and is air and moisture stable. Tertiary phosphine sulphides also, on H_2O_2 oxidation, give the corresponding phosphine oxides (see Section III.B.4 for details). Iron-phosphole complexes **24** are known⁶⁰ to be oxidized by H_2O_2 to **25** ($\text{R} = \text{Ph}$; $\text{R}^1 = \text{R}^2 = \text{Me}$; $\text{X} = \text{O}$). The decomplexed products, **24**, in turn,

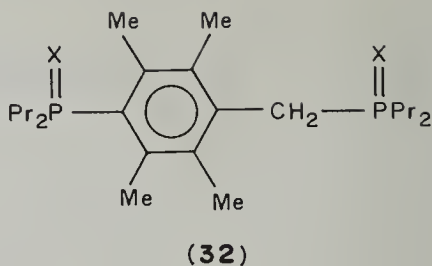
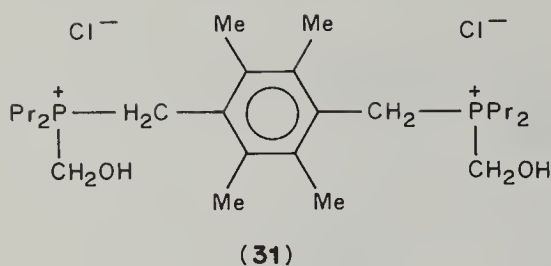


SCHEME 1. Preparation of phosphole oxides.

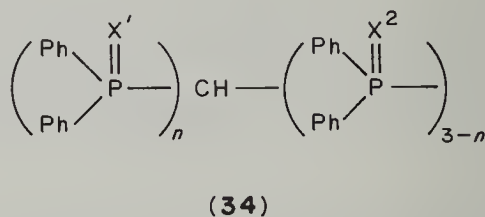
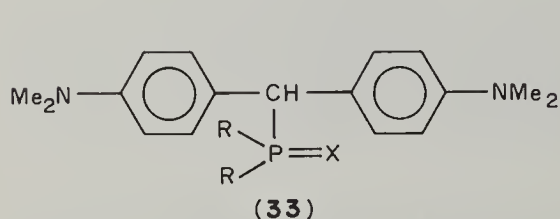
were prepared by treating the iron phosphole complex with AlCl_3 and then with ammonia solution. Treatment of **24** with BzCl , Et_3N and water gave the ring expanded product **26** (Scheme 1).

H_2O_2 oxidation of diphosphines **27** ($\text{R} = \text{Me}$, Bu , Ph ; $\text{R}' = \text{Et}$, Bu , Pr , Me_2CH , pentyl, hexyl; $\text{X} = \text{nil}$) are known to give⁶¹ the oxides in 62–68% yields. Compounds **27**, in turn, are prepared by ring opening of the diphosphacyclopentanes **28** with organolithium compounds, RLi , to give **29**, followed by reaction of **29** with $\text{R}'\text{Br}$. Tertiary phosphines **1** ($\text{R} = \text{alkyl}$) on oxidation with H_2O_2 give⁶² the corresponding oxides. **1** ($\text{X} = \text{nil}$), in turn, are prepared by treatment of RMgBr with PCl_3 in thf . Allylic phosphine oxides are likewise formed by H_2O_2 oxidation⁶³ of **30** ($\text{R} = \text{H}$, Et), prepared by reaction of Ph_2PLi in thf with $\text{MeCR}=\text{CHCH}_2\text{COOC}_6\text{H}_3\text{Cl}_2\text{-2,6}$. Oxidation of the phosphonium salts **31** with $\text{H}_2\text{O}_2\text{-MnO}_2$ is reported to give arylenebismethylenephosphine oxide⁶⁴ **32** ($\text{X} = \text{O}$). Compounds **31** are prepared by reaction of $\text{Pr}_2\text{PCH}_2\text{OH}$ with arylenebis(methyl halides).

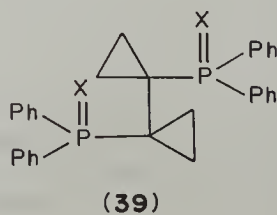
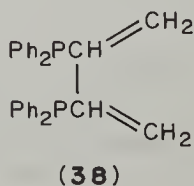
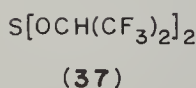
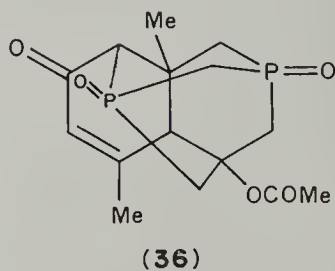
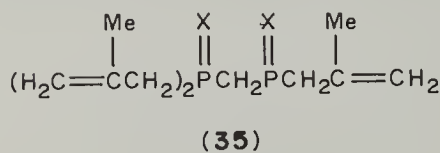




H_2O_2 is known to oxidize the leuco dyes **33** ($\text{R} = \text{Et}$, CMe_3 , Ph ; $\text{X} = \text{nil}$) to the phosphine oxides **33** ($\text{X} = \text{O}$). Polydentate ligands containing P of the type **34** ($\text{X}^1 = \text{O}$; $\text{X}^2 = \text{S}$; $n = 1, 2, 3$) are prepared⁶⁵ by H_2O_2 oxidation of **34** ($\text{X}' = \text{nil}$).

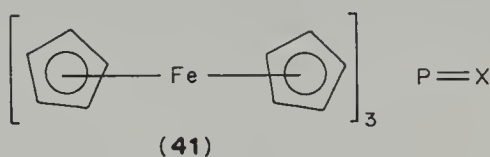
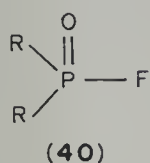


Olefinic phosphines, **35** ($\text{X} = \text{nil}$), on oxidation with H_2O_2 , give⁶⁶ the phosphine oxides **35** ($\text{X} = \text{O}$). These on further oxidation with ozone followed by a multiple aldol reaction on the product, gives the phosphaheterocycle **36**. Phosphine oxide **5** ($\text{R} = \text{Ph}$; $\text{R}^1 = 2\text{-MeOC}_6\text{H}_4$; $\text{X} = \text{O}$) is prepared by H_2O_2 oxidation of the corresponding **5** ($\text{X} = \text{nil}$), which in turn is prepared by the reaction of Ph_2PCl with $2\text{-MeOC}_6\text{H}_4\text{MgBr}$. Similarly, $2\text{-XC}_6\text{H}_4\text{X}'$ ($\text{X} = \text{X}' = \text{halides}$) on reaction with 2 mol equiv. of LiPPh_2 in the presence of furan, followed by oxidation⁶⁸ with H_2O_2 , gives **5** ($\text{R} = \text{Ph}$, $\text{R}^1 = 2\text{-ClC}_6\text{H}_5$). Likewise, 50 g of **5** ($\text{R} = \text{CO-2}$, $6\text{-Cl}_2\text{C}_6\text{H}_3$; $\text{R}' = 2,5\text{-xylyl}$; $\text{X} = \text{nil}$) in MeCN , on treatment with 150 ml of 30% H_2O_2 at 60°C , gives⁶⁹ the corresponding oxide ($\text{X} = \text{O}$).



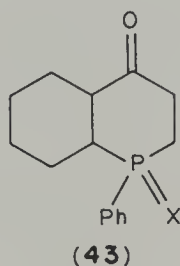
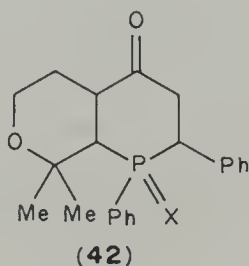
c. *By oxides of sulphur.* Aqueous sodium sulphite has been used to oxidize⁷⁰ the phosphine-iodine complex R_3PI_3 (see Section III.C.1). Sulphoxylate **37** is known⁷¹ to oxidize Me_3P to its oxide. Recently Dziwok *et al.*⁷² have used $Me_2S(=CH_2)O$ to convert 2,3-(bisphenylphosphinyl)buta-1,3-diene **38** by double cyclopropanation and oxidation to the phosphine oxide **39** ($X = O$). SO_2 is reported to react with Me_3P to give³⁷ both Me_3PO and Me_3PS . $(Me_3SiO)_2SO_2$ is known⁷⁴ to react with $PhPCl_2$ at $140^\circ C$ for 2 h to produce $(Me_3SiO)_2P(O)Ph$, Me_3SiCl and SO_2 .

d. *By oxides of nitrogen.* Hydroxylamine hydrochloride in refluxing pyridine has been used⁵⁷ to oxidize chiral cyclic tertiary phosphines stereospecifically. Reactions of nitrosyl fluoride, FNO, with dialkylphosphines R_2PH is reported to give⁷⁵ the corresponding oxide along with the substitution of H by F. Thus 0.026 mol of dibutylphosphine, on treatment with FNO at -50 to $-68^\circ C$, gave **40** ($R = Bu$, Me) in 7.3% yield.



Photochemical transfer of oxygen from heterocyclic *N*-oxides to phosphine sulphide has also been reported⁷⁶ (see Section III.B.4). Enantiomeric phosphine **12** ($R = Me$; $R' = Ph$; $R^2 = Pr$; $X = nil$) and diastereomeric phosphorinanes are thus stereospecifically oxidized⁷⁷ by tertiary amine oxides.

e. *By other inorganic oxidants.* Substituted phosphines and nickel halide complexes, e.g. $[(Ph_3P)_2NiX_2]$ ($X = Cl, Br, I$) are known⁷⁸ to be quantitatively oxidized to the corresponding oxides by sodium chlorite. Use of ClO_2 as the oxidizing agent led to the preparation of $(R_3P=O)_2 \cdot NiCl_2$ ($R = Ph$, cyclohexyl) and $[\{Ph_2P(=O)CH_2\}_2NiCl_2]$. Oxidation of triferrocenylphosphines **41** with MnO_2 , $KMnO_4$ or oxygen over alumina gave the corresponding oxides⁷⁹ ($X = O$) in 83, 64 and 15% yields, respectively. $KMnO_4$ has also been used to oxidize^{80,81} oxaphosphabicyclodecanones **42** and **43** ($X = nil, O$).



Mercury(II) acetate has been used to oxidize⁸² Me_3P , forming a 1:1 adduct $Me_3PO \cdot AcOH$, which is also formed in 73–81% yield by reaction of Me_3PO with $RCOOH$ ($R = H, Me$). This adduct on treatment with sodium methoxide gives $Me_3PO \cdot MeOH$ and sodium acetate.

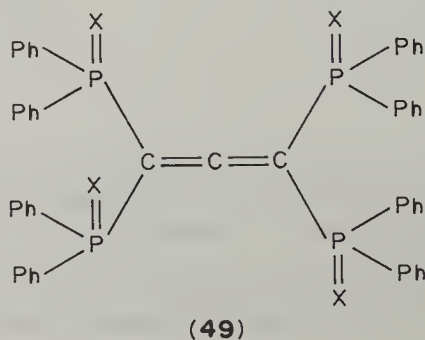
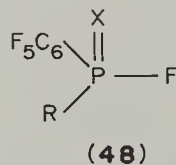
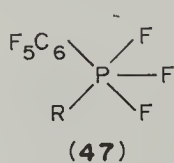
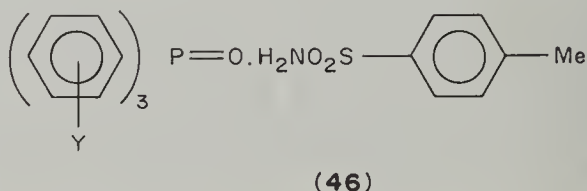
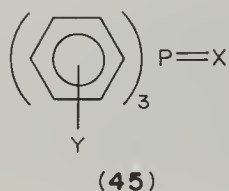
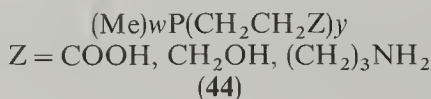
Triphenylphosphine can be oxidized⁸³ with 2–3 mol equiv. of MnO_2 in kerosene. Thus Ph_3P (1 mol) was oxidized by MnO_2 (3 mol) in kerosene (1750 ml) at $140-150^\circ C$ for 5–6 h

to give $\text{Ph}_3\text{P}=\text{O}$ in 80% yield. R_3P is also oxidized⁸⁴ to its oxide with KMnO_4 in acetone, the product being obtained by repeated extraction of the black residue with chloroform. R_3P are oxidized with FSO_2Cl at room temperature to give⁸⁵ $\text{R}_3\text{P}=\text{O}$.

f. By miscellaneous oxidants. Tributylphosphine, on mixing with methyl pyruvate under nitrogen at 40–45 °C for 1 day, is reported⁸⁶ to give the oxide in 90% yield along with dimethylmethylene dicarboxylate. Diethyl mesoxalate also has been used as an oxidizing agent in the same reaction. A mixture of Ph_3P and ethyl pyruvate on heating for 1 h at 140 °C forms $\text{Ph}_3\text{P}=\text{O}$ in 58.9% yield.

The anaerobic aqueous alkaline oxidation⁸⁷ of **44**, ($w=0-2$; $y=3-w$) and ($p\text{-OHC}_6\text{H}_4$)₃P gives a stoichiometric amount of hydrogen and the corresponding phosphine oxides. ($\text{Y-C}_6\text{H}_4$)₃P reacts⁸⁸ with chloramine-T in ethanol to give **45** ($\text{X}=\text{NSO}_2\text{C}_6\text{H}_4\text{Me-}p$), which on hydrolysis with water gives the phosphine oxide **45** ($\text{X}=\text{O}$) along with $\text{H}_2\text{NO}_2\text{SC}_6\text{H}_4\text{Me-}p$, together forming a strongly hydrogen-bonded adduct **46**. $(\text{Me}_3\text{Si})_2\text{O}$ is reported⁸⁹ to oxidize $\text{C}_6\text{F}_5\text{PRF}_3$ (**47**) to **48** ($\text{X}=\text{O}$). Compound **47** is prepared by the reaction of $\text{C}_6\text{F}_5\text{PRY}$ ($\text{Y}=\text{NEt}_2$) with HCl or HBr , thus forming the halides ($\text{Y}=\text{Cl}, \text{Br}$), which in turn react with NaF in MeCN to give the fluoro derivative ($\text{Y}=\text{F}$). This on further reaction with AsF_3 gives **47**. $\text{C}_6\text{F}_5\text{PRNEt}_2$ was prepared by reaction of $\text{Et}_2\text{NP(R)Cl}$ ($\text{R}=\text{Me}, \text{Et}, \text{CMe}_3, \text{Ph}$) with $\text{C}_6\text{F}_5\text{MgBr}$.

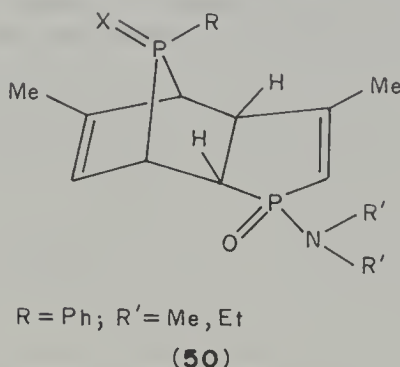
Tertiary phosphines **5** ($\text{R}=\text{Me}, \text{Et}$; $\text{R}'=\text{octadecyl}, \text{octyl}, \text{dodecyl}, \text{hexadecyl}, \text{hexyl}, \text{tetradecyl}$; $\text{X}=\text{nil}$) on oxidation with *tert.*-butyl peroxide give the oxides **5** ($\text{X}=\text{O}$). The phosphines **5** are prepared by treatment of dialkylphosphines with an alkene⁹⁰.



Tetrakis(diphenylphosphino)allenes **49** ($X = \text{nil}$) were oxidized with bistrimethylsilyl peroxide, $(\text{Me}_3\text{SiO})_2$, to give the corresponding oxide^{91,92} **49** ($X = \text{O}$) (see Section III.A.2.b for the preparation of the phosphine **49**).

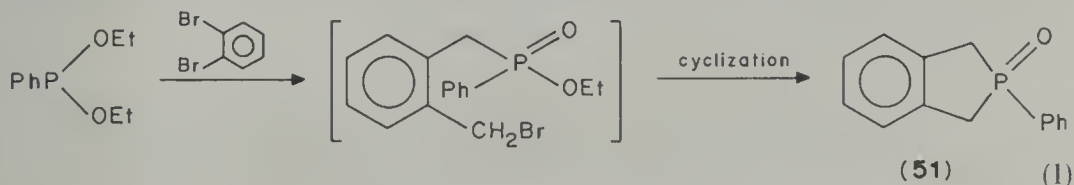
Trimethylsilyl *tert*-butyl peroxide, $\text{Me}_3\text{CSiOOSiCMe}_3$, is known to react^{93a} with Ph_3P to give the oxide (itself being converted to $\text{Me}_3\text{SiOCMe}_3$ in the process). Bis(trimethylsilyl) peroxide is a versatile^{93b} reagent for the selective generation of the oxyphosphoryl group. It oxidizes phosphines to the oxides with retention of configuration at phosphorus. It also converts the thiophosphoryl function to the oxophosphoryl function with inversion of configuration at phosphorus.

Et_3P is known to be converted into its oxide by reaction⁹⁴ with dimethylacetylene dicarboxylate in presence of water, forming dimethyl pyruvate along with other products. The tricyclic phosphine **50** ($X = \text{nil}$) is reported⁹⁵ to be oxidized ($X = \text{O}$) by treatment with Me_3COOH . Compound **50** ($X = \text{nil}$) was in turn prepared by the reaction of the phosphinous chloride of the phosphine **50** ($R = \text{Cl}$; $X = \text{nil}$) with PhMgBr . Haloalkylphosphine oxides are prepared⁹⁶ by oxidative halogenation of tertiary hydroxyalkyl phosphines. Thus **1** [$R = \text{HO}(\text{CH}_2)_3$; $X = \text{nil}$] on treatment with HCl gives **5** [$R = \text{HO}(\text{CH}_2)_3$; $R' = \text{H}$; $X = \text{O}$].

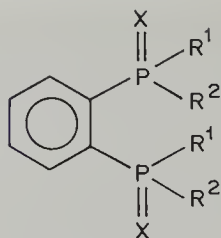


2. Through reaction of organometallics with P^{III} compounds

a. With P^{III} esters. 2-Phenylisophosphindoline-2-oxide (**51**) is prepared⁹⁷ by reaction of phenylphosphinic acid esters with *o*-xylene dibromide in the presence of $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{CMe}_2)_2$ through a Michaelis–Arbuzov rearrangement. The cyclization can also be brought about by treatment with HSiCl_3 . The reaction of MeMgBr and $(\text{EtO})_2\text{POH}$ with RI is reported⁹⁸ to give the oxide **5** [$R = \text{Me}$; $R' = \text{F}_3\text{C}(\text{CF}_2)_7\text{CH}_2$, $\text{F}_3\text{C}(\text{CF}_2)_5(\text{CH}_2)_2$, $\text{F}_3\text{C}(\text{CF}_2)_3(\text{CH}_2)_3$, $\text{F}_3\text{C}(\text{CF}_2)_9(\text{CH}_2)_2$]. The reaction of PhRPOH ($R = \text{Bu}$, PhCH_2 , *n*-hexyl) with $\text{R}'\text{Br}$ ($R' = \text{Ph}$, *o/p*-tolyl, *p*- AcC_6H_4 , *p*- AcNC_6H_4 , *p*- $\text{Me}_2\text{NC}_6\text{H}_4$, *p*- PhC_6H_4 , 2-naphthyl, *p*- NCC_6H_4) in the presence of $[\text{Pd}(\text{PPh}_3)_4]$ and Et_3N gives⁹⁹ phosphine oxides of the type **12** ($R^2 = \text{Ph}$).



Biphosphine oxide ligands **52** ($X = \text{O}$) for transition metal complexes have been prepared¹⁰⁰ by reaction of *o*-difluorobenzene with $\text{R}^1\text{R}^2\text{P}(\text{O})\text{M}^+$ ($\text{M} = \text{alkali metal}$). The

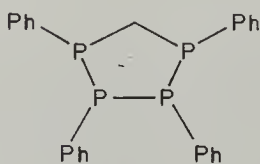


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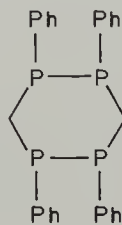
latter is prepared *in situ* by treating R^1R^2POH with an alkali metal hydride. Compound **52** ($X = O$) on reduction with $PhSiH_3$ at $120^\circ C$ gives the phosphine ($X = nil$). Tertiary phosphine oxides are prepared¹⁰¹ by reaction of primary aliphatic or aromatic halides with activated sodium phosphinates, which in turn are prepared by treating dialkylphosphine oxide with complex bases $NaNH_2$ -*tert*-BuONa. Ph_2POH reacts with $R'hal$ ($R' = PhCH_2$, Et, Me_2CH , cyclohexyl, menthyl; $hal = Cl, Br, I$) in the presence of $NaAlH_2(OCH_2CH_2CMe)_2$ to give¹⁰² phosphine oxides of the type **5** ($R = Ph$).

Alkylarylphosphine oxides of the type **5** ($R = Me$, $R' = CH_2C_6H_3Cl_2$ -3,4) can be prepared¹⁰³ by the addition of sodium hydride to a cooled solution of 50% Me_2POH in isobutyl alcohol and 3,4-dichlorobenzyl chloride in toluene at 20 – 45 and 50 – $55^\circ C$.

b. With P^{III} halides. PCl_3 is reported to react¹⁰⁴ with trialkylaluminium under nitrogen at 120 – $145^\circ C$ to give alkylchlorophosphines, which on treatment with carbon in the presence of Et_3N at high temperature and pressure, followed by oxidation, give the corresponding oxides. Phenylphosphine dichloride reacts¹⁰⁵ with sodium acetylide to yield the phosphine, **5** ($X = nil$; $R = -C\equiv CH$; $R' = Ph$) in 52% yield, which is then oxidised ($X = O$) to give the oxide in 80–90% yield. Grignard reaction of arylphosphinyl halides $Ph_{3-n}PCl_n$ with aryl halides, BrC_6H_4Et , followed by oxidation with H_2O_2 gave^{19b} phosphine oxides of type **5** in 21–89% yield. As a variation of this reaction, Baudler *et al.*¹⁰⁶ obtained 1,2,4,5-tetraphenylcyclo-3,6-dicarba-1,2,4,5-tetraphane (**54**) in 19% yield by metallation of the phospholane **53** and subsequent reaction with CH_2Cl_2 .

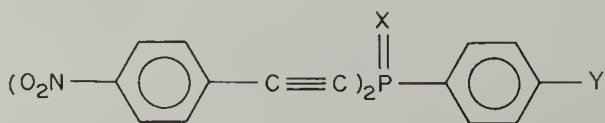


(53)



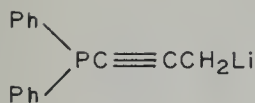
(54)

Aryl-substituted P^{III} halides on reaction¹⁰⁷ with aryl-substituted copper acetylides in the ratio 1:2, e.g., $p-O_2NC_6H_4C\equiv CCu$ in thf, containing catalytic LiCl or LiBr, gave, on oxidation with H_2O_2 , the oxide **55**. A similar reaction with PCl_3 gave $(p-O_2NC_6H_4C\equiv C)_3P$, which polymerized during recrystallization.

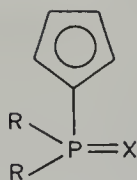


$Y = H, Cl, OMe, NMe_2$

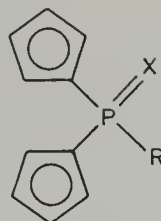
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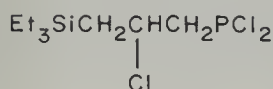
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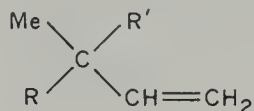
(58)

Tetrakis(diphenylphosphino)allenes **49** ($X = \text{nil}$) were prepared⁹¹ in 56% yield by reacting the lithium derivative of the acetylenic phosphine **56** with diphenylchlorophosphine **19** ($R = \text{Ph}$; $X = \text{nil}$).

Cyclopentadienylthallium is allowed¹⁰⁸ to react for 1 h at room temperature with P^{III} halides such as R_2PCl or RPhCl_2 ($R = \text{Ph}, \text{Me}$) in diethyl ether, yielding 40–100% CpPR_2 **57** ($X = \text{nil}$) and Cp_2PR **58** ($X = \text{nil}$), respectively, which on H_2O_2 oxidation gave the corresponding oxides ($X = \text{O}$). Reaction of P^{III} dihalides with organometallics has been used to prepare phosphine oxide dyes⁵⁶. Thus reaction of **59** with PhMgBr , followed by oxidation, gives the phosphine oxide **5** ($R = \text{Ph}$; $R' = \text{CH}_2\text{CH}=\text{CH}_2$; $X = \text{O}$; see Section III. A. 1.b for its conversion to an azo dye, **21**). Compound **59** was prepared by the reaction of $\text{Et}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ with PCl_5 in benzene at -15°C when an adduct was formed which was decomposed with phosphorus and CS_2 at -20°C .

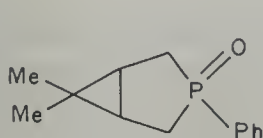


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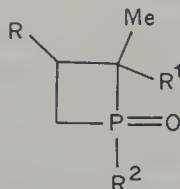


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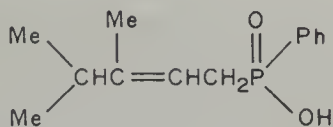
In a variation of the reaction of organometallics with P^{III} halides, phosphorus heterocycles are prepared by the reaction¹⁰⁹ of unsaturated compounds with a complex of a P^{III} halide with AlCl_3 , e.g. addition of **60** ($R = \text{CH}=\text{CH}_2$; $R' = \text{Me}$) to the dichlorophenylphosphine. AlCl_3 complex in CH_2Cl_2 at room temperature followed by quenching with aqueous NaHCO_3 gives the phosphabicyclo[3.1.0]hexane **61** and the vinylphosphetane **62** ($R = \text{CH}=\text{CH}_2$; $R^1 = \text{Me}$; $R^2 = \text{Ph}$). Reaction of **60** ($R = \text{Ph}$) with $\text{PhPCl}_2.\text{AlCl}_3$ complex resulted in the formation of **62** ($R = R^2 = \text{Ph}$; $R^1 = \text{CH}=\text{CH}_2$), whereas with $\text{PhPBr}_2.\text{AlCl}_3$ in dichloromethane a mixture of **61** and **62** was obtained. Use of dibromomethane in the above reaction, however, resulted in the formation of the open-chain derivative **63**. A similar reaction of $\text{MePCl}_2.\text{AlCl}_3$ with camphene gave after hydrolysis the phosphetane oxide¹¹⁰ **64** and the chlorophosphetane oxide **65**.



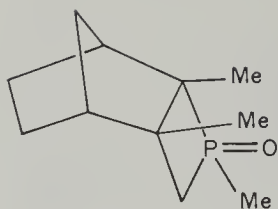
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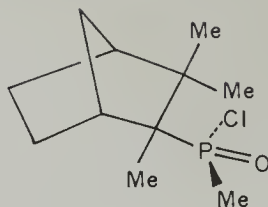
(62)



(63)



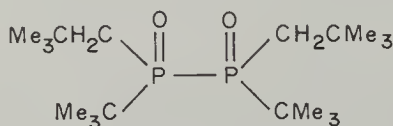
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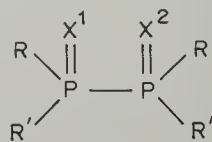
(65)

Phosphine oxides of the type **12** (R^1 and R^2 = substituted phenyl; R = *tert.*-alkyl) are prepared¹¹¹ by alkylation of the $AlCl_3$ complex of the corresponding **19** (R = aryl; X = nil) at 20–160 °C. Diaryl(tertiaryalkyl)phosphine oxide **5** (R = unsubstituted Ph; R' = alkyl; X = O) can be prepared likewise^{112,113} by reacting a complex of **19** (R = aryl; X = nil) with $AlCl_3 \cdot HCl$ and an alkylating agent in diethyl ether and heating.

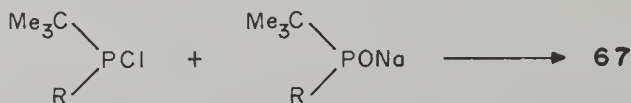
Alkoxyethylphosphine oxides are prepared in 35–80% yields by reaction¹¹⁴ with Grignard reagents, e.g. $(EtOCH_2)_3P=O$ was prepared in 44% yield by reaction of $Cl_2P(O)CH_2OEt$ with $EtOCH_2MgCl$. Bis(*p*-chlorophenyl)methylphosphine oxide is prepared¹¹⁵ by reacting *p*-chlorophenylmagnesium bromide with phosphine dichloride in thf. Alkyl(di-*tert.*-butyl)phosphine oxide **5** ($R' = Me, Et$) is formed by refluxing¹¹⁶ **19** ($R = Me_3C$; X = nil) with $R'ONa$ in MeOH for 1 h. Tertiary phosphine oxides of the type **5** ($R = R'$) or **1** ($R = R' = C_{1-12}$ -alkyl or aryl; $X = O$ or S) are obtained¹¹⁷ by refluxing **19** with a mixture of the halo derivative of the hydrocarbon in the presence of a metal, generally magnesium. Grignard reaction of *tert*-butylphosphinic dichloride with Me_3CCH_2MgBr , followed by oxidation¹¹⁸, gives oxide **5** ($R = Me_3CCH_2$; $R' = Me_3C$; $X = O$) together with diphosphine dioxide **66**. The phosphine oxides **67** ($R = Me_3C, Me_2CH, Me_2CHCH_2, Bu, Ph$; $R' = Me_3C$; $X^1 = nil$; $X^2 = O$) are prepared¹¹⁹ by the reaction of Me_3CPRCl with $Me_3CPRONa$.



(66)

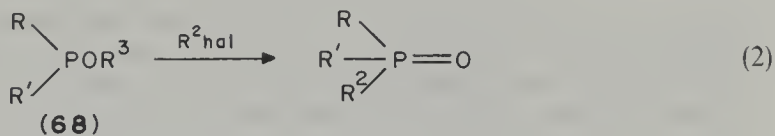


(67)

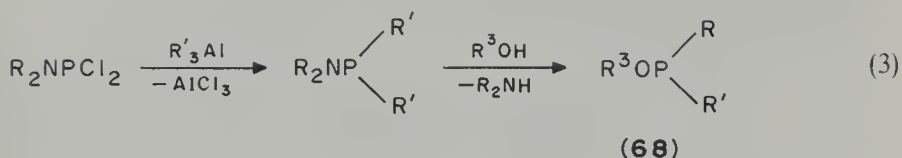


3. Through Michaelis–Arbuzov rearrangement

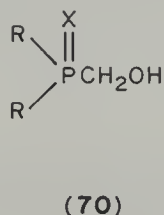
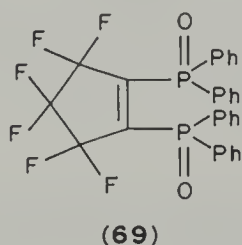
A convenient method for preparing tertiary phosphine oxides consists in the reaction of phosphinite esters **68** [(a) $R = R'$; (b) $R \neq R'$] with alkyl halides (reaction 2). The rearrangement offers a very facile pathway for the formation of a C—P bond and has been reviewed elsewhere¹²⁰. Compound **68** is obtained as in reaction 3. Thus methyl iodide reacts¹²¹ vigorously with **68** ($R = R' = Et$) at room temperature to yield **5** ($R = Et$; $R' = Me$; $X = O$). Alkyl halides seem to be more reactive than aryl halides, in keeping with the general reluctance of the aryl groups to undergo nucleophilic substitution.



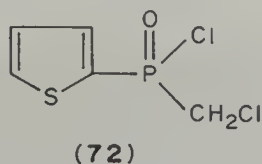
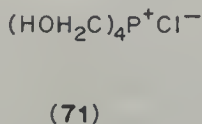
Hal = Cl, Br, I; α -halocarbonyl compounds, etc.



Ethyl diphenyl phosphinite reacts on refluxing^{16a} with 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene to give perfluorocycloalk-1-enyl-1,2-ylenediphosphoryl compounds **69**, useful as metal extractants and sequestering agents. Some phosphinite esters undergo self-isomerization to the oxides, even in absence of any alkyl halides. Thermal isomerization is also fairly common, e.g. methylphosphine oxides can be prepared in 77.8% yield by the thermal rearrangement¹²² of **70** (R = R' = Me) in phenyl cyanide at 130°C in 8 h. Toluene, xylene, octane, decalin and *o*-dichlorobenzene have also been used as solvents in the reaction.



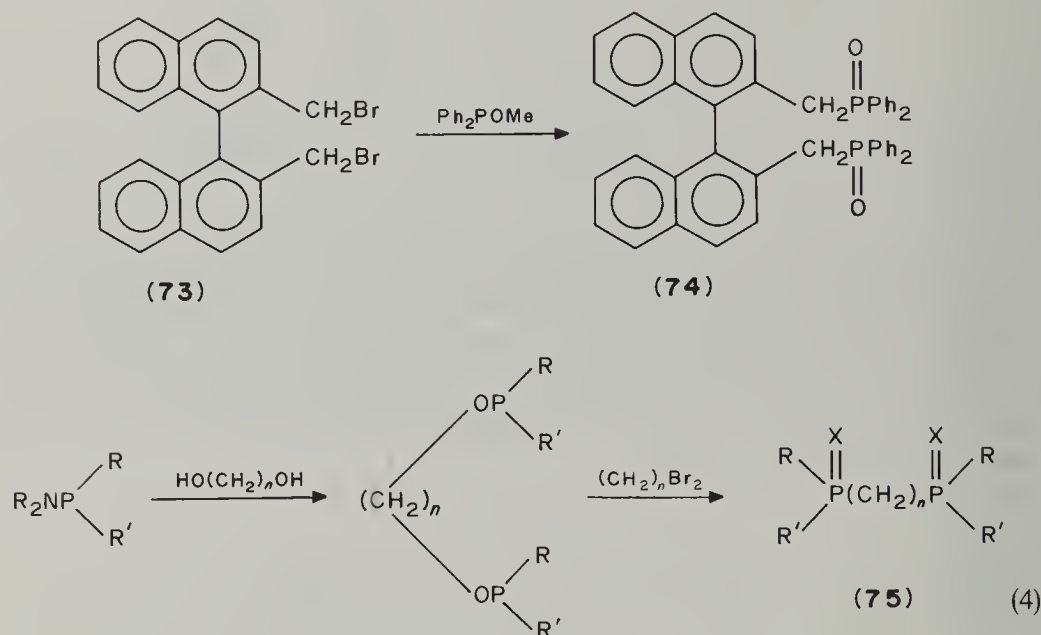
Tetramethylphosphonium halides **71** also undergo rearrangement¹²³ on heating at 190–200°C in presence of HCl gas to give **70** (R = CH₂OH; R' = Me; X = O). Me₃P or (AcOCH₂)₃P, on heating at 160–180°C in the presence of HCl gas with simultaneous removal of the low-boiling products by distillation, yields¹²⁴ the phosphine oxide **5** (R = ClCH₂; R' = Me; X = O). Irradiation of hydroxymethylphosphines **70** (R' = CH₂OH; X = nil) in an inert gas is also known¹²⁵ to give the rearranged product, e.g. hydroxymethyldimethylphosphine (108 g) when irradiated for 8 h at 25°C under nitrogen gives 79% of **70** (R = R' = Me), which on further irradiation at 30°C in dichloromethane for 9 h under argon gives trimethylphosphine oxide in 91.85% yield.



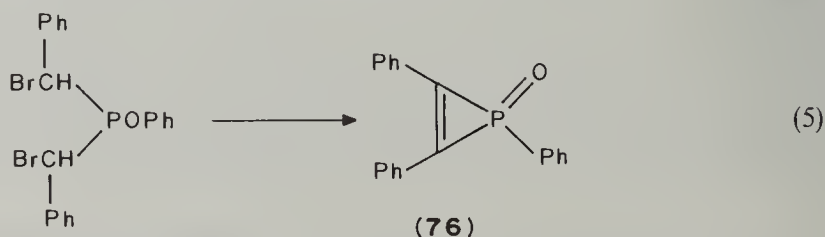
Dichlorophosphines undergo rearrangement on reaction with paraformaldehyde¹²⁶, e.g. 2-thienyldichlorophosphine on heating at 135°C for 4 h gives **72** in 33% yield. The

yield of **72** is further increased to 74.5% by heating with additional paraformaldehyde. Likewise, chlorodimethylphosphine on treatment with formaldehyde in dry benzene is known to give¹²⁷ chloromethyldimethylphosphine oxide.

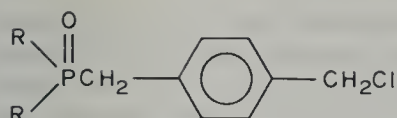
Arbuzov reaction of (*S*)-(-)-2,2'-bis(bromomethyl)-1,1'-binaphthyl (**73**) with Ph_2POMe results in the formation¹²⁸ of the corresponding oxide **74**. $\text{R}_2\text{NPRR}'$ on reaction with α,ω -alkanediols, followed by reaction with alkylene dibromide, rearranges¹²⁹ to form the phosphine oxide **75** ($\text{X} = \text{O}$).



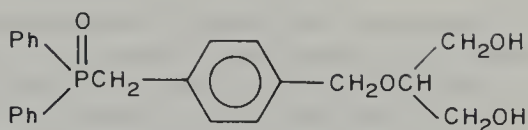
Phosphine oxides containing upto four phosphorus atoms (**16**) have also been prepared¹³⁰ from the phosphinites **68** ($\text{R} = \text{R}'$), by reaction with trischloromethylphosphine. Triphenylphosphine oxide **76** has been synthesized^{131a} starting from **68a** ($\text{R} = \text{R}' = \text{PhCHBr}$; $\text{R}^3 = \text{Ph}$). Addition of 1,5-diazabicyclo[4.3.0]non-5-ene to a benzene solution of **68a** gave the phosphacyclopropene **76**, which at 120°C gave $\text{PhC}\equiv\text{CPh}$. Addition of aqueous NaOH to **76** gave (*cis*-1,2-diphenylvinyl)phosphinic acid. The preparation of oxaphosphirane phosphine oxides has also been reported^{131b}.



Some specific phosphine oxides (**77**), useful as flame retardants in polyurethanes, are prepared¹³² by reaction of phosphinite **68a** ($\text{R} = \text{R}' = \text{Ph}$, tolyl; $\text{R}^3 = \text{Me}$, Et) with $p\text{-Cl/BrCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl/Br}$, which was further reacted with glycerol or glycols to give **78**. Thus a mixture of methyldiphenyl phosphinite (216.2 parts) and aryl halide (175.1 parts), when stirred for 1 h at $90\text{--}100^\circ\text{C}$ followed by 1 h at $120\text{--}130^\circ\text{C}$, gives **77** ($\text{R} = \text{Ph}$), which on stirring with glycerin (138.1 parts) and sodium carbonate (58.0 parts) for 2 h at $100\text{--}130^\circ\text{C}$ gives **78** (440.1 parts).

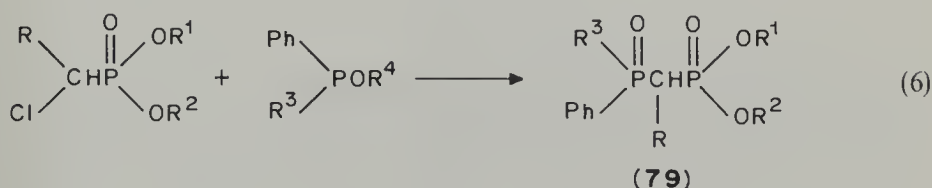


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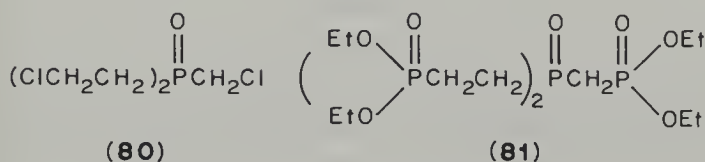


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The reaction of α -halo compounds with phosphinites also leads to the formation¹³³ of phosphine oxides **79** ($\text{R}, \text{R}', \text{R}^2 = \text{H}, \text{Ph}; \text{R}^3 = \text{Ph}; \text{R}^4 = \text{Et}, \text{Me}_2\text{CH}$) (reaction 6). Tris(chloroethyl)phosphine oxide and **80** underwent Michaelis–Arbuzov rearrangement on heating at 170°C with triethyl phosphite to give the oxides **81** and **82** ($\text{R} = \text{OEt}$) in high yield. Compound **80** is, in turn, prepared by the chlorination of tris(hydroxyethyl)phosphine oxide and **5** ($\text{R} = \text{HOCH}_2\text{CH}_2; \text{R}' = \text{CH}_2\text{OH}; \text{X} = \text{O}$). Tris(chloroethyl)phosphine oxide also undergoes an Arbuzov reaction¹³⁴ with butyldiphenyl phosphinite to give the tetra(tertiary phosphine) oxide **82** ($\text{R} = \text{Ph}; \text{X} = \text{O}$).

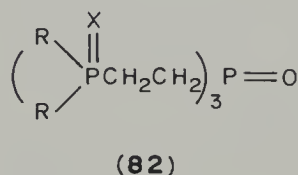


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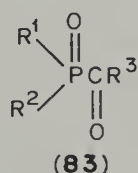


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(81)

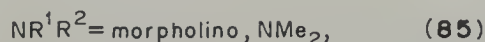
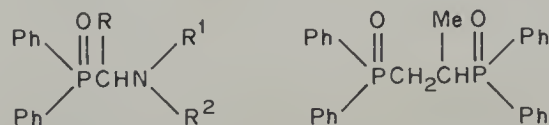


(82)



(83)

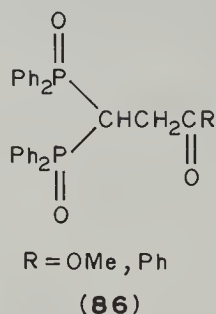
Acyl-substituted phosphine oxides **83** are prepared^{135,136} by treating the phosphinite **68b** ($\text{R} = \text{aryl}; \text{R}' = \text{C}_{1-16}\text{-alkyl, cycloalkyl, aryl, S- or N-heterocycle}$) with R^2COhal ($\text{hal} = \text{Cl, Br, I}; \text{R}^2 = \text{C}_{1-16}\text{-alkyl, cycloalkyl}$) as in equation 2. Thus, 2,6-MeOC₆H₃COCl is heated for 3 h at 50°C with methyldiphenyl phosphinite to give **83** ($\text{R}' = \text{R}^2 = \text{Ph}; \text{R}^3 = 2, 6\text{-MeOC}_6\text{H}_3$). Arbuzov reaction or Mannich-type condensation of Ph_2POH with aldehydes or secondary amines results in the formation¹³⁷ of the phosphine oxides **84** ($\text{R} = \text{H, alkyl, Ph, CH=CHPh, CH=CHMe, SMe, SPh, cyclohexyl}$).



(84)

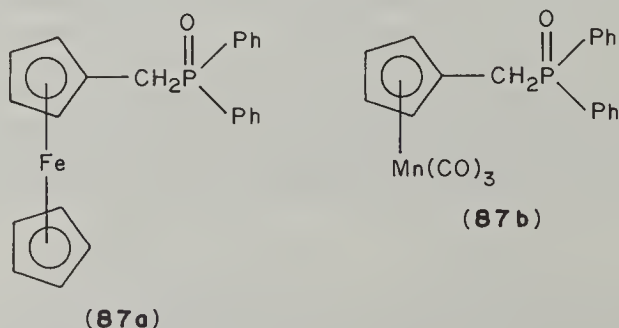
Condensation of R_2POH ($R = Et, Ph$) with unsaturated halides or 1,3-dienes, in the presence of a phase-transfer catalyst, results in the formation of a phosphine oxide containing β,γ -unsaturated groups. Thus $BrCH_2CH=CH_2$ reacts with Et_2POH in the presence of KOH and Katamin AB to give¹³⁸ **5** ($R = Et$; $R' = CH_2CH=CH_2$; $X = O$). Similarly, the alkyl(tetraphenylethylene)diphosphine dioxide **85** is prepared¹³⁹ by reaction of Ph_2POH with $CH_2=CHCHBr$, which gives $Ph_2P(O)CH_2CH=CH_2$. The latter on further reaction with Ph_2POH gives **85**.

Reaction of Ph_2POH with $Ph_2P(O)CH=CHCOR$ at $100-150^\circ C$ under an inert gas gives¹⁴⁰ the oxide **86** whereas reaction¹⁴¹ with $BzCH_2CH_2NMe_2HCl$ at $100-110^\circ C$ for 3 h in $MeOH$ gives the oxide **5** ($R = Ph$; $R' = CH_2CH_2Bz$) in 80% yield. Alkylation of R_2POH with $R'hal$ gives¹⁴² phosphine oxides of the type **5**. Thus, $[Me(CH_2)_7]_2POH$, on reaction with $PhCH_2Cl$ in the presence of $(Bu_4N)_2SO_4$, gives the oxide **5** [$R = Me(CH_2)_7$; $R' = CH_2Ph$].



Addition of Et_2POH to $p-R^2C_6H_4N=CHPh$ gives **5** ($R = Et$; $R' = p-R^2C_6H_4NHCHPh$, where $R^2 = COOMe/Et$; $X = O$) in 20.5% yield¹⁴³; Et_2POH is prepared by the hydrolysis of Et_2PCl . Likewise, the reaction¹⁴⁴ of R_2POH ($R = \text{pentyl, hexyl, heptyl}$) with $hal(CH_2)_nCOOH$ ($hal = Cl, Br, I$; $n = 1,2$) or with $hal(CH_2)_nCOOR^2$ ($R' = \text{alkyl}$) gives the oxide **5** [$R' = (CH_2)_nCOOR^2$, where $R^2 = H$ or alkyl]. Reaction of $(Me_3C)_2POLi$ with Me_3CCOCl gives¹⁴⁵ **5** [$R = Me_3C$, $R' = C(O)CMe_3$; $X = O$].

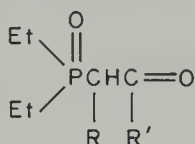
$Ph_2P(O)CH_2Cl$, prepared from Ph_3P and $ClCH_2OMe$ in four steps, reacts¹⁴⁶ with cyclopentadienyllithium in benzene on refluxing for 4–5 h to give a mixture of $Ph_2P(O)CH_2R$ ($R = 1\text{- or }2\text{-cyclopentadienyl}$). These oxides react with $[CpFe(CO)_2]_2$ and $[Mn_2(CO)_{10}]$ to give ferrocene and cymantrene complexes **87a** and **87b**.



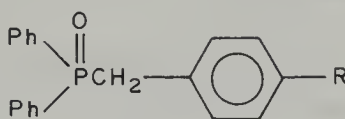
4. Through reactions of halophosphines

Chlorodimethylphosphine reacts with methanol at $20-30^\circ C$ with the elimination of methyl chloride, removed at $50^\circ C$, and the mixture neutralized at $20^\circ C$ with 50% $NaOH$, followed by distillation, to give dimethylphosphine oxide in 90% yield¹⁴⁷.

A general method for preparing tertiary phosphine oxides of the type **5** is by the reaction¹⁴⁸ of dimethylchlorophosphine with $Y(CH_2)_nR'$ ($Y = Cl, Br$; $R' = \text{alkyl, alkenyl, benzyl, functionally substituted alkyl}$; $n = 0-9$; $X = \text{nil}$), followed by treatment with an appropriate oxo or hydroxy compound. Secondary chlorophosphines **19** ($X = \text{nil}$) react with cyclic ketones¹⁴⁹ at $100-120^\circ\text{C}$ in a sealed system to give the oxide **5** ($R' = \text{cycloalkyl}$). Reaction of diethylchlorophosphine with α -halo ketones¹⁵⁰ gives **88** ($R, R' = H, Me$ or Me, Et). Chlorodiphenylphosphine on treatment with benzyl alcohol¹⁵¹ gave phosphinate esters, which rearranged to give the phosphine oxides **89** ($R = H, Me, MeO, Cl$).

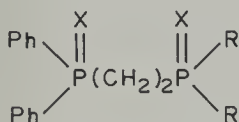


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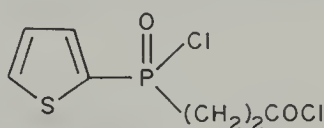


(89)

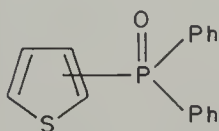
Compounds **19** ($R = Ph$; $X = \text{nil}$) are reported to react with diol ethers¹⁵² in the presence of a tertiary amine. Thus a mixture of $(HOCH_2CH_2)_2O$ (1.2 mol) and pyridine (2.4 mol) in diethyl ether, on treatment with Ph_2PCl , gives **90** ($R = Ph$; $X = O$) in 52% yield. Treatment of a diarylphosphine halide with lithium, followed by reaction with *trans*- $ClCH=CHCl$ for 1.5 h at -20°C and then oxidation, gave the *trans* isomer of the phosphine⁵⁴ **18** ($X = O$; for details see Section III. A.1.b). Reaction of dichloro-2-thienylphosphine with acrylic acid at 60°C for 3 h yielded¹⁵³ the corresponding oxide **91** in 74.5% yield; 2- and 3-thienylphosphine oxides **92** are also known¹⁵⁴. Reaction of 2,2'-methylenebis(cyclohexanone) with PH_3 in dioxane containing HCl results in the formation¹⁵⁵ of the 10-oxo-10-phosphaperhydroanthracene system **93**. Addition of RPX_2 ($R = Ph, Me$; $X = Br, Cl$) to cyclohepta-1,3-diene led to the



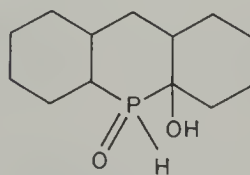
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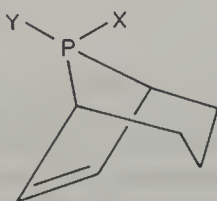
(91)



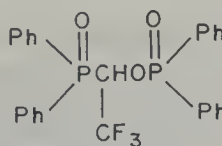
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(93)

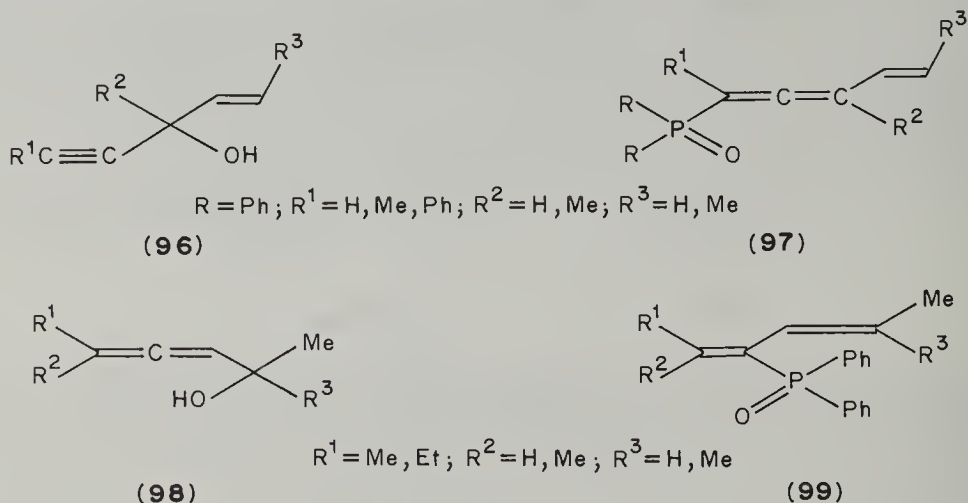


(94)

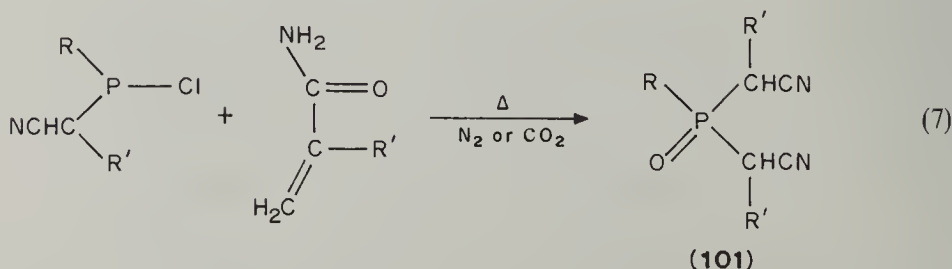
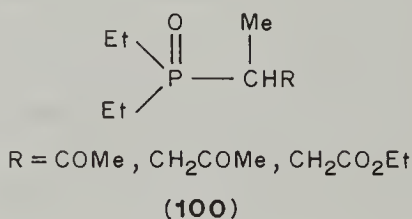


(95)

formation¹⁵⁶ of bicyclic phosphine oxide epimers **94** [(a) X = R; Y = O; (b) X = O; Y = R]. Reaction of **19** (R = Ph; X = nil) with trifluoroacetic acid at 160–170 °C is known to give¹⁵⁷ **95** in 92% yield. Reaction of **19** (R = aryl, alkyl) with enyols **96** is reported¹⁵⁸ to give eneallenes **97**, whereas a similar reaction with allenols **98** produces **99**, involving a [2,3]-sigmatropic reaction at phosphorus.

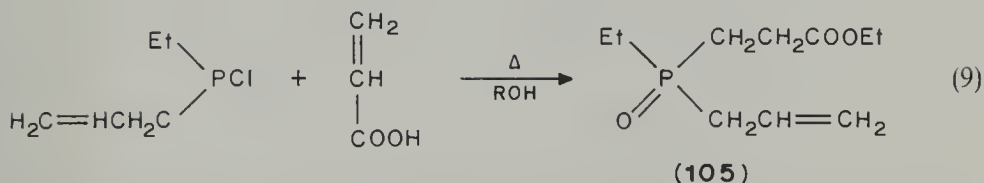
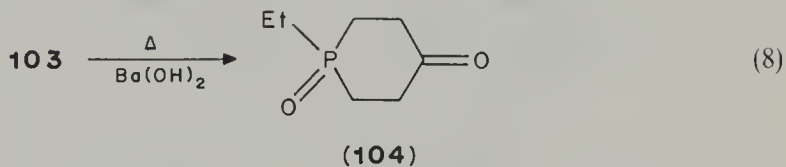
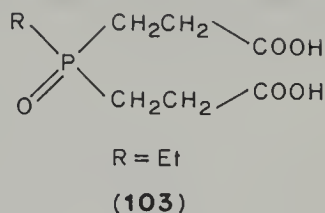
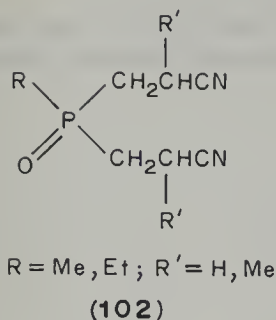


Reaction of **19** with α,β -dicarbonyl compounds also gives¹⁵⁹ the oxide, e.g. the reaction of chlorodiethylphosphine with MeC(O)R results in the formation of **100**. Alkyl(β -cyanoalkyl)chlorophosphines, on heating at 100 °C with amides of α,β -unsaturated carbocyclic acids in an atmosphere of nitrogen or carbon dioxide, yielded¹⁶⁰ alkylbis(β -cyanoalkyl)phosphine oxide **101**.

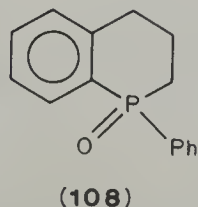
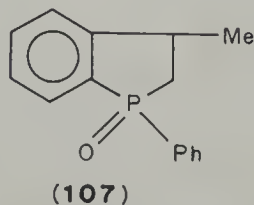
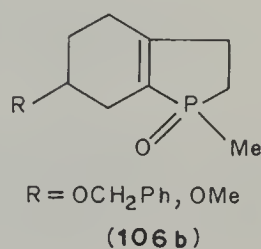
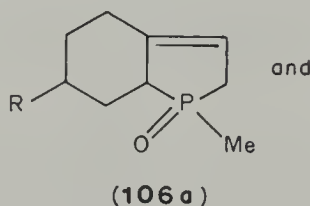
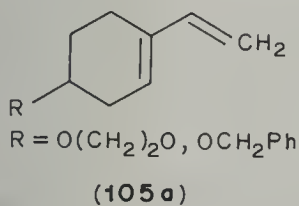


Bifunctional oxides **102** are formed in reaction 7 on heating¹⁶¹ the corresponding chlorophosphine in an inert atmosphere. Compound **102** (R' = H) on hydrolysis gave the acid **103**, which on reaction with PCl₅ was converted into the chloride. Pyrolysis of **103** with Ba(OH)₂ gave the phosphorinane **104** on cyclization.

The reaction of an olefinic phosphine with acrylic acid, followed by esterification, gives **105** by equation 9.

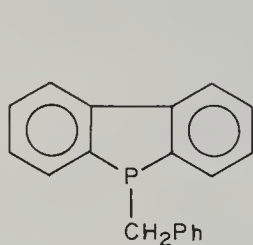


McCormack cycloaddition of dichloromethylphosphine to 1-vinylcyclohexenes, **105a**, are known to give¹⁶² hexahydrophosphindole oxide **106** in 49.6–72.7% yield. Phosphindoline (**107**) and phosphinoline (**108**) systems have also been conveniently prepared by El-Deek *et al.*¹⁶³ in 40–70% yield in a one-step cyclization reaction of diphenylalkenylphosphine oxides **5** (R = Ph; R' = CH₂CH=CH₂) by heating at 180 °C in the presence of polyphosphoric acid.

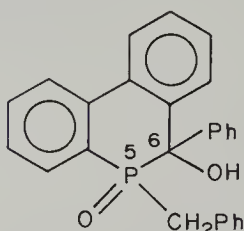


The phosphole **109**, on reaction¹⁶⁴ with benzyl chloride in triethylamine and water, gives 6-phenyl-5-phosphaphenanthrene (**110**) in 90% yield. Baudler and Reuschenbach¹⁶⁵ reported the synthesis of tetraphenylcyclotetraphosphine **112** by the cyclo-condensation of **111** with phenyl-*tert*-butylphosphine. Compound **112** (R = Ph)

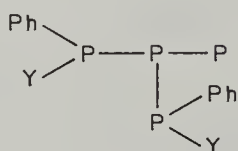
was unstable at room temperatures in solution and rearranged to oligomeric pentaphenylcyclopentaphosphine, whereas **112** ($R = \text{Bu}^t$) was remarkably stable (for oxidation³⁴ of **112**, see Section III.A.1.a).



(109)

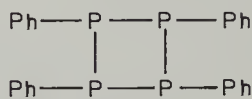


(110)



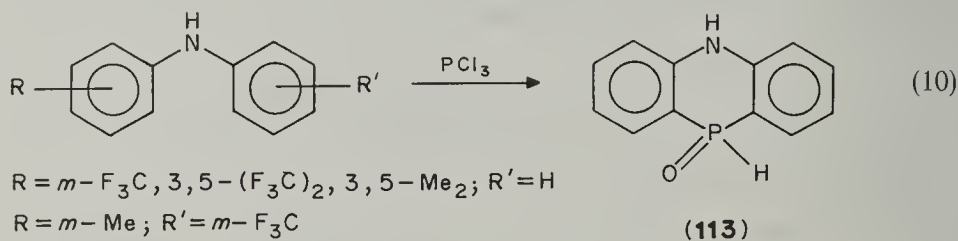
$Y = K, \text{SiMe}_3$

(111)

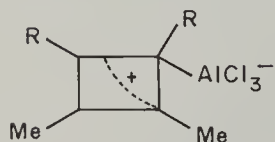


(112)

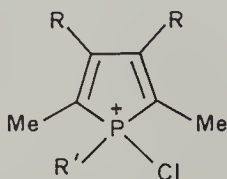
Dihydrophenophosphazines **113** are prepared¹⁶⁶ by the interaction of diarylamines with PCl_3 , resulting in cyclization (reaction 10). Reaction of AlCl_3 complexes of cyclobutadienes **114** with $\text{R}'\text{PCl}_2$ ($\text{R}' = \text{Ph}, \text{Me}$) in CH_2Cl_2 at -50°C gave¹⁶⁷ the phospholium salts **115**, which, on aqueous NaOH work-up, gave the phosphole oxides **116** in 78% and 66% yields.



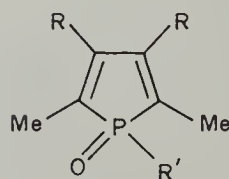
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(114)



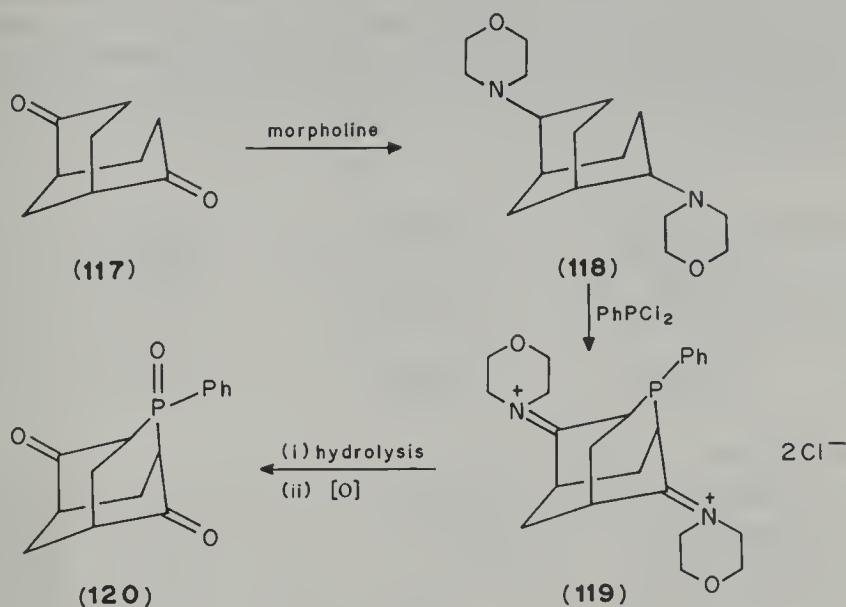
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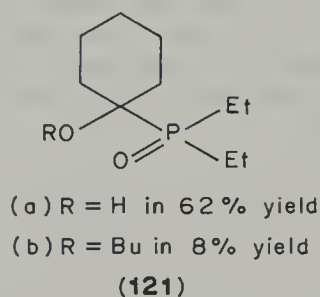
(116)

Kukhar *et al.*¹⁶⁸ reported the synthesis of 2-phenyl-2-phosphaadamantane-4,8-dione-2-oxide **120** in 28% yield by hydrolysing the bisiminium salt **119**, followed by its oxidation. Compound **119** in turn is prepared by treating bicyclononadiene **117** with morpholine and cyclizing the resultant bicyclononadiene **118** with dichlorophenylphosphine, followed by oxidation (Scheme 2). The reaction of **19** ($R = \text{Et}; X = \text{nil}$) with cyclohexanone¹⁶⁹ in

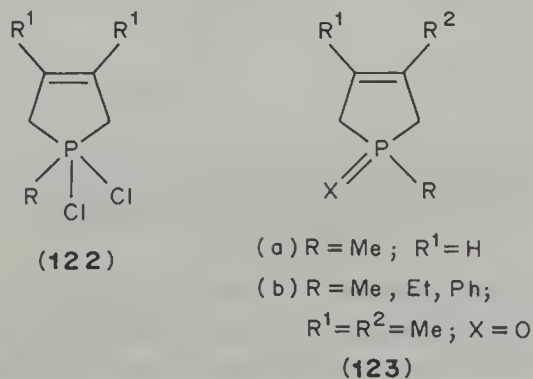
the presence of butanol, butanethiol or AcOH gives a multi-component mixture. The reaction in the presence of butanol thus gives **121**.



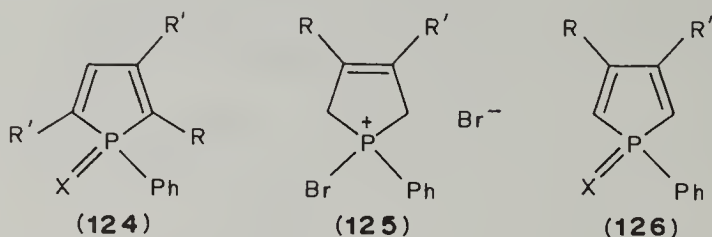
SCHEME 2. Preparation of phosphaadamantane-2-oxide.



Cycloaddition of dichloroalkylphosphine to butadiene and isoprene yields¹⁷⁰ dichlorophospholines **122**, which are hydrolysed to give phospholinones **123** in 43–95% yield. Cyclocondensation of dichlorophenylphosphine with two equivalents of enamines

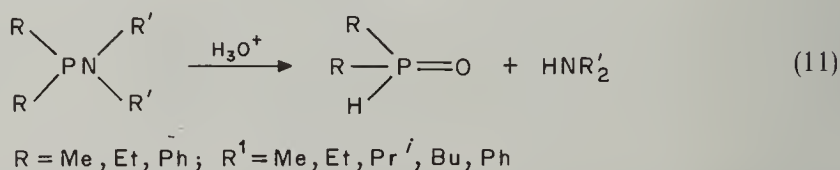


at room temperature has been reported¹⁷¹ to give 2-amino-1-phenylphosphole in 30–35% yield, which on oxidation gives the oxide **124** (R = piperidino, R' = Me, Et; R = pyrrolidino, R' = Et; X = nil, O). Application of pressure to the cycloaddition of dibromophenylphosphine to buta-1,3-dienes reduces the reaction¹⁷² time from days to hours, giving phospholinium bromide **125**, which readily undergoes elimination to produce phosphole **126** (X = nil) in 75–77% yield, which could be oxidized to the corresponding oxide.



5. Through hydrolysis of $R_2PNR'_2$ compounds

Secondary phosphine oxides are prepared¹⁷³ in 90–100% yield by hydrolysis of $R_2PNR'_2$ in presence of HCl, H_2SO_4 or H_3PO_4 at 30 °C (reaction 11). In a variation, dimethylphosphine oxide is prepared¹⁷⁴ in 80–95% yield by hydrolysis of $R_2PNR'_2$ (R = Me, Et, Ph; R' = Me, Et, H) with water in benzene at –20 to 100 °C under an atmosphere of nitrogen. In another variation¹⁷⁵, the hydrolysis of Me_2PR [R = Cl, OPh, NMe_2 , NEt_2 , $N(CHMe_2)_2$, $NHPh$] also yields the above phosphine oxide in 45–97.5% yield. Secondary phosphine oxides **127** (R¹ and R² = C_{1–6}-alkyl) are prepared in high yields and high purity by acidic hydrolysis¹⁷⁶ of dialkylchlorophosphines or their HX addition products with aqueous non-oxidizing mineral acids. Thus, **19** (R = Me; X = nil) in concentrated HCl was poured steadily at –5 °C under nitrogen into water and the mixture was adjusted to pH 6.5 with aqueous NaOH at 20–30 °C, to give the oxide in 97.5% yield.

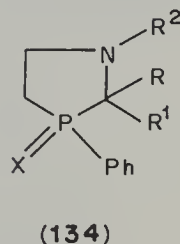
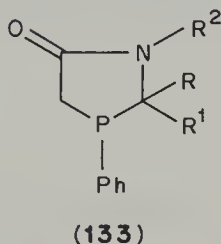
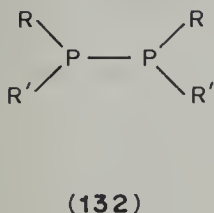
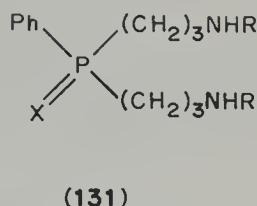
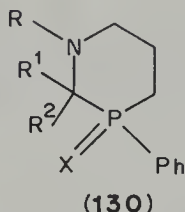
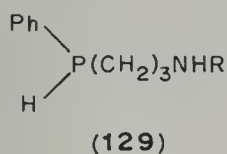


Dimethylphosphine halides are known¹⁷⁷ to react with sodium methoxide to give Me_2POMe , which rearranges to trimethylphosphine oxide in presence of methyl iodide or is hydrolysed to **127** (R¹ = R² = Me) via intermediate **128**.

6. Through reaction of P^{III} compounds with reactive groups

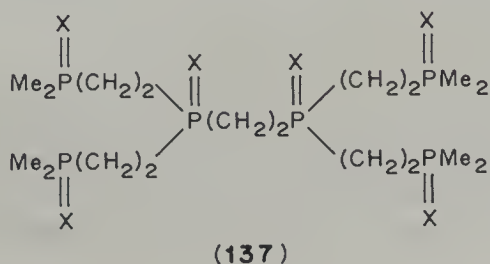
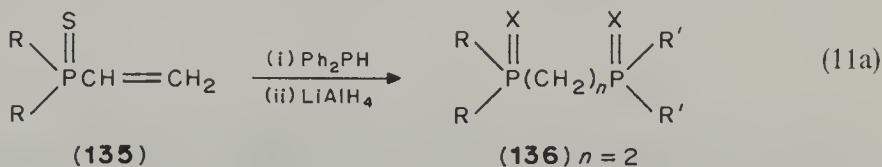
3-Aminopropylphosphines **129** on cyclization¹⁷⁸ with $R^1C(O)R^2$ give 1,3-azaphosphinanes **130**. Both **130** (X = nil) and **131** (X = nil), on H_2O_2 oxidation, give the oxide

(X = O). Compounds **130** (X = nil) and **131** (X = nil) are prepared by heating PhPH_2 and $\text{H}_2\text{C}=\text{CHCH}_2\text{NHR}$ in the presence of azobisisobutyronitrile (AIBN). The reaction of diarylaminomethyl-substituted tertiary phosphines with primary or secondary phosphines causes cleavage¹⁷⁹ of the P—C bond, to form a new P—P bond. Thus, treatment of $\text{Ph}_2\text{PCH}_2\text{N}(\text{Et})_2$ with Ph_2PH yields **132** (R = R' = Ph) and HNEt_2 . Similarly, reaction of $\text{PhP}(\text{CH}_2\text{N}(\text{Et})_2)_2$ and PhPH_2 gives novel cyclic phosphines **8** and **53** (R = Ph; X = nil), together with HNEt_2 and MeNEt_2 (see Section III.A.1.a. for oxidation of **8** and **129**).



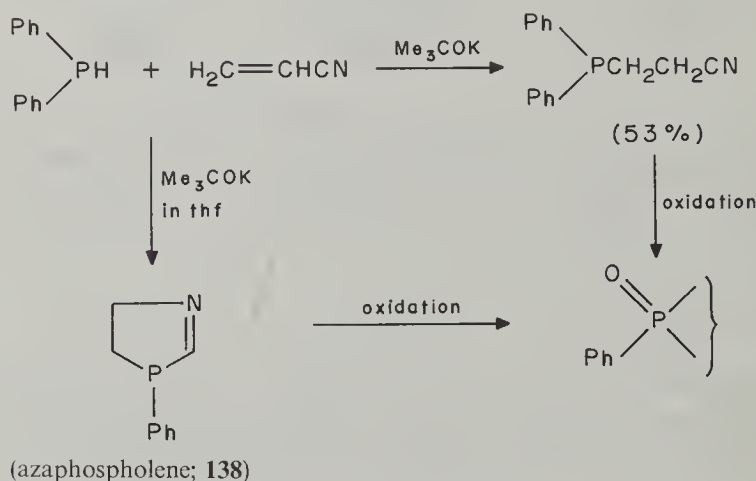
C—P bond cleavage is known in the reaction¹⁸⁰ of tertiary phosphine oxides substituted at the α -carbon by electronegative functional groups such as ethers, thioethers and carbonyl with BCl_3 to give high yields of secondary phosphine oxides. BF_3 and BBr_3 are also known to react but with a lower yield of the C—P bond cleavage products. Substituents with β -carbons also reacted but with a lower yield.

1,3-Azaphospholanes **134** are synthesized¹⁸¹ by the addition of Schiff bases, semi- or thiosemi-carbazones, to $\text{PhPHCH}_2\text{COOH}$ followed by intramolecular condensation resulting in the formation of **133**, which on treatment with LiAlH_4 ($>\text{C}=\text{O} \rightarrow >\text{CH}_2$) followed by oxidation gives **134**. Base-catalysed addition of P—H bonds to vinyl double bonds has been used by King and Cloyd¹⁸² to prepare methylated poly-tertiary phosphines **136** (reaction 11a). Thus, addition of a primary or secondary phosphine to

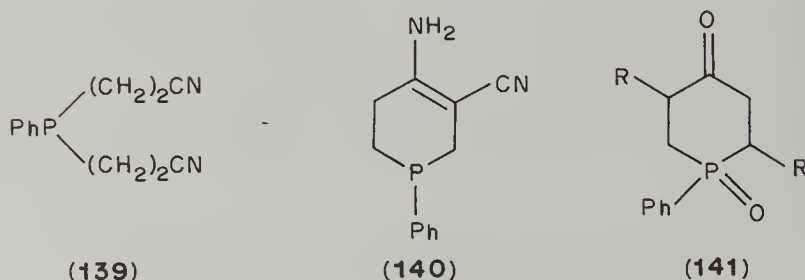


135, followed by desulphurization with LiAlH_4 in boiling dioxane solution, produced **136** ($\text{R} = \text{Me}$; $\text{R}' = \text{Ph}$; $\text{X} = \text{nil}$) (reaction 11a). Similarly, **135** reacted with PhPH_2 to give **17** ($\text{X} = \text{nil}$). Using this method, linear P-6 polyphosphines **137** and polyphosphine oxides with up to ten phosphorus atoms have been prepared. All the phosphines **17**, **136** and **137** ($\text{X} = \text{nil}$) have been oxidized⁵¹ to the corresponding phosphine oxides ($\text{X} = \text{O}$; see Section III.A.1.b for details). P—H bonds are reported¹⁸³ to add to the vinyl derivatives under mild conditions in presence of free radicals. Di-, tri- and tetra-(tertiary phosphines) have been synthesized by this method.

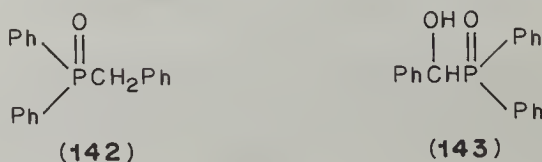
Diphenylphosphine is known to react¹⁸⁴ with acrylonitrile in two different ways, depending on the conditions (Scheme 3). The reaction of phenylphosphine with acrylonitrile gives¹⁸⁵ **139**, which on treatment with Me_3COK cyclizes to give **140**. This, on refluxing with 6M HCl followed by oxidation, gives 1-oxo-1-phenyl-4-phosphorinane **141** ($\text{R} = \text{H}$).

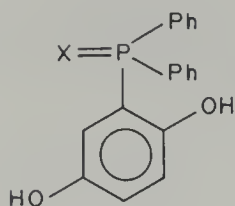


SCHEME 3. Reaction of diphenylphosphine with acrylonitrile.

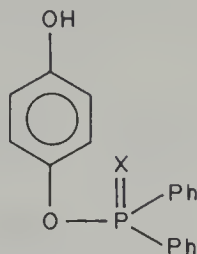


Reaction of $[\text{Ph}_2\text{P}(\text{O})]\text{M}$ (where $\text{M} = \text{Na}$, MgCl or ZnCl) with aromatic carbonyl compounds gave¹⁸⁶ different phosphine oxides **142** or **143** depending on the metal used. Compound **142** was produced with $\text{M} = \text{Na}$ or ZnCl , whereas with $\text{M} = \text{MgCl}$ **143** was produced along with benzoin and benzil. Reaction of $\text{Ph}_2\text{P}(\text{O})\text{M}$ with *p*-benzoquinone gives the phosphine oxides **144** ($\text{X} = \text{O}$) and **145** ($\text{X} = \text{O}$).



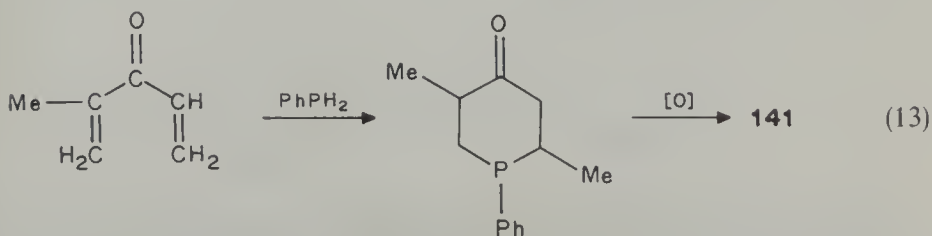
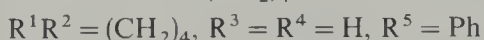
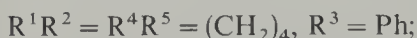
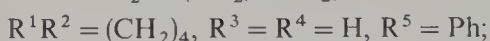
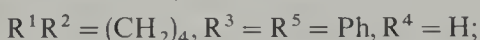
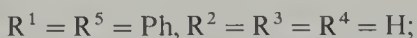
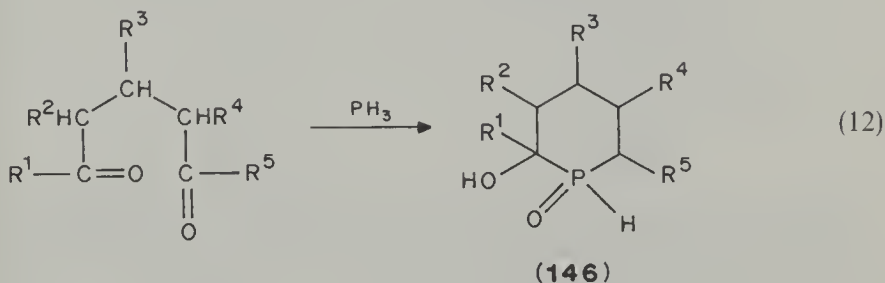


(144)

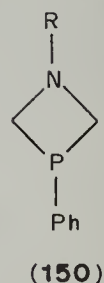
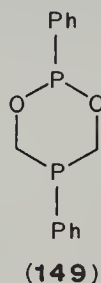
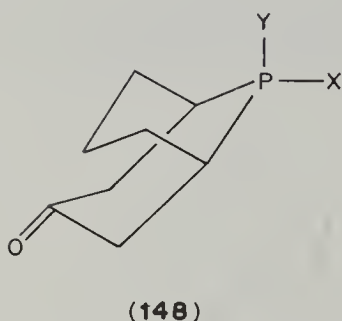
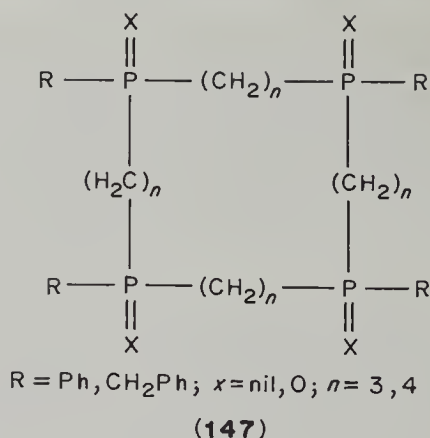


(145)

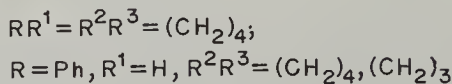
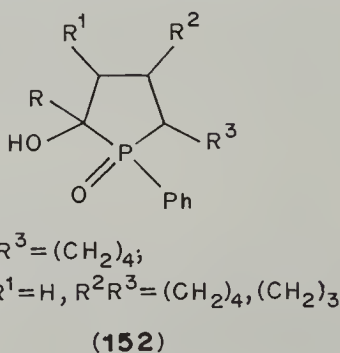
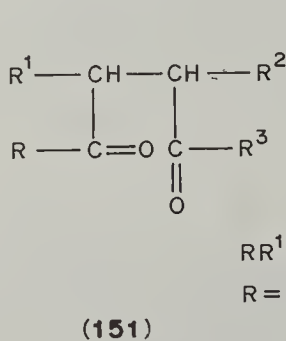
Dihydrophosphorin systems **26** are formed¹⁸⁷ by ring expansion of phospholes **25** ($R = \text{Ph}$) on reaction with $R'\text{COCl}$ ($R' = \text{Ph}$, *o*-, *m*-, *p*- MeC_6H_4 , *p*-anisyl, *p*-chlorophenyl, *p*- $\text{F/NO}_2\text{-C}_6\text{H}_4$ and 2/3-thienyl) and water. Phosphorinane oxides **146** are obtained by cyclization¹⁸⁸ of 1,5-diketones with PH_3 (reaction 12). Phosphorinane ring systems **141** ($R = \text{Me}$) are also formed by the reaction¹⁸⁹ of phenylphosphine with 1,4-dienes (reaction 13). Reaction of $R'\text{P}(\text{CH}_2\text{OH})_2$ with propylene oxide in triethylamine yielded⁵³ the phosphine oxides **5** [$R = \text{CH}_2\text{CH}(\text{Me})\text{OH}$] in 41.6–47.8% yield (see Section III.A.1.b for their oxidation).



Multi-membered oligophosphacycloalkanes **147** were prepared by Horner *et al.*¹⁹⁰ in a five-step synthesis starting from $\text{Bz}(\text{CH}_2)_n\text{Bz}$ and appropriate phosphorus compounds. Reaction of cycloocta-2,7-dienone with phenylphosphine, followed by oxidation, leads to the formation¹⁹¹ of phosphabicyclo[3.3.1]nonan-3-one-9-oxides **148** [(a) *syn* isomer, $X = \text{O}$, $Y = \text{Ph}$; (b) *anti* isomer, $X = \text{Ph}$, $Y = \text{O}$].

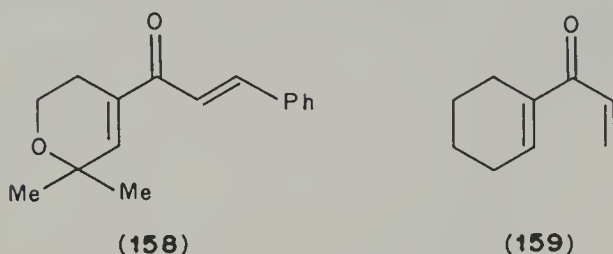
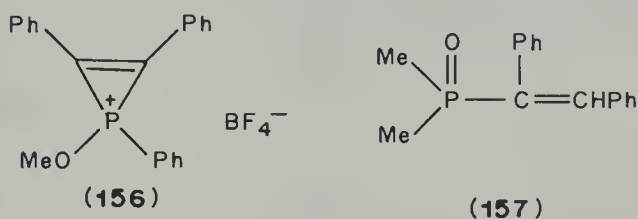
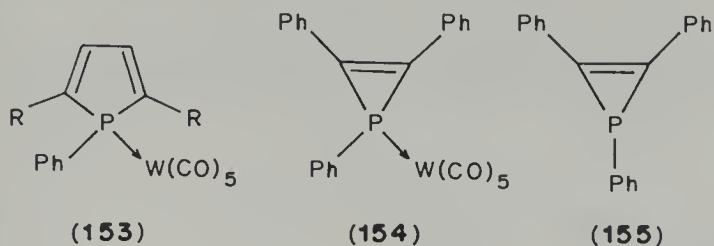


Reaction of alkenes **60** ($\text{R} = \text{R}' = \text{Me}$) with phosphorus trihalides in the presence of a catalyst results in the formation¹⁹² of a phosphetane ring, which on hydrolysis gives 1-chloro-2,2,3-trimethylphosphetane **62** ($\text{R} = \text{R}' = \text{Me}$; $\text{R}^2 = \text{Cl}$). 1,3-Azaphosphatidine systems **150** were synthesized¹⁹³ in 20–85% yield by the reaction of **149** with RNH_2 ($\text{R} = \text{Ph}, \text{PhCH}_2, \text{Br/Me-C}_6\text{H}_4$) or in 34% yield by refluxing^{193b} bis(anilinomethyl)phenylphosphine [$\text{PhP}(\text{CH}_2\text{NHPh})_2$] in ethanol for 3 h. Reaction of 1,4-diketones **151** with phenylphosphine on cyclization gives the phospholanes¹⁹⁴ **152** in 23–50% yield.

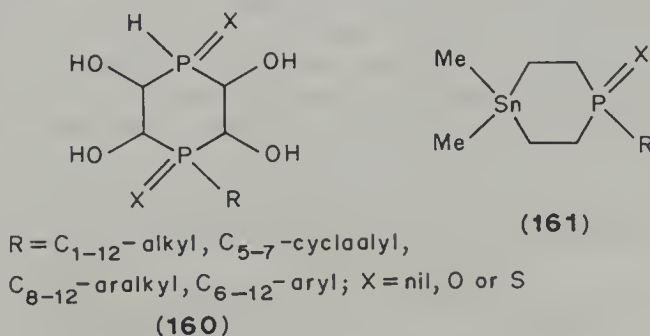


Phosphole complexes **153** ($\text{R} = \text{Ph}$) have been directly converted¹⁹⁵ into phosphirene complexes **154** by reaction with methylacetylene dicarboxylate, followed by decomplexation of **154** with iodine and *N*-methylimidazole to form **155**, which reacted with $\text{Me}_3\text{O}^+\text{BF}_4^-$ sluggishly to yield **156**. This was cleaved instantly at room temperature with neutral phosphine to give the corresponding vinyl phosphine oxide **157**. Oxaphosphabicyclodecanones (**42**; $\text{X} = \text{nil}$) are prepared⁸⁰ in 29% yield by cyclizing pyran **158** with phenyl phosphine, which on oxidation gave the oxide ($\text{X} = \text{O}$). Use of cyclohexenyl vinyl

ketone **159** (in place of **158**) in ethanol containing NaOEt gave⁸¹ **43** (X = nil) in 49% yield, which when oxidized with KMnO_4 in acetone gives the oxide (X = O).

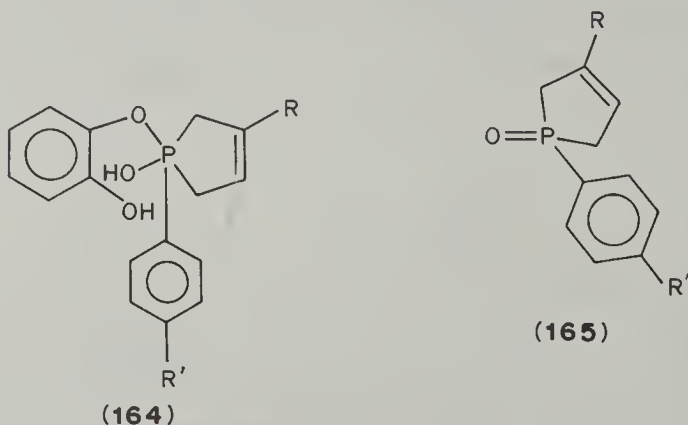
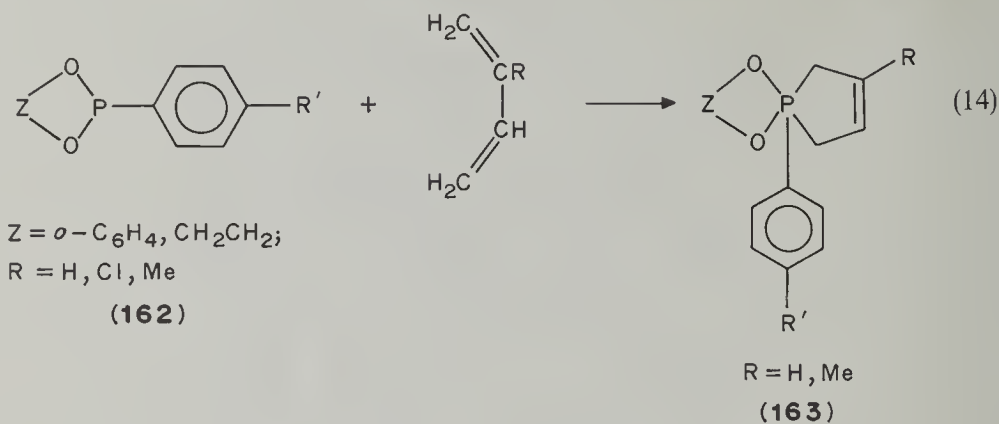


Reaction of but-2-ene and PH_3 in presence of AIBN has been reported⁴⁸ to give *sec*-butylphosphine, which is further alkylated with oct-1-ene at 80°C in the presence of AIBN to give *sec*-butyldi-*n*-octylphosphine, oxidized by H_2O_2 to its oxide. Robertson and Gallivan¹⁸ have synthesized 1,4-disubstituted 2,3,5,6-tetrahydroxy-1,4-diphosphorinanes **160** by reaction of propylphosphine in thf with 40% aqueous glyoxal, followed by oxidation with 30% H_2O_2 . Weichmann *et al.*¹⁹⁶ have reported the formation of 1-organo-4,4'-dimethyl-1,4-phosphastanninanes **161** (X = O) by the hydrostannylation of the alkyldivinylphosphine $\text{RP}(\text{CH}=\text{CH}_2)_2$ with Me_2SnH_2 , followed by oxidation.



Condensation of glycollic and pyrocatecholic esters of arylphosphonous acids (**162**) with 1,3-diene hydrocarbons is reported¹⁹⁷ to give the phospholanes **163**. Heating **163**

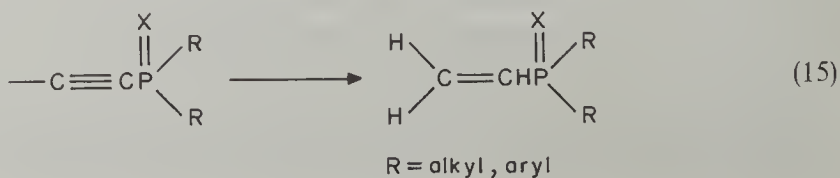
(Z = *o*-C₆H₄) with water gave the partial ester **164**, which with excess of acetyl chloride gave the phospholane **165**.



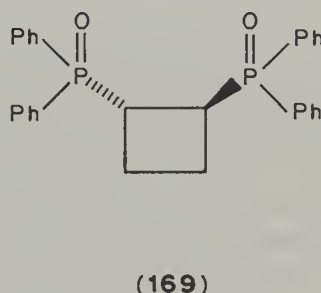
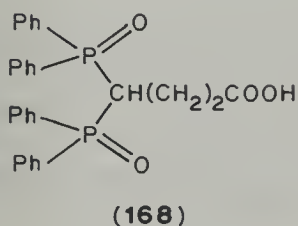
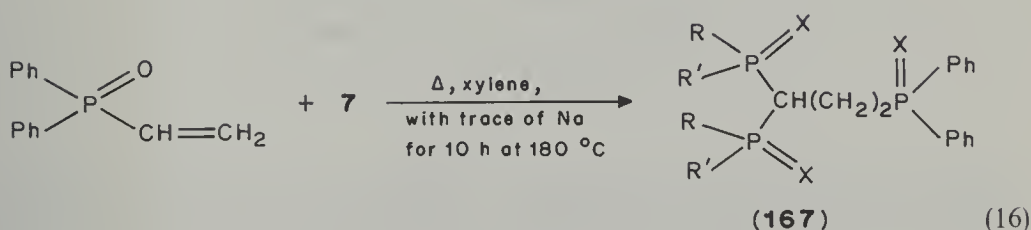
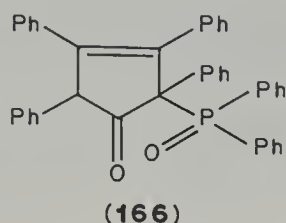
B. Reactions Involving Conversion of an Already Present P^V Nucleus

1. Through reactions of phosphine oxides.

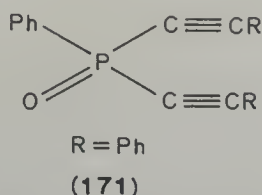
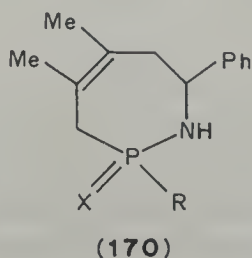
A variety of 1-(*tert*-alkynyl)-1-phosphine oxides **5** (R' = alkynyl; X = O) can be reduced¹⁹⁸ to *trans*-β-substituted vinylphosphine oxides, employing NaBH₄ as a reducing agent (reaction 15). Highly pure phosphine oxides of type **5** were prepared in high yields and short reaction times by the reaction^{199a,b} of secondary phosphine oxides with α-olefins at 130–200 °C without catalytic action, with UV irradiation or in the presence of catalysts such as *tert*-butyl peroxide (TBP) or azobis(isobutyl)diacetate (ABD) under an inert atmosphere. Thus octadec-1-ene (326 g) and TBP (0.3 g) were added within 3 h to dimethylphosphine oxide at 145 °C under nitrogen and heated for 5 minutes at 160 °C to give **5** (R' = *n*-C₈H₁₇) in 94% yield. Phosphine oxides of the type **5** have recently been prepared²⁰⁰ by the reaction of R₂P(O)H (R = alkyl, aryl) with R'hal (R' = alkyl, alkenyl, PhCH₂; hal = Cl, Br, I) in the presence of alcohols R'OH at 90–210 °C.



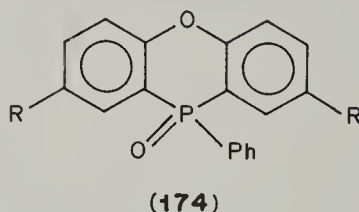
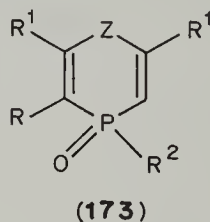
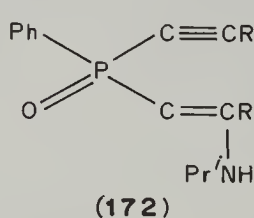
Diphenylphosphine oxide is known to react²⁰¹ with tetraphenylcyclopentadienone in the presence of dimethylamine with a 1,6-addition in which phosphorus is attached in the α -position to the carbonyl group, to give **166**. Phosphine oxides **7** (See Section III.B.3 for preparation), having an active methylene group, react²⁰² with unsaturated compounds to give new phosphine oxides **167** ($R = R' = \text{Ph}$; $X = \text{O}$) (reaction 16). Similarly **7** ($R = R' = \text{Ph}$; $X = \text{O}$) reacts with ethyl acrylate followed by alkaline hydrolysis to yield **168**.



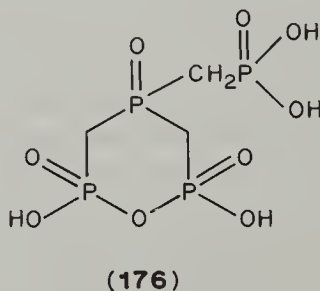
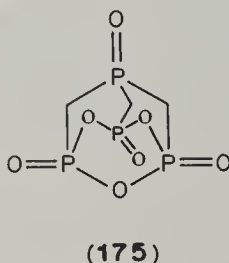
Oxidative coupling with $\text{CuCl}-\text{CuCl}_2$ of the 1,4-dicarbocations obtained from lithiation of **75** ($R = R' = \text{Ph}$; $X = \text{O}$; $n = 4$) gives²⁰³ (\pm)-*trans*-bis(1,2-diphenylphosphinyl)cyclobutane (**169**). Thus, BuLi (70 mmol) in 15% hexane is added to the phosphine oxide **75** ($R = R' = \text{Ph}$; $n = 4$) (25 mmol) in thf with cooling, then CuCl (5 mmol) is added, followed by CuCl_2 (55 mmol), and oxygen is passed through the system to give **169** in 37% yield. These compounds are useful as ligands in metal complexes.



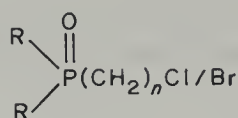
The lithium derivatives of 1-oxo-3-phospholane systems **123** ($R' = R^2 = \text{Me}$) are reported to react²⁰⁴ with benzonitrile at -70°C with the formation of a seven-membered ring, which on hydrolysis yielded azaphosphepine oxide **170** ($X = \text{O}$) in 42% yield. Diacetylenic phosphine oxides **171** ($R = \text{Ph}$; $X = \text{O}$) could be converted into **172** in 82% yield by reaction¹⁰⁵ with isopropylamine followed by acidic hydrolysis. Addition of H_2S , H_2Se , H_2Te , H_2O or H_2NEt to **171** under nucleophilic conditions also gives rise²⁰⁵ to new ring systems **173** ($R = \text{H}$; $R^1 = \text{H, Me, Me}_3\text{C}$; $R^2 = \text{Ph, cyclohexyl}$; $Z = \text{S, Se, Te, O or NEt}$) by cyclization. Compounds **172** could also be cyclized¹⁰⁵ with sodium methoxide to give oxaphosphorinanes **173** ($X = \text{O}$) in 86% yield. Dibenzooxaphosphorinane derivatives **174** are also known²⁰⁶.



Treatment of tris(chloroethyl)phosphine oxide with tertiary amines gives trivinylphosphine oxide **1** ($R = \text{CH}=\text{CH}_2$) in high yields²⁰⁷, whereas its reaction with **5** ($R = \text{Ph}$, $R' = \text{Bu}$; $X = \text{O}$) gives the tetraoxide **16** ($R = \text{Ph}$; $X = \text{O}$). Likewise, **5** ($R = \text{ClCH}_2\text{CH}_2$; $R' = \text{ClCH}_2$; $X = \text{O}$) on treatment with triethylamine yields²⁰⁸ chloromethyldivinylphosphine oxide **5** ($R = \text{CH}=\text{CH}_2$, $R^1 = \text{ClCH}_2$; $X = \text{O}$). Partial anhydrides of alkylidenephosphonylphosphine oxides (**176**), used as calcium-sequestering agents, were prepared¹⁵ from the complete anhydrides **175** by addition of sodium hydroxide solution (final pH 7.6), yielding **176** as the trisodium salt.

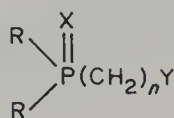


Dialkylhaloalkylphosphine oxides **177** were prepared²⁰⁹ by reaction of **178** ($X = \text{O}$; $Y = \text{OH}$) with COCl_2 or BrCOCOBr . Thus, **178** ($R = \text{Me}$; $Y = \text{OH}$; $n = 1$) on treatment with COCl_2 in CH_2Cl_2 at ca 30°C yielded the oxide ($Y = \text{halogen}$; $R = \text{Me}$; $n = 1$) in 96% yield. Tris(chloromethyl)phosphine oxide **1** ($R = \text{ClCH}_2$; $X = \text{O}$) was prepared²¹⁰ by hydrolysis of tris(acetoxymethyl)phosphine oxide **1** ($R = \text{CH}_2\text{OAc}$).



(177)

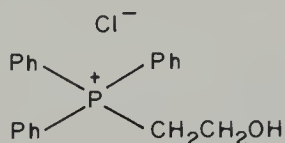
R = Me, Et, Pr, Bu;



(178)

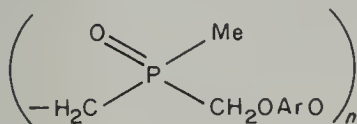
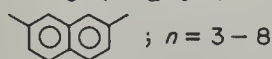
 $n = 1, 2$

Asymmetrically substituted ethylenebis(phosphine oxides) **90** (R = Bu) were synthesized in 74% yield by reaction of the halide **178** (R = Ph; $n = 2$; Y = Cl) with dibutylphosphine oxide in the presence of butyllithium²¹¹. The halide **178** in turn was prepared in 88.5% yield by refluxing the hydroxyethyl compound **178** (R = Ph; $n = 2$; Y = OH) with PCl_5 for 10 min in benzene; the hydroxyethyl compound was prepared in 59.5% yield by hydrolysing the phosphonium salt **179** with KOH.

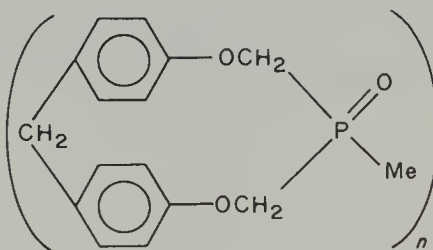


(179)

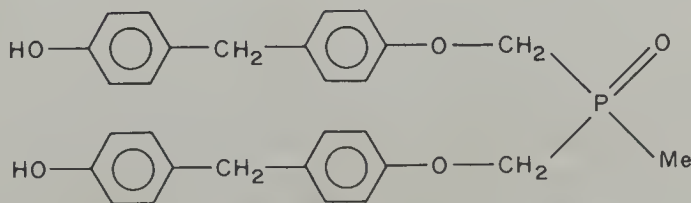
Oligomeric phosphine oxide ethers **180** or **181** are reported to be prepared²¹² by polycondensation of equimolecular amounts of methyl- or ethyl-dichloromethylphosphine oxide and disodium bisphenolates in water or xylene. Phosphine oxide ethers with terminal OH groups (**182**) were obtained by using excess of bisphenolates in the above reaction.

Ar = $p\text{-C}_6\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{-}p$, $p\text{-C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{-}p$,

(180)



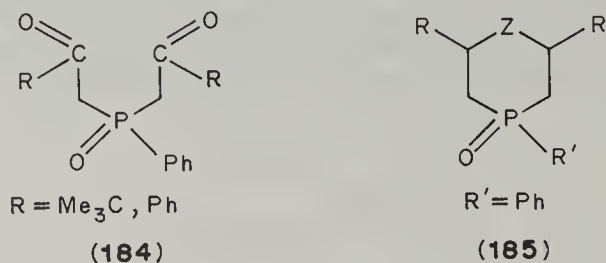
(181)



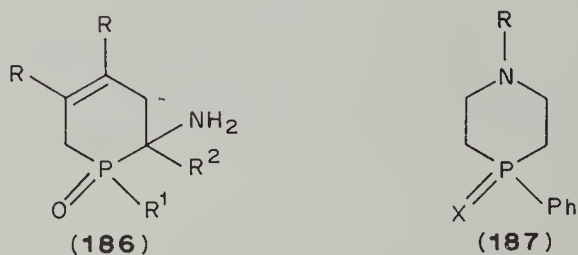
(182)

Vinyl phosphine oxides of the type **5** ($\text{R}' = \text{CH}=\text{CH}_2$) react²¹³ with dithiophosphonic acids on heating at 45–75°C in an organic solvent to give **183** (R = R' = alkyl, aryl;

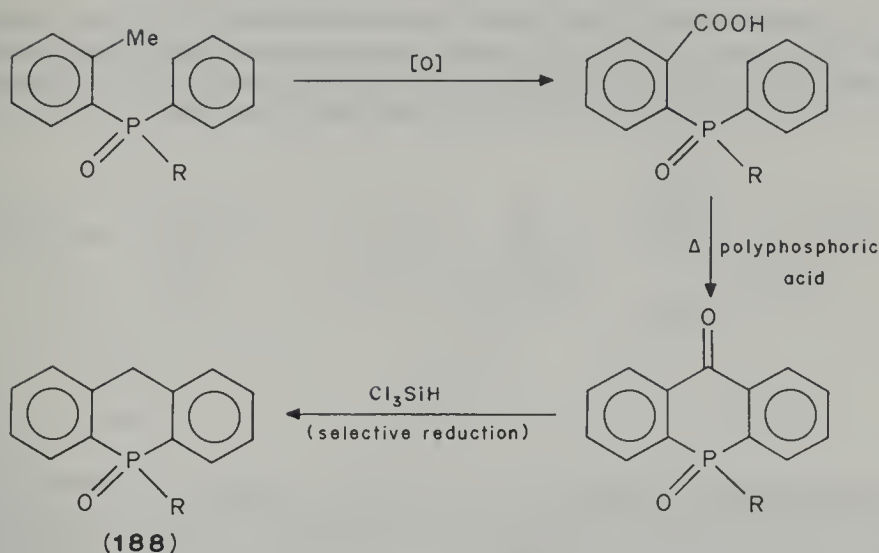
X = O) (equation 17). Heterocyclic phosphine oxides, i.e. 1,4-thiaphosphorinanes **185** (Z = S), were formed in 60–63% yields by cyclizing²¹⁴ **184** with P₂S₅.



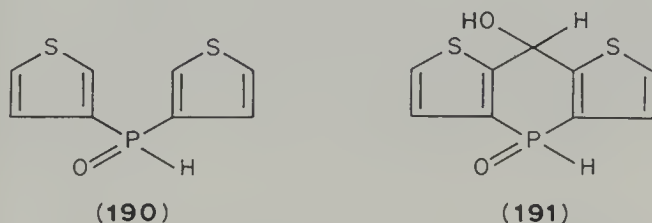
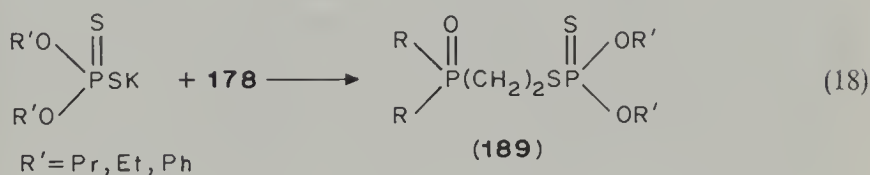
3-Phospholenes **123** are reported to react²¹⁵ with RCN to give 1-aza-2-phosphacyclohepta-4,6-dienes **169** (X = O), which undergo ring contraction to **186** (R = Me, R¹ = Ph; R² = Ph, C₆H₄NMe₂, C₆H₄N, Et₂) on treatment with HSiCl₃. 4-Phenylperhydro-1-4-azaphosphorinane-4-oxides **187** (X = O) are synthesized²¹⁶ in almost quantitative yields by refluxing divinylphosphine oxide with a 20% excess of MeNH₂ or aqueous alkylamine for 6 h. Divinylphenylphosphine oxide in turn was prepared in 72% yield by the reaction of 2 mol of vinylmagnesium bromide with dichlorophenylphosphine in thf at -70 °C. Seagull *et al.*²¹⁷ have prepared dibenzophosphorins **188** (R = Ph) starting from the phosphine oxide **5** (R = Ph, R' = *o*-tolyl; X = O) (Scheme 4).



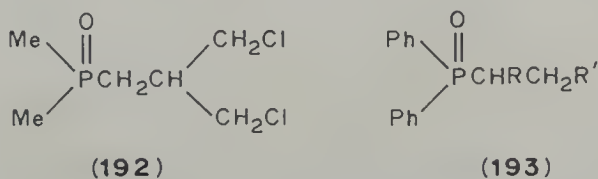
Phosphine oxides **189**, containing a dithiophosphoric acid moiety, were prepared²¹⁸ either by the reaction of alkylthiophosphoric acid with **5** (R = alkyl; R¹ = vinyl; X = O) or by the reaction of the potassium salt of dialkylthiophosphoric acid with **178** (R = Et, Ph; n = 2; Y = Cl). Bilithiation of di-3-thienylphosphine oxides **190** gave 2,2-dianions, which on treatment with esters cyclized²¹⁹ to give 1,4-dithieno-1,4-dihydrophosphorin systems **191**. Tris(trifluoroalkyl)phosphine oxides were prepared²²⁰ by electrochemical fluorination of **1** (R = C₅₋₈-alkyl) in anhydrous hydrofluoric acid. The above phosphine oxides **1** were first brominated in HF and then electrolysed in another procedure. Thus, tri-*n*-octylphosphine oxide (145 g) in HF (40 g) and bromine (180 g) on electrolysis gave tris(*n*-perfluorooctyl)phosphine oxide^{220b}.



SCHEME 4. Synthesis of dibenzophosphorin-10-ones.

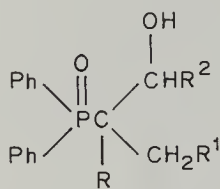


Bisphosphine oxides **136** ($R = \text{alkyl}$; $R' = \text{ethyl}$; $X = \text{O}$) were prepared²²¹ in 43–92% yields by heating the oxide **5** ($R = \text{alkyl}$; $R' = \text{vinyl}$; $X = \text{O}$) with diethylphosphine oxide in absolute xylene for between 1.5 and 5 h at 140 °C. Chloroalkylphosphine oxides **178** ($Y = \text{Cl}$; R and $n = \text{Me}$, 1; Me_2CH , 1) are prepared²²² by chlorination of the hydroxy derivative **178** ($Y = \text{OH}$) with HCl. Bis(chloromethyl)methyl- and trichloromethyl-phosphine oxides and oxide **192** were prepared similarly.

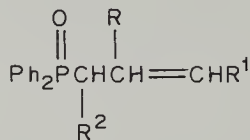


Davidson and Warren²²³ used the diphenylphosphine oxide $\text{Ph}_2\text{P}(\text{O})$ group in organic synthesis by activating a series of C—C bond-forming reactions from successive carbon

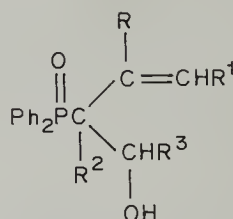
atoms by migration along a developing carbon framework. Thus, **193** reacted with $R^2\text{CHO}$ in the presence of BuLi to give **194**, the tosylate of which solvolyses in carboxylic acids, with migration of the $\text{Ph}_2\text{P}(\text{O})$ group to give **195**, which, in turn, further increases the carbon chain by reaction with BuLi and $R^3\text{CHO}$ to give **196**.



(194)

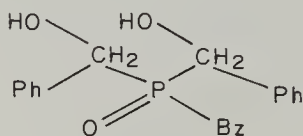


(195)

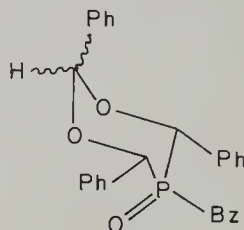


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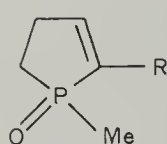
Benzylbis(α -hydroxybenzyl)phosphine oxide **197** is known to react²²⁴ with benzaldehyde to give 5-benzyl-2,4,6-triphenyl-1,3,5-dioxophosphorinane-5-oxide (**198**) (both *dl*- and *meso*-epimers). The lithio derivative of phospholene oxides **199** ($R = \text{Li}$) are reported²²⁵ to be readily carbonated to the corresponding carboxylic acid **199** ($R = \text{COOH}$). Dialkylphosphine oxides react with oxazolidine derivatives **200** to give²²⁶ the tertiary phosphine oxides **201**. Thus, **200** (30 g) was added dropwise to diethylphosphine oxide (28 g) and the mixture was heated for 1 h at 50–60 °C to give **201** ($R = \text{Et}$) in 98% yield. Bodalski *et al.*²²⁷ have synthesized 2-phospholene-1-oxide (**199**) derivatives by heating equimolar amounts of secondary benzylphosphine oxides with α,β -unsaturated compounds in thf. The reaction occurs via a 1,4-adduct, which rearranges to a carbonium ion, followed by cyclization to give the product.



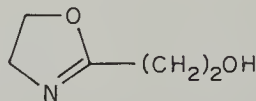
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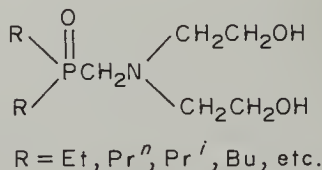
(198)



(199)

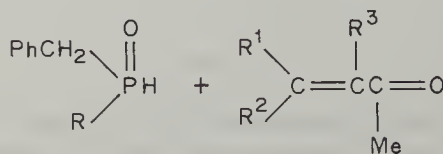


(200)



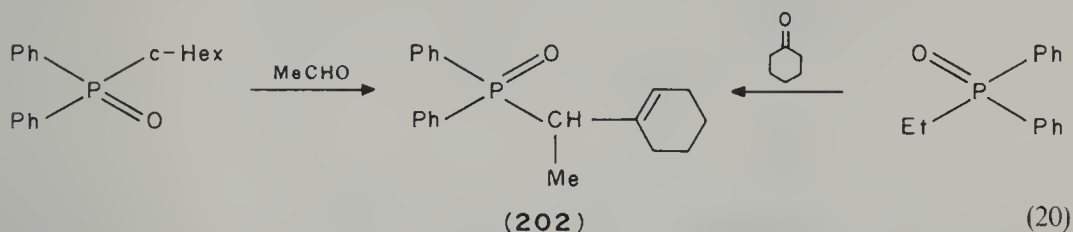
$R = \text{Et}, \text{Pr}^n, \text{Pr}^i, \text{Bu}, \text{etc.}$

(201)

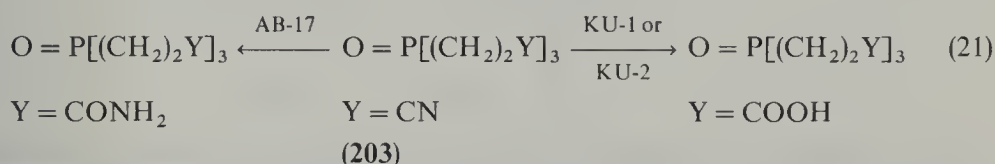


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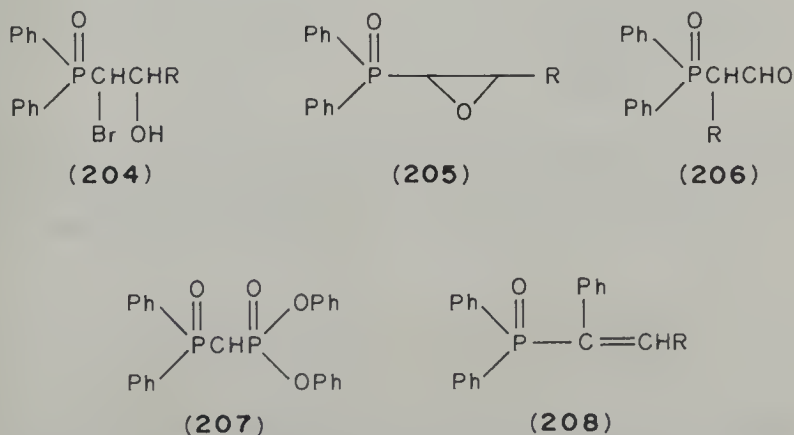
Cyclohexyldiphenylphosphine oxide is reported to react²²⁸ with acetaldehyde to give **202** in which the cyclohexyl group has migrated to the carbonyl carbon, followed by elimination of water. The same product was also obtained by the reaction of **5** ($R = \text{Ph}$; $R' = \text{Et}$; $X = \text{O}$) with cyclohexanone (reaction 20).



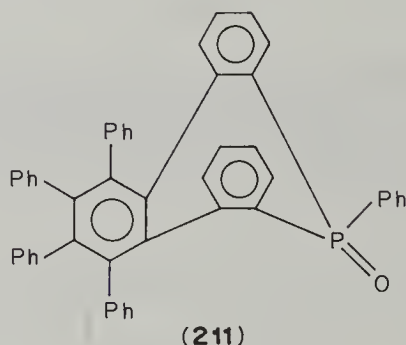
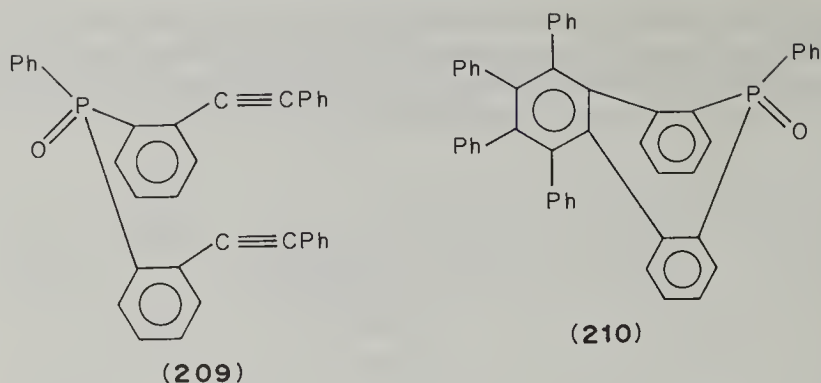
Tris(β -cyanoethyl)phosphine oxide **203** ($Y = \text{CN}$) is reported²²⁹ to be hydrolysed by heating in water at 90–95 °C in the presence of strongly acidic cation exchangers, e.g. KU-1 or KU-2, giving **203** ($Y = \text{COOH}$). However, hydrolysis at 60–65 °C in the presence of strongly basic anion exchangers, e.g. AB-17, gave 60–80% **203** ($Y = \text{CONH}_2$) (reaction 21).



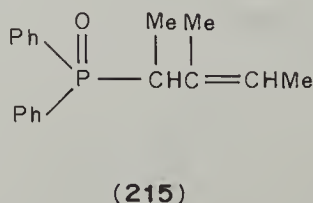
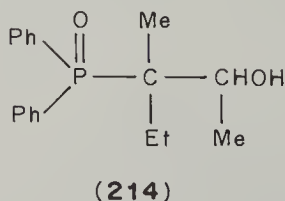
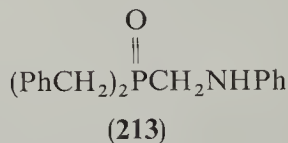
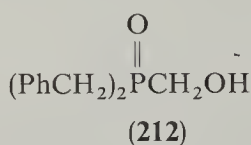
Dehydrohalogenation of **204** with KOH in hexametapal or dmf is reported²³⁰ to give oxirenes **205** in 65–70% yields, which rearrange to **206** in presence of F_3CCOOH . Reaction of phosphine oxide **207** with RCHO is known²³¹ to give 12–50% α -phosphinyl-substituted stilbenes **208** ($R = \text{Ph}$, 2,4-pyridyl, 1,2,4-quinolyl) and diphenylphosphoric acid, the size of R determining whether the product is the *cis* or the *trans* isomer. Thus, with $R = \text{Ph}$ or pyridyl the *trans* product predominates, whereas with quinolyl the *cis* isomer is the major product.



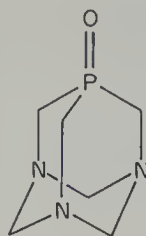
Transition metal-catalysed cyclization of **209** with tolane resulted in the formation²³² of conformationally isomeric tribenzo[*b, d, f*]phosphine oxides **210** and **211**.



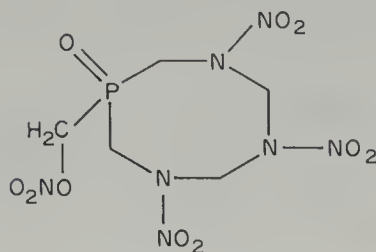
Dibenzylphosphine oxide is reported²³³ to react with formaldehyde and aniline to give **212** by heating at 60–70 or 100–110 °C, the yield depending on the ratio of the reactants and the temperature. On raising the temperature to 160–170 °C, **213** was formed, which was also obtained by the reaction of aniline with **212** at 160–170 °C. Conversion of (2-hydroxyalkyl)diphenylphosphine oxides into allyl phosphine oxides by acid-catalysed migration is also known²³⁴. Thus, **214** on refluxing in benzene for 6 h with *p*-tolylsulphonic acid gives **215** in 90% yield.



Siele²³⁵ prepared the derivative of 1,3,5,7-triazaphosphocine (**217**) by nitration, nitrosation and acetylation of 1,3,5-triaza-7-phosphaadamantane-7-oxide (**216**). Oxidation of 3-phospholines with H₂O₂ in the presence of potassium osmate is known²³⁶ to give the 3,4-dihydroxy derivative **218** (R = Me). The cycloaddition of **5** (R = Ph, R' = propynyl; X = O) with diazoalkanes is known²³⁷ to give diphenylphosphoryl-3*H*-

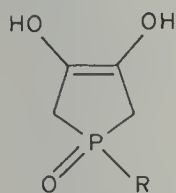


(216)

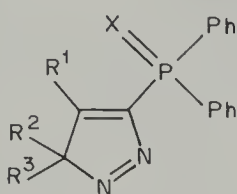


(217)

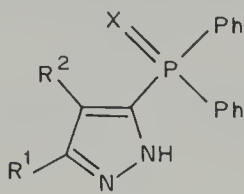
pyrazole **219** ($X = O$), which on heating in toluene or treating with chloroform at room temperature, rearranges to give **220** ($R^1 = \text{Me}$, $R^2 = \text{Ph}$; $R^1 = R^2 = \text{Ph}$). Cycloaddition of phenyl azide with diphenylpropenylphosphine oxide leads to the formation²³⁸ of triazoles **221**.



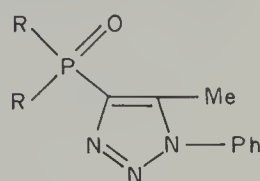
(218)



(219)



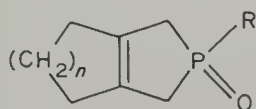
(220)



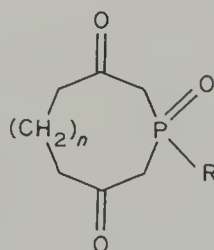
$R = \text{Et}, \text{Ph}$

(221)

Quin and Middlemas²³⁹ prepared large-ring compounds by ozonolysis of 3-phospholene derivatives **222**, bearing a cyclohexane ring fused at the double bond, when 7-9-membered heterocyclic P-rings **223** ($R = \text{Me}, \text{Ph}$; $n = 0-2$) were obtained.

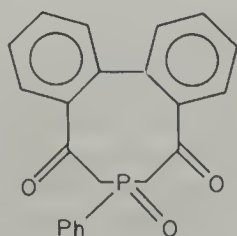


(222)

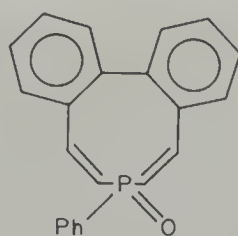


(223)

The 5,6-double bond of phenanthrene fused to a 3-phospholene oxide ring was likewise cleaved by ozone to yield a dibenzo derivative **224** of **223** ($R = \text{Ph}$; $n = 2$). This ring is non-planar and rigid. Reduction of **224**, followed by dehydration, yielded the first reported example of a phosphonin oxide, **225**.

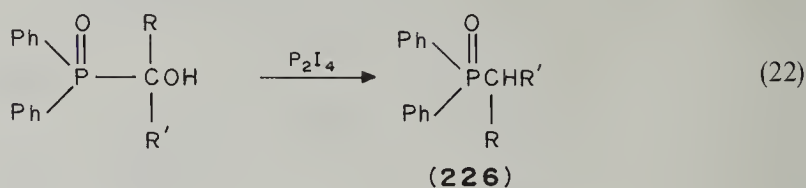


(224)

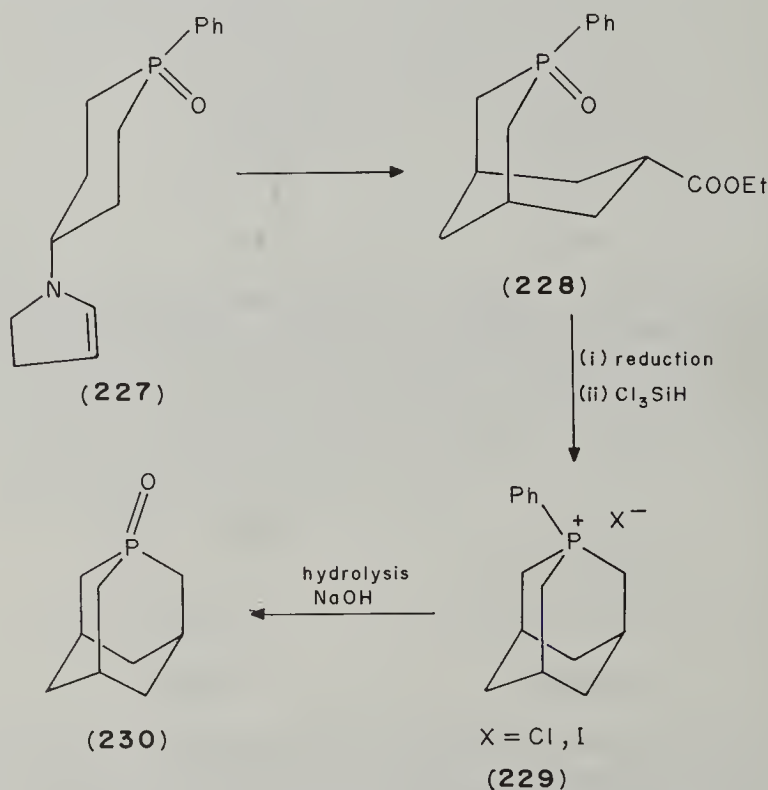


(225)

The α -hydroxy group of a phosphine oxide can be deoxygenated²⁴⁰ by reaction with diphosphorus tetraiodide, giving **226** [$R = H, Me$; $R' = Me, Et$; $RR' = (CH_2)_5$] in

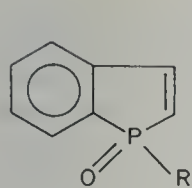


73–100% yield. The annelation reaction between 1,2,3,6-tetrahydro-1-phenyl-4-(1-pyrrolidiny)phosphorin-1-oxide (**227**) and $(\text{BrCH}_2)\text{CHCOOEt}$ resulted²⁴¹ in a mixture of two stereoisomers of the 3-phosphabicyclo[3.3.1]nonane derivative **228**. The keto function in **228** was reductively removed to give the $-\text{CH}_2\text{OH}$ group, which on cyclization followed by hydrolysis gave **230** (Scheme 5).

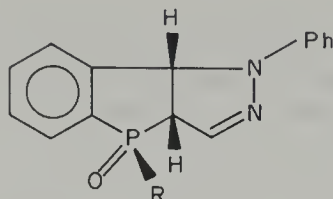


SCHEME 5. Synthesis of 1-phosphaadamantane.

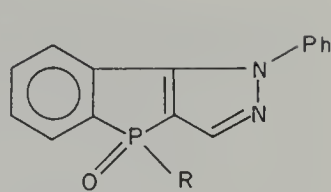
Cycloaddition of diphenylnitrilimine to phosphindole oxide **231** ($R = \text{Me}, \text{Ph}$) proceeds regio- and stereo-specifically to give²⁴² pyrazolophosphindoles **232** in 90–95% yield. Further oxidation with $\text{CuCl}_2\text{--LiCl}$ gives the oxidation product **233** quantitatively. The fulvalene ylide **234** is known to undergo²⁴³ a Stevens rearrangement on refluxing in toluene to give the spirophosphine **235** ($X = \text{nil}$) in almost quantitative yield. On oxidation this gave the oxide **236** ($X = \text{O}$). Long-chain phosphine oxides of the type **237** were prepared²⁴⁴ in 80% yields by treating chloromethyldimethylphosphine oxide with the sodium salt of **70** ($R = R' = \text{Me}$; $X = \text{O}$, $n = 0\text{--}2$).



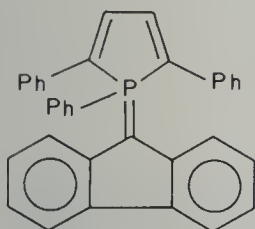
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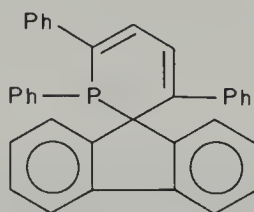
(232)



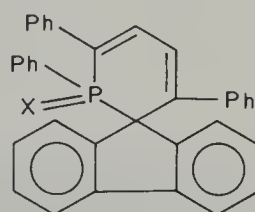
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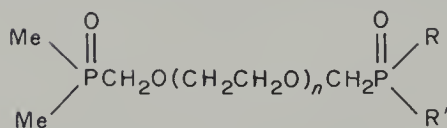
(234)



(235)

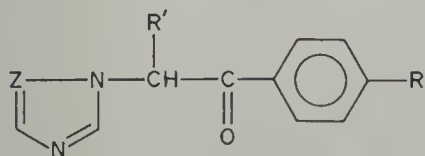


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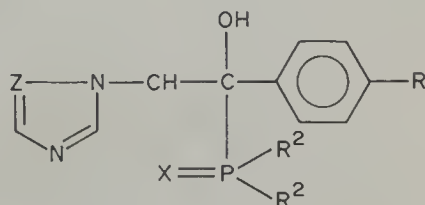
(237)

Δ^3 -Phospholenes **123** ($R' = H$) are known²⁴⁵ to be isomerized to Δ^2 -phospholenes by heating at 160–200 °C in the presence of catalytic amounts of base such as alkali or alkaline earth metal oxides, hydroxides or carbonates. Thus, **123** ($R' = Me$, $R^2 = H$) (300 g) was heated for 4 h at 180 °C in the presence of 1.0 wt% CaO to give 54% **199** ($R = COOH$). Secondary phosphine oxides react with triazolyl and imidazolyl ketones **238** to give phosphorylated alcohols **239** ($R^2 = Me$, CH_2Ph , Ph ; $X = O$) having fungicidal activity¹³. Reaction of dialkyl(4-methylaryl)phosphine oxide with paraformaldehyde or $CH_2(OMe)_2$ in concentrated HCl at 70–90 °C leads to the formation²⁴⁶ of **5** [$R = alkyl$, $R' = 3$ -(chloromethyl)-4-methoxyaryl; $X = O$]. It has been shown²⁴⁷ that chloromethylation is dependent on the substituents present in the phenyl ring. β -Carboxyethylphosphine oxides are prepared by hydrolysis²⁴⁸ of β -carbalkoxyethylphosphine oxides at 90–95 °C in the presence of a strongly acidic ion-exchange resin.



$R = H, F, Cl$; $R' = H, Ph, 1,2,4$ -triazolyl;
 $Z = N, CH$

(238)



(239)

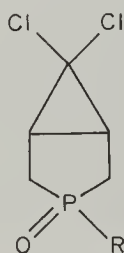
m-(Nitroaryl)dialkylphosphine oxides on reduction with PhNHNH_2 at $115\text{--}160^\circ\text{C}$ produce²⁴⁹ **5** [$\text{R} = \text{alkyl}$; $\text{R}' = m\text{-(aminoaryl)}$; $\text{X} = \text{O}$]. Reaction of **5** ($\text{R} = \text{Ph}$; $\text{R}' = \text{OMe}$; $\text{X} = \text{O}$) with acetyl chloride under a nitrogen atmosphere gives²⁵⁰ the oxide **5** ($\text{R} = \text{Ph}$, $\text{R}' = \text{Acetyl}$; $\text{X} = \text{O}$). Reaction of **177** ($\text{R} = \text{Bu}$, octyl; $n = 1$; $\text{Y} = \text{Br}$) with aldehydes produces²⁵¹ the α -hydroxy-substituted phosphine oxides **5** [$\text{R}' = \text{CH}(\text{OH})\text{Z}$, where $\text{Z} = \text{H}$, Ph or substituted phenyl]. Reaction of phosphine oxides **5** ($\text{R}' = \text{CHBr-CR}^1\text{R}^2\text{OAc}$) with an alkali metal alcoholate in an aliphatic alcohol leads to the formation²⁵² of epoxyalkylphosphine oxides **240**.



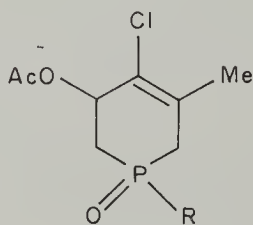
(240)

Tertiary phosphine oxides of the type **12** [R and $\text{R}^1 = \text{linear or branched } \text{C}_{1-18}\text{-alkyl, Ph}$; $\text{R}^2 = \text{CH}(\text{R}^3)\text{OCH}_2\text{R}^5$, where $\text{R}^3 = \text{H}$ or CH_2R^4 ($\text{R}^4 = \text{H}, \text{C}_{1-11}\text{-alkyl, Ph}$) and $\text{R}^5 = \text{alkyl}$] are obtained by reaction²⁵³ of the phosphine oxide **12** [$\text{R}^2 = \text{CH}(\text{R}^3)\text{OH}$; R, R^1 and R^3 as above] with halomethyl derivatives in the presence of phase-transfer catalysts. Thus, reaction of dioctylphosphine oxide with HCHO in the presence of a base gives hydroxymethyldioctylphosphine oxide. Likewise, treatment with BuBr in presence of tetrabutylammonium sulphate gives dioctyl(butoxymethyl)phosphine oxide. Diarylvinylphosphine oxides **12** ($\text{R}, \text{R}^1 = \text{Ph, tolyl}$) are formed by dehydrochlorination²⁵⁴ of **12** [R and R^1 as above; $\text{R}^2 = \text{CH}(\text{Cl})\text{Me}$; $\text{X} = \text{O}$] with alkali at $20\text{--}100^\circ\text{C}$, in a two-phase system containing 5–40% aqueous alkali in CHCl_3 or CCl_4 . Similarly, oxide **5** ($\text{R} = \text{Ph}$, $\text{R}' = \text{CH}=\text{CR}^2\text{R}^3$; $\text{X} = \text{O}$) can be prepared²⁵⁵ by condensing **178** ($\text{R} = \text{Ph}$; $n = 1$; $\text{Y} = \text{Li}$) with $\text{R}^1\text{R}^2\text{CO}$ ($\text{R}^1 = \text{R}^2 = \text{Me}$, *p*-anisyl; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H, Me, Ph}$) followed by treatment with SOCl_2 –pyridine.

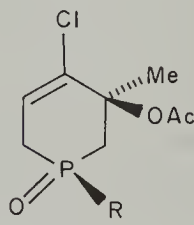
The cyclopropane ring in the dichlorocarbene adducts of alkylmethylphospholene oxides **241** ($\text{R} = \text{Me, Bu}$) can be opened up with mercury acetate–acetic acid²⁵⁶ to form the tetrahydrophosphorin oxide diastereoisomers **242** and **243**. Dibenzophosphole-5-



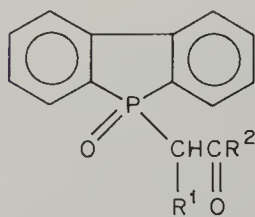
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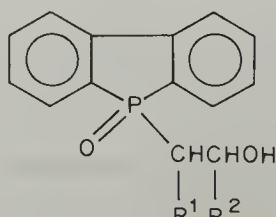
(242)



(243)

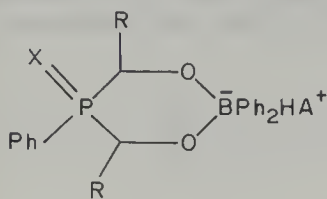


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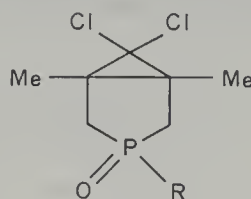


(245)

oxides containing an α -carbonyl group (**244**) [$R^1 = \text{Me, Et, (CH}_2\text{)}_2\text{OH}$; $R^1 = \text{Me, Ph, (CH}_2\text{)}_n\text{OH}$ with $n = 2, 3, 5$ and $R^2 = (\text{CH}_2\text{)}_3\text{OSiPh}_2\text{CMe}_3, 2\text{-furyl, 2-pyridyl, cyclohexyl, 3,4-methylene, dioxyphenyl}$], on reduction²⁵⁷ with NaBH_4 , give *threo*-alcohols **245**, whereas reduction with NaBH_4 , CeCl_3 or $\text{Zn(BH}_4\text{)}_2$ gives the *erythro* form of **245**.

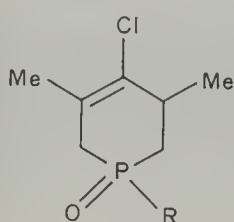


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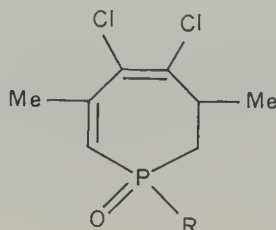


(247)

Boratadioxaphorinanes **246** ($R = \text{H}$; $X = \text{O}$) are prepared²⁵⁸ by the reaction of $\text{Ph}_2\text{BOCH}_2\text{CHMe}_2$ with **5** ($R = \text{CH}_2\text{OH, R}' = \text{Ph}$; $X = \text{O}$) in the presence of amines A ($A = \text{Pr}_2\text{NH, } p\text{-Me C}_6\text{H}_4\text{, NH}_2$). Methylphospholene-1-oxide **123** ($R = \text{Ph, R}' = \text{Me}$) reacts²⁵⁹ with dichlorocarbene in the presence of triethylbenzylammonium chloride and NaOH to give dichloromethylphosphabicyclo[3.1.0]hexane-1-oxides (**247**), which react under the same conditions to give the dihydrophosphorins **248** and phosphacyclopentatrienes **249**.

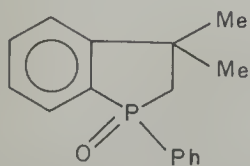


(248)

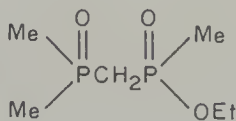


(249)

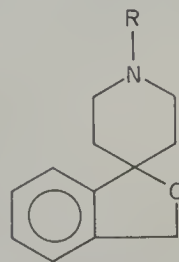
β -Hydroxyalkylphosphine oxides on acid-catalysed dehydration initially give allyl- or vinyl-phosphine oxide, which cyclise to give five- or six-membered rings. Thus, dehydration of **5** [$R = \text{Ph}$; $R' = \text{CH}_2\text{C(Me)}_2\text{OH}$; $X = \text{O}$] with H_3PO_4 (98%) initially gives the oxide **5** [$R = \text{Ph}$; $R' = \text{CH}_2\text{C(Me)}=\text{CH}_2$; $X = \text{O}$], which cyclizes²⁶⁰ to give **250**. Chloromethyldimethylphosphine oxide (200 g) reacts slowly²⁶¹ at 140°C with MeP(OEt)_2 (215 g) to give the dioxide **251**. Reaction of the former with the amine **252** ($R = \text{H}$) on heating at 100°C for 20 h in dmf containing K_2CO_3 gives²⁶² the oxide **252** [$R = \text{CH}_2\text{P(O)Me}_2$].



(250)

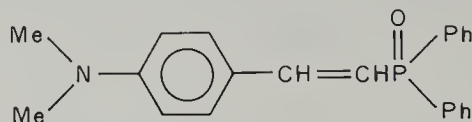


(251)

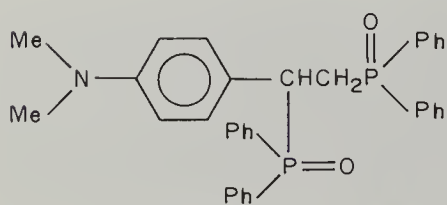


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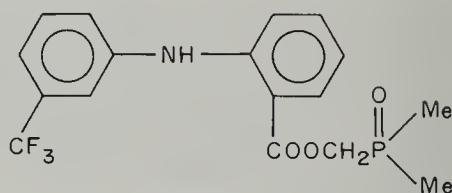
β -Nitrostyrenes react with diphenylphosphinite esters **68** ($R = R' = \text{Ph}$; $R^3 = \text{Me, Et, CHMe}_2$) in MeCN below 0°C to form 1,2-bis(phenylphosphinyl)arylethanes usually as the major product²⁶³ together with *trans*- β -styryldiphenylphosphine oxide. Thus, *p*-Me₂NC₆H₄CH=CHNO₂ produces 0.3% *trans*-**253** and 66–85% **254**. The phosphine oxide **255**, prepared by treating chloromethyldimethylphosphine oxide with the corresponding sodium carboxylate in dmf at 150°C , has anti-inflammatory properties²⁶⁴.



(253)

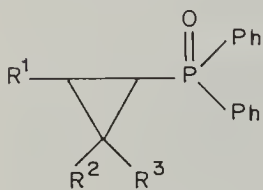


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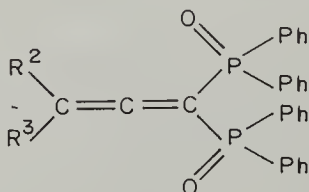


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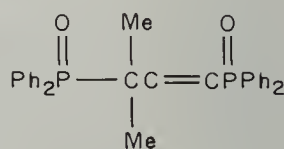
The photochemical ring opening of **219** ($X = \text{O}$) gives diphenylphosphorylvinylcarbenes via diazomethane intermediates²⁶⁵. These carbenes cyclize to give good yields of phosphorylated cyclopropenes **256**. Thus, **219** ($R^1 = \text{H}$; $R^2 = R^3 = \text{Me}$; $X = \text{O}$) produces **256** in 97% yield. Photolysis of **219** [$R^1 = \text{P}(\text{O})\text{Ph}_2$; $R^2 = \text{Me, Ph}$; $R^3 = \text{Me}$; $R^2 = R^3 = \text{Ph}$] gives **257** in addition to cyclopropenes **256**, whereas when $R^2 = \text{Me}$ and $R^3 = \text{Ph}$ it rearranges to **258**.



(256)

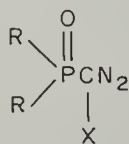


(257)

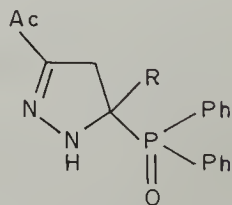


(258)

Diazomethylphosphoryl compounds **259** ($R = \text{OEt}$, $Y = \text{H}$) on lithiation give the lithiated product ($Y = \text{Li}$), which after acylation and silylation was transformed²⁶⁶ with PhCHO and chloral into an aldol-like product **260**. Bromination or iodination of **259**

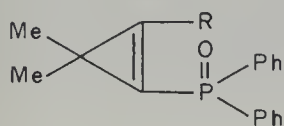


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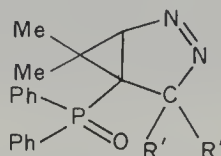


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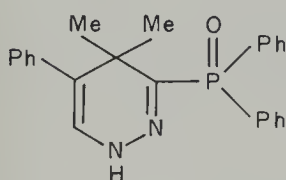
(R = alkyl, aryl; Y = Ag) with BrCN or iodine gives the halo derivative (Y = Br, Cl), which on acylation with R'COCl (R' = Me, CMe₃, Ph, β -anisyl, *P*-BrC₆H₄) gives the acyl derivative of **259** [Y = C(O)R']. Cyclopropenylphosphine oxides **261** [R = H, Me, Ph, P(O)Ph₂] undergo regiospecific reaction²⁶⁷ with diazoalkanes R'₂CN₂ (R' = Me, Ph; R'₂ = 9-fluorenylidene) to give **262**. Treatment of the cycloadduct **262** with ethanolic KOH resulted in isomerization to give 1,4-dihydropyridazines **263** and **264**.



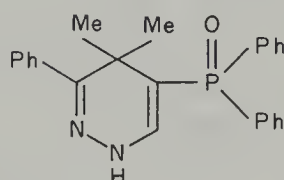
(261)



(262)

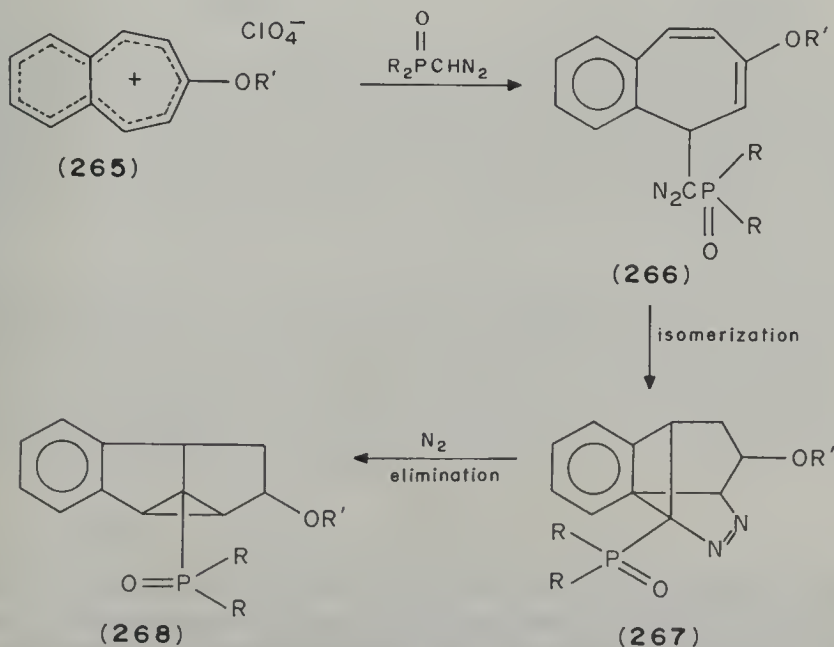


(263)



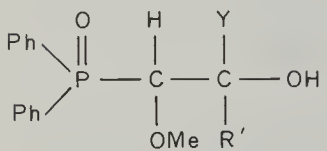
(264)

Intramolecular cycloaddition of 5-(diazomethyl)-5*H*-benzocycloheptenes **266** leads to their isomerization²⁶⁸ to **267**, which by thermal elimination of nitrogen are converted into the tetracycles **268**. Compounds **266** are prepared by electrophilic substitution by diazoalkane of 7-alkoxybenzocycloheptenylium perchlorate **265** (R' = Me, CHMe₂, CH₂Ph) (Scheme 6).



SCHEME 6. Intramolecular cycloaddition of 5-(diazomethyl)-5*H*-benzocycloheptenes.

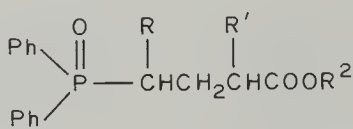
Phosphine oxides **5** [$R = \text{Ph}$, $R' = \text{CH}(\text{R}^2)\text{OMe}$, where $\text{R}^2 = \text{H}, \text{Me}$], on reaction with $\text{LiN}(\text{CHMe})_2$, give the lithium derivative [$\text{R}' = \text{C}(\text{Li})(\text{R}^2)\text{OMe}$], which reacts with aldehydes and ketones to give separable diastereoisomeric adducts. Treatment of these diastereoisomers with base gives the vinyl ether geometrical isomers, e.g. reaction of **5** ($R = \text{Ph}$, $R' = \text{CH}_2\text{OMe}$, $X = \text{O}$) with $\text{LiN}(\text{CHMe})_2$ followed by reaction with aldehydes gives²⁶⁹ the adducts **269**. Phosphine oxide **270** ($R = \text{H}, \text{Me}$; $\text{R}^1 = \text{H}, \text{Ph}$; $\text{R}^2 = \text{Me}, \text{Et}, \text{Ph}$, hexyl, cyclopropyl) undergoes acyl transfer²⁷⁰ when treated with $(\text{Me}_2\text{CH})_2\text{NLi}$ to give 73–96% **271** [$\text{Y} = \text{C}(\text{O})\text{R}^2$], which on reduction with NaBH_4 gives *threo*-alcohol **271** [$\text{Y} = \text{CH}(\text{OH})\text{R}^2$]. Horner's reaction of the dioxide **272** with $\text{RC}_6\text{H}_4\text{CHO}$ ($R = \text{H}, m-, p-\text{NMe}_2, o-, m-, p-\text{OMe}$) produces²⁷¹ 24–93% *trans*-oxide **273**.



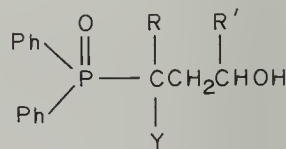
(a) $\text{R}' = (\text{CH}_2)_5\text{Me}$; $\text{Y} = \text{H}$

(b) $\text{R}' = \text{H}$; $\text{Y} = (\text{CH}_2)_5\text{Me}$

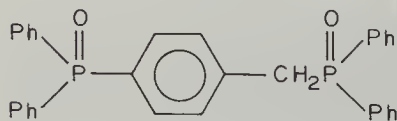
(269)



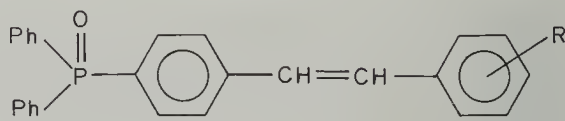
(270)



(271)

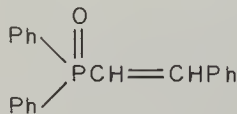


(272)

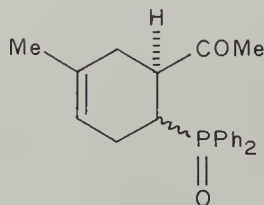
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(273)

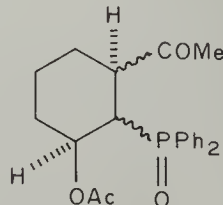
Carbonyl alkenylation of **5** [$R = \text{Ph}$, $R' = \text{CH}(\text{Li})\text{R}^2$, where $\text{R}^2 = \text{SnPh}_3, \text{PbPh}_3, \text{SbPh}_2, \text{TePh}$; $X = \text{O}$] by reaction²⁷² with aldehydes proceeds readily to give diphenylphosphoryl-substituted alkenes in high yields. Thus, benzaldehyde on reaction with **5** [$R = \text{Ph}$, $R' = \text{CH}(\text{Li})\text{SnPh}_3$; $X = \text{O}$] at -70°C in *thf* gives **274** in 92% yield. Reaction of oxide **5** ($R = \text{Ph}$, $R' = \text{CH}=\text{CHCOMe}$; $X = \text{O}$) with isoprene and acetic acid gives²⁷³ adducts **275** and **276**.



(274)



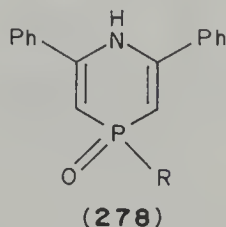
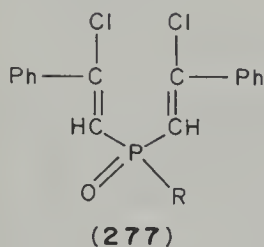
(275)



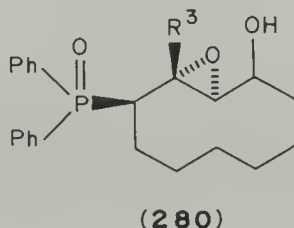
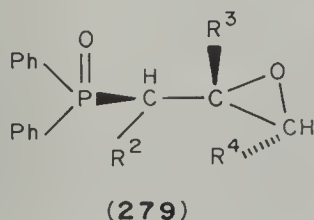
(276)

Phosphine oxides of the type **12** (R, R^1 and $\text{R}^2 = \text{hydrocarbyl}$; $X = \text{O}, \text{S}$) are prepared²⁷⁴ in two steps by the reaction of dihydrocarbylphosphine oxides (or sulphides) with alkali metal (M) amides to give $\text{R}(\text{R}^1)\text{PXM}$, followed by treatment of the latter with organic halides R^2Y . Thus, reaction of dioctylphosphine oxide with $\text{NaNH}_2\text{--NaOCMe}_3$

followed by treatment with PhBr gives **5** ($R = \text{octyl}, R' = \text{Ph}; X = \text{O}$). Triphenyl- and tribenzyl-phosphine oxides have been reported recently to react²⁷⁵ with alkali metals in liquid ammonia to give diphenyl- and dibenzyl-phosphinite ions, respectively, in high yields. These react under photostimulation with aryl halides by the $S_{\text{RN}}1$ mechanism to produce aryldiphenyl- and aryldibenzyl-phosphine oxides of the type **5**. Tribenzyl-phosphine oxide, on consecutive debenzylation with alkali metals followed by photo-stimulated reaction with aryl halides, could part with all the aromatic moieties and produce unsymmetrical triarylphosphine oxides of the type **12**. 1,4-Azaphosphorin oxides **278** ($R = \text{Ph}, -\text{C}\equiv\text{CPh}$) are prepared²⁷⁶ by cyclizing the halovinyl phosphine oxide **277** [$R = \text{Ph}(\text{Cl})\text{C}=\text{CH}, \text{Ph}$] with ammonia in dmf.



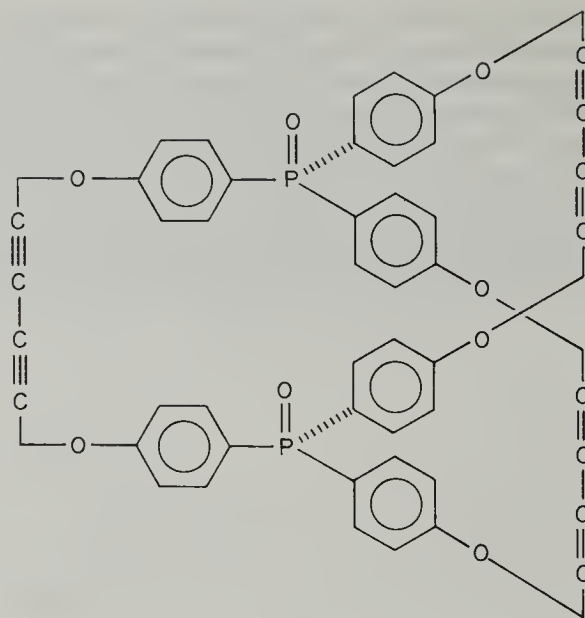
Reaction of **5** ($R = \text{Ph}, R' = \text{Et}; X = \text{O}$) with BuLi and PhCHO in thf-hexane at between -78°C and room temperature over 24 h forms (1*RS*, 2*SR*)- and (1*RS*, 2*RS*)-oxide **5** [$R = \text{Ph}; R' = \text{CH}(\text{Me})\text{CH}(\text{Ph})\text{OH}$], respectively²⁷⁷. Stereoselective peracid epoxidation of allylic and 6-hydroxyallylic diphenylphosphine oxides has been studied by McElroy and Warren²⁷⁸. Thus (*E*)-5-oxide [$R = \text{Ph}; R' = \text{CH}(\text{R}^2)\text{C}(\text{R}^3)=\text{CHR}^4$, where $\text{R}^2 = \text{pentyl}, \text{Me}, \text{Pr}; \text{R}^3 = \text{Me}, \text{Et}, \text{H}$ and $\text{R}^4 = \text{Me}, \text{Me}_2\text{CH}$] on epoxidation with *m*-chloroperbenzoic acid gives **279**. Similarly, the hydroxyallyl compound produces **280**.



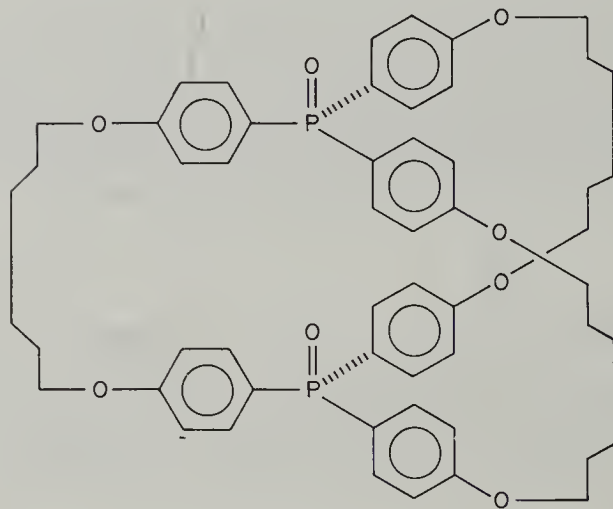
Friedrichsen and Whitlock²⁷⁹ have prepared some macrocyclic phosphine oxides (**281** and **282**) starting from the reaction of tris(4-hydroxyphenyl)phosphine oxide with propargyl bromide in acetone in the presence of K_2CO_3 . The tris(4-propargyloxyphenyl)-phosphine oxide thus obtained cyclizes in the presence of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in pyridine to give the macrocycle **281** together with its *exo-endo* isomer. On hydrogenation, **281** gives the macrocycle **282** in 47% yield whereas the *exo-endo* isomer of **281** gives the *exo-endo* isomer of **282** on hydrogenation in 53% yield.

2. Through decomposition/hydrolysis of phosphonium salts

Hexaalkyliodobis(phosphonium)pentaiodide **283a** on hydrolysis at room temperature in benzene for 1 h yields a 1:1 complex of the resultant phosphine oxide. Hydrolysis²⁸⁰ for 10 h gives **283b** in 80% yield. Oxidative degradation of the phosphonium chloride **284a** with chlorine at pH 5–7 is reported²⁸¹ to give tris(hydroxyethyl)phosphine oxide,

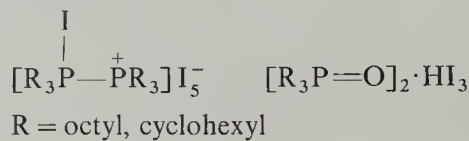


(281)



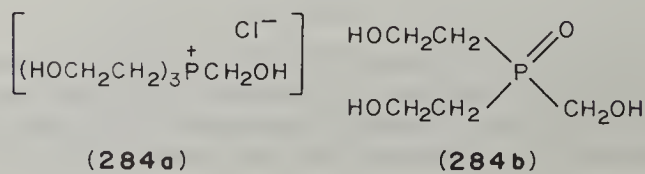
(282)

whereas at pH 1-3 **284b** is obtained.



(283a)

(283b)

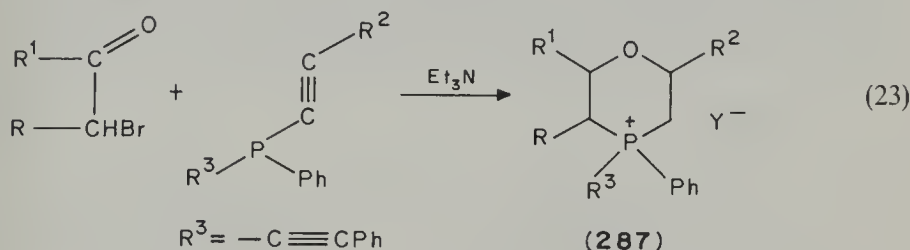


POCl_3 reacted with triethylphosphine to give the dichlorophosphoryl phosphonium²⁸² salt **285** in 80–90% yield, which on alkaline or aqueous hydrolysis was converted into the triethylphosphine oxide. Compounds **75** ($\text{R}' = \text{Ph}$; $\text{X} = \text{S}$) and **286** were similarly prepared. However, this procedure could not be applied to Ph_2PPh_2 because of steric hindrance. The phosphonium bromide obtained by heating²⁸³ the phosphine **123** ($\text{R} = \text{Ph}$, $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$; $\text{X} = \text{nil}$) with alkyl bromide ($\text{R} = \text{octadecyl}$) at 105–115 °C for 2 h under nitrogen, on treatment with aqueous Na_2CO_3 for 5 min, yielded the oxide **12** ($\text{R} = \text{methylbutenyl}$, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{octadecyl}$) by cleavage of a $\text{P}-\text{C}$ bond.

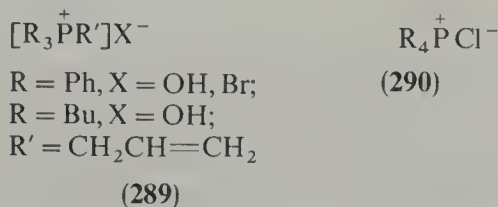
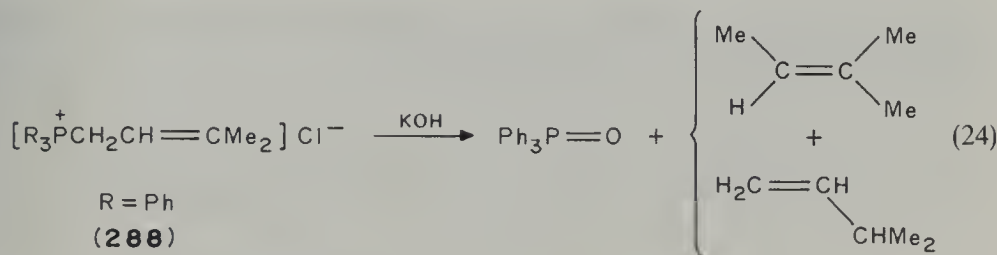


The steric course of the alkaline cleavage of phosphonium salts has been described by Luckenbach²⁸⁴. The cleavage results in more or less complete inversion of configuration at the phosphorus atom depending on the nature of the R group.

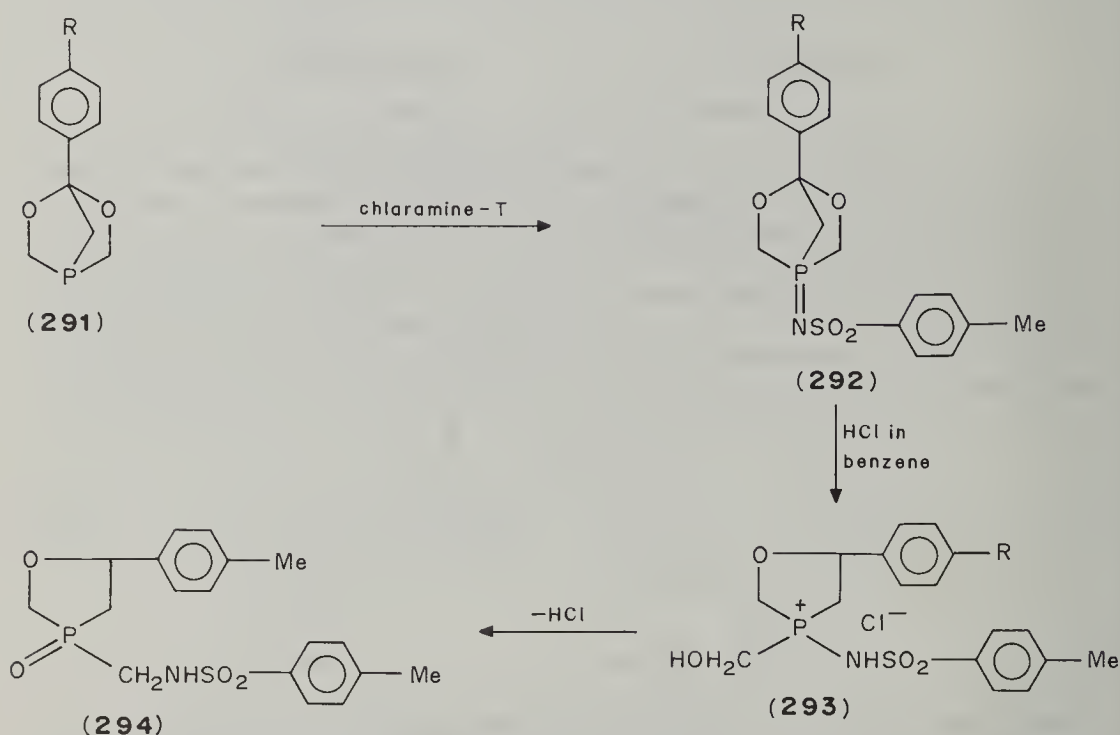
4-Phosphoniapyran salts **287** ($\text{Y} = \text{Br}$, ClO_4) on basic hydrolysis²⁸⁵ with NaOH , Ag_2O or KOH yielded 4-oxo-4-phenyloxaphosphorin systems **173** ($\text{R} = \text{Ph}$, $p\text{-NO}_2\text{C}_6\text{H}_4$; $\text{R}' = \text{PhC}\equiv\text{C}$, $\text{MeC}\equiv\text{C}$, Ph ; $\text{R}^2 = \text{H}$, Me , Ph ; $\text{Z} = \text{O}$). Compound **287**, in turn, was prepared in 55% yield by the cycloaddition²⁸⁶ of diacetylenic phosphines with α -halo ketones by stirring them together for 96 h at room temperature in the presence of Et_3N (reaction 23).



Decomposition of the phosphonium salt **288** containing a γ -methylallyl or γ,γ -dimethylallyl group results in anomalous cleavage²⁸⁷ yielding the phosphine oxide and isomeric alkenes, e.g. decomposition of **288** by aqueous KOH gave 65% of a mixture of alkenes and 70% of Ph_3PO . Analogous decomposition of **288** ($\text{R} = \text{Bu}$) gave 60%

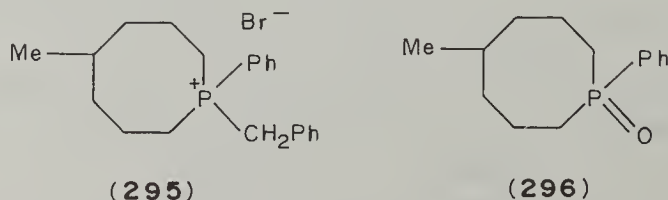


Bu_3PO and 61% of a mixture of alkenes. Similar alkaline cleavage²⁸⁸ of **289** yielded trialkylphosphine oxide and propene. Hydroxymethylphosphonium chloride **290** ($\text{R} = \text{CH}_2\text{OH}$) on reaction with aniline gave²⁸⁹ **290** ($\text{R} = \text{CH}_2\text{NHPh}$), which on treatment with Et_3N , followed by oxidation, yielded diazaphosphorinane oxide **22** ($\text{R} = \text{H}$, $\text{R}'\text{CH}_2\text{-NHPh}$; $\text{X} = \text{O}$). 1,3-Oxaphospholene oxide **294** was prepared²⁹⁰ in 61–96% yield from the oxaphospholene salt **293** by dehydrochlorination (Scheme 7); **293** in turn was prepared by treating aryl dioxaphosphabicycloheptenes **291** with chloramine-T for 2 h at 20°C , followed by treatment of the resultant **292** with 1% HCl in benzene for 24 h.



SCHEME 7. Synthesis of 1,3-oxaphospholene oxide.

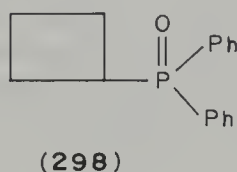
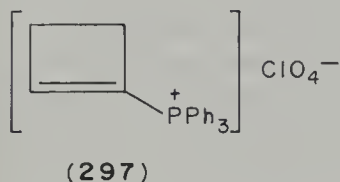
The stereochemistry of the cleavage of phosphocane derivatives **295** by alkaline hydrolysis has been shown by Marsi and Burns²⁹¹ to proceed predominantly with inversion of configuration at phosphorus to give **296**.



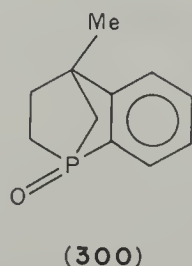
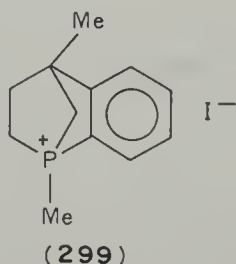
Thermal decomposition of $\{\text{R}_2\text{P}^+(\text{CH}_2\text{OH})_2\}\text{Cl}^-$ is known²⁹² to give phosphine oxide, e.g. dimethylbis(hydroxymethyl)phosphonium chloride gave 74.3% Me_3PO . Similarly, **290** ($\text{R} = \text{Me}$) on heating in a stream of air^{293a} at 80°C gave **1** ($\text{R} = \text{Me}$; $\text{X} = \text{O}$) in 83% yield. Compound **1** ($\text{R} = \text{Me}$; $\text{X} = \text{O}$) can also be obtained^{293b} by the alkaline hydrolysis of **290** ($\text{R} = \text{Me}$) with two mol equiv. of 50% aqueous NaOH . Likewise, the salts **289**

(R = Ph, Bu; R' = OCH₂CH₂Br) on hydrolysis with water or alcohol give the corresponding²⁹⁴ oxides. The phosphonium salts **289** (R = Ph; R' = 2-pyridyl, 2-quinolyl, 2-benzothiazolyl) on hydrolysis²⁹⁵ give **1** (R = Ph; X = O). Compound **289** in turn is prepared by heating Ph₃P with R'X (R' = 2-pyridyl, 2-quinolyl, 2-benzothiazolyl, 2-benzoxazolyl; X = Br, Cl, I). Compound **289** [R = Ph; R' = —C(R²)=CHR³, where R², R³ = (CH₂)_n; X = ClO₄] on hydrolysis gives²⁹⁶ **5** (R = Ph, R' = —CR²=CHR³; X = O).

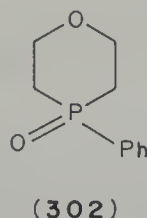
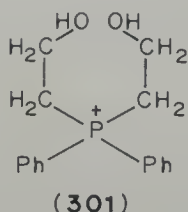
Alkylation of the phosphine **75** (R = R' = Ph; X = nil; n = 1) with PhCH₂Br in toluene at 80 °C gives the phosphonium salt, which on hydrolysis with aqueous alkali produces²⁹⁷ the phosphine oxide **75** (X = O). Hydrolysis of a solution of the phosphonium salt **297** (4 mmol) with NaOH (4 mmol) in MeOH-H₂O (2:3) for 5 h gave 1-cyclobutylphosphine oxide **298** in 80% yield²⁹⁸.

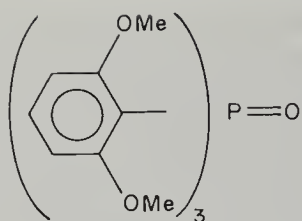


1-Phosphabicyclooctane phosphine oxides **300** are formed²⁹⁹ by treatment of the methiodide of the phosphonium salt **299** with KOH. Methane is eliminated from the molecule. Owing to the constraint of the bridgehead structure, nucleophiles attack the methiodide of 3,4-benzo derivative **299** to displace the *p*-methyl group in preference to the benzylic moiety. Such displacement of a methyl group in preference to a benzylic group is very unusual and is due to the influence of the cage structure on the reactivity at phosphorus.

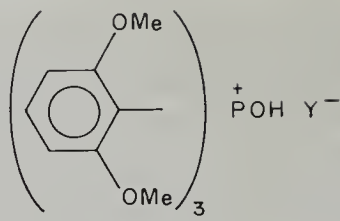


Diphenylbis(β-hydroxyethyl)phosphonium chloride (**301**) cyclizes during alkaline cleavage³⁰⁰ with NaOH to give oxaphosphorinane **302** in 75% yield. The hydroxyphosphonium salt **304**, obtained by the reaction of acids with tris(2,6-dimethoxyphenyl)-phosphine oxide **303**, is fairly stable and forms (with ClO₄⁻ salts) stable 1:1 adducts with various amines. An unexpected property of **303** is that it is highly soluble in water and reacts³⁰¹ with acids to give **304**. The phosphine oxide **303** is prepared by the oxidation³⁰² of the corresponding phosphine with H₂O₂; on treatment with HClO₄, **303** gives **304** (Y = ClO₄).





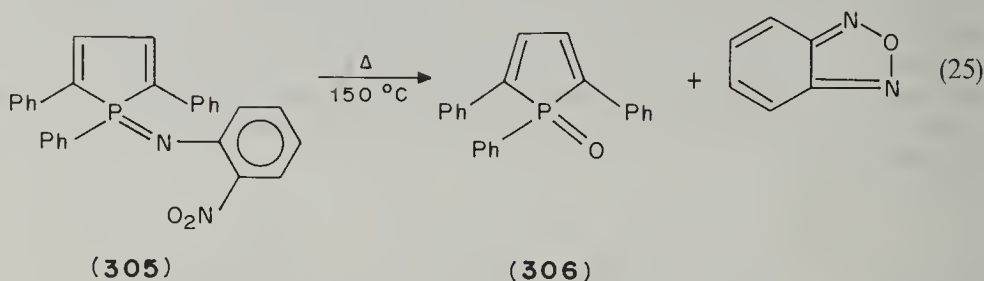
(303)

Y = ClO₄, BF₃

(304)

3. Through hydrolysis of dihalophosphoranes/imines/P=N bonds

Tetraphenylmethylenediphosphine bis(*N*-phenylimine) **7** (R = R' = Ph; X¹, X² = NPh) on reaction³⁰³ with *p*-nitrobenzaldehyde in refluxing xylene for 11 h gave the corresponding phosphine oxide **7** (X = O) in 81% yield. Thermolysis of *o*-nitroaryliminophosphole **305** at 150 °C was reported³⁰⁴ to give 1,2,5-triphenylphosphole oxide **306** and the benzofuran. The *N*-phenyl derivatives **305** in turn were prepared from the corresponding phospholes.



4. Through oxidation of phosphine sulphides/selenides

Phosphine sulphides are known⁷⁶ to be oxidized to oxides through the photochemical transfer of oxygen from heterocyclic *N*-oxides. Thus, triaryl sulphides **1** (R = *p*-R'C₆H₄, where R' = H, Me, Cl, MeO, MeOOC; X = S) were converted into the corresponding oxides (X = O) in 29–38% yields on irradiation with 3-methylpyridazine-2-oxide in dichloromethane.

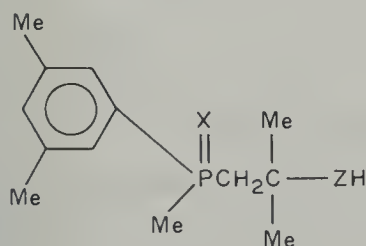
A general method for conversion of thiophosphoryl and selenophosphoryl groups into phosphoryl groups is available³⁰⁵ through ozone oxidation. For example, **12** (R = R¹ = R² = Et, Ph; X = S, Se) is quantitatively oxidized to the oxide by ozone at –75 °C. The reaction is stereoselective and proceeds with retention of configuration at the phosphorus atom.

Phosphine oxides are prepared by the reaction of dimethyl sulfoxide with phosphine sulphides in acidic solution^{306,307}. These conversions proceed with complete inversion of configuration at the central phosphorus atom. Thus, (*R*)-(+)-methylphenylpropylphosphine sulfide gives the (*S*)-(–)-oxide. Similarly, (*S*)-(–)-benzylmethylphenyl and (*S*)-(–)-methylphenyl-*t*-butyl phosphine sulphides yield the corresponding (*R*)-(+)-oxides. The dmso oxidation is catalysed by iodine³⁰⁸. Dimethyl selenoxide is also known³⁰⁹ to oxidize the thio- and seleno-phosphoryl compounds to the phosphoryl analogues. Phosphine oxides have also been prepared by the oxidation of phosphine

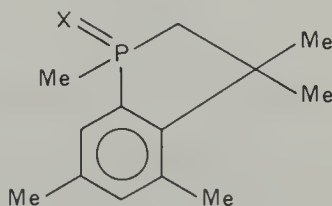
sulphides with H_2O_2 . The oxidation is carried out³¹⁰ at 40–80 °C in at least 20–50 wt% of a C_{1-6} -carboxylic acid or anhydride. Thus, bis(*p*-(chlorophenyl)phenylphosphine sulphide (18.16 g) in acetic acid (50 ml) was treated with 35% H_2O_2 (4.51 ml) at 70 °C for 30 min to give the corresponding oxide in 97% yield. The same reaction takes 12 h in methanol. H_2O_2 oxidation of sulphides can also be carried out³¹¹ in a solution containing 2–20 wt% of an optionally halogenated aliphatic carboxylic acid, e.g. when **12** ($\text{R} = \text{Me}$, $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{Ph}$; $\text{X} = \text{S}$) (25 g) is dissolved in methanol (50 g) and acetic acid (6.3 g) is added to the solution at 45–50 °C, subsequent treatment with 35% H_2O_2 (11.7 ml) gives the oxide **12** ($\text{X} = \text{O}$) in 90% yield.

Tertiary aryl phosphine oxides **5** ($\text{R} = p\text{-FC}_6\text{H}_4$, $\text{R}' = \text{Ph}$; $\text{X} = \text{O}$) are also prepared by the H_2O_2 oxidation³¹² of the corresponding sulphides ($\text{X} = \text{S}$); see Section IV.B.2 for the preparation of **5** ($\text{X} = \text{S}$). The oxidative desulphurization by H_2O_2 is also aided by the presence of inorganic acid catalysts³¹³. Thus, a refluxing mixture of phenylbis(*p*-chlorophenyl)phosphine sulphide (0.01 mol) and 32% HCl (25 ml) on treatment with 30% H_2O_2 (3.4 ml) followed by refluxing for 5 h gives the corresponding oxide in 81% yield. The stereochemistry of the oxidation of thiono- and seleno-phosphoryl compounds with H_2O_2 has been described by Stec *et al.*³¹⁴ They proceed with net retention of configuration at the phosphorus atom.

Phosphine sulphide to phosphine oxide exchange reactions are also known³¹⁵. Thus, treatment of the sulphide **307** ($\text{X} = \text{S}$, $\text{Z} = \text{O}$) with polyphosphoric acid at 140–150 °C for 4 h gives the oxide **308** ($\text{X} = \text{O}$) on cyclization, in 47% yield. Under milder conditions, i.e. on reaction with $\text{MeSO}_3\text{H}-\text{P}_2\text{O}_5$ at room temperature, the sulphide alcohol **307** ($\text{X} = \text{S}$; $\text{Z} = \text{O}$) gives the oxide thiol **307** ($\text{X} = \text{O}$; $\text{Z} = \text{S}$), which cyclizes to **308** ($\text{X} = \text{O}$) on heating with polyphosphoric acid at 145 °C.



(307)



(308)

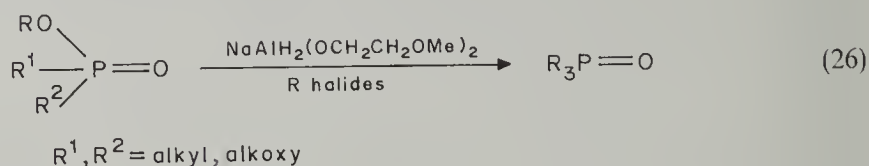
Oxidation of phosphine sulphide is also carried out using sulphuric acid or sulphonic acid at 70–200 °C in an inert aprotic solvent³¹⁶, e.g. Ph_3PS (5 g) on heating with 96% H_2SO_4 (15 ml) for 9 h at 140–150 °C and cooling, followed by extraction, gave Ph_3PO (3.8 g). Metalloporphyrins are known to catalyse³¹⁷ oxidative desulphurization/deselenation at pentavalent phosphorus. Manganese(III) mesotetraphenylporphyrin chloride in the presence of $\text{Bu}_4\text{N}^+ 10_4^-$ helps in the oxidative desulphurization, which is further aided by the presence of imidazole. Thus, Ph_3PS reacts with periodate to give the corresponding oxide in 33% yield. Addition of the manganese(III) complex increases the yield to 59% and addition of imidazole gives Ph_3PO in 81% yield. Cumyl hydroperoxide in the presence of magnesium and iron mesotetraphenylporphyrins also have been reported³¹⁸ to catalyse the oxidative desulphurization of the phosphine sulphides.

Oxidative desulphurization/deselenation at P^{V} is also known to be carried out with photogenerated peroxide species³¹⁹ such as those obtained from the photooxidation of dihexyl sulphide and diphenyldiazomethane. Thus, Rose Bengal-photosensitized oxidation of dihexyl sulphide in methanol–chloroform in the presence of Ph_3PSe or Ph_3PS gave

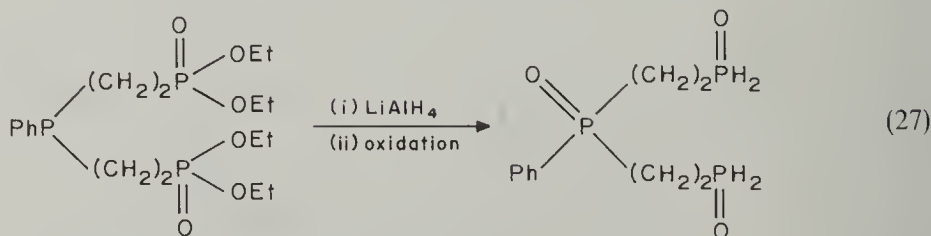
Ph_3PO in 100% and 37% yield, respectively. Baxter *et al.*³²⁰ have reported the oxidative desulphurization of Ph_3PS to Ph_3PO by irradiation in the presence of the photoinitiator $\text{RC(O)P(O)R}'_2$ in acetonitrile and oxygen for 10 h. Oxidative desulphurization of **1** ($\text{R} = \text{Ph}, \text{Bu}$; $\text{X} = \text{S}$) has also been carried out by reaction³²¹ with COCl_2 in MeCN for 24 h, to obtain the corresponding oxides ($\text{R} = \text{Ph}, \text{Bu}$) in yields of 95 and 99%, respectively. Use of CSCl_2 in the above reaction reduced the yields to 74 and 95%, respectively.

5. Through reduction of phosphonates and phosphinates

Phosphine oxides are reported³²² to be formed by the reduction of phosphonates, phosphinates and phosphate esters, with sodium bis(2-methoxy ethoxy)aluminium hydride, followed by the addition of either primary or secondary alkyl halides (reaction 26). Sodium aluminiumdiethyldihydride has also been used for the reduction of phosphorus esters³²³, followed by reaction with alkyl halides. The yields are generally comparable to those obtained by using a Grignard reaction, but the procedures involved in reaction 26 are much simpler.

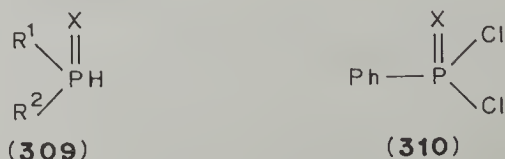


Reduction of phosphonates with LiAlH_4 is known³²⁴ to give phosphines, which could be oxidized to the oxides (reaction 27).



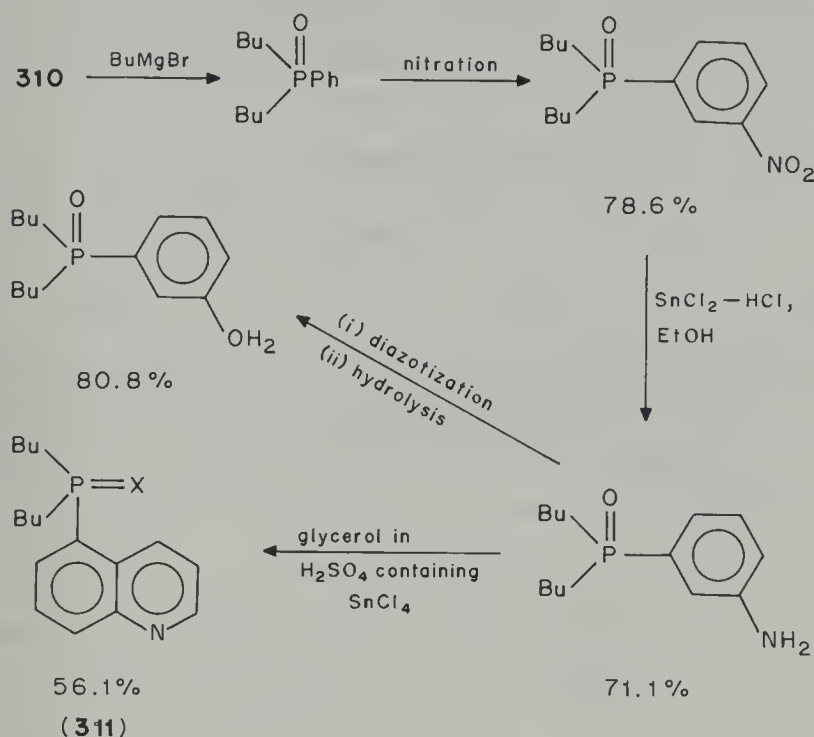
6. Through reaction of organometallics/reactive species with P^{V} halides/oxyhalides

The reaction of Grignard reagents containing tertiary aliphatic radicals with phosphonic dichlorides yields phosphine oxides **5**, **67** or **309** ($\text{X} = \text{O}$), depending on the nature of the reactants³²⁵. Tertiary phosphine oxides based on organomagnesium compounds can be prepared³²⁶ by the reaction of organomagnesium compounds with PCl_5 or its organic derivatives at 20–80 °C in an inert solvent such as benzene, followed by treatment with aqueous NH_4Cl .



Kormachev *et al.*³²⁷ converted dialkylaryl-, arylalkyl- and arylalkynyl-phosphine oxides **5** ($\text{X} = \text{O}$) into quinolinylphosphine oxide derivatives **311** ($\text{X} = \text{O}$) by a series of

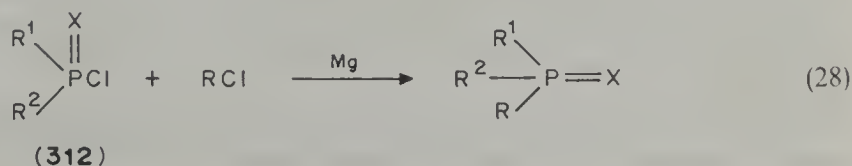
reactions involving nitration with a 26.3:71.7:2. $\text{HNO}_3\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ mixture at 60–90°C, followed by reduction of the nitro group to an amino group and Skraup's synthesis (Scheme 8). The starting oxide **5** in turn is prepared by the reaction of alkylmagnesium bromide with **310** ($\text{X} = \text{O}$), in 74.1% yield.



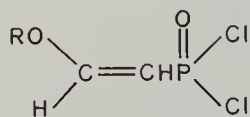
SCHEME 8. Preparation of phosphine oxides involving Skraup's synthesis.

A Grignard reaction of **312** ($\text{R}^1 = \text{Ph}$; $\text{X} = \text{O}$) with *o*-bromotoluene yields³²⁸ the starting phosphine oxide (see Scheme 4: synthesis of dibenzophosphorins), which on oxidation followed by cyclization with polyphosphoric acid gives **188**. Phosphine oxides of the type **5** are prepared¹¹⁷ by treating **312** ($\text{R}^1 = \text{R}^2 = \text{C}_{1-12}\text{-alkyl or aryl}$; $\text{X} = \text{O}$) with alkyl halides and metals, preferably magnesium, in a refluxing organic solvent, 80–90% (by volume) of hydrocarbon with b.p. > 110°C and 10–20% (by volume) of ether with b.p. > 64°C as a mixed organic solvent (reaction 28). The addition of alkyl halides and phosphorus(V) chlorides to magnesium in the organic solvent gave improved yields.

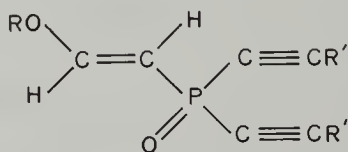
Reaction of $(\text{BrCH}_2\text{CH}_2)_2\text{POCl}$ in benzene with $\text{R}'\text{MgBr}$ (1 mol) in diethyl ether at 0–5°C (for $\text{R}' = \text{Et}$) or 30°C (for $\text{R}' = \text{Ph}$) gave the oxide **5** ($\text{R} = \text{CH}_2\text{CH}_2\text{Br}$; $\text{X} = \text{O}$), which on heating in presence of Et_3N gave the vinyl derivative ($\text{R} = \text{CH}=\text{CH}_2$) by elimination of HBr from **5**, with 50–98% yield³²⁹. Phosphine oxides of the type **1** were prepared^{19a} by Grignard reaction of POCl_3 with RCl or RBr [$\text{R} = \text{C}_{5-12}\text{-alkyl}$, PhCH_2CH_2 , $\text{Ph}(\text{CH}_2)_3$, cyclohexyl]. Thus, magnesium in diethyl ether was treated with octyl chloride in xylene for more than 1 h, followed by refluxing the product with POCl_3 for 2.5 h and hydrolysis with water, to give trioctylphosphine oxide in 80% yield.



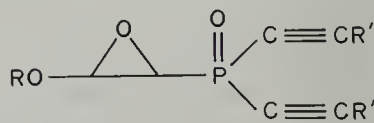
Reaction of alkylmagnesium and lithium derivatives with PCl_5 in the ratio of 3:1 has been reported³³⁰ to give R_3PO ($\text{R} = \text{Bu}, \text{Ph}$), whereas when they are in the ratio 1:4 the product is R_3P . Treatment of Ph_2PCl_3 with $\text{R}'\text{Li}$ is known³³¹ to give $\text{Ph}_2\text{PR}'\text{Cl}_2$ ($\text{R}' = \text{Et}, \text{Pr}, \text{CHMe}_2, \text{Bu}, \text{CMe}_3, \text{Ph}, p\text{-tolyl}$), which on hydrolysis yields the oxide **5**. Tertiary phosphine oxides **315** of acetylenic and diacetylenic series containing an α -epoxy ring are prepared³³² by epoxidation of **314**, which in turn is prepared by the reaction of sodium acetylide with the vinylphosphine oxide dichloride **313**.



(313)

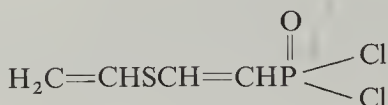


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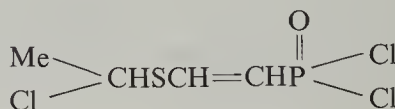


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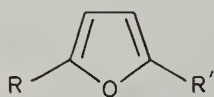
Reaction of divinyl sulphide with PCl_5 at $0-5^\circ\text{C}$ in dry benzene yielded³³³ **173** ($\text{R} = \text{R}' = \text{H}; \text{R}^2 = \text{Cl}; \text{Z} = \text{S}$) in 33.6% yield as a crystalline product, together with 10.2% of **316** and 27.8% of **317**. The reaction of 2-furyllithium **318** ($\text{R} = \text{H}, \text{Me}, \text{NO}_2; \text{R}' = \text{Li}$) with dialkyl chlorophosphates $(\text{RO})_2\text{P}(\text{O})\text{Cl}$ is known to give tris(2-furyl)phosphine oxide³³⁴ **319** ($\text{X} = \text{O}$).



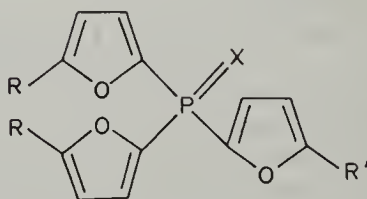
(316)



(317)



(318)



(319)

C. Miscellaneous Reactions

1. Reaction of elemental phosphorus with alkyl halides

Electrochemical reduction of yellow phosphorus in the presence of alkyl halides is reported³³⁵ to give phosphine oxides, usually mixed with other products. Thus, electrolysis of a mixture of ethyl iodide (250 g) and white phosphorus (in 150 ml of methanol) in the presence of KOH in methanol (at 60 g l^{-1} concentration) as anolyte gave 44% Et_3PO together with ethane and hydrogen. The use of sodium methoxide in place of KOH improved the yield of the oxide to 46.2%. Electrochemical reduction of phosphorus evidently occurred first, followed by reaction of the product with alkyl halide and proton.

Octyl iodide and red phosphorus is known to give³³⁶ trioctylphosphine oxide in 89% yield in trituration with iodine followed by heating for 1.5 h at $210-215^\circ\text{C}$, cooling and

treatment with aqueous Na_2SO_3 . Tris-cyclohexyl-, -hexyl-, -heptyl- and -nonyl-phosphine oxides were similarly prepared in 72, 81, 96 and 95% yields, respectively. Kirsanov *et al.*³³⁷ prepared the oxides by alkylation of red phosphorus with alkyl iodides in presence of catalytic amounts of iodine, resulting in the formation of a complex $\text{R}_3\text{P}\cdot\text{I}_3$, which was oxidized on decomposition with alcohol to give the $\text{R}_3\text{PO}\cdot\text{I}_2$ complex. This was then decomplexed by treatment with aqueous Na_2SO_3 (see also Section III.A.1.c).

Tertiary phosphine oxides with dissimilar alkyl groups have been prepared³³⁸ by treating white phosphorus with a mixture of metallic magnesium and alkyl iodides and (or) chlorides at 130–170 °C. When alkyl chlorides were used solutions of white phosphorus in these halides were added to a mixture of magnesium and alkyl halides. When alkyl chlorides with up to five carbon atoms were used, the reactions were carried out in the presence of 5 mol% of the corresponding alkyl iodides. Polyphosphine oxides have been prepared³³⁹ by treating white phosphorus at 170–200 °C with a mixture of alkyl halides or alkylene dihalides and magnesium, followed by treatment of the reaction mixture with alkali at 300 °C. In another variation of the above procedure, secondary alkylphosphine oxides were prepared by treating³⁴⁰ white phosphorus with the respective alkyl halides and magnesium or zinc at 120–210 °C, followed by alkaline hydrolysis at 270 °C.

Malovik *et al.*^{70a} have reported details of the commercial production of the oxides **1** (R = isopentyl, C_7H_{15} – C_9H_{19} , *sec*-octyl; X = O) by treatment of PI_3 with ROH . Treatment of alkyl iodides with phosphorus, catalysed by iodine, gave the intermediate $\text{R}_3\text{P}\cdot\text{I}_2$, which yielded **1** (X = O) on treatment with Na_2CO_3 . The iodine was regenerated from the aqueous solution of sodium iodide obtained from the decomposition of $\text{R}_3\text{P}\cdot\text{I}_3$ with Na_2SO_3 in the final step of the production. This regeneration^{70b} was achieved by either oxidation with NaNO_2 or reduction with sulphonates or methyl sulphate.

One-pot synthesis of phosphine oxides has also been carried out by Bornancini *et al.*³⁴¹ by reaction of elemental phosphorus with sodium in liquid ammonia when ionic species were formed, which reacted with alkyl halides (hal = Cl, Br, I) under irradiation to form **1** (X = O) by an $\text{S}_{\text{RN}}1$ mechanism, in 40–75% yield.

Trialkylphosphine oxides R_3PO (R = C_{1-6} -alkyl) have also been prepared³⁴² by the reaction of red phosphorus with alkyl iodide in presence of $[\text{IR}_3\text{PET}_3]^+\text{I}_5^-$ or I_2 as catalyst. Thus, Et_3PO is formed³⁴³ by heating a mixture of red phosphorus, EtI and $[\text{IEt}_3\text{PPeEt}_3]^+\text{I}_5^-$ at 200 °C for 8 h. This process can be further simplified³⁴⁴ by decomposing hexaalkylphosphorane phosphonium pentaide, with alcohol, followed by treatment with 40–50% alkali in the presence of 0.2–0.4 wt% of an inorganic oxidizing agent. Phosphorus and dimethyl ether, on reaction at 200–400 °C, are reported to produce³⁴⁵ Me_3PO .

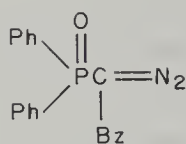
2. Photophosphorylation reactions

Irradiation of hydroxymethylphosphines **70** (R' = CH_2OH ; X = nil) under an inert gas is reported¹²⁵ to give phosphine oxides of the type **5** or **1** (see section III.3 for details).

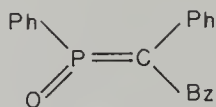
Trapping reactions³⁴⁶ of α -benzoylbenzylidenephénylphosphine **321**, generated photochemically from the diazophosphine oxide **320**, with aldehydes and ketones, e.g. with benzophenones, are known to give cyclic phosphine oxide **322** formed by $[4 + 2]$ cycloaddition, together with **323** and **324**.

1,3,4-Triphenyl-3-phospholene oxide **123** ($\text{R} = \text{R}^1 = \text{R}^2 = \text{Ph}$; X = O) on photocyclization³⁴⁷ formed the phenanthrophospholene derivative **325**, which on ozonolysis²³⁹ yielded the nine-membered ring diketone **224**. This was reduced by NaBH_4 to the diol and then dehydrated with POCl_3 -pyridine to give *cis*-*trans*-dibenzophosphonin oxide **326**, the first known example of a phosphonin oxide.

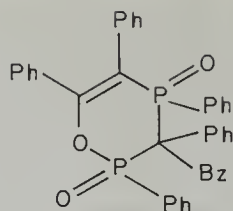
Photochemical transfer of oxygen from heterocyclic *N*-oxides to phosphine sulphides



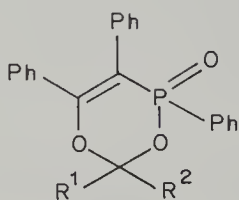
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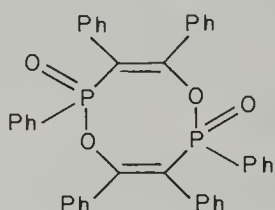
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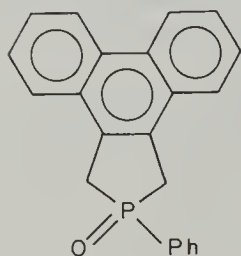
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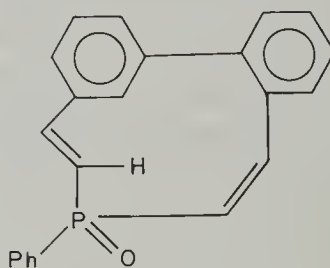
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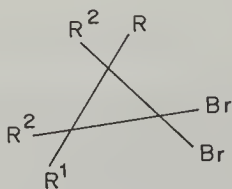


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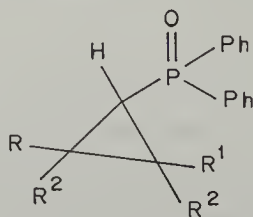


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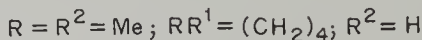
have been reported⁷⁶, e.g. the sulphides **1** ($R = p\text{-R}'\text{C}_6\text{H}_4$, where $R' = \text{H, Me, Cl, MeO, MeOOC}$; $X = \text{S}$) were converted to the corresponding oxides in 29–38% yields on irradiation with 3-methylpyridazine-2-oxide in CH_2Cl_2 . Diphenylphosphide ions react³⁴⁸ photochemically with *gem*-dibromocyclopropanes **327** in liquid ammonia or dmsO to give the phosphine oxide **328** in 38–49% yield.



(327)



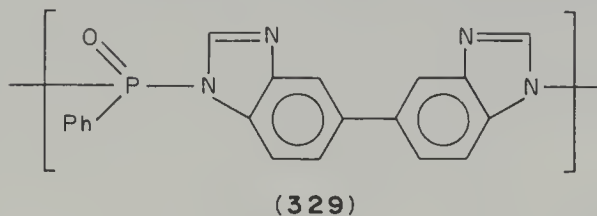
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3. Polymerization of unsaturated phosphine oxides

Vinylphosphine oxides **5** ($R' = \text{CH}=\text{CH}_2$, $R = \text{H, Me}$; $X = \text{O}$) are polymerized³²⁹ in the presence of an organomagnesium catalyst to give mouldable polymers¹⁰ with high stability. Thus, **5** ($R = \text{OCH}_2\text{CH}_2\text{Cl}$; $R' = \text{CH}=\text{CH}_2$; $X = \text{O}$) was polymerized under

nitrogen in toluene at 0°C in the presence of BuMgCl to yield a film which strongly adhered to glass. In a similar manner, **5** ($\text{R} = \text{Bu}$, $\text{R}' = \text{CH}=\text{CH}_2$; $\text{X} = \text{O}$) was polymerized in the presence of EtMgCl , Bu_2Mg or CH_2CHMgCl . Similarly, **5** ($\text{R} = \text{Ph}$; $\text{R}' = \text{CH}=\text{CH}_2$; $\text{X} = \text{O}$) and styrene react together on heating in benzene^{11a} for 6 days at 60°C in a 1:1 ratio in the presence of catalytic amounts of $\text{Me}_2\text{C}(\text{CN})\text{N}=\text{N}(\text{CN})\text{CMe}_2$ in an evacuated tube. After filtration and treatment with MeOH , a polymer was precipitated which did not burn in the open. A dark-coloured solid polymeric product with unit formula (**329**) was prepared⁹ by treating 5,5'-bisbenzimidazole with diimidazole-1-ylphenylphosphine oxide or dipyrrol-1-ylphenylphosphine oxide. These polymers are good adhesives, giving tough surface coatings. The synthesis of oligomers and polymers from phosphine oxides has been reviewed by Borisov *et al.*³⁴⁹.



Some heterocyclic phosphines are mentioned in the literature for which the corresponding phosphine oxides have not been reported. These phosphines are listed in Table 1. They should give the oxides on oxidation.

TABLE 1. Some phosphines, the oxides of which have not been reported

Name	Structure	Reference
Bicyclic phosphine		350
Phosphor-III adamantane		351
Tetraphenyleyclotetraphosphine		165
	$\text{R} = (\text{a})\text{Ph}; (\text{b})\text{Bu}'$	
1,2-Diphosphaacyclobut-3-ene		352
6-Phenyl-5-phosphaphenanthrene		164

(continued)

TABLE 1. (continued)

Name	Structure	Reference
1,5-Diaza-3,7-diphosphacyclooctane		353
1,5-Diaza-3-phosphacycloheptane		354
Azaphosphetane		193
Bicyclic C-P heterocycles		355
3-Keto-5-phenylphosphabenzenes		356
Phospha-heterocycle		357
1,2-Bis(di- <i>tert</i> -butylcyclotriphosphinyl)-3,4-di- <i>tert</i> -butylcyclotetraphosphine-P ₁₀ R ₆ type		358
Polyphosphine-P ₁₂ R ₄ and-P ₁₃ R ₅ structure type		359
Octa- <i>tert</i> -butyldodecaphosphine(8)-P ₁₂ R ₈ structure type		360

R = *tert*-butyl

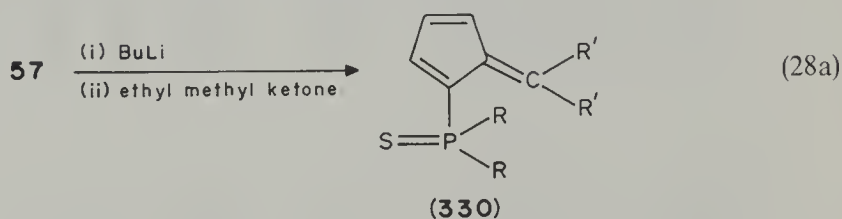
IV. METHODS OF PREPARATION OF PHOSPHINE SULPHIDES

This subject has been reviewed previously²¹⁻²⁴. Many of the general methods of preparation are common with those used to prepare the oxides. Usually the sulphides are produced more easily.

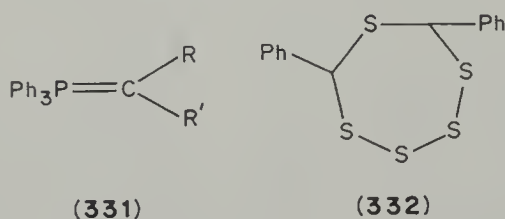
A. Reactions Involving the Conversion of P^{III} to P^V

1. Through sulphurization of phosphines

a. Through addition of sulphur. Poly(tertiary phosphine) sulphide **16** and **17** ($X = S$; see Section III.A.1.b) are prepared⁵¹ by reacting the phosphines **16** and **17** ($X = \text{nil}$) with sulphur in boiling benzene. Mathey and Lampin¹⁰⁸ prepared the diarylcyclopentadienylphosphine sulphide **57** ($X = S$; $R = \text{Ph}$) by boiling the corresponding phosphine **57** ($X = \text{nil}$; see Section III.A.2.c) with sulphur in a suitable solvent. The sulphide, on treatment with BuLi followed by treatment with ethyl methyl ketone, yielded the corresponding fulvene **330** in 20–70% yield (reaction 28a).



Some phosphines react with sulphur to produce the sulphide, as shown in Table 2. Incidentally, these phosphines, on oxidation, give phosphine oxides also. Reaction of alkylidenetriphenylphosphoranes **331** with sulphur is known³⁶⁴ to give the phosphine sulphides. When $R = \text{H}$ and $R' = \text{Ph}$ in **331**, reaction with sulphur gave the triphosphine sulphide and 1,2,3,4,6-pentathiepane (**332**).



Reaction of silylated iminodiphosphanes **333** ($X = \text{nil}$) with sulphur³⁶⁵ yielded the sulphide **333** ($X = S$), which, on hydrolysis gave the secondary phosphine sulphide **309** ($X = S$; $R^1 = R^2$) and $R_2\text{POONH}_4$. Compounds **333** ($X = \text{nil}$) were prepared by the reaction of **67** ($R = R'$; $X^1 = X^2 = \text{nil}$) with Me_3SiN_3 together with **334**.

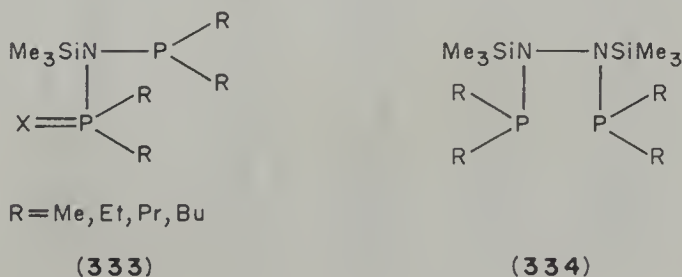
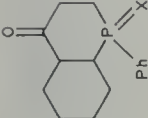
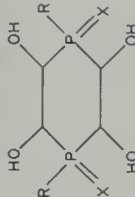

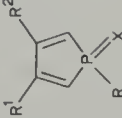
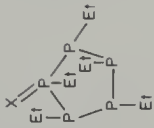
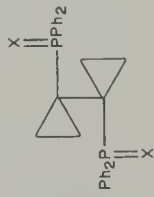
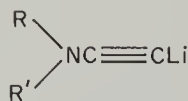


TABLE 2. List of phosphines sulphurated by reaction with sulphur

Name	Structure of the phosphine (X = nil), sulphide (X = S)	Formula No. in text	Section in text	References	Remarks
2-Bis(diphenylphosphino)methyl- pyridine		9	III.A.1.a	35	
<i>N,N</i> -Disubstituted-5-phenyl- diazaphosphorinane		22	III.A.1.b	58	
Cyclopropylidenebis(diphenyl- phosphine)		23	III.A.1.b	59	Sulphide obtained in 88% yield
Tetrakis(diphenylphosphino)allene		49	III.A.1.f	91,92	
2-Phenyl-2-phosphabicyclo[4.3.0]- nonan-5-one		11	III.A.1.a	37,36	Reaction at 40–60 °C with sulphur
Tricyclic phosphine		50	III.A.1.f	95	

Oxaphosphabicyclodecanone		42,43	III.A.6	80,81	
1,4-Diphosphorinane		160	III.A.6	18	
1,4-Phosphastanninane		161	III.A.6	196	
3,4-Dialkylphosphole		116	III.A.5	167	
Tris(trichloromethyl)phosphine	$(\text{ClCH}_2)_3\text{P}=\text{X}$	1	III.A.3	362	Heating with S at 60–80 °C in the presence of 0.2–0.6% of active carbon
Pentaethylcyclopentaphosphine		8	III.A.1.a	363	
1,1-Bis(diphenylphosphino)-bicyclopentyl		39	III.A.1.c	72	The oxide (X = O) on reduction with $\text{HSiCl}_3\text{--NEt}_3$ gives the phosphine (X = nil) which on treatment with sulphur gives the sulphide (X = S)

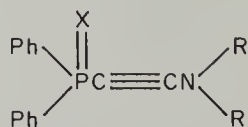
Reaction of acetylenic phosphines **336** ($X = \text{nil}$) with sulphur leads to the formation³⁶⁶ of the sulphides **366** ($X = \text{S}$); **336** ($X = \text{nil}$) in turn were prepared in 33–57% yield by the reaction of chlorodiphenyl phosphines **312** ($R' = R^2 = \text{Ph}$; $X = \text{nil}$) with the lithium derivative **335** at -10°C in diethyl ether under nitrogen. Reaction of **336** with $R^2\text{SOON}_3$ in chloroform led to the formation of a crystalline equilibrium mixture of **337** and **338** ($X = \text{S}$) by diazo group transfer.



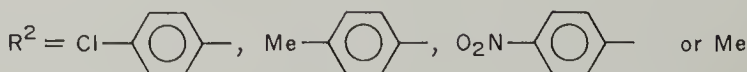
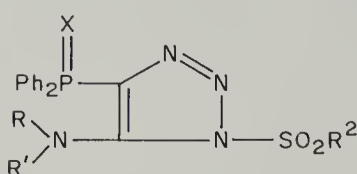
$\text{R} = \text{Et}, \text{Me}, \text{CH}_2\text{Ph}, \text{Ph}$;

$\text{R}' = \text{Et}, \text{Ph}$

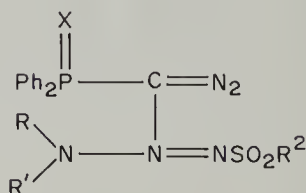
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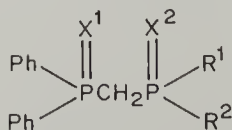


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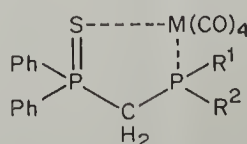


(338)

(Phosphinomethyl)phosphine sulphides **339** ($X^1 = \text{S}$; $X^2 = \text{nil}$) on reaction³⁶⁷ with sulphur give the disulphide **339** ($X^1 = X^2 = \text{S}$; $R^1, R^2 = \text{Me}, \text{Et}, \text{Ph}, \text{PhCH}_2$). The sulphide **339** ($X^1 = \text{S}$, $X^2 = \text{nil}$), on reaction with Group VI metal carbonyls, gives a complex **340** ($\text{M} = \text{Mo}, \text{Cr}, \text{W}$), with phosphorus and sulphur bonded to the metal in a six-membered chelate ring. On heating, the sulphur transfers to the more basic phosphorus atom, forming **339** ($X^1 = \text{nil}$, $X^2 = \text{S}$). Disecundary phosphine sulphides **75** ($\text{R} = \text{Ph}$; $\text{R}' = \text{H}$; $n = 2, 4$ and 6 ; $X = \text{S}$) were prepared³⁶⁸ by treating the corresponding bisphosphine **75** ($X = \text{nil}$) with sulphur. The disulphide **75** ($n = 1$; $X = \text{S}$; $\text{R} = \text{R}' = \text{Me}$) on treatment with lithium gave the lithium derivative, which on reaction with dimethylthiophosphoryl chloride **19** ($\text{R} = \text{Me}$; $X = \text{S}$) gave a novel mesomeric stabilized carbanion³⁶⁹, the tris(dimethyl thiophosphinyl)methanide **341**. Diastereoisomerically pure (–)-(Rp)-O-menthyl methyl phenylphosphinite and O-methyl ethyl phenylphosphinite underwent stereospecific alkylation with alkyl lithium ($\text{R} = \text{Pr}$) to give chiral tertiary phosphines with very high optical purity. These phosphines on sulphuration³⁷⁰ with S_8 gave (–)-S-methyl propyl phenylphosphine sulphides. Similar sulphuration was obtained with other chiral phosphines. Reaction of adamantylphosphine **342** ($X = \text{nil}$) with sulphur

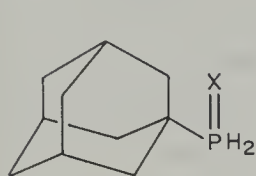
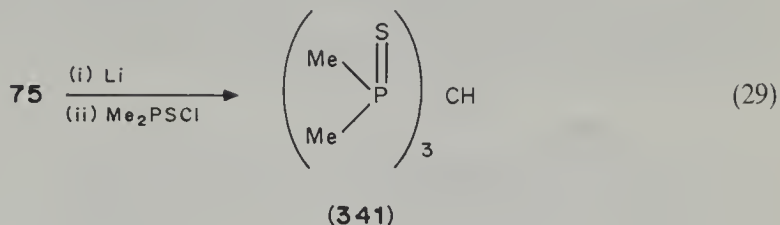


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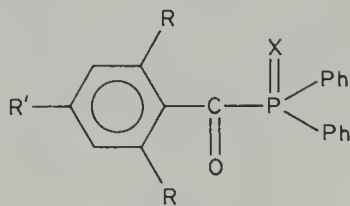


(340)

at 85–90 °C gives the corresponding sulphide³⁷¹ **342** (X = S). Acylphosphine sulphides **343** (X = S), used as photoinitiators, are formed by the reaction³⁷² of sulphur with the phosphine **343** (X = nil; R = MeO; R' = H).

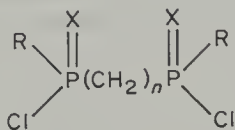


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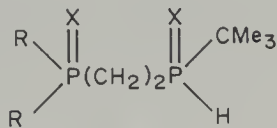


(343)

1-*tert*-Butylphosphinoethane derivative **345** (R, R' = Ph; X = nil) and bis-*tert*-butylphosphinoethane **345** (R = Bu'; R' = H; X = nil) on reaction³⁷³ with sulphur give the corresponding sulphides **345** (X = S). The bisphosphine **345** (R = Bu'; R' = H; X = nil) is prepared by the reaction of *tert*-butylmagnesium chloride with halophosphine **344** (R' = Cl; n = 2; X = nil), when one chlorine on each phosphorus is replaced by a CMe₃ group. This on reduction gives **345** (X = nil; R = CMe₃; R' = H). The diphenylphosphinoethane derivative **345** (R = R' = Ph; X = nil) is prepared by treatment of the lithium derivative of the *tert*-butylphosphine LiP(H)CMe₃ with **178** (x = nil; R = Ph; n = 2; Y = Cl).

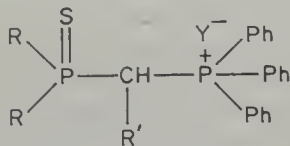
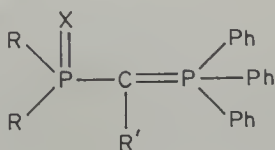


(344)



(345)

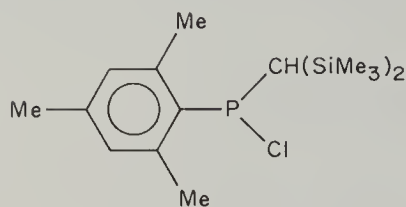
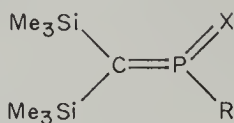
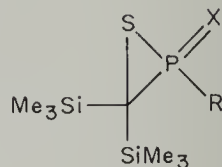
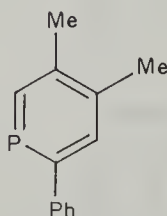
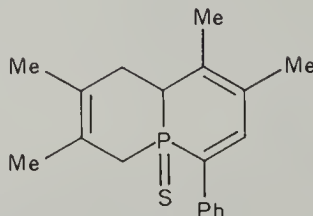
The sulphides **346** (X = S), produced in 53–59% yield by reaction of sulphur on the phosphine **346** (X = nil), showed triad thiophosphorylmercapto ylide tautomerism (S=P—CH ⇌ HS—P=C) on reaction³⁷⁴ with halogen acids HY (Y = Cl, Br), yielding the corresponding phosphonium salt. The above tautomerism is dependent on the nature of the substituents on the central carbon atom.



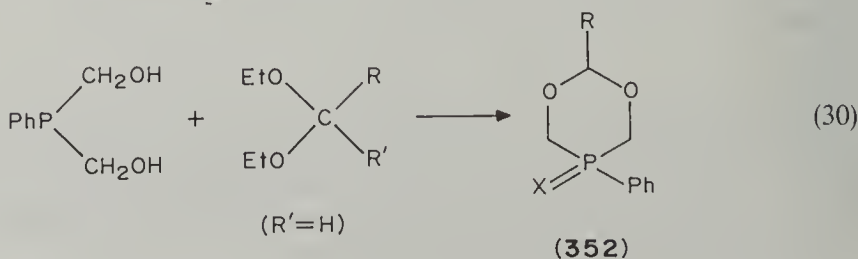
R = Bu, Ph; R' = —O₂SC₆H₄Me-*p*, COOMe

(346)

The methylene phosphine **348** ($X = \text{nil}$) is smoothly oxidized³⁷⁵ by elemental sulphur to the three-membered ring sulphide **349** ($X = \text{S}$). The phosphine **348** ($X = \text{nil}$) is prepared³⁷⁶ by dehydrohalogenation of **347** ($R = \text{mesityl}$) with 1,8-diazabicyclo[5.4.0]-undec-7-ene. Alcaraj and Mathey³⁷⁷ prepared a bicyclic C-P heterocyclic phosphine sulphide (**351**) by the reaction of 2-phenyl-4,5-dimethylphosphorin (**350**) with S_8 , followed by cycloaddition with 2,3-dimethylbutadiene.

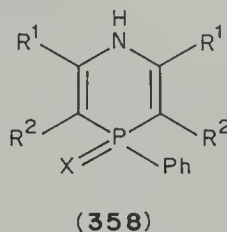
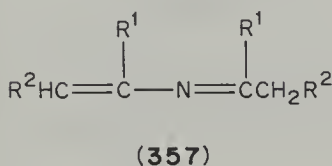
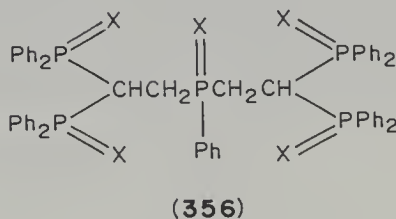
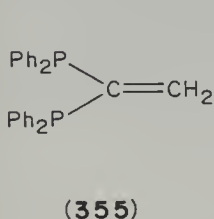
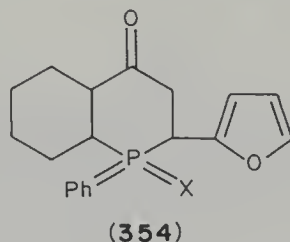
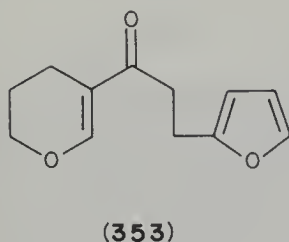
**(347)****(348)****(349)****(350)****(351)**

5-Phenyl-1,3-dioxaphosphorinane systems **352** ($X = \text{nil}$), on reaction with sulphur³⁷⁸, gave the 5-thio derivatives **352** ($X = \text{S}$). The phosphines **352** ($X = \text{nil}$; $R = \text{furyl, Me, Ph}$) were prepared in 7.3–41% yield³⁷⁹ according to equation 30. Alkyl bis(trifluoromethyl)phosphine sulphides of the type **5** ($R = \text{CF}_3$; $X = \text{S}$), used as reference standards in gas chromatography, are prepared by sulphuration³⁸⁰ of the corresponding phosphines ($R = \text{CF}_3$; $R' = \text{C}_{1-30}\text{-alkyl}$; $X = \text{nil}$). These in turn may be prepared by the reaction of halobis(trifluoromethyl)phosphine with RMgBr .



2-Thio-2-phosphabicyclo[4.4.0]decanone sulphide **354** ($X = \text{S}$) is formed³⁸¹ by reaction of the phosphine **354** ($X = \text{nil}$) with sulphur. The phosphine in turn is prepared by cycloaddition of phenylphosphine with furan derivative **353**. Progressive reaction of bis2,2-bis(diphenylphosphino)ethylphenylphosphine **356** ($X = \text{nil}$) with sulphur gives³⁸² the corresponding sulphide **356** ($X = \text{S}$). The phosphine, in turn, is prepared in 85% yield, through the potassium *tert*-butoxide-catalysed reaction of the phosphine **355** with phenylphosphine. 1,4-Dihydroazaphosphinine sulphides **358** ($X = \text{S}$) are formed on reaction of S_8 with the phosphinines **358** ($X = \text{nil}$). These in turn are synthesized³⁸³ in

75–85% yield by the cyclocondensation of dichlorophenylphosphines with 2-aza-1,3-dienes **357** ($R' = \text{Ph}$; $R^2 = \text{Me, Et, Pr}$) in hexane followed by hydrolysis. Thus, reaction of **357** ($R' = \text{Ph}$; $R = \text{Me}$) with PhPCl_2 in the presence of Et_3N gave 1,4-dihydro-³-azaphosphinines **358** ($X = \text{nil}$).

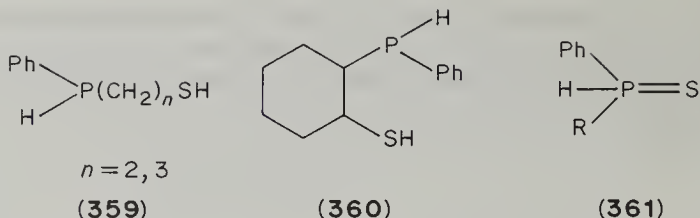


b. Through addition of sulphides/SO₂. Chan and Goldwhite³⁸⁴ reported the formation of trimethyl sulphide from the corresponding phosphine by reaction with SO₂. However, some phosphine oxide is also produced in the reaction. Generally, fully oxidized acid is formed when the primary and secondary phosphines react with SO₂. Thus, phenyl- and diphenyl-phosphines give $\text{PhP}(\text{O})(\text{OH})_2$ and $\text{Ph}_2\text{P}(\text{O})\text{OH}$, respectively.

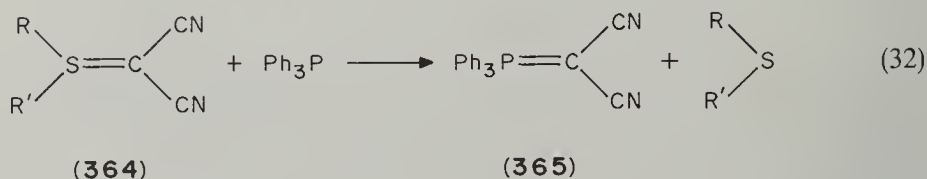
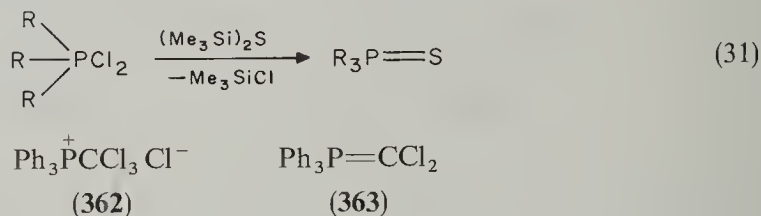
POCl_3 adducts of R_3PO ($R = \text{alkyl, aryl}$), on reaction with Ag_2S at 120–150 °C, give the corresponding tertiary phosphine sulphides³⁸⁵. The adducts are formed by reaction of POCl_3 with R_3PO in the molar ratio 1:2–3.

c. Through sulphur transfer agents. Trialkyl- and triaryl-phosphines **1** ($R = \text{Et, Ph}$; $X = \text{nil}$) and bisphosphines **75** ($n = 0, 1, 2$; $R' = \text{Ph}$; $X = \text{nil}$) are known to be converted²⁸² into the corresponding sulphides ($X = \text{S}$) in yields of 70–90%, through direct sulphur transfer by reaction with PSCl_3 . The 1:1 adducts with thiourea diethylazodicarboxylate are also known³⁸⁶ to convert Ph_3P to its sulphide (in the process being itself converted to carbodiimides).

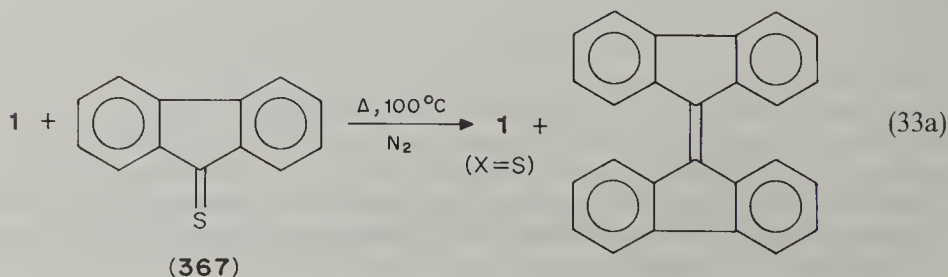
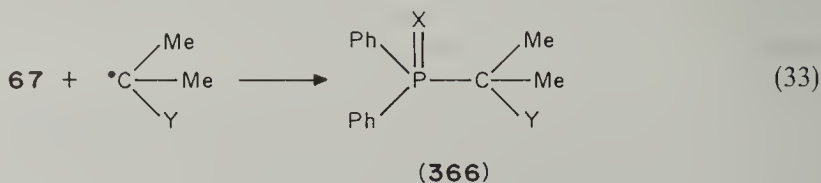
ω -Mercaptoalkylphenylphosphines, e.g. **359** and **360**, on reaction with oxygen gave³⁸⁷ alkylphenylphosphine sulphides **361**. Compounds **359** and **360** were prepared by the reaction of $\text{Ph}(\text{H})\text{PNa}$ with $\text{Cl}(\text{CH}_2)_n\text{SH}$ ($n = 2, 3$) and cyclohexene sulphide. In the sulphides **359**, **360** and **361**, the hydrogen bound to sulphur is more acidic than that bound to phosphorus, as is evident by its preferential reaction with BuLi and Na and its reaction with ethylene and propylene oxide.

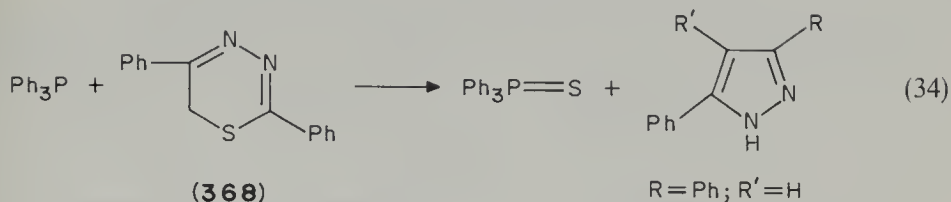


Phosphine sulphides are also obtained by reaction³⁸⁸ of tertiary phosphine dihalides with $(\text{Me}_3\text{Si})_2\text{S}$ (reaction 31). $\text{Me}_2\text{P}(\text{S})\text{Cl}$ is also known to act as a sulphur transfer agent³⁸⁹ in converting tributylphosphine to its sulphide. $(\text{Bu}_3\text{Sn})_2\text{S}$ is known to be unreactive to Ph_3P in thf, MeCN or hydrocarbon solvents. However, it reacts at room temperature with CCl_4 to give the intermediate adduct **362**, which then reacts with $(\text{Bu}_3\text{Sn})_2\text{S}$ to give Ph_3PS together with Bu_3SnCl and a phosphorus-containing resinous product derived from **363**. Sulphonium dicyanomethylides **364** (where $\text{R} = \text{R}' = \text{benzyl}$ or alkyl) react with Ph_3P to give the corresponding sulphides³⁸⁹. However, when $\text{R} = \text{R}' = \text{aryl}$ the transylidation reaction yields **365** according to equation 32.

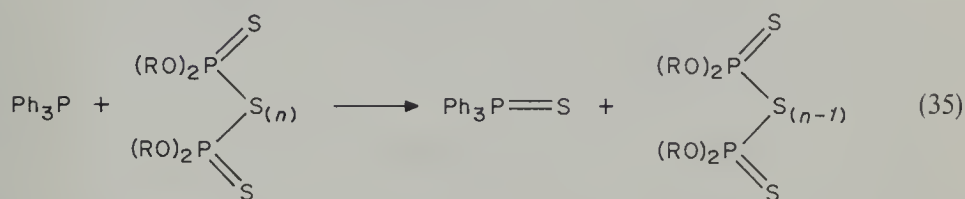
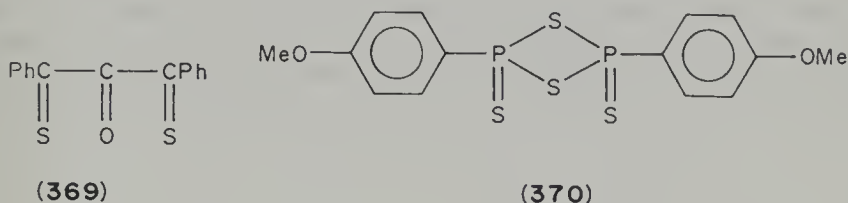


Tetraphenyldiphosphine **67** ($\text{R} = \text{R}' = \text{Ph}$; $\text{X}^1 = \text{X}^2 = \text{nil}$) is reported to react with carbon radicals to give **366** ($\text{X} = \text{nil}$; $\text{Y} = \text{CN}$, COOMe), which on sulphuration³⁹⁰ yield the sulphides **366** ($\text{X} = \text{S}$). 9-Fluorenoethione **367** is also known to act as a sulphur transfer agent, being itself converted into 9,9'-bifluorenyl in the process³⁹¹, e.g. on reaction with **1** ($\text{R} = \text{Bu}$; $\text{X} = \text{nil}$) (equation 33a). The thiadiazine **368** converts Ph_3P to Ph_3PS , being itself converted into pyrazole in the process³⁹², by ring contraction (equation 34).



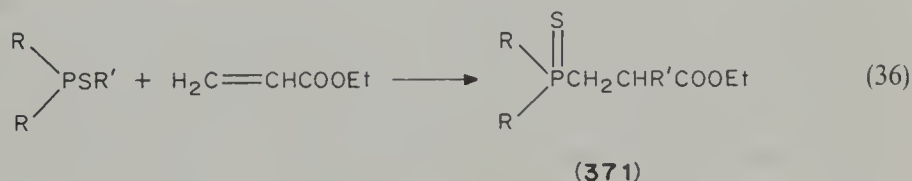


2-Oxo-1, 3-dithio-1,3-diphenylpropane (369) is also known to convert Ph_3P into Ph_3PS . However, some Ph_3PO is also formed in the reaction³⁹³. Diethyl dithiophosphorochloridite converts³⁹⁴ Ph_3P into Ph_3PS in 61% yield. Lowesson's reagent (370) has also been used³⁹⁵ for sulphurization of R_3P ($\text{R} = \text{P}, \text{Ph}, \text{Me}_2\text{OH}$), by refluxing them together in benzene. Phosphorus-containing polysulphides are also reported to convert³⁹⁶ phosphines into phosphine sulphides as in equation 35.

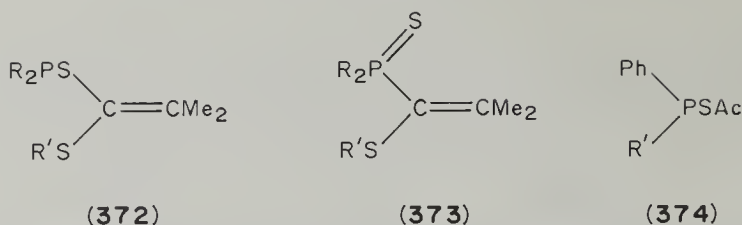


2. Through reactions of P^{III} compounds

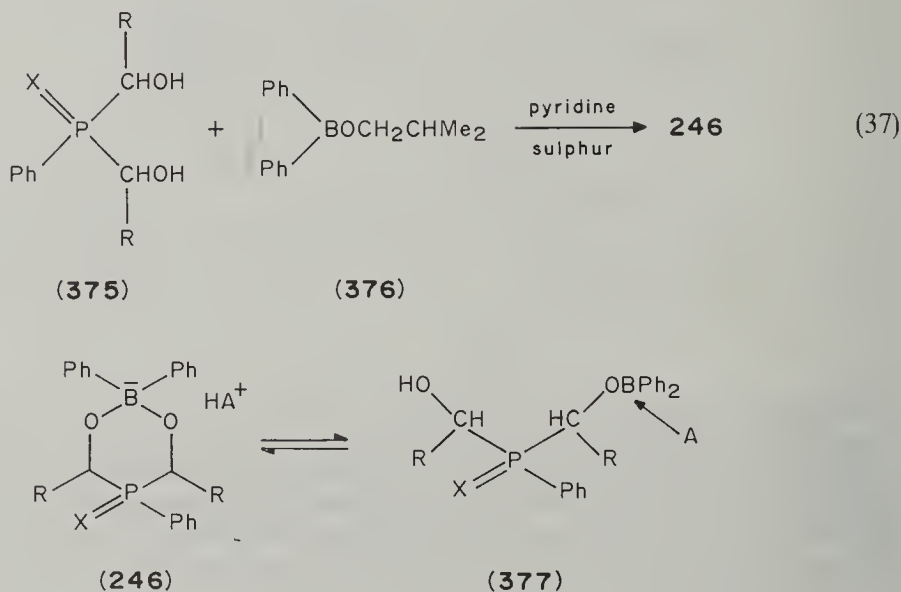
Phosphine sulphide 371 has been prepared by the reaction³⁹⁷ of an alkylthio-phosphonous acid with acrylic acid derivatives in the presence of sodium ethoxide in alcohol as a catalyst (equation 36). Dimethylphosphine halides, on reaction with methanethiols (and their sodium salts), give Me_2PSMe . The latter, on reaction¹⁷⁷ with MeI , gives the phosphonium salt $\text{Me}_3\text{P}^+\text{SMeI}^-$, which on melting at 170°C gives the sulphide 1 ($\text{R} = \text{Me}; \text{X} = \text{S}$).



The Friedel-Craft's reaction of benzene, sulphur and PCl_3 is reported to give³⁹⁸ Ph_3PS in good yields. The thiovinyl esters of P^{III} are known to give phosphine sulphides on rearrangement³⁹⁹. Thus, thermal rearrangement of 372 gives the phosphine sulphide 373 in 26–43% yields. Compounds 374 ($\text{R} = \text{Et}; \text{R}' = \text{Me}, \text{Et}$) are prepared in 42–87% yields by the reaction of dialkyl chlorophosphines with $\text{Me}_2\text{CHC}(\text{S})\text{SR}'$ in the presence of Et_3N in diethyl ether.



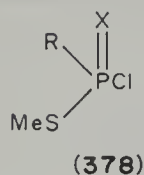
S-Acetyl thiophosphinites **374** are known⁴⁰⁰ to rearrange to phosphine sulphides **12** ($\text{R}' = \text{Et}, \text{Ph}$; $\text{R}^2 = \text{Ac}$; $\text{X} = \text{S}$). Compounds **374** were prepared by the reaction of phenylalkylchlorophosphines **312** ($\text{X} = \text{nil}$; $\text{R}' = \text{Et}, \text{Ph}$) with AcSH in the presence of Et_3N . The reaction of bis(α -hydroxyalkyl)phenylphosphines **375** ($\text{X} = \text{nil}$) and isobutyl-diphenyl borate **376** in the presence of a tertiary amine A, such as pyridine, and sulphur, is reported⁴⁰¹ to give dioxaboratophosphorinanes **246** ($\text{R} = \text{H}, \text{Me}_2\text{CH}$; $\text{X} = \text{S}$) in 25–45% yield. Thus, **246** exists in equilibrium with its open-chain form **377** ($\text{R} = \text{H}$, $\text{X} = \text{S}$; $\text{Y} = \text{NEt}_3$; $\text{R} = \text{Et}, \text{Me}_2\text{CH}$, $\text{X} = \text{S}$, $\text{Y} = \text{NEt}_3$) which is formed in 66% yield, by the treatment of phenylphosphine with CH_2O followed by reaction with **376** and pyridine, and then with sulphur ($\text{R} = \text{H}$, $\text{X} = \text{S}$, $\text{A} = \text{pyridine}$).



Sequential arylation of PCl_3 in the presence of AlCl_3 is also known⁴⁰². Thus, PCl_3 , AlCl_3 and benzene were heated at 80°C for 6 h, followed by reaction with fluorobenzene and sulphur for 20 h to give **5** ($\text{R}' = \text{Ph}$; $\text{R} = o-, m-, p\text{-FC}_6\text{H}_4$; $\text{X} = \text{S}$), *para* isomer 70%, *ortho* isomer 4.0% and also **5** ($\text{R} = \text{Ph}$, $\text{R}' = p\text{-FC}_6\text{H}_4$) 2.2% together with **1** ($\text{R} = p\text{-FC}_6\text{H}_4$; $\text{X} = \text{S}$) in 5.4% yield. A similar reaction of P(S)Cl_3 with PhF and AlCl_3 , followed by reaction with benzene, gave **5** ($\text{R}' = \text{Ph}$; $\text{R} = p\text{-FC}_6\text{H}_4$; $\text{X} = \text{S}$) in 80% yield together with its *ortho*-isomer in 0.7% yield, and **1** ($\text{R} = p\text{-FC}_6\text{H}_4$; $\text{X} = \text{S}$) in 2.3% yield. MeP(S)Cl_2 likewise, when treated with AlCl_3 and PhF followed by treatment with benzene, gave sulphide **12** ($\text{R} = \text{Ph}$, $\text{R}^1 = \text{Me}$, $\text{R}^2 = o-, m-, p\text{-C}_6\text{H}_4$), *para* isomer in 94.3% together with the *ortho* isomer in 3.8% yield.

1,4-Cycloaddition⁴⁰³ of alkylthiophosphines **378** ($\text{R} = \text{Me}, \text{Ph}$; $\text{X} = \text{nil}$), by heating them with 1,3-dienes at $70\text{--}100^\circ\text{C}$ gave 3-phospholene sulphides **25** ($\text{R} = \text{Me}$, $\text{R}^1 = \text{R}^2 = \text{Me}$; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$; $\text{R} = \text{Ph}$, $\text{R}^1 = \text{R}^2 = \text{Me}$). The reaction proceeds via [1 + 4]cycloadducts, which in some cases were isolated. Compounds **378** ($\text{R} = \text{Me}, \text{Et}$,

Ph) were prepared in 65–78% yield by methylthiolation of RPCl_2 with MeSH in the presence of trimethylamine.



B. Reactions Involving the Conversion of an Already Present P^{V} Nucleus

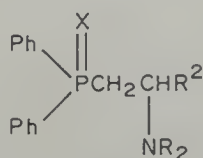
1. Through reactions of phosphine sulphides

Reduction of a variety of diaryl- and dialkyl-alk-1-ynylphosphine sulphides **5** (R = aryl, alkyl; R' = alkynyl; $\text{X} = \text{S}$) by LiAlH_4 leads to the formation of *trans*- β -substituted vinyl sulphides¹⁹⁸ (see equation 15). The phosphol-3-enes **123** ($\text{R} = \text{Me}$; $\text{R}^1 = \text{R}^2 = \text{Ph}$; $\text{X} = \text{S}$) react²¹⁵ with R^3CN ($\text{R}^3 = \text{Ph}$, substituted Ph, 2-furyl, 2-thienyl, 4-pyridyl) to give 29–62% **170** ($\text{X} = \text{S}$), which on reaction with HSiCl_3 underwent ring contraction to **186** ($\text{X} = \text{S}$) (see also Section III.B.1). Diphenylphosphine sulphide on reaction⁴⁰⁴ with BuLi gives the lithium derivative, which on reaction with MeI gives **5** ($\text{R}' = \text{Me}$; $\text{X} = \text{S}$). Reaction of **19** ($\text{X} = \text{S}$; $\text{R} = \text{Ph}$) with magnesium yielded $\text{Ph}_2\text{P}(\text{S})\text{MgCl}$, which on further reaction with **19** ($\text{R} = \text{Ph}$; $\text{X} = \text{S}$) yielded **67** ($\text{X} = \text{S}$) through the formation of a P–P bond.

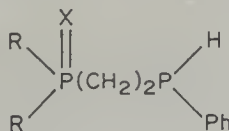
Reaction of $\text{Ph}_2\text{P}(\text{S})\text{M}$ ($\text{M} = \text{Li}, \text{MgCl}, \text{Al}$) with *p*-benzoquinone¹⁸⁶ yielded **144** together with **145** ($\text{X} = \text{S}$). However, with $\text{M} = \text{FeCl}$ in $\text{Ph}_2\text{P}(\text{S})\text{M}$, the products were phosphinothioate **145** ($\text{X} = \text{S}$) (see also Section III.A.6). Quinolyl derivatives of phosphine sulphides **311** ($\text{X} = \text{S}$) can be prepared by a series of reactions³²⁷, as detailed in Scheme 8, starting from dichlorophenylphosphine sulphide **310** ($\text{X} = \text{S}$) (see Section III.B.6).

The $[3 + 2]$ cycloaddition of alkynyldiphenylphosphine sulphides with substituted diazoalkanes yield²³⁷ thiophosphorylpyrazoles **219** ($\text{X} = \text{S}$) (see also Section II.B.1). Secondary phosphine sulphides **309** ($\text{R}' = \text{R}^2$; $\text{X} = \text{S}$) are known to react with triazolyl and imidazolyl ketones **238** to give thiophosphorylated alcohols **239** ($\text{X} = \text{S}$), having fungicidal activity¹³ (see also Section III.B.1).

The addition of dialkylamines to vinylphosphine sulphides **5** ($\text{R} = \text{Ph}$; $\text{R}' = \text{CH}=\text{CHR}^2$; $\text{X} = \text{S}$) leads⁴⁰⁵ to the formation of **379** ($\text{R}^2 = \text{H}, \text{Me}$; $\text{NR}_2 = \text{Et}_2\text{N}, 1\text{-pyrrolidinyl}, \text{piperidino}$; $\text{X} = \text{S}$). Compound **379** ($\text{X} = \text{S}$; $\text{R}^2 = \text{Me}$) was also prepared by reduction of the oxide **379** ($\text{X} = \text{O}$) with Cl_3SiH to phosphine **379** ($\text{X} = \text{nil}$), followed by its reaction with sulphur. Base-catalysed 1:1 addition of dimethylvinylphosphine sulphide **5** ($\text{R} = \text{Me}$) to phenylphosphine and to alkyl- and dialkyl-phosphines^{406,407} gives crystalline sulphides **380** ($\text{X} = \text{S}$), which undergo desulphurization with LiAlH_4 in boiling dioxane to give the phosphines **380** ($\text{X} = \text{nil}$). Similar base-catalysed 1:1 addition of PhPH_2 to **5** ($\text{X} = \text{S}$; $\text{R} = \text{R}' = \text{Ph}$) gives **380** ($\text{R} = \text{Ph}$). Sulphurization of phosphines has been used as a means of protecting the trivalent phosphorus in the synthesis of methylated poly(tertiary phosphines)^{182,183,324}. 1-Phenyl-3,4-dimethylphosphole sulphide **25** ($\text{X} = \text{S}$) reacted with *tert*-butyllithium at -170°C under argon, to give an anion which reacted⁴⁰⁸

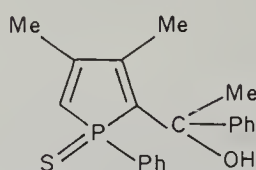
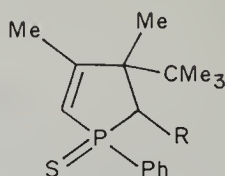


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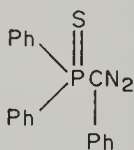
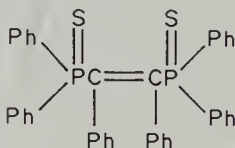
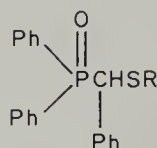


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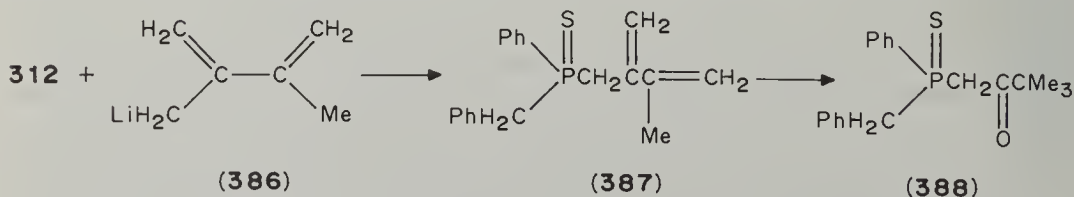
with aldehydes and ketones to give the corresponding derivatives, e.g. reaction with acetophenone gave **381** in 10% yield. Reaction of **25** ($X = S$) with excess of Me_3CLi gave a 3-*tert*-butylated derivative **382** [$R = \text{CMe(Ph)OH}$].

**(381)****(382)**

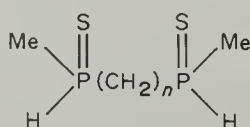
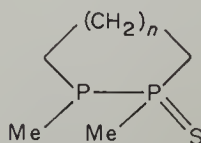
Tetraalkyldiphosphine disulphides **67** ($R = R' = \text{Me, Et, Bu; } X = S$), on reaction with alkyl halides R^2Y give phosphine sulphides **5** ($X = S$; $R = \text{Me, Et, PhCH}_2, \text{Bu}$) in 73–90% yield, by cleavage⁴⁰⁹ of the P—P bond. (Diphenylphosphinothioyl)phenyl diazomethane (**383**) on thermolysis in refluxing xylene gave the phosphine sulphide (carbene dimer) **384** in 88% yield⁴¹⁰, whereas refluxing in aqueous dioxane produced **384** together with **385** in 8% and 72% yield, respectively. Compound **384** was prepared in 37% yield by treating⁴¹¹ benzylidiphenylphosphine sulphide **5** ($R = \text{Ph; } R' = \text{CH}_2\text{Ph; } X = S$) with PhLi followed by its reaction with $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{N}_3$.

**(383)****(384)****(385)**

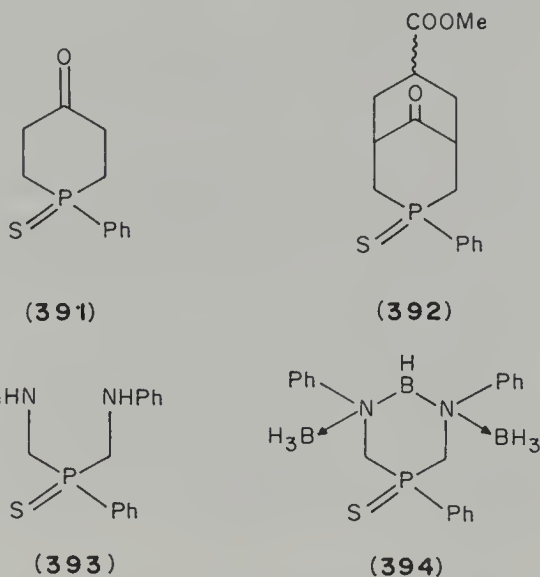
The facile transformation, via a pinacol rearrangement, of butadienyldiphosphine sulphide **387** into β -ketophosphine sulphide **388** (Scheme 9), has been reported⁴¹². Compound **387** is produced in 70% yield by the reaction of **312** ($R = \text{Ph, } R' = \text{PhCH}_2$; $X = S$) with the lithium derivative **386**. Phosphine sulphides of the type **389** ($n = 3, 4$), on reaction with $\text{Me}_2\text{NSiMe}_3$, are known to cyclize⁴¹³ to form the monosulphides **390** ($n = 1, 2$) of 1,2-diphosphenes or 1,2-diphosphanes. Akhmetova *et al.* reported⁴¹⁴ the synthesis of 7-(methoxycarbonyl)-3-phenyl-3-phosphabicyclo[3.3.1]nonan-9-one-3-



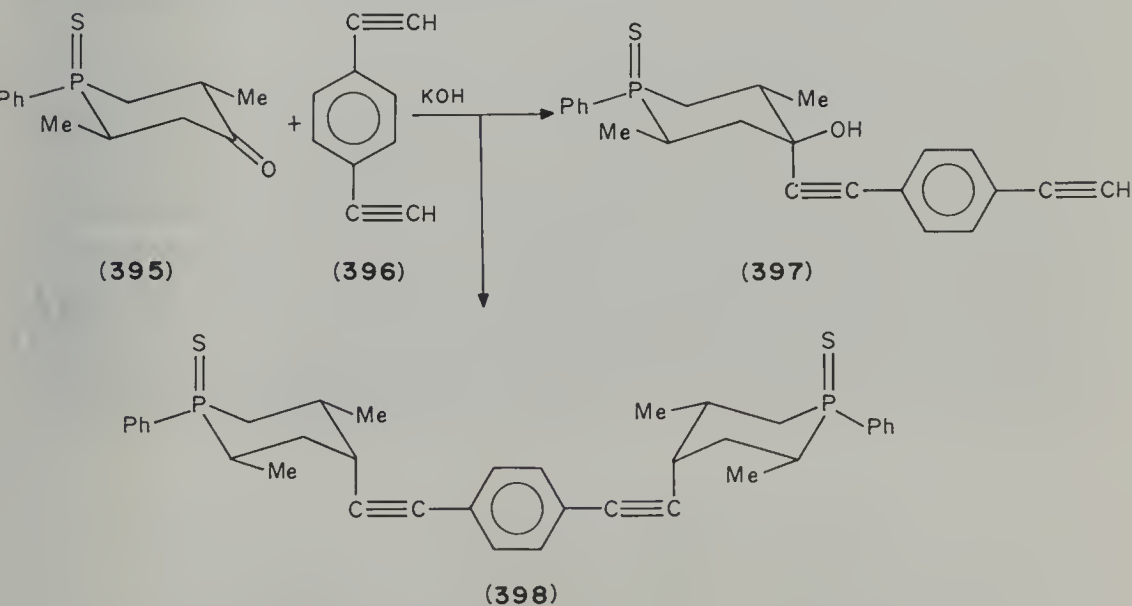
SCHEME 9. Conversion of butadienyldiphosphine sulphide.

**(389)****(390)**

sulphide (**392**) in 30% yield by treating phosphorinane sulphide (**391**) with pyridine, followed by cyclization of the enamine with $(\text{BrCH}_2)_2\text{CHCOOMe}$. 1,3-Diborane-1,3,2,5-diazaboraphosphorinane sulphide (**394**) are prepared in 86% yield by cyclizing⁴¹⁵ **393** with B_2H_6 .



Stereoselective ethynylation of the *trans* isomer of phosphorinan-4-one (**395**) with **396** in the presence of KOH or NaNH_2 gave⁴¹⁶ the alcohol **397** and glycol **398** in the ratio 85:15 in liquid ammonia- NaNH_2 (Scheme 10).



SCHEME 10. Reaction of *trans*-thioxophosphorinan-4-one with *p*-diethynylbenzene.

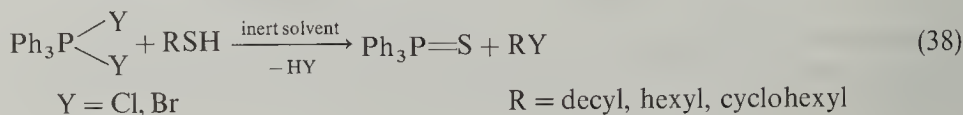
2. Through reactions of P^{V} halides

Reaction of dichlorophenylphosphine sulphide **310** ($\text{X}=\text{S}$) with 2 mol equiv. of vinylmagnesium bromide in thf at -70°C gave divinylphenylphosphine sulphide **5**

($R = CH=CH_2$; $R' = Ph$; $X = S$), which on refluxing with a 20% excess of methylamine or aqueous alkylamine, afforded almost quantitative amounts of azaphosphorinane-4-sulphide **187** ($X = S$). Treatment of **187** ($X = O$; see Section III.B.1) with P_2S_5 in hot benzene also gave the sulphide **187**.

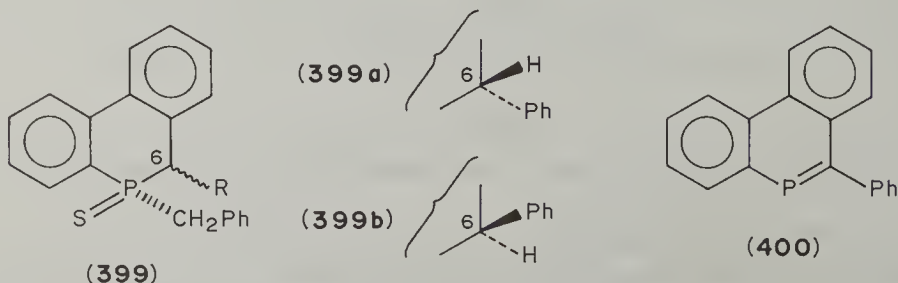
The reaction of 2-furyllithium **318** ($R' = Li$) with dialkyl chlorothiophosphates is reported³³⁴ to give, through successive replacements of OR groups, the tris(2-furyl)sulphide **319** ($X = S$; see Section III.B.6). Phenylthiophosphoryl dichloride **310** ($X = S$), on Friedel–Craft's reaction with halobenzene, gives the sulphide **5** ($R' = Ph$), e.g. a mixture of the above chloride (2 mol), $AlCl_3$ (5 mol) and fluorobenzene (12 mol) was refluxed for 18 h under nitrogen to give the sulphide **5** ($R = p-FC_6H_4$, $R' = Ph$).

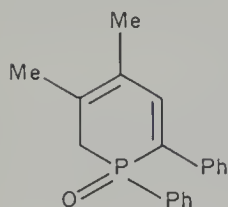
Tertiary phosphine sulphides and organic halides have been coproduced⁴¹⁷ by heating a thiol or dithiol, preferably in an inert solvent, with tertiary phosphine dihalide (reaction 38). Thus, Ph_3P (0.01 mol) in dry MeCN (60 ml) was stirred well at 0 °C whilst bromine (0.01 mol) was added over a period of 15–20 min. This was followed by the rapid addition of decane-1-thiol (0.01 mol) to the reaction mixture. The solvent was distilled off at 81 °C, accompanied by evolution of HBr. 1-Bromodecane was finally distilled at 138–139 °C/30 mmHg in 76% yield. The residue was then triturated with diethyl ether–pentane, followed by recrystallization from absolute alcohol to obtain Ph_3PS . Chlorophosphines **312** ($X = nil$) on reaction with the lithium derivative of methyl-diphenylphosphine sulphide⁴¹⁸, prepared by reaction of Ph_3PS with methylolithium, gave phosphinomethylphosphine monosulphide **339** ($X^1 = S$; $X^2 = nil$; $R^1 = Me_2CH$, Ph ; Ph , Me ; Ph , Et ; Me_2CH , $CHMe_2$).



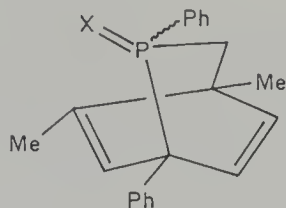
3. Through sulphurization of phosphine oxides

The *trans* isomers of tetraaryl- and -alkyl-vinylidenediphosphine dioxides **18** ($X = O$), on heating⁵⁴ for 2 h at 120 °C with sulphur, give the disulphide **18** ($X = S$) in 86% yield (see also Section III.A.1.b). The phosphaphenanthrone **110** is reported¹⁶⁴ to react with P_4S_{10} to give the isomeric phenanthrene thione **399** ($R = \alpha$ - or β -Ph; see Section III.A.4). Nickel-catalysed thermolysis of **399** at 275 °C gave 6-phenyl-5-phosphaphenanthrene **400**. Dialkylphosphine oxides $R_2P(O)H$ on reaction with P_4S_{10} at –30 to 20 °C in CH_2Cl_2 under nitrogen yielded⁴¹⁹ the corresponding sulphides **309** ($X = S$) in 55.5–62% yield. Phosphabicyclooctadiene oxide **402** ($X = O$) on sulphurization with P_4S_{10} yielded⁴²⁰ the corresponding sulphide **402** ($X = S$). The oxide **402** was prepared, in turn, by Diels–Alder reaction of the phosphorin-1-oxide **401** with dimethylacetylene dicarboxylate.



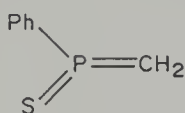


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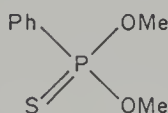


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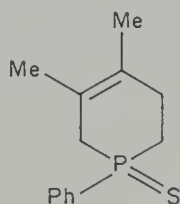
The sulphide **402** ($X = S$) on refluxing with toluene generated the C-unsubstituted methylenephosphine sulphide **403**, which was trapped by methanol or 2,3-dimethylbutadiene to give **404** or **405**.



(403)



(404)



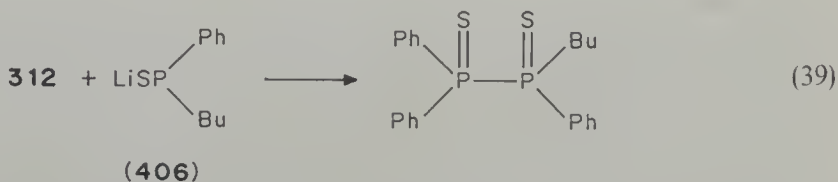
(405)

Reaction of sulphur with phospholes **25** ($R = R' = \text{Me}$; $X = \text{O}$) led to the formation⁴²¹ of the sulphides **25** ($X = S$). Phospholes **25** ($X = \text{nil}$) were prepared by the cyclization of alkyl- or aryl-halophosphines in the presence of a tertiary amine with pK_a 5–11, e.g. treatment of a mixture of PhPBr_2 and PhPCl_2 with $\text{H}_2\text{C}=\text{C}(\text{Me})=\text{CH}_2$ in CH_2Cl_2 in the presence of α -picoline gave **25** ($R = R' = \text{Me}$; $X = \text{nil}$) in 83.5% yield.

Optically active phosphine oxides of the type **12**, on reaction with boron trisulphide, give the corresponding sulphides⁴²² with high stereospecificity and net retention of configuration at phosphorus, e.g. (+)-(R)-cyclohexylmethylphenylphosphine oxide gave 76% of the corresponding sulphide with 95% optical purity.

4. Through reaction of $\text{P}_2\text{S}_5/\text{P}^V$ sulphur halides with organometallics or alkyl halides

Grignard reaction of PSCl_3 with alkyl halides yielded^{19a} phosphine sulphide **1** (see also Section III.A.2.b). Phosphine sulphides of the type **5** ($X = S$) are prepared by the reaction⁸⁵ of **12** ($R^1 = R^2$; $X = S$) with alkyl halides in the presence of magnesium (see Section III.B.6). Phosphorus thioxychloride reacts⁴²³ with cyclohexylmagnesium chloride to give **309** ($X = S$), **67** ($R = R'$; $X = S$) and **1** ($X = S$; $R = \text{cyclohexyl}$). 1-Butyl-1,2,2-triphenyldiphosphine disulphide was prepared⁴²⁴ by heating **312** ($R^1 = R^2 = \text{Ph}$; $X = S$) with **406** (reaction 39).



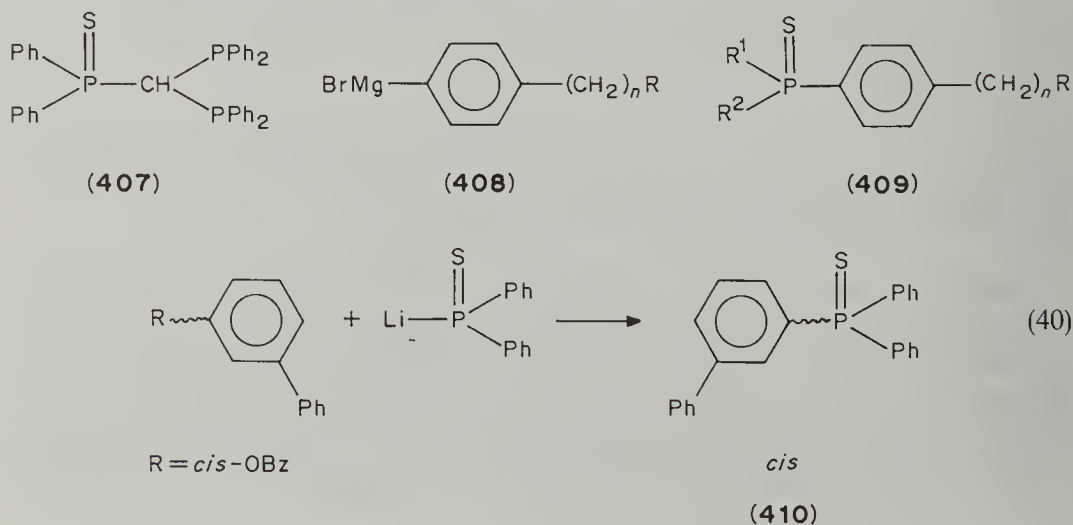
(406)

Dialkyl- and diaryl-phosphonothioic halides of the type **312** ($X = S$) and alkyl- and aryl-phosphinothioic dihalides **310** ($X = S$) are prepared by reaction⁴²⁵ of alkyl halides

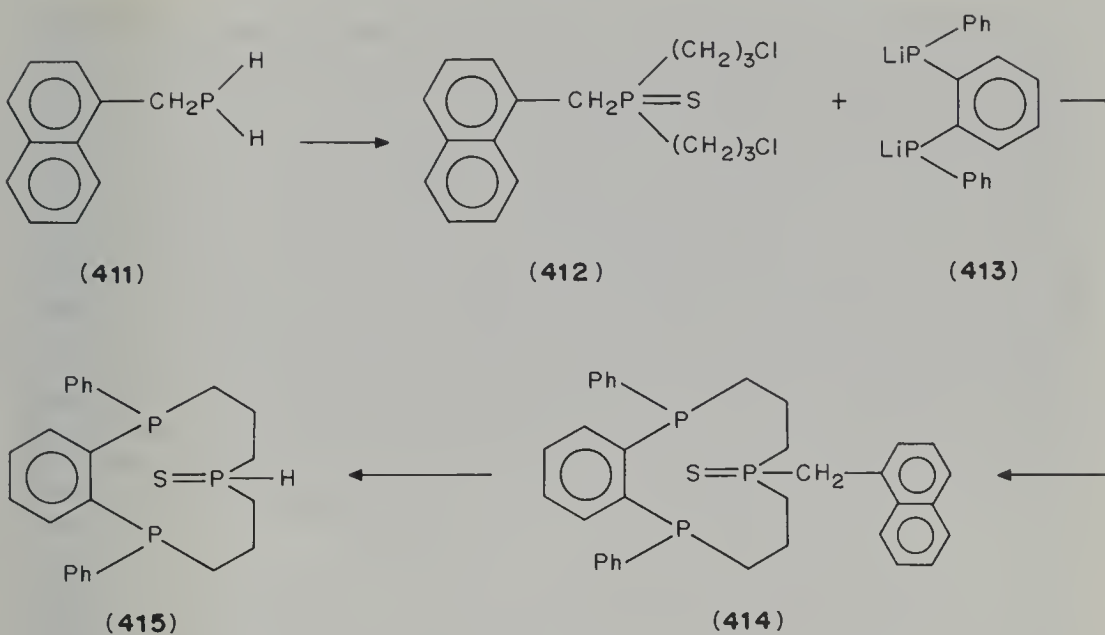
with P_4S_3 at 250–339 °C. Thus, P_4S_3 (0.02 mol) and methyl chloride (0.118 mol) on heating at 235–240 °C for 12 h gave **312** ($R^1 = R^2 = R$; $X = S$) and **310** ($R = \text{Me, Bu, Ph, C}_{1-20}\text{-alkyl, C}_{5-6}\text{-cycloalkyl}$; halide = Cl, Br). Compounds **312** ($X = S$) are used for increasing the effectiveness of flotation of copper ores.

The reaction of thiophosphoryl chloride with PhLi gives the corresponding phosphine sulphides⁴²⁶ of the type **1**. Thus, $P(S)Cl_3$ on reaction with PhLi gives Ph_3PS in 80% yield. The reaction proceeds via a metal–halogen exchange reaction, e.g. the reaction of $PSCl_3$ and BuLi gives, after hydrolysis, several products such as $Bu_2P(S)H$, Bu_3PS and $Bu_4P_2S_2$.

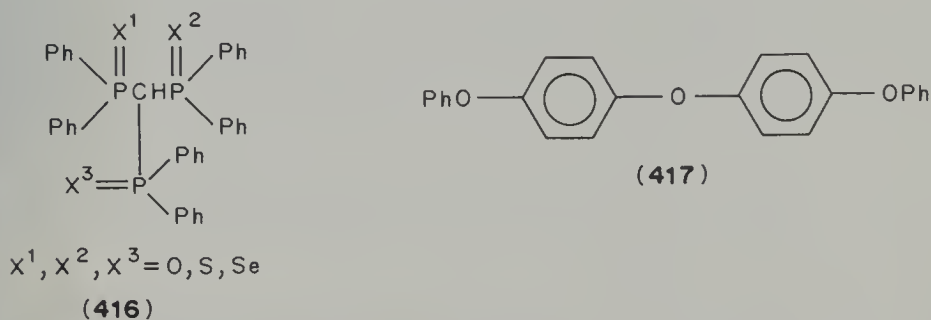
The (dialkylphosphino)diphenylphosphinomethane monosulphides **67** ($X^1 = S$, $X^2 = \text{nil}$; $R = \text{tert-butyl}$) were prepared⁴²⁷ in 43% yield by treating $Ph_2P(S)CH_2Li$ with **312** ($R^1 = R^2 = \text{tert-butyl}$; $X = \text{nil}$). A similar reaction⁴²⁸ of the lithium derivative of methyl diphenylphosphine sulphide with **312** ($R^1 = R^2 = \text{Ph}$; $X = \text{nil}$) gave **407** in 66% yield. Grignard reaction of **312** ($R^1 = R^2 = \text{Me, Et}$; $X = S$) with **408** ($R = \text{OMe, OSiMe}_3$) gave⁴²⁹ the phosphine sulphide **409**. Fiaud⁴³⁰ reported a stereoselective synthesis of allylic diphenylphosphine sulphide (**410**) in high yields by the palladium-catalysed substitution of allylic carboxylates with lithium diphenyl thiophosphides in thf containing $[Pd(PH_3)_4]$ at room temperature, with an overall retention of configuration (equation 40). Kyba and Liu⁴³¹ prepared the P_3 macrocyclic phosphine-6-sulphide **415** by the reaction of bis(3-chloropropyl)-1-naphthylmethylphosphine sulphide (**412**) with bis(lithiophenylphosphino)benzene (**413**) to give **414**, followed by quantitative removal of 1-naphthylmethyl moiety with potassium naphthalenide (Scheme 11). 1-Naphthylmethylphosphine sulphide has been used as a protecting group for a P–H bond in a secondary phosphine and to convert 1-naphthylmethylphosphine (**411**) into **412**.



Polydentate phosphorus-containing ligands of the type **34** and **416** can be prepared from their neutral precursors⁴³² by proton abstraction with LiOMe. Phosphine sulphides of the type **5** ($R = \text{halogen, Me, MeOC}_6\text{H}_4$; $R' = \text{lower alkyl, aryl, X = S}$), useful in the preparation of fire-resistant polyoxyphenylenes, are prepared⁴³³ from aryl- and alkyl-thiophosphoryl dihalides (**310**) and halobenzenes in the presence of Friedel–Craft's catalysts. Thus, refluxing $PhP(S)Cl_2$ (0.3 mol) with chlorobenzene (2 mol) and anhydrous $AlCl_3$ (1.6 mol) for 8 h gave bis(*p*-ClC₆H₄)phenylphosphine sulphide in about 80% yield. Similarly, stirring $P(S)Cl_3$ (0.1 mol) and $AlCl_3$ (0.5 mol) with **417** (0.7 mol) at 150 °C for 6 h gave a polymer in 36% yield. Compound **5** ($R = \text{p-ClC}_6\text{H}_4$; $R' = \text{Ph}$; $X = S$) is also prepared by two variations⁴³⁴ of a Friedel–Craft's reaction involving either treating

SCHEME 11. Synthesis of 11-P₃ macrocyclic phosphine sulphide.

benzene with PCl_3 and then the resulting unisolated intermediate with sulphur and halobenzene (halo = F, Cl, Br) (> 2 mol), or heating halobenzene with P(S)Cl_3 and then the unisolated intermediate with benzene. In both cases the reaction mixture is heated between 70 and 150 °C in the presence of an Al(halo)_3 catalyst. Thus, benzene (0.1 mol) and PCl_3 (0.1 mol) were heated for 6 h at 80 °C under nitrogen in the presence of AlCl_3 (0.22 mol) and the resultant mixture was treated with sulphur (0.1 mol) and chlorobenzene (0.6 mol) and a refluxed for a further 6 h to give bis(*p*-chlorophenyl)phenylphosphine sulphide in 65% yield.



An efficient Friedel–Craft's-type preparation of Ph_3PS and its derivatives was reported by Olah *et al.*⁴³⁵, involving AlCl_3 -catalysed reactions of benzenes (or substituted benzenes) with P_4S_{10} . Tertiary halogen ($\text{X} = \text{F}, \text{Cl}, \text{Br}$)-substituted phenylphosphine-sulphides **5** are prepared by heating⁴³⁶ a mixture of PSCl_3 with halobenzene, followed by addition of substituted benzene and continued heating. Thus, a mixture of PSCl_3 (0.75 mol) and AlCl_3 (1.34 mol) in cyclohexane was refluxed for 8 h, followed by addition of toluene (3 mol) and refluxing for a further 5 h, when **5** ($\text{R} = p\text{-F-C}_6\text{H}_4$; $\text{R}' = p\text{-MeC}_6\text{H}_4$; $\text{X} = \text{S}$) was produced in 85% yield. Tertiary phosphine sulphides of the type **1** ($\text{R} = \text{Me}, \text{Et}, \text{Bu}, \text{Ph}$; $\text{X} = \text{S}$) are also prepared⁴³⁷ by the reaction of phosphorus with alkyl sulphides R_2S at 200–400 °C.

V. METHODS OF PREPARATION OF PHOSPHINE SELENIDES AND TELLURIDES

Selenophosphines and related compounds have been reviewed^{22,23,438}. Some phosphine selenides have novel inclusion properties and act as highly selective hosts, e.g. 1,2-bis(diphenylphosphinoselenoyl)ethane **90** ($R = \text{Ph}$; $X = \text{Se}$) acts very selectively for *p*-xylene⁴³⁹. Thus, **90** ($R = \text{Ph}$; $X = \text{Se}$) formed stable inclusion compounds when crystallized from various pure solvents. However, when **90** ($X = \text{Se}$) was crystallized from certain solvent mixtures, there was remarkable guest selectivity. The preference shown for **90** ($X = \text{Se}$) is general for *para*-disubstituted mononuclear aromatics of similar size. The sulphide analogue of **90** also exhibited significant inclusion properties. Compound **90** ($R = \text{Ph}$; $X = \text{Se}$) (3 g) was dissolved in a mixture (25 ml) of equal volumes of *o*-, *m*-, *p*-xylene and ethylbenzene at 100 °C and the solution was cooled at 0.5–1 °C min⁻¹ and inoculated with *p*-xylene crystals at 360 K to give the *p*-xylene adduct (2.9 g), which was thermally decomposed to give a product containing 95.5% *p*-xylene, 2.5% ethylbenzene, 1.2% *m*-xylene and 0.8% *o*-xylene. The crystal structure of the inclusion compound contains three host and one guest molecule in a unit cell. The adduct is of true clathrate type, with the highly ordered *p*-xylene guest being accommodated in an effectively closed case.

Brown *et al.*⁴⁴⁰ measured the exchange of selenium between tertiary phosphine selenides and analogous tertiary phosphines and found it to be fairly fast on the NMR time scale at elevated temperature. In this it resembles the phosphine tellurides, where rapid tellurium transfer⁴⁴¹ has been observed in $\text{R}_3\text{P}^+\text{Te}^-\text{R}_3$. The corresponding sulphide derivatives redistribute themselves in analogous systems much more slowly.

Phosphine tellurides have been used recently for the chemical transport⁴⁴² of tellurium under very mild conditions, i.e. they find application in the preparation of semiconductor materials.

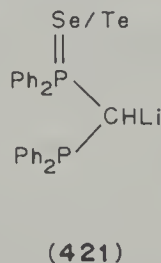
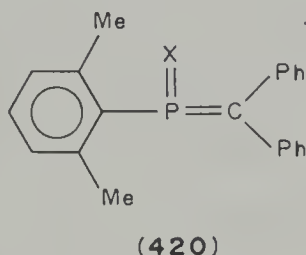
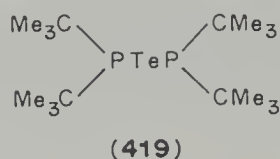
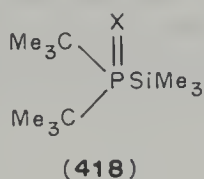
A. Reactions Involving Conversion of P^{III} to P^{V}

Diphenylphosphine selenide was prepared⁴⁴³ by heating red selenium suspended in benzene with diphenylphosphine for 10 min at 70 °C. Dibutylphosphine selenide was obtained by passing H_2Se into a benzene solution of dibutyl(diethylamino)phosphine.

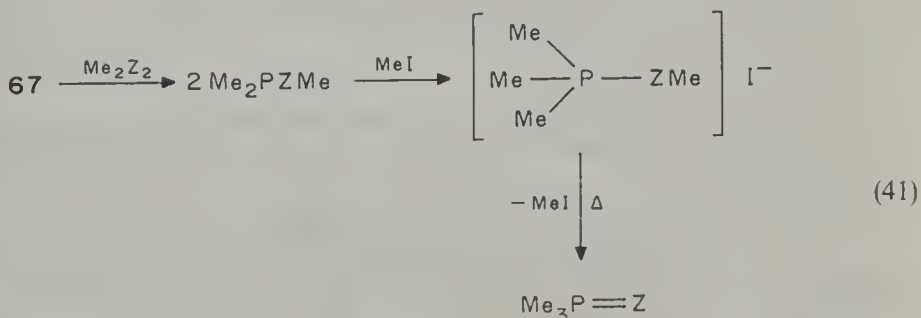
$\text{Ph}_4\text{As}^+\text{Te}^-\text{CN}$, on treatment with excess of Ph_3P in MeCN containing LiClO_4 , is known to give $\text{Ph}_3\text{P}^+\text{Te}^-\text{PPh}_3$ in which the $\text{P}-\text{Te}-\text{P}$ configuration could be regarded⁴⁴⁴ as one in which there is normal bond between tellurium and one of the phosphorus atoms, whereas the interaction between tellurium and the other phosphorus atom is weak. Tertiary phosphine selenides are also formed through selenium abstraction⁴⁴⁵ in the reaction of diethyl diselenide with tertiary phosphines. Thus, photochemical deselenation of Et_2Se_2 by diphenylmethylphosphine gave **5** ($R = \text{Ph}$, $R' = \text{Me}$; $X = \text{Se}$) in high yield together with Et_2Se .

CSe_2 also is known⁴⁴⁶ to react with Ph_3P in the presence of metal carbonyls to give Ph_3PSe . Aryl phosphines of the type **1** ($R = \text{Ph}$, *p*- ClC_6H_4 or *o*-, *m*-, *p*- MeC_6H_4) react with SeO_2 suspended in benzene–ethanol solution to give R_3PSe together with R_3PO in different proportions depending on the phosphine, the relative proportions of the reagents and the solvent⁴⁴⁷. Similar reaction of SeS_2 with Ph_3P gave a solid solution of Ph_3PS and Ph_3PSe on refluxing⁴⁴⁸ for 2 h in excess of benzene. Insertion of tellurium⁴⁴⁹ into **418** ($X = \text{nil}$) gave **418** ($X = \text{Te}$), which, however, disproportionated to give **419** and $(\text{Me}_3\text{Si})_2\text{Te}$. Alkenebis(monophenylphosphine chalcogenides) **75** ($R = \text{Ph}$; $R' = \text{H}$; $X = \text{Se}$; $n = 2$) were prepared by treating the corresponding phosphine **75** ($X = \text{nil}$) with selenium³⁶⁸. Reaction of **420** ($X = \text{nil}$) with selenium in benzene leads to the formation of stable *p*-2,6-dimethylphenyl-*C-C*-diphenylselenophosphine⁴⁵⁰ **420** ($X = \text{Se}$), which is stable at room temperature but decomposes on heating with partial regeneration

of the starting materials. No reaction, however, was observed between **420** ($X = \text{nil}$) and tellurium. The reactions of tri-*tert*-butyl phosphine with selenium and tellurium proceed quantitatively with formation⁴⁵¹ of the corresponding selenide and tellurides. The lithium derivatives of **7** ($R = R' = \text{Ph}$; $X^1 = X^2 = \text{nil}$) on treatment⁴⁵² with elemental selenium or tellurium give the mono-selenium or tellurium derivatives **421**. Reaction of acetylenic phosphines **336** ($X = \text{nil}$) with selenium leads to the formation³⁶⁶ of the selenide **336** ($X = \text{Se}$, see also Section IV.A.1.a). Tetrakis(diphenylphosphino) allene **49** ($X = \text{nil}$), 2-phosphabicyclononanone **11** ($X = \text{nil}$), phosphastanniananes **161** ($X = \text{nil}$), 3,4-dialkylphosphole **116** ($X = \text{nil}$), and pentaethylcyclopentaphosphine **8** ($X = \text{nil}$) (see Table 2 for further details) are all converted into their selenides ($X = \text{Se}$) by reaction with selenium. Likewise, dioxaphosphorinanes **352** ($X = \text{nil}$) also gave the selenide³⁷⁸ ($X = \text{Se}$), as did 2-phosphabicyclodecanone **354** (see section IV.A.1.a), phosphabicyclodecanone⁸¹ **43** (see Section II.A.1.e) and oxaborataphosphorinanes **246** ($X = \text{nil}$) (see Section IV.A.2), on reaction with selenium.



The exchange reaction of tetramethyl bisphosphines **67** ($R = R' = \text{Me}$; $X = \text{nil}$) with dimethyl dichalcogenides Me_2Z_2 ($Z = \text{S}, \text{Se}, \text{Te}$) leads to the formation⁴⁵³ of the corresponding methyl chalcogenides Me_2PZMe . These on reaction with MeI give the phosphonium salt (see also ref.177), which is converted to the corresponding chalcogenide on heating (reaction 41).



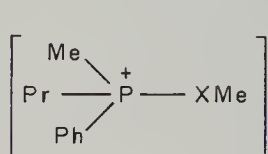
A simple and efficient method of preparing aromatic tertiary phosphine selenides is through the reaction of phosphines with potassium selenocyanate in acetonitrile (reaction 42)⁴⁵⁴. The reaction is specific for selenium and does not occur with the oxygen or sulphur analogues.



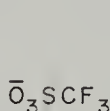
B. Reactions Involving Conversion of an Already Present P^V Nucleus

Phenylselenophosphoryl acid chloride **310** (R' = Ph; X = Se) on Friedel–Craft's reaction with halobenzenes³¹² gives the selenide **5** (X = Se; R' = Ph) (see Section IV.B.2 for details). Phosphine selenides of the type **1** and **5** (X = Se) were prepared by the reaction⁴⁵⁵ of organomagnesium compounds with selenophosphorus acid chlorides. Thus, the reaction of diethylselenophosphoryl chloride with R'MgBr gave 61.8–72.9% of **5** (R = Et, R' = Et, Ph; X = Se) and the reaction of PhMgBr with PhP(Se)Cl₂ gave Ph₃PSe in 35.4% yield. Grim and Walton prepared⁴⁵⁶ variously substituted **416** (X¹, X² = Se, S or O and X³ = nil; X¹ = Se, S and X², X³ = nil; X¹ = Se, X² = S and X³ = nil) by reaction of Ph₂P(Z)CH₂Li with Ph₂P(X)Cl (Z = Se, S, O or nil).

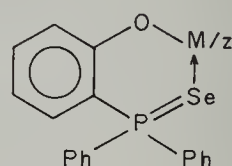
Stereospecific interconversion of chiral thiophosphines into selenophosphines has also been reported⁴⁵⁷. Thus, the conversion of chiral methylpropylphenylphosphine sulphide into the selenide and *vice versa* were accomplished by treatment of **422** (X = Se, S) with NaSeH or NaSH, respectively. Both reactions occur with retention of configuration at phosphorus and high stereospecificity. (2-Hydroxyphenyl)diphenylphosphine selenide **423** (X = Se) has been prepared⁴⁵⁸ in 77% yield by heating the corresponding oxide **423** (X = O) with selenium. The selenide **423** (X = Se) forms complexes **424** with metals M (M = Cu, Ni, Co, Zn) in 72–85% yields.



(422)



(423)



(424)

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CHAPTER 7

Chemical properties and reactions of phosphine chalcogenides

R. S. EDMUNDSON

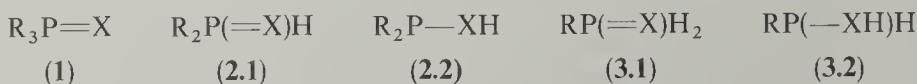
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I. INTRODUCTION

Tertiary phosphines, R_3P , and their chalcogenide derivatives, (1) ($X = O, S, Se$ or Te), have been known since the early days of organophosphorus chemistry. The latter group is characterized by the possession of three, formally single, phosphorus—carbon bonds, in addition to the bond between the phosphorus and chalcogen atom, and whose character may vary considerably depending on both the group(s) R and the element X . The series of so-called tertiary compounds is thus clearly distinguishable from similar derivatives of secondary and primary phosphines which possess one and two phosphorus—hydrogen bonds, respectively.



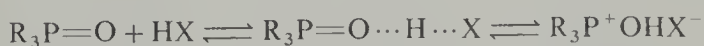
An important feature of the chemistries of the secondary and primary phosphine chalcogenides, where these compounds actually exist, is their participation in the dyad prototropic equilibria $2.1 \rightleftharpoons 2.2$ and $3.1 \rightleftharpoons 3.2$. The secondary and primary phosphine chalcogens are thus each able to form two series of derivatives based on tri- or

tetra-coordinate geometry. Those derivatives having tricoordinate structures are not the direct concern of the present chapter, which, in addition to describing the reactions of the tertiary phosphine chalcogenides, also reviews briefly reactions of the secondary and primary phosphine derivatives, particularly those which directly involve the phosphorus—hydrogen bond itself.

The tertiary phosphine oxides were, for a long time, considered to be amongst the most stable organophosphorus compounds with regard to both thermal stability and the action of common chemical reagents. Thus, triphenylphosphine oxide is thermally stable up to about 450 °C, although the higher chalcogenides are less so. The oxides are now known, however, to be more reactive than was at one time thought. The chemical reactivity of a tertiary phosphine chalcogenide is a function of the particular chalcogen present, in addition to the nature of the organic ligands attached to phosphorus. Indeed, part of the usefulness of many such compounds depends on the ease of cleavage of a phosphorus—carbon bond.

The nature of the P=X bond is not a subject of detailed discussion in this chapter, although a very brief general consideration is perhaps desirable. Although widely represented as a phosphorus-to-chalcogen double bond, the true nature of the bond depends on the individual element X, and also on the nature of the electronic interactions between phosphorus and the ligands R, e.g. whether these are halogen atoms or organic groups. It has been suggested, for instance, that the phosphoryl bond in a simple trialkylphosphine oxide has almost triple bond character.

Whatever the true nature of the P=X bond in any particular phosphine chalcogenide, such compounds are well known to form complexes through the atom X with an extremely wide range of compounds, including oxides, halides and other derivatives of both metals and non-metals. Phosphine oxides, in particular, form strong hydrogen bonds with carboxylic acids, phenols, alcohols and even more weakly bonding species such as CHCl_3 , to yield complexes of various stoichiometries, mostly detectable spectroscopically, but sometimes isolable; triphenylphosphine oxide forms isolable hydrates. With strong mineral acids, the structure of the complex may lie between that of a simple hydrogen-bonded species and a fully protonated ion (Scheme 1). Hydrogen bonding, normally intermolecular, as in the cases just mentioned, and for appropriately separated groups as in the oxide $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_n\text{OH}$ when $n = 4$, is intramolecular for $n = 1-3$ [†].



SCHEME 1

The basicity of a tertiary phosphine oxide is due to the nucleophilic character of the phosphoryl group and its desire to protonate; as a class, such oxides are weaker bases than the corresponding tertiary amine oxides, but are stronger bases than similar carbonyl compounds.

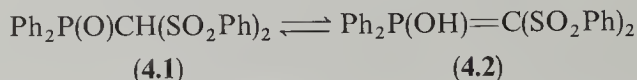
Organic derivatives of the phosphinoyl* group, $\text{H}_2\text{P}(\text{O})-$, exert an electron-attracting effect by induction or mesomerism, in appropriate environments, to an extent dependent on the attached organic groups. This electronic influence leads to enhanced acidity of compounds having hydrogen atoms on carbon bonded directly to phosphorus, and a greater potential for tautomerism. Thus, 1-(diphenylphosphinoyl)propan-2-one,[†]

*This terminology is becoming more widely accepted (IUPAC) than the term phosphinyl, although the latter is used by *Chemical Abstracts*; for further discussion of terminology, see Chapter 1 of Volume 1.

[†]This compound might also be termed (2-oxopropyl)diphenylphosphine oxide. Both types of nomenclature will be used interchangeably in this chapter.

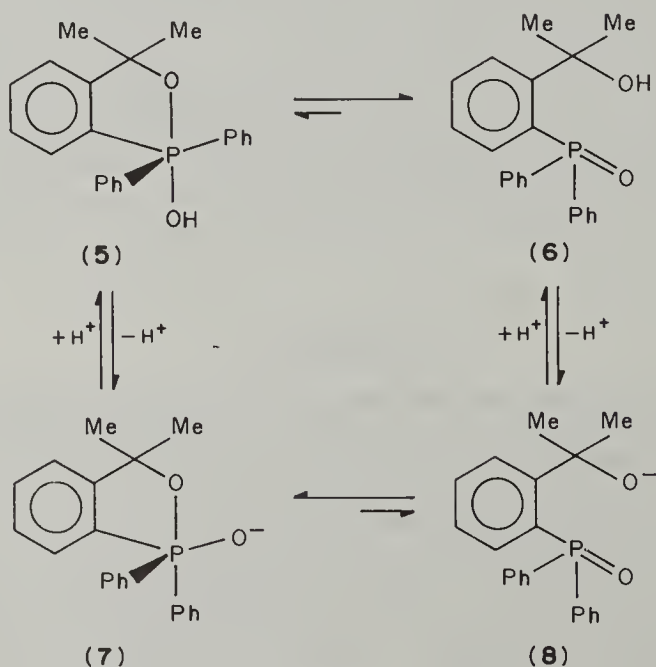
$\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{COMe}$, contains about 2% of an enol (i.e. oxygen acid) form, an enol content very much greater than that in acetone itself or even in benzyl methyl ketone².

Evidence for prototropy involving the phosphoryl group in tertiary phosphine oxides seems to have come to light only recently. Diphenylphosphinoylbis(phenylsulphonyl)-methane normally exists in the CH form (4.1) and is a relatively strong acid with $\text{p}K_{\text{a}}$ 3.27 in 95% aqueous EtOH. The rapid acidification of a solution of its sodium salt leads to samples enriched in the form 4.2, as evidenced by the presence of two signals in its ^{31}P NMR spectrum, and the formation of an *O*-Me derivative on reaction with MeI, Me_2SO_4 or CH_2N_2 . The ylide form reverts to the CH acid form when such samples are recrystallized^{3,4}.



There is also some evidence for the limited occurrence of 'ring-chain' tautomerism involving the phosphoryl group as exemplified in Scheme 2. Although the equilibrium between structures 5 and 6 lies well over to 6, the equilibrium between 7 and 8 is strongly biased towards the pentacoordinate form 7⁵.

The chemical reactions of phosphine oxides^{6,7} and sulphides, selenides and tellurides^{8,9} have been reviewed; the reader should consult those sources for most literature references published before about 1965. The emphasis in this chapter is on those reactions discovered or developed during the last two to three decades, and the scope covers reported developments up to the end of 1990, with *Chemical Abstracts* surveyed to the end of Volume 113.



SCHEME 2

The chemistry of phosphine chalcogenides is discussed here in terms of the properties of the $\text{P}=\text{X}$ bond and the reactions of the organic ligands attached to phosphorus. Included is a special section dealing with phosphine oxide carbanions and the special role they play in organic synthesis (the Horner reaction). Other sections deal with the

stability of the intervening phosphorus—carbon bond and the chemistry of secondary and primary phosphine chalcogenides, treated separately because of the special properties endowed on these compounds by the phosphorus—hydrogen bond.

II. REACTIONS OF THE CHALCOGENIDE GROUP

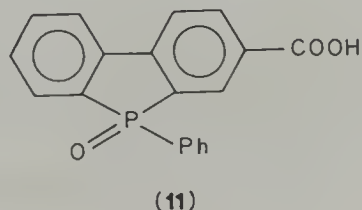
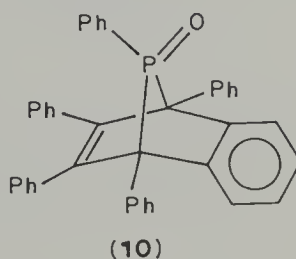
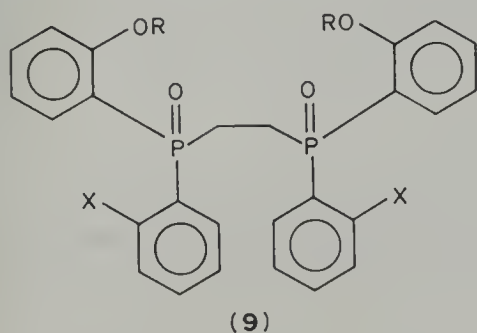
This section is intended as an outline of those reactions by which the chalcogenide group, $P=X$ ($X = O, S, Se$ or Te) can be removed so as to leave the corresponding phosphine, and also the various reactions by means of which one such group may be converted into another or to yet other groupings. Both types of sequence are of importance in synthetic organophosphorus chemistry.

A. Reduction of Quinquevalent Tetracoordinate Compounds to Tervalent Tricoordinate Compounds

The removal of the $P=X$ bond from phosphine chalcogenides can be achieved through the use of a wide variety of types of reagents acting under very varied conditions. Not all of the reactions described would necessarily be considered as being of value for synthetic purposes, since it has often been found that slight variations in experimental conditions may lead to an unexpected outcome with respect to either the nature or the stereochemistry of the reaction product(s).

1. Phosphines from phosphine oxides

The potential for the use of simple metal hydrides in reductions of phosphine oxides to phosphines has not been fully explored. Successful reductions of simple trialkyl- and triaryl-phosphine oxides to the respective phosphines have been performed with the hydrides of calcium or aluminium. CaH_2 reduces Ph_3PO to Ph_3P , the yield of the latter decreasing with increase in reaction temperature, but some cleavage to benzene and Ph_2PH , which may be accompanied by the liberation of diphenylphosphinic acid, is also observed¹⁰. AlH_3 is a better reagent for the reduction of the oxides **9** ($X = H$ or



OR; R = H, Me, Et or Bu')¹¹. Ph₃P(O) has also been reduced by trialkylboranes, dimeric dialkylboranes and borane-trialkylamine complexes, and even by a triphenylphosphine-borane complex at 120–150 °C¹², but the reduction may also be achieved by the use of SmI₂ in thf–hmpa at lower temperatures¹³. Oxides with at least one P-aryl grouping are reduced in moderate yield by a stoichiometric amount of [Cp₂TiCl₂]-Mg in thf, and the yields for the series Ph_nP(O)Me_{3-n} increase as *n* increases; other tertiary phosphine oxides, e.g. Bu₃PO, may not be reduced by this reagent¹⁴.

Much more attention has been focused on the use of LiAlH₄ and other complex hydrides. Ca(AlH₄)₂ is useful for the reduction of trialkylphosphine oxides but not for the triaryl analogues. On the other hand, LiAlH₄ reduces Ph₃PO satisfactorily in diethyl ether, but reactions in solvents with higher boiling points are again accompanied by fission to Ph₂PH; nevertheless, several successful reductions with LiAlH₄, with yields in the range 60–80%, have been reported^{15,16}. Neither LiAlH₄ nor LiAlH(OBu')₃ was of value in attempted reduction of phosphine oxides at the low temperatures necessarily required to prevent valence isomerization of phosphonin 1-oxides¹⁷, and attempted reduction of a bridged phosphine oxide (**10**) also failed because of the elimination of the phosphorus bridge and the formation of 1,2,3,4-tetraphenylnaphthalene¹⁸.

Although the use of LiAlH₄, with its known ability to reduce a wide range of functional groups, might thus seem to have distinct disadvantages for synthetic purposes, one of its main drawbacks is, without doubt, the possibility of reduction accompanied by racemization. Some optically active phosphine oxides, e.g. (*S*)-(–)-Bu'MePhPO, have been reduced with little loss of optical purity¹⁹, whereas for other compounds, e.g. 5-phenyl-5*H*-dibenzophosphole-3-carboxylic acid 5-oxide (**11**), reduction to the phosphine is accompanied by reduction of the COOH group and by complete racemization.

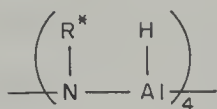
In 1969, Mislow and coworkers²⁰ reported that phosphine oxides may undergo stereomutation in the presence of LiAlH₄ even before the actual reduction process has commenced. In thf at room temperature, (+)-MePhPrPO is almost completely racemized before 10% reduction has occurred; similar observations were made with the *cis* and *trans* forms of 1-phenyl-2,2,3,4,4-pentamethylphosphetane 1-oxide, stereomutation being completed within 10 min. Complexes of the type Li[Al(OHPR₃)₄] may play a role in such stereochemical changes²⁰.

The addition of CeCl₃ to mixtures of triarylphosphine oxides and LiAlH₄ in thf results in much increased yields of the phosphines, although again this may be accompanied by complete racemization, a feature found for (*S*)-(2-An)MePhPO²¹. Reduction of phosphine oxides with NaBH₄ occurs only in the presence of CeCl₃; initially this reaction yields the phosphine-BH₃⁻ complex (60–90%) from which the borane may be removed, with retention of configuration relative to the starting oxide, by treatment with Et₂NH²².

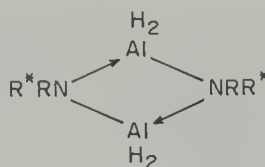
Reduction of phosphine oxides with simultaneous asymmetric induction has been observed following the use of the chiral aminoalanes **12** and **13** (where R* represents a chiral organic group). Reduction of racemic MePhPrPO with the alane **13** derived from methyl-(*S*)-2-phenylethylamine afforded a 30% yield of the phosphine possessing about 20% induced optical activity. Potential difficulties in the widespread use of the procedure are well illustrated by the reduction of 3-methyl-1-phenyl-3-phospholene 1-oxide (**14**),[†] when both the extent and the sign of the induced optical activity are dependent on the presence of Et₃N, and also the reaction temperature within fairly narrow limits²³.

Far more extensively used than any of the hydride or other metal reagents hitherto mentioned have been a variety of silicon compounds. A mixture of methylchlorosilanes reduces Ph₃PO in very high yield but the scope of this reduction procedure has not

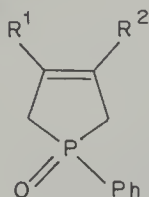
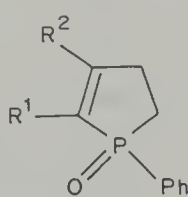
[†]Such compounds may also be referred to (and currently are in *Chemical Abstracts*) as 2,5-dihydro-1*H*-phospholes.



(12)



(13)

(14) $R^1 = \text{Me}; R^2 = \text{H}$ (15) $R^1 = R^2 = \text{Me}$ (16) $R^1 = R^2 = \text{H}$ (17) $R^1 = \text{H}; R^2 = \text{Me}$ (18) $R^1 = R^2 = \text{H}$ (19) $R^1 = \text{Ph}; R^2 = \text{H}$

been explored²⁴. Polysiloxanes, $(\text{OSiHMe})_n$, may be employed in the presence or absence of a solvent, but higher temperatures are required for the reduction of triarylphosphine oxides; yields of about 60–90% have been achieved using diethylene glycol dimethyl ether as solvent, and the reagent has been used successfully with the cyclic oxides **15** and **17**¹⁰.

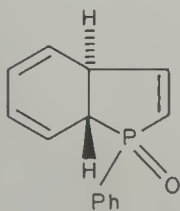
Much attention has been focused on the use of trichlorosilane and the phenylsilanes, $\text{Ph}_n\text{SiH}_{1-n}$. Advantages in the use of the phenylsilanes as reducing agents include their ready availability, either commercially or through the reduction of the corresponding chlorides with LiAlH_4 , and the high reaction yields coupled, under appropriate circumstances, with very high stereospecificity with retention of configuration. Phenylsilane has been used for the reduction of allylic phosphine oxides (**20**) and the phosphine oxide moiety $\text{R}_2\text{P}(\text{O})(\text{CH}_2)_n$ —bound to a solid support²⁵, and also phosphine oxides having the general structures $\text{Ar}_2\text{P}(\text{O})\text{Me}$ ²⁶ and $\text{RMeP}(\text{O})\text{Ph}$ ²⁷. Indeed, phenylsilane has been described as the reagent of choice for the reduction of phosphine oxides²⁸.



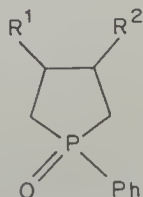
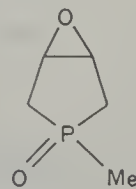
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(21)

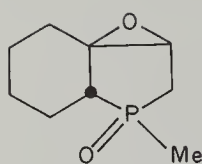
Diphenylsilane reduces the α -(diphenylphosphinoyl)alkyl cyanides **21** ($n = 1, 3$ or 4)²⁹, and both mono- and di-phenylsilane reagents have been employed in the reduction of *P*-oxides of phospholenes, e.g. **15**, **18** and **19**¹⁰, **16** and **22**³⁰, phospholanes, e.g. **23** and **24**^{31,32}, epoxides of types **25–27**³³ and simple phosphorinanes and phosphhepanes **28–30**^{28,34}.



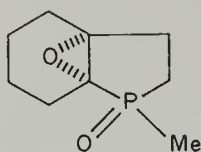
(22)

(23) $R^1 = \text{H}, R^2 = \text{Me}$ (24) $R^1 = R^2 = \text{Br}$ 

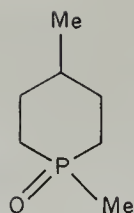
(25)



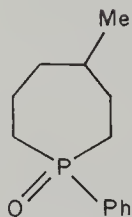
(26)



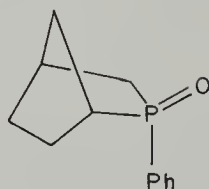
(27)



(28)



(29)



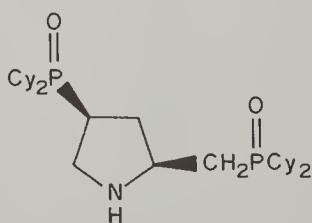
(30)

Phenylsilane deoxygenates (*R*)-(-)-(PhCH₂)MePrPO to the (*S*)-(+)-phosphine of comparable optical purity, and a similar result is observed for (*S*)-(-)-(PhCH₂)MePhPO, i.e. reaction with retention of configuration³⁵; by contrast, the same reagent reduces (*R*)_P-(menthyl)MePhPO to a 9:1 mixture of the (*S*)_P and (*R*)_P phosphines³⁶. Epoxy, cyano, bromo and vinyl groups are evidently tolerated by the phenylsilane reagents.

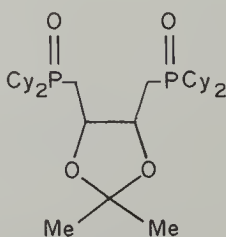
Trichlorosilane (silicochloroform), SiHCl₃, has been the most widely examined of all the silicon hydrides for the deoxygenation of phosphine oxides. It is a powerful reagent, capable of reducing many types of phosphine oxides; at the same time, however, it is one which has to be used with some caution, particularly with regard to the assignment of configurational changes at phosphorus, and it is recommended that such assignments in the product phosphines be checked by re-oxidation with H₂O₂ (retention of configuration) or by spectroscopic means, e.g. ¹³C NMR spectroscopy.

In a pioneering study, Horner and Balzer³⁷ showed that trichlorosilane reduced phosphine oxides with retention of configuration; however, reduction in the presence of Et₃N or, even better, Bu₃N, resulted in inversion of configuration at phosphorus, whereas the use of pyridine or *N,N*-diethylaniline brought about no such change. In practice, the reagent is employed with or without added base in a solvent (CHCl₃, benzene or a higher boiling aromatic), generally under reflux conditions. Phosphine oxides so reduced include trialkyl³⁸, dialkylaryl^{39,40}, alkyl-diaryl^{41,42} and triaryl^{38,43} derivatives, in which several functional groups, including CN, COOH, COOR, NO₂,

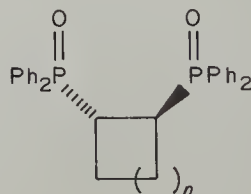
(*n* = 2 or 3)⁵² and **37**⁵³



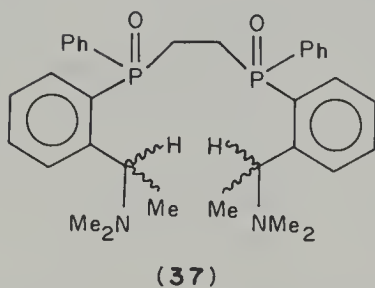
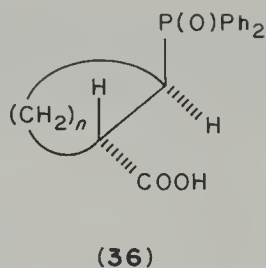
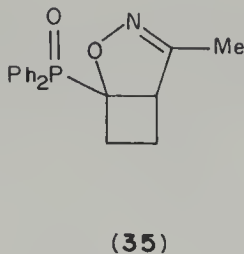
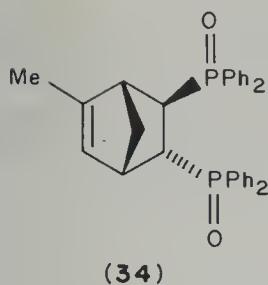
(31)



(32)

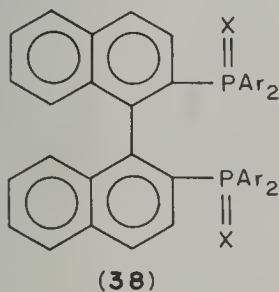


(33)

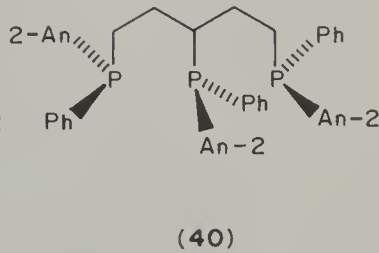
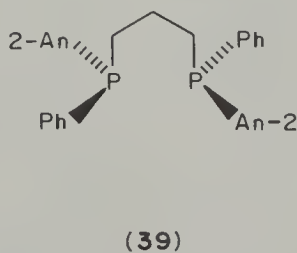


NR_2 , NR_3^+ or OMe , particularly when attached to aromatic rings, are unaffected by the reagent. Other phosphine oxides of some special interest and which have been successfully reduced include 2-(dicyclohexylphosphinoyl)-4-[(dicyclohexylphosphinoyl)methyl]pyrrolidine (31)⁴⁴, 4,5-bis[(dicyclohexylphosphinoyl)methyl]-2,2-dimethyl-1,3-dioxolane (32)⁴⁵ and the diphenylphosphinoyl compounds 9^{11,46,47}, 33 ($n=0$ ⁴⁸ or 1⁴⁹), the enantiomers of methylmorphos dioxide (34)⁵⁰, 35⁵¹, racemic 36.

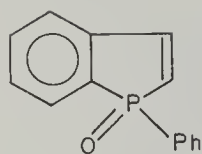
Other applications include the syntheses of optically active forms of the binaps ligands 38 ($\text{X} = \text{lone pair}$; $\text{Ar} = \text{Ph}$, 4-tol, or 4-Bu^tC₆H₄) from the resolved forms of the binaps dioxides 38 ($\text{X} = \text{O}$)⁵⁴, and of the ligands 39 and 40 (using *N,N*-diethylcyclohexylamine as base in MeCN)⁵⁵, during which inversion at phosphorus was assumed to have taken place. In the presence of Et₃N, the reagent reduced (*R*)-(menthyl)methylPhPO to a 4:1 mixture of (*R*)_P and (*S*)_P phosphines, i.e. with largely, but by no means exclusively, inversion³⁶.



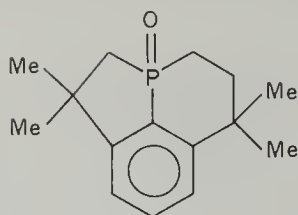
An = anisyl



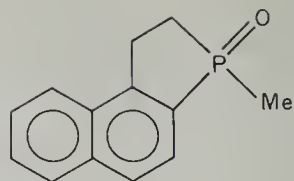
The many types of cyclic phosphines oxides possessing the phosphorus atom in a non-bridging position, which have been reduced to the corresponding phosphines by trichlorosilane, in the presence or otherwise of added amine, include phospholes and their benzo derivatives, e.g. 41⁵⁶; phospholenes and their benzo derivatives, e.g. 42⁵⁷, 43⁵⁸, 44⁵⁹, 45 and 46⁶⁰, 47⁶¹, 48 and 49⁶²; 17³⁷; 5,10-dihydrodibenzo [*b*,*e*]phosphorins,



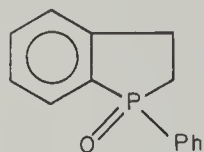
(41)



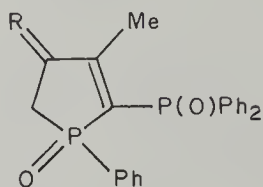
(42)



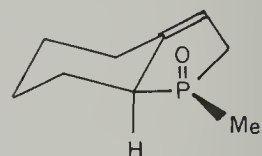
(43)



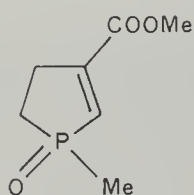
(44)

(45) R = CH₂

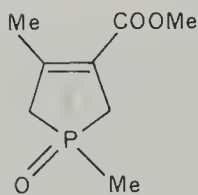
(46) R = O



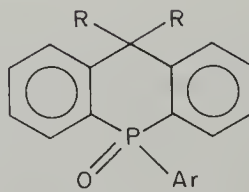
(47)



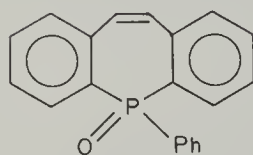
(48)



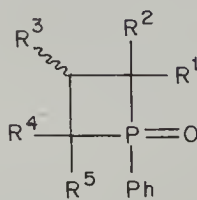
(49)

(50) R₂ = O; Ar = Ph

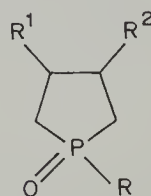
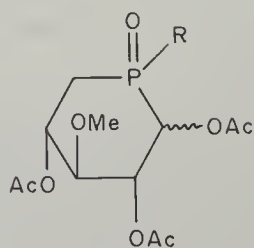
(51) R = Me, Ar =



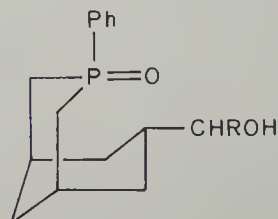
(52)



(53)

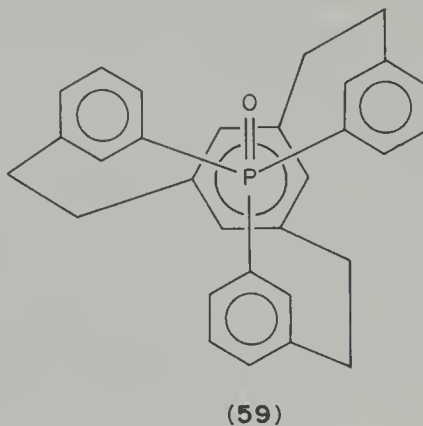
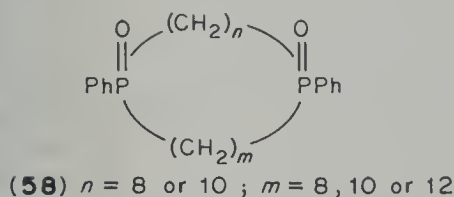
(54) R = Me; R¹ = H; R² = Me(55) R = CH₂Ph; R¹ = R² = Br

(56)

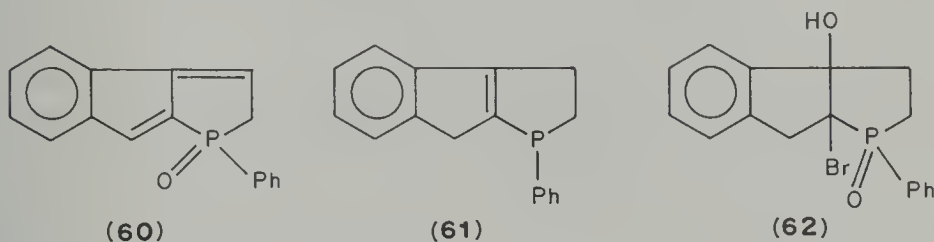


(57)

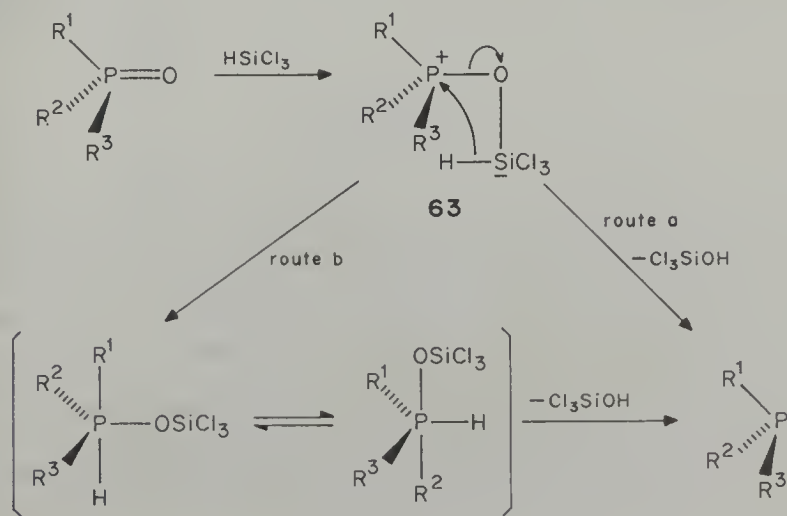
e.g. **50**⁶³ and **51**⁶⁴; 5-phenyl-5*H*-dibenzo[*b, f*]phosphepin 5-oxide **52**⁶⁵; the phosphetanes **53** ($R^1-R^5 = H$ or Me)⁶⁶; phospholanes, e.g. **54**⁶⁷ and **55**⁶⁸; phosphorinanes **56** ($R = Et$ or Ph)⁶⁹; **57** ($R = H$ or Ph)^{70,71}; the large-ring compounds **58**⁷²; and the phosphacyclopentane **59**⁷³. Within these systems, OAc, OMe, Br, CH₂OH, CR₂OH and COOMe groups appear to tolerate the reagent.



A few examples exist for which unfortunate side-reactions become prominent. Thus, attempted reduction of the oxide **60** yields the phosphine **61**, also obtained when **62** is similarly reduced. In the presence of pyridine, **60** is simply deoxygenated⁷⁴.

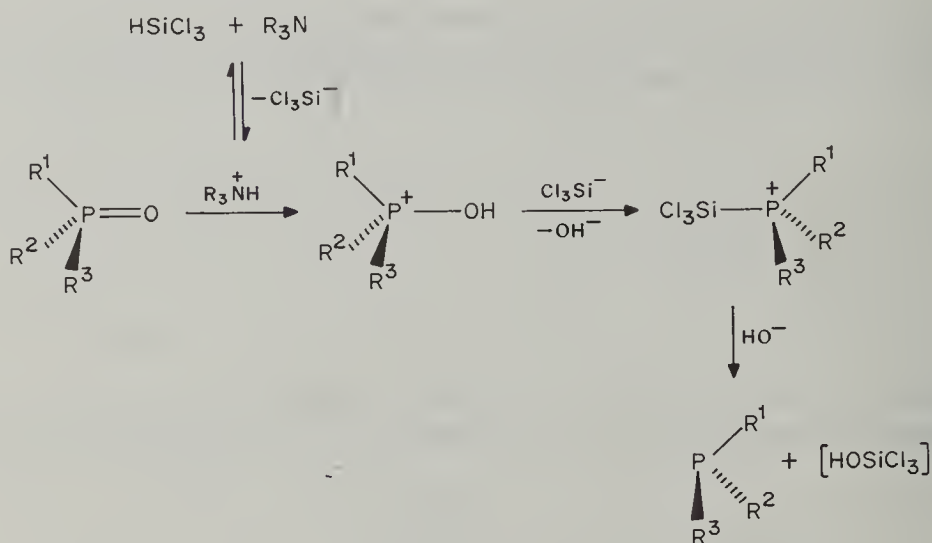


Horner and Balzer³⁷ rationalized their original observations on the trichlorosilane reduction of phosphine oxides, with net retention, with an explanation (Scheme 3)



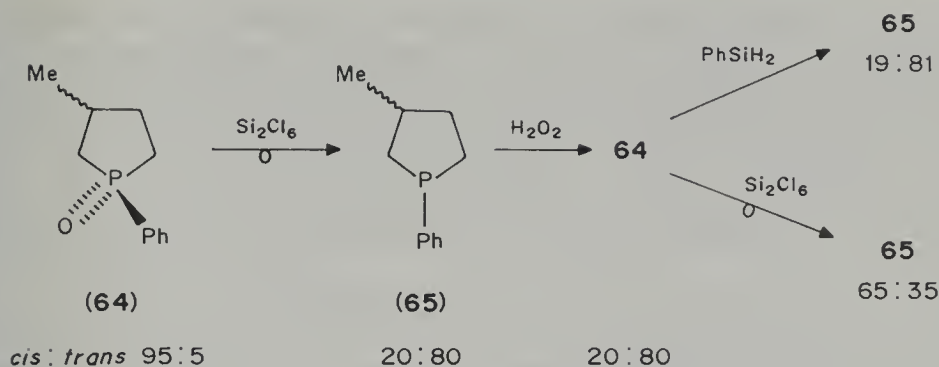
involving complexation and a hydride shift followed (route a) by direct loss of silicon; later authors raised the possibility of the intermediacy of pentacoordinate species (route b), possibly resulting from a rearrangement of structure **63**⁷⁵.

To rationalize the net inversion observed when the oxides are reduced in the presence of Et_3N , Horner and Balzer stressed the importance of complexation between the reagent and the added tertiary base (and certainly such complexation is well known to occur), but this consideration has been shown to be unimportant⁷⁵. More striking is the possible relevance of base strength. When a base with $\text{p}K_{\text{B}} < \text{ca } 5$ (Et_3N , $\text{p}K_{\text{B}} 3.26$) is used, largely inversion of configuration is observed. Largely retention of configuration is to be noted using those bases with $\text{p}K_{\text{B}}$ of $\geq \text{ca } 7$ (pyridine, $\text{p}K_{\text{B}} 8.81$; Et_2NPh , $\text{p}K_{\text{B}} 7.44$). Moreover, the type of base is also of some importance; the use of primary or secondary amines can lead to results entirely different from those observed with tertiary amines. A further complicating feature is the dependence of the final stereochemical outcome on the nature of the reaction solvent; HSiCl_3 with Et_2NPh in benzene or dibutyl ether reduces $(\text{PhCH}_2)\text{MePhPO}$ largely with retention of configuration, but in acetonitrile the reaction proceeds with predominant inversion. A mechanism proposed later⁷⁵ for the inversion process is outlined in Scheme 4, but here again there remains the question as to the possible participation of pentacoordinate intermediates in the later stages.



SCHEME 4

The potential usefulness of disilane derivatives with Si—halogen bonds as reducing agents was suggested by two features of silicon chemistry: the known reducing power of such compounds, and the fact that the freshly prepared adduct from HSiCl_3 and Et_3N liberated hydrogen when placed in aqueous base. Thus, the oxides MePhP(O)R ($\text{R} = \text{allyl}, \text{PhCH}_2$ or 4-An), each of 100% optical purity, were reduced to the corresponding phosphines of 67, 95, and 94% optical purities, respectively, and with inverted configurations, when treated with Si_2Cl_6 , similar results being obtained with the use of Si_3Cl_8 ⁷⁵. Configurational inversions were also noted in the reductions of $(R)\text{-Bu}^t\text{MePhPO}$ ⁷⁶, and both $(R)_\text{P}$ and $(S)_\text{P}$ -(menthyl) MePhPO ³⁶. Extensive inversion also occurred in the reduction of a 95:5 *cis:trans* mixture of 3-methyl-1-phenylphospholane 1-oxides (**64**) (Scheme 5)³².

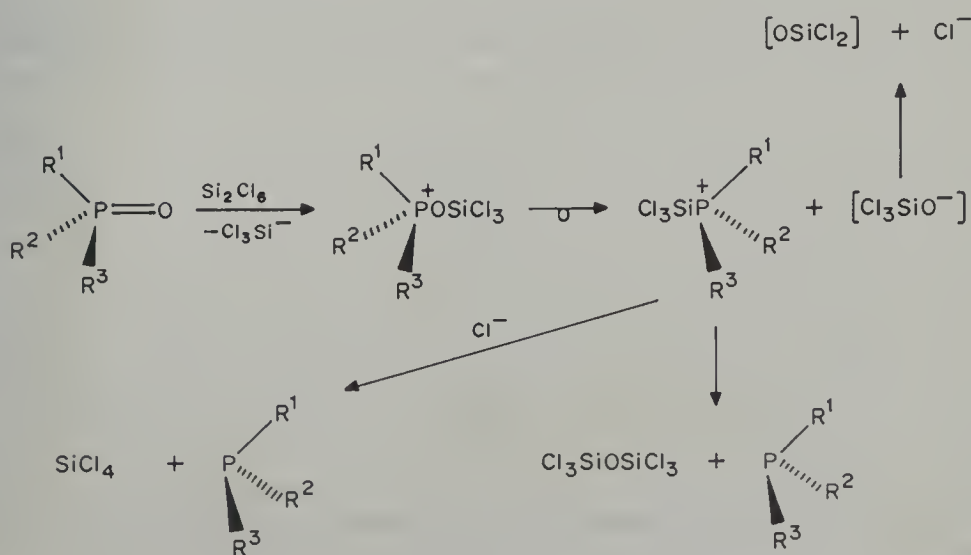


SCHEME 5

The lack of stereospecificity in reductions by Si_2Cl_6 has been attributed to the formation of SiCl_4 and the stereomutation that this compound is known to cause^{77,78}. When the phosphine **65** was treated with SiCl_4 , the *cis:trans* composition ratio 20:80 became 45:55³². At room temperature, SiCl_4 causes complete stereomutation of $(\text{PhCH}_2)\text{MePhPO}$ in MeCN during 20 min, and the degree of stereomutation increases if the contact time between substrate/product and Si_2Cl_6 reagent (and thus also SiCl_4) is greater than about 5 min.

A proposed mechanism (Scheme 6) for reductions with Si_2Cl_6 accommodates the formation of SiCl_4 , and the sequence probably proceeds via the intermediate $\text{R}^1\text{R}^2\text{R}^3\text{P}(\text{OSiCl}_3)\text{SiCl}_3$, which is unlikely to undergo isomerization since the more electronegative groups are already in the apical positions of a trigonal bipyramid.

Phosphetane 1-oxides are reduced by silicon reagents under conditions significantly milder than those normally required for unbranched acyclic phosphine oxides, although the outcome of such reductions may be less predictable. There appears to be no stereospecificity dependence on the presence, or otherwise, of a tertiary base (Et_3N , pyridine) for reductions with SiHCl_3 which, for this group of substrates, has been used with^{66,79,80} or without base^{79,81}; in the presence of Et_3N , SiHCl_3 reduces hexamethyl-



SCHEME 6

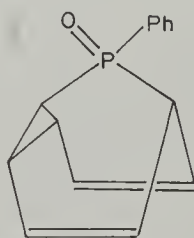
phosphetane 1-oxide with retention of configuration, and although the same reagent in the presence of pyridine also reduces 2,2,3-trimethyl-1-phenylphosphetane 1-oxide stereospecifically, the reduction of the latter phosphetane oxide by SiHCl_3 in the presence of Et_3N depends on the ratio of substrate to reagents for the stereochemical outcome. Other reagents which have been used with phosphetane substrates include 'silicone fluid'⁸¹, PhSiH_3 ⁸² and Si_2Cl_6 ⁷⁸. 4-Methyl-4-phosphatetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane 4-oxide (**66**) is reduced, with 100% yield, to the *endo* phosphine (inversion) with SiHCl_3 alone⁸³ but to a mixture of *endo* and *exo* products in the ratio 2:1 when pyridine is present⁷⁹.

As the severe angular constraint present in the phosphetane ring is relaxed, as it is in the monocyclic phospholane and larger saturated ring systems, reduction of the oxides to the parent phosphines by silicon reagents proceeds more predictably with retention of configuration.

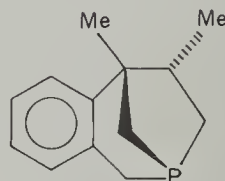
A structural feature which has been shown to have a pronounced effect on the final reaction outcome is the constraint imposed by phosphorus at a bridgehead position. When the phosphorus bridge produces no particular strain, reductions of *P*-oxides proceeds normally, as has been found for compounds **67** with SiCl_6 ¹⁸, *endo*-3-phenyl-3-phosphabicyclo[3.2.1]octane 3-oxide (**30**) with PhSiH_3 and compound **68** with SiHCl_3 alone^{34,84}, the phosphines being obtained essentially with retained stereochemistry and no loss of phosphorus bridge.



(66)



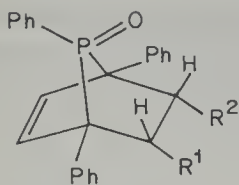
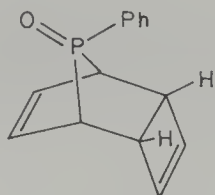
(67)



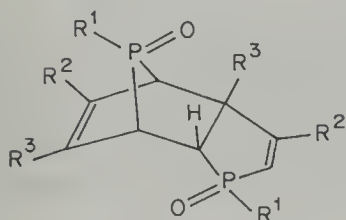
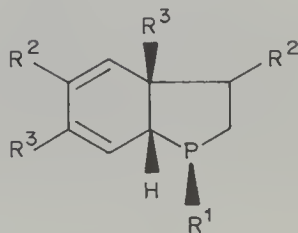
(68)

Many compounds in the 7-phosphanorbornene system, of which **10** is one, behave unusually towards silicon reducing agents. Thus, with Si_2Cl_6 ,⁷⁹ **10** loses the phosphorus bridge to yield 1,2,3,4-tetraphenylnaphthalene, as it does when treated with LiAlH_4 ¹⁸. Initially, the *syn*-1,4,7-triphenyl-7-phosphabicyclo[2.2.1]hept-5-enes **69** and **70** with SiHCl_3 -pyridine yield the corresponding *syn*-phosphines, but for each the main isolable product is $(\text{PhP})_4$. With SiHCl_3 alone, 9-phenyl-9-phosphatricyclo[4.2.1.0^{2,5}]nona-3,7-diene 9-oxide (**71**) is reduced but the product rapidly loses bridgehead phosphorus as PhPH_2 to give cyclooctatetraene; addition of pyridine to the initial reduction mixture allows the isolation of the expected *anti*-phosphine in ca 80% yield.

The most unusual results relate to the 3a,4,7,7a-tetrahydro-4,7-phosphindine-1*H*-phosphindoles **72–76**, recognizable as phosphole 1-oxide dimers. When treated with SiHCl_3 in boiling benzene, these compounds lose the bridging phosphorus as R^1PH_2 and the 1- R^1 -*cis*-3a,7a-dihydrophosphindoline (**78**, $\text{R}^1 = \text{Me}$ or Ph) co-products are isolable^{59,79}. The presence of pyridine, although not always required, as, for example, for **74** and **75**, certainly allows normal reductions to proceed with high yields and with retention of molecular geometry. Reductions of the same compounds with PhSiH_3 consistently afforded the bisphosphines with inverted geometry at the bridgehead phosphorus atom as the main products (ca 70%), together with the isomer with retained *syn* geometry as the minor products (8–27%).

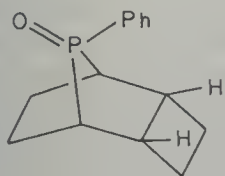
(69) $R^1 = \text{CN}$; $R^2 = \text{H}$ (70) $R^1 = R^2 = \text{COOMe}$ 

(71)

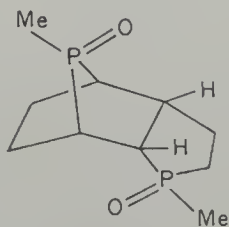
(72) $R^1 = \text{Me}$; $R^2 = R^3 = \text{H}$ (73) $R^1 = \text{Ph}$; $R^2 = R^3 = \text{H}$ (74) $R^1 = R^2 = \text{Me}$; $R^3 = \text{H}$ (75) $R^1 = \text{Ph}$; $R^2 = \text{Me}$; $R^3 = \text{H}$ (76) $R^1 = R^2 = R^3 = \text{Me}$ (77) $R^1 = \text{Ph}$; $R^2 = R^3 = \text{Me}$ 

(78)

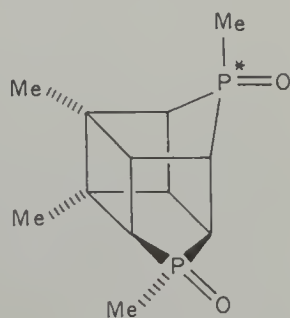
The fragmentations with loss of bridgehead phosphorus are examples of retro-cycloaddition reactions (in this case retro-McCormick reactions) and they do not occur for fully saturated analogues. The 7-phosphanorbornane **79** and 1-*syn*-8,8-dimethyl-2,3,3a,4,5,6,7,7a-octahydro-4,7-phosphinidine-1*H*-phosphole (**80**) are reduced by SiHCl_3 with configurational retention in 93% and 30% yields, respectively. The cage compound **81** is reduced by SiHCl_3 alone with inversion of P^* stereochemistry, but, in the presence of pyridine, or when PhSiH_3 is employed, the stereochemistry is retained at both phosphorus centres.



(79)



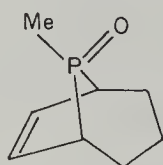
(80)



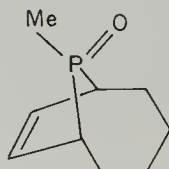
(81)

Angular constraint can be relieved by enlarging the component rings of such molecules. Both 8-phosphabicyclo[3.2.1]octene **82** and its homologue **83**, as mixtures of *syn* and *anti* isomers, afford mixtures of the phosphines of comparable stereochemical content

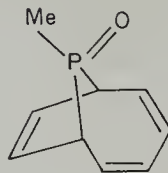
when deoxygenated with SiHCl_3 irrespective of the presence, or otherwise, of pyridine; interestingly, the 9-phosphabicyclo[4.2.1]nonatriene **84** with SiHCl_3 alone gives only phosphine with retained geometry.



(82)

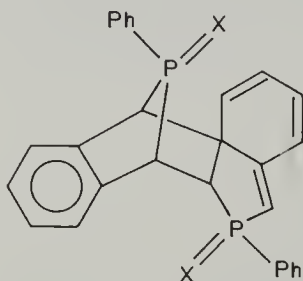


(83)

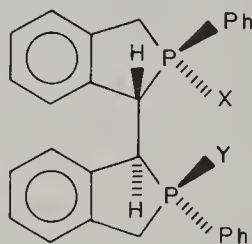


(84)

Compound **85** behaves even more unusually when treated with SiHCl_3 . In the presence of Et_3N at ambient temperature, cleavage occurs at one of two possible positions to give the bisphosphindoline monoxide (**86.1**). Loss of PhPO from a bridging position evidently does not occur, nor does reduction to the bisphosphine **86.2** unless the reaction temperature is raised to 60°C ; both products may be oxidized to the bisoxide⁸⁴.



(85)

(86.1) $\text{X} = \text{lp}^\dagger$, $\text{Y} = \text{O}$ (86.2) $\text{X} = \text{Y} = \text{lp}^\sigma$

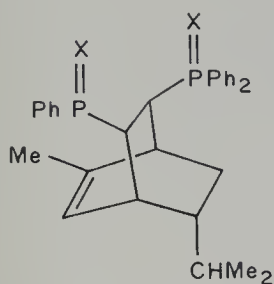
There are thus many opportunities to make erroneous predictions about the stereochemical outcome of reductions of phosphine oxides with silicon-containing reagents; nevertheless they are powerful reagents. The existence of isomerization and retro-cycloaddition processes calls for the participation of pentacoordinate intermediates.

2. Phosphines from phosphine sulphides, selenides and tellurides

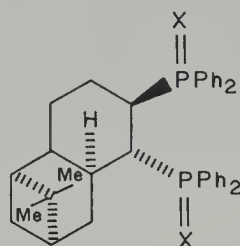
Several types of tertiary phosphine sulphides have been desulphurized successfully by a wide variety of reagents under conditions which have ranged from mild to severe. Iron powder, NaH at $250\text{--}300^\circ\text{C}$ or Na with naphthalene⁸⁵ were amongst the earliest reagents used. Sodium under boiling toluene has been the reagent of choice for alkyldiarylphosphine sulphides; specifically, this reagent has been used in the synthesis of (*S,S*)-phellanphos (**87**) ($\text{X} = \text{lp}$) and norphos (**88**) ($\text{X} = \text{lp}$) by the removal of the thiophosphoryl sulphur from the corresponding sulphides, in turn obtained from phellandrene and nopadiene, respectively⁸⁶. Unlike oxygen from a phosphine oxide, sulphur is removable from a phosphine sulphide under Birch conditions [Li-NH_3 (1)]. By contrast to the high reactivity shown towards Ph_3PS , sodium with naphthalene fails to desulphurize $\text{Me}_2\text{P(S)CH}_2\text{CH}_2\text{P(S)Me}_2$, a compound also unreactive to LiAlH_4 in thf ⁸⁷. Nevertheless, LiAlH_4 in dioxane has proved popular as a desulphurizing agent. Luchenbach⁸⁸, using

[†] $\text{lp} = \text{Lone pair of electrons.}$

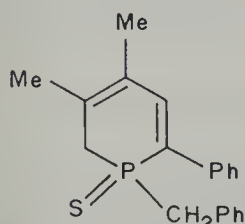
(*R*)-(+) -MePhPrPS showed that, in either thf or dibutyl ether at 65 °C, LiAlH₄ removed the sulphur with complete retention of configuration at phosphorus. The 1,2-dihydrophosphorin 1-sulphide **89** was desulphurized by nickel powder at high temperature, but also suffers debenzylation to 2-phenyl-4,5-dimethylphosphorin⁸⁹.



(87)



(88)



(89)

In studies on poly(tertiary phosphine) ligands, King and coworkers resorted to their synthesis through the corresponding sulphides, since this obviated the need to work with more volatile and obnoxious phosphines; the synthesis of the target compounds was completed by the removal of sulphur with LiAlH₄ in boiling dioxane. In this way the phosphine sulphides Me_nP(S) (CH=CH₂)_{n-3} proved more attractive starting materials than the corresponding phosphines. An example of their use is illustrated in Scheme 7^{90,91}.

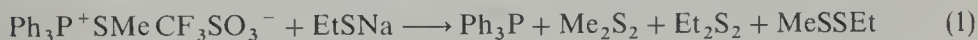


SCHEME 7

Amongst the more recent developments in desulphurization processes is the use of metal complexes. Mathey found that the slight reduction to the phosphine when 3,4-dimethyl-1-phenyl-3-phospholene 1-sulphide was treated with nickelocene at 110 °C for 20 h increased if the reaction was carried out in diglyme^{92,93}. Most of the product phosphine was evidently incorporated into a complex, but could be liberated from that with NaCN in MeOH, or by *N*-methylimidazole⁹⁴ or (MeO)₃P⁹⁵. The treatment of a tertiary phosphine sulphide with [Fe(CO)₅] at 130–150 °C yields the complex [R₃PFe(CO)₄] which, with CuCl₂ in MeOH, gives [(R₃P)₂Fe(CO)₂Cl₂]; when heated, or when treated with *N*-methylimidazole, such complexes release the phosphine in a process compatible with the presence of alcohol and carbonyl functions. This procedure appears to have the advantage over the nickelocene process in being less sensitive to steric hindrance around phosphorus⁹⁶.

Additional to its use for the deoxygenation of tertiary phosphine oxides, Si_2Cl_6 has also been employed for the removal of sulphur from phosphine sulphides¹⁰⁴. The use of chiral phosphine sulphides has demonstrated the stereospecificity of the reaction with retention of configuration at phosphorus¹⁰⁷.

A well characterized indirect method for the removal of sulphur or selenium from a tertiary phosphine sulphide or selenide consists in the formation of a quaternary salt (Section II.C) with subsequent removal of the chalcogen as a disulphide or deselenide. Thus, electrolysis of the salt $\text{Ph}_3\text{P}^+\text{SMe MeSO}_4^-$ yields 69% Ph_3P . The cleavage of the salts is also accomplished when they are treated with sodium ethylthiolate, as exemplified in equation 1¹⁰⁸. That cleavage of the quaternary salts occurs with retention of configuration is shown by the formation of (*R*)-(+)- Bu^tEtPhP from the (*S*)-(+)-sulphide via the (*S*)-(–)-methylthiophosphonium triflate¹⁰⁸.

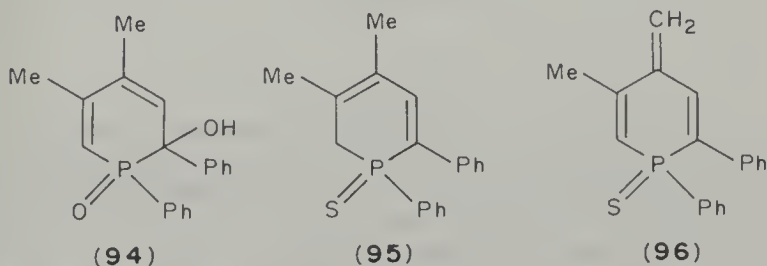


In the case of particularly reactive compounds, e.g. tris(2,6-dimethoxyphenyl)-phosphine sulphides, a solution of an alkyl- or aryl-thiol (rather than its sodium salt) in MeOH is sufficient to complete the reaction¹⁰⁹. Other quaternary salts of the same type have been cleaved by KCN in the presence of 18-crown-6 in CH_2Cl_2 ¹¹⁰.

B. Interconversions of Quinquevalent Tetracoordinate Compounds

1. Phosphine sulphides, selenides or tellurides from phosphine oxides

Early reports indicated that tertiary phosphine sulphides could be prepared from the corresponding phosphine oxides by simply heating them with elemental sulphur at a moderate to high temperature, but such reports appear not to have been substantiated. Triarylphosphine oxides yield the corresponding sulphides when heated with P_4S_{10} ^{98,111} and enantiomers of MePhPrPO yield the racemic sulphide with the same reagent¹¹², although optically active sulphides do not racemize under the same conditions. The fused-ring tetrahydrophosphorin 1-oxide **90.2** has been converted into the sulphide¹⁰¹, while the dihydrophosphorin 1-oxide **94** suffered dehydration and rearrangement during the sulphurization reaction with the same reagent to give **95** and **96**¹¹³.



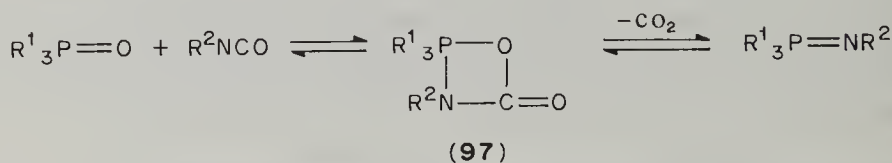
It is perhaps surprising that 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulphide (Lawesson's reagent), generally thought to be sulphurization reagent superior to P_4S_{10} , appears to have been used very seldom, a rare example of its use being in the conversion of the *endo*-dimeric phosphole dioxide **77** into the corresponding disulphide¹¹⁴.

An unusual sulphurization reagent is B_2S_3 which, within the narrow range of substrate compounds examined, affords moderate conversions of phosphine oxides into the sulphides; stereospecificity was 65% with predominant retention of configuration for acyclic oxides, with some slight loss of optical purity, but with the loss in the latter for isomeric phosphetane oxides¹¹⁵.

The reported formation of 5-phenyl-5*H*-dibenzophosphole 1-selenide, and of Ph_3PSe , by treatment of the corresponding oxides with $\text{Se-KH}_2\text{PO}_4$ at 270–370 °C, is possibly no more than sequential deoxygenation and selenation¹¹⁶.

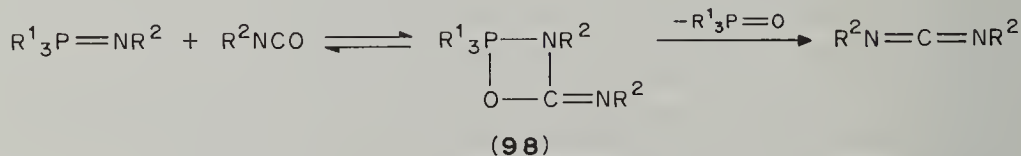
2. Phosphine imides from phosphine oxides

The first observations on the catalytic role of tertiary phosphine oxides on the formation of carbodiimides from isocyanates appear to have been made by Monagle and coworkers¹¹⁷, who, from a study of the kinetics of the liberation of CO_2 , recognized that the interaction occurred in two distinct stages. The first stage leads, via a four-membered ring pentacoordinate intermediate or transition state (97), to a phosphine imide as in Scheme 9. The sequence is reversible; phosphine imides are known to react with carbonyl compounds, including CO_2 , when, in the latter case, isocyanates are formed.

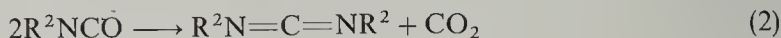


SCHEME 9

The second stage, as in the Scheme 10, consists in the interaction of the imide and a second mole of isocyanate in a rapid process also proceeding through a similar type of intermediate or transition state. The overall reaction is that represented in equation 2.

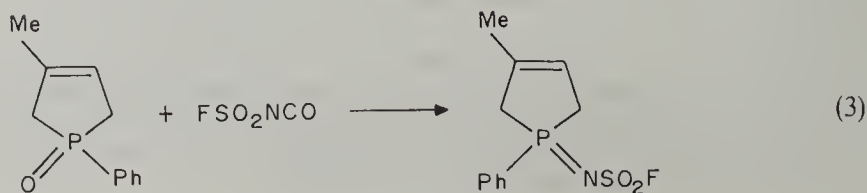


SCHEME 10



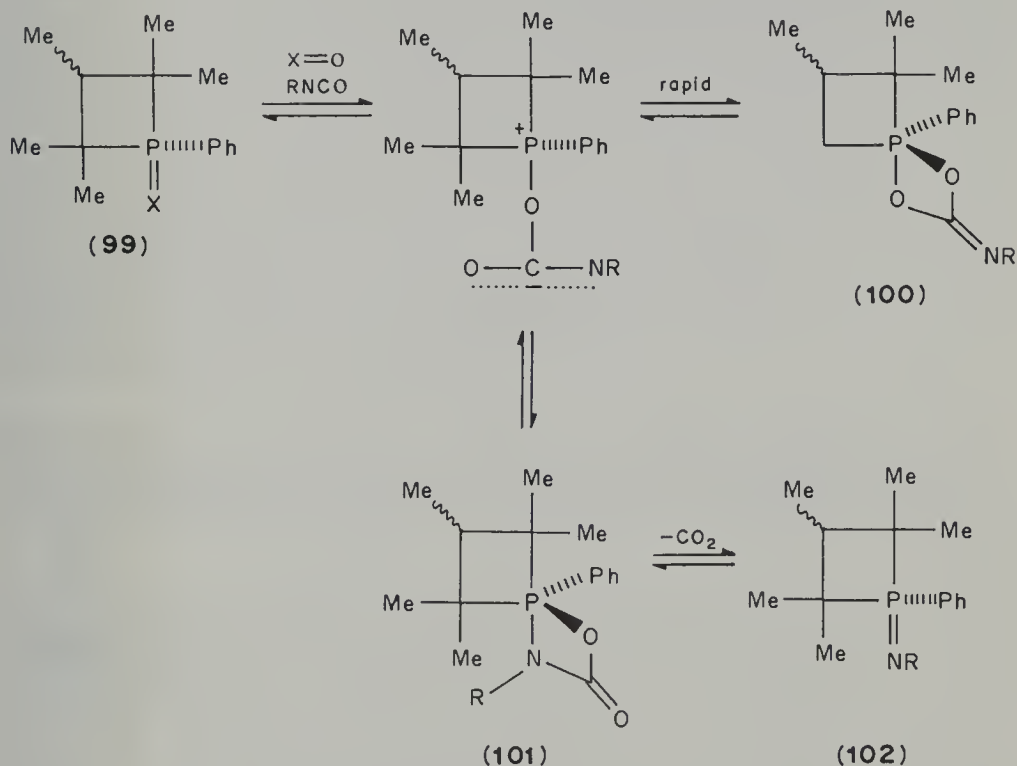
The first stage (Scheme 9) is rate determining, the reactions of phosphine imides with R^2NCO being 10^5 – 10^7 times faster than those of, for example, the oxides $\text{Ph}_n\text{P}(\text{O})\text{Et}_{3-n}$. 1-Phenylphospholane 1-oxide is 10^3 times more reactive than $\text{PhP}(\text{O})\text{Et}_2$ as a catalyst, whereas the ratio of catalytic power of the imide is only ca 10^{118} . The most effective catalyst is 3-methyl-1-phenyl-3-phospholene 1-oxide.

The formation of an imide from an isocyanate and a phosphine oxide (reaction 3) has since been demonstrated by other workers, but in this case the reaction proceeds no further¹¹⁹.



The results of a study on the liberation of ^{18}O (as CO_2) from an oxide enriched at the phosphoryl group were also consistent with the overall picture represented in Schemes 9 and 10¹²⁰ but, because of difficulties in the interpretation of the kinetic results, Aksnes and Frøyer¹¹⁸ proposed the participation of betaine intermediates which cyclize to give **97** and **98**.

Hall and Smith¹²¹ investigated the stereochemical course of the reactions between cyclic phosphine oxides, as exemplified by the geometric isomers of phosphetane 1-oxides, and the isocyanates RSO_2NCO ($\text{R} = \text{Cl}$ or 4-tol). Both *cis*- and *trans*-2,2,3,4,4-pentamethyl-1-phenylphosphetane 1-oxide gave imides with retention of configuration at phosphorus (Scheme 11).



SCHEME 11

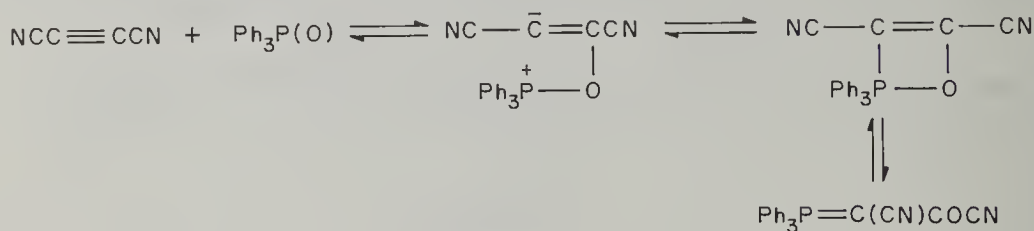
The proposed mechanism takes into account the types of betaine suggested by Aksnes and Frøyer¹¹⁸, and which lead to pentacoordinate species of undetermined structure, although **101** is thought to be more probable than **100**. The reaction for the corresponding sulphide (**99**, $\text{X} = \text{S}$) was slower and 2 mol of TsNCO were required for each mole of sulphide, leading to **102** together with TsNCS via **99** ($\text{X} = \text{O}$). The formation of diphenylcarbodiimide from PhNCO and Ph_3PS at 165°C had already been noted in 1964 by Maier⁸.

In a second study, the reactions of acyclic phosphine oxides were shown to be slower than those of the phosphetane oxides; optically active oxides, e.g. enantiomers of $(\text{PhCH}_2)_2\text{MePhPO}$, are racemized faster (half-life ca 40 min) than the rate of formation of the imides (half-life ca 36 h). Three possible mechanisms were considered for the formation of a monocyclic phosphorane intermediate after initial betaine formation but, unfortunately, computer simulation of the kinetics failed to distinguish conclusively between them¹²².

The feature distinguishing between the results of these two studies is clearly the constraint placed on stereomutational processes within any intermediate(s) by the presence of the phosphetane ring; this must occupy an equatorial-axial position in any pentacoordinate intermediate, and its formation would be followed by a collapse to give **102** with retention of configuration.

3. Phosphine methylenes (ylides) from phosphine oxides

Scheme 12 summarizes the remarkable interaction between triphenylphosphine oxide and acetylenes containing electronegative groups in a retro-Wittig reaction. The reactions between Ph_3PO and the acetylenes $\text{RC}\equiv\text{CR}'$, where $\text{R}=\text{R}'=\text{CF}_3$ or COOMe , and $\text{R}=\text{CN}$, $\text{R}'=\text{H}$, occur in the temperature range $120\text{--}200^\circ\text{C}$ ¹²³.

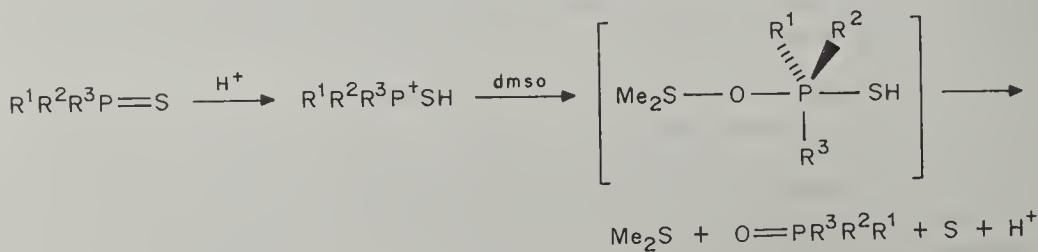


SCHEME 12

4. Phosphine oxides from phosphine sulphides, selenides or tellurides

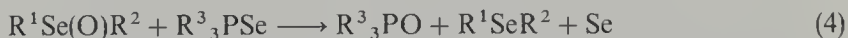
Tertiary phosphine sulphides are relatively stable compounds which undergo atmospheric oxidation only on prolonged exposure, and they are therefore unlike the corresponding selenides and tellurides, which are much more readily oxidized and which also liberate the chalcogen on exposure to light and particularly on contact with surfaces¹⁰².

Many of the more powerful oxidizing agents not only convert the $\text{P}=\text{X}$ grouping ($\text{X}=\text{S}$, Se , or Te) into $\text{P}=\text{O}$, but also bring about additional, perhaps unwanted, reactions. Thus the action of nitric acid on Ph_3PS yields tris(3-nitrophenyl)phosphine oxide, also obtainable by the direct nitration of Ph_3PO ; other dialkylarylphosphine sulphides behave analogously¹²⁴. The treatment of (*R*)-(+)- MePhPrPS with HNO_3 at room temperature yields the (*S*)-(–)-oxide in a highly stereospecific reaction with inversion; when N_2O_4 is used, there is marked racemization in addition to retention of configuration¹²⁵. KMnO_4 or acid dichromate readily convert $\text{P}=\text{S}$ into $\text{P}=\text{O}$, but simultaneously bring about the oxidation of, for example, alkyl groups attached to aromatic rings. MePhPrPS is oxidized by KMnO_4 -pyridine with predominant inversion of configuration at phosphorus. The same phosphine sulphide is oxidized by H_2O_2 , and unlike the case of the corresponding selenide, the stereospecificity is here unaffected by experimental conditions such as change of solvent and reaction temperature¹²⁶.

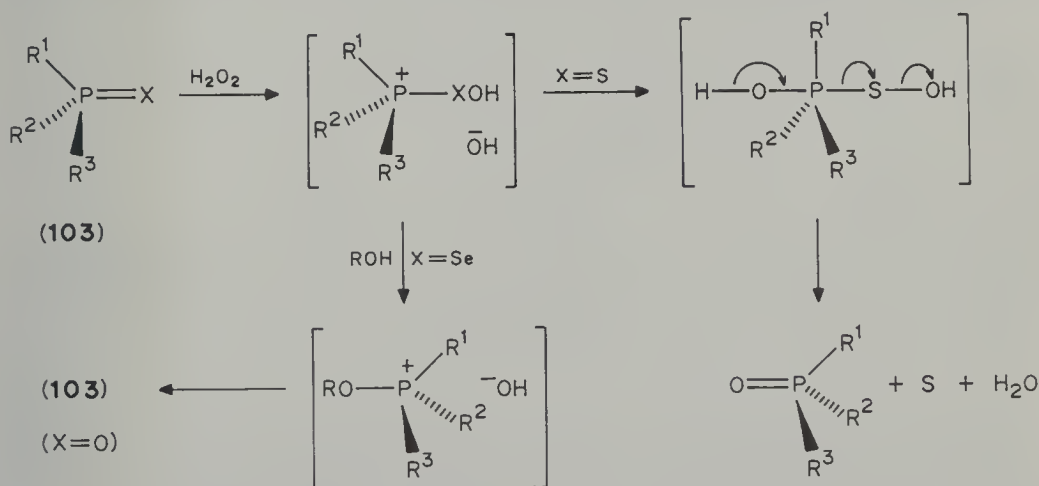


SCHEME 13

Following earlier proposals by Mikołajczyk in 1966, Luchenbach also suggested the use of dmsO under acidic conditions, and showed that with tertiary phosphine sulphides and, incidentally, tertiary arsine sulphides also, the oxidation proceeded with predominant inversion of configuration (Scheme 13)^{127,128}. This stereochemical outcome was also recognized by Mikołajczyk in a revision of the earlier conclusions, the reactions being catalysed by acid or iodine (5%)¹²⁹. The reaction, equally applicable to tertiary phosphine selenides^{129,130}, is also catalysed by metalloporphyrins aided by added imidazole¹³¹. Tertiary phosphine selenides are oxidized in high yield by selenoxides (equation 4)¹³² with retention of configuration accompanied by some racemization¹³³.



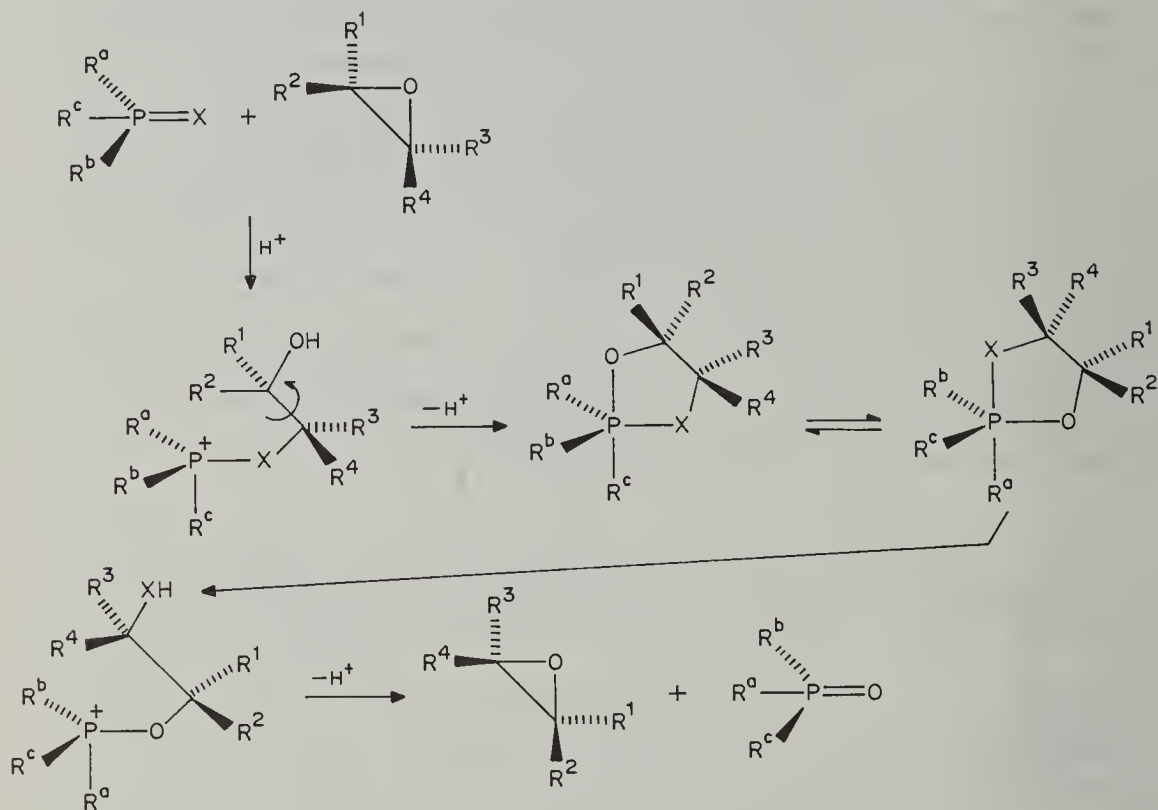
By contrast to the reactions involving tertiary phosphine sulphides, the stereochemical course of the oxidation of the phosphine selenides with H_2O_2 depends on the solvent system. Net retention of configuration is observed for solutions in MeOH or EtOH, but the introduction of thf to methanolic solutions, or the use of entirely different solvents, e.g. acetone, pyridine, nitromethane or even Bu^tOH , leads to inversion of configuration. The effect of reaction temperature then depends, in the case of selenides only, on the particular solvent; stereospecificity for reactions in $MeNO_2$ is independent of temperature, but for ethanolic solutions a rise in reaction temperature improves the stereospecificity. This is possibly the result of a lowering of the stability of a pentacoordinated intermediate so reducing the time available for stereomutation; the net retention of configuration observed for reactions in primary alcohols has been explained by assuming direct participation of the solvent (Scheme 14)¹²⁶.



SCHEME 14

Other peroxidic substances useful for the oxidation of tertiary phosphine sulphides and selenides include dioxiranes¹³⁴ and bis(trimethylsilyl) peroxide¹³⁵; reactions with the latter reagent are catalysed by $AlCl_3$ and occur at room temperature, when they are relatively quick for the selenides but slow for sulphides. Photogenerated peroxides oxidize both sulphides and selenides in the presence of Rose Bengal in yields which depend appreciably on the solvent^{136,137}. Ozone, successful in the oxidation of Ph_3PS and Ph_3PSe , reacts with $MePhRPS$ ($R = Pr$ or $PhCH_2$) with essentially complete retention of configuration^{138,139}.

The synthesis of thiiranes and their selenium analogues from oxiranes also represents the conversion of R_3PX ($X = S$ or Se) into the corresponding oxides; reactions, with high yields, are conducted in the presence of trifluoroacetic acid. By using a variety of oxiranes and Bu_3PSe , evidence has been collected to suggest the intermediacy of pentacoordinate compounds (Scheme 15). Selenium is retained in combined form for reactions involving epoxycyclohexane, and for those with 2-hexyloxirane selenium is liberated only on warming the reaction mixtures^{101,140}.



SCHEME 15

The oxidative removal of sulphur or selenium from the phosphine chalcogenide is also achievable using $(CF_3CO)_2O$ in CH_2Cl_2 , in a reaction accelerated by the presence of pyridine. Optically active sulphides suffer complete racemization, selenides with net inversion and a high degree of racemization; however, optically active oxides are also racemized. Pentacoordinate species of the type $R_3P(OCOCF_3)(SCOCF_3)$ are thought to be involved^{141,142}.

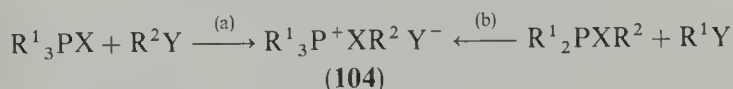
The treatment of triarylphosphine sulphides with $SOCl_2$ at room temperature can give large yields of the phosphine oxide accompanied, in the case of Ph_3PO itself, by ca 25% of Ph_3PCl_2 ; under different conditions (Section II.D), the latter may be the main product, but even so its formation allows an indirect means of reaching the oxide which may be obtained through several reactions of the dichloride¹⁴³. An additional, but again indirect, procedure for chalcogen interchange consists in the decomposition of quaternary salts $R^1_3P^+SR^2X^-$ (Section II.C) with alkali, a reaction explored originally as early as 1907 by Hantzsch⁶⁻⁹.

C. Quaternary Phosphonium Compounds from Phosphine Chalcogenides

Early work by Mann and Watson¹⁴⁴ demonstrated that the treatment of pyridinylphosphine sulphides, $\text{Ph}_n(2\text{-pyr})_{3-n}\text{PS}$, with MeI under sealed-tube conditions (no reaction occurring in boiling benzene) resulted in complete fragmentation of the phosphine sulphide; the products included 2,2'-bipyridinyl bismethiodide together with trimethylsulphonium iodide, when $n = 2$; the former bis(methiodide) was also obtained from $(2\text{-pyr})_3\text{PO}$. When $n = 0$, the products were 2,2'-bipyridinyl monomethiodide and trimethyl(2-pyridinyl)phosphonium iodide¹⁴⁴.

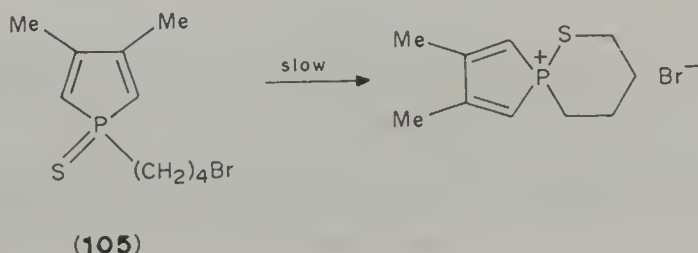
In general, alkoxy- and related phosphonium salts of the type **104** are obtainable by either of the two reactions indicated briefly in Scheme 16. Because of the lower nucleophilic power of the $\text{P}=\text{O}$ group, phosphine oxides would be expected to be the least reactive of the chalcogenides in reaction (a). Normally, reactions of the oxides with simple alkyl halides do not occur, or the resultant salts are unstable, but some others, e.g. $\text{R}_3\text{P}^+(\text{OSiMe}_3)\text{I}^-$, from R_3PO ($\text{R} = \text{Et}$, Ph , or Me_3SiCH_2) and Me_3SiI , are isolable. Route (b) also generally fails to give isolable products, but such salts with $\text{X} = \text{O}$ are assumed to have been formed early during the course of Arbuzov reactions. The use of trialkyloxonium salts (Meerwein's salts) $\text{R}_3\text{O}^+\text{Y}^-$, where R is Me or Et and Y^- is PF_6^- , SbCl_6^- or BF_4^- , is advantageous for trialkylphosphine oxides^{145,146}, triarylphosphine oxides¹⁴⁷ or cyclic phosphine oxides¹⁴⁸. Elsewhere, dimethyl sulphate or sulphonic acid esters, e.g. $\text{CF}_3\text{SO}_2\text{OR}$ ($\text{R} = \text{Me}$ or Me_3Si), have been employed.

A relatively recent observation is of interest since it shows that the nature of the product from a triarylphosphine oxide and an oxonium salt depends on the manner of mixing; in addition to the 'normal' ethoxytriphenylphosphonium salt, oxybisphosphonium salts, $\text{Ph}_3\text{P}^+\text{OP}^+\text{Ph}_3\text{2Y}^-$, $\text{Y}^- = \text{BF}_4^-$ or CF_3SO_3^- , have been prepared¹⁴⁹.



SCHEME 16

Not surprisingly, the formation of similar quaternary phosphonium salts from phosphine sulphides or higher phosphine chalcogenides is easier. Although Ph_3PS does not react with alkyl halides under normal conditions, it does so with trialkyloxonium salts^{109,150}. In the case of more highly 'activated' phosphine sulphides, e.g. tris(2,6-dimethoxyphenyl)phosphine sulphide, direct reaction is feasible with alkyl bromides or iodides in benzene at room temperature to give isolable salts which are thermally stable¹⁰⁹. The phosphole sulphide **105** undergoes slow intramolecular quaternization¹⁵¹. Unusually, Ph_3PS reacts with NO^+BF_4^- to give the poorly stable salt $\text{Ph}_3\text{P}^+\text{SSP}^+\text{Ph}_3(\text{BF}_4^-)_2$ ¹⁵². Tertiary phosphine tellurides also react directly with MeI to give isolable methiodides of reasonable thermal stability¹⁵³.



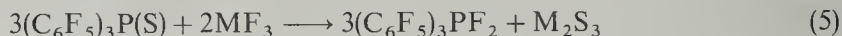
The crystalline salts isolated from reactions between phosphine oxides and phosphoryl or thiophosphoryl halides are thought to have the structure $R_3P^+OP(Y)X_2 X^-$ ($Y = O$ or S , $X = Cl$ or Br)¹⁵⁴.

Alkaline hydrolysis of alkoxy- or alkythio-phosphonium salts may, or may not, provide phosphine oxides with retained configuration at phosphorus; the phosphonium salts themselves retain the configuration of the chalcogenide from which they are prepared^{107,108}. (S)-(+) -Me(2-Np)PhPO and (S)-(-) -MePhPrPS yield (ethyl)phosphonium salts which, on alkaline hydrolysis, give oxides in which the configuration at phosphorus has been retained; on the other hand, similar treatment of the (ethyl) quaternary salt from (R)-(+)-Bu^tMePhPO affords the oxide with inverted configuration⁷⁶.

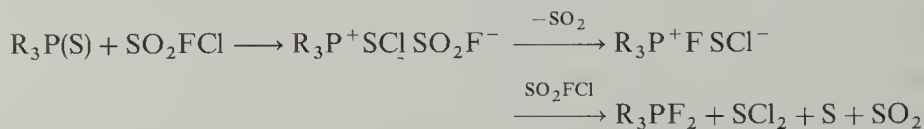
D. Quinquevalent Pentacoordinate Compounds (Phosphoranes) from Phosphine Chalcogenides

Like the corresponding oxides, tertiary phosphine sulphides may be converted into the dichlorophosphoranes R_3PCl_2 by the action of hot $SOCl_2$ ¹⁴³; other reagents which have been used for the oxides include oxalyl chloride¹⁵⁵, phosgene¹⁵⁶, methyl chloroformate¹⁵⁵ and PCl_5 ¹⁵⁷.

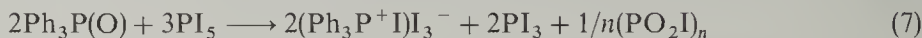
The analogous difluorophosphoranes have been obtained from the phosphine oxides with SF_4 or EF_3 ($E = As$ or Sb) and by the use of the latter reagents with trialkylphosphine sulphides¹⁵⁸. The reaction shown in equation 5 is also known¹⁵⁹. Difluorophosphoranes are also obtainable from the sulphides by the action of sulphuryl chloride fluoride (Scheme 17)¹⁶⁰.



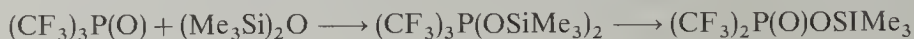
The reactions between tertiary phosphine oxides and certain sources of iodine are complicated by the known propensity of phosphorus to form ionic polyhalides. The reactions between PI_5 and tricyclohexyl- and triphenyl-phosphine oxides have been investigated in some detail¹⁶¹. Tricyclohexylphosphine oxide yields Cy_3PI_2 together with POI_3 on the pathway to $Cy_3P^+I_3^-$, and further reaction between the latter and POI_3 furnishes more of the diiodophosphorane. Polyiodides up to and including the hepta-iodide have been identified in the product mixtures the compositions of which depend on the ratios of reactants (equations 6 and 7).



SCHEME 17

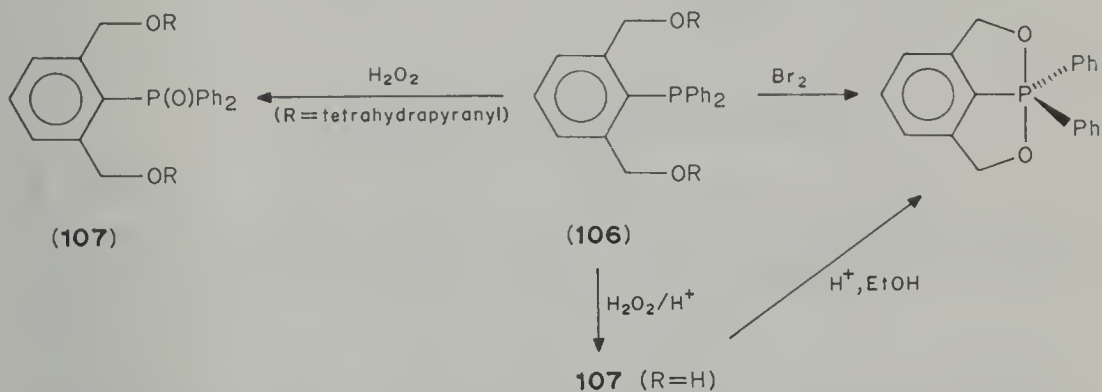


A simple dioxyposphorane has been identified spectroscopically as a product from the interaction of tris(trifluoromethyl)phosphine oxide and hexamethyldisiloxane (Scheme 18). Chemical identification followed from its ready transformation into trimethylsilyl bis(trifluoromethyl)phosphinate¹⁶².

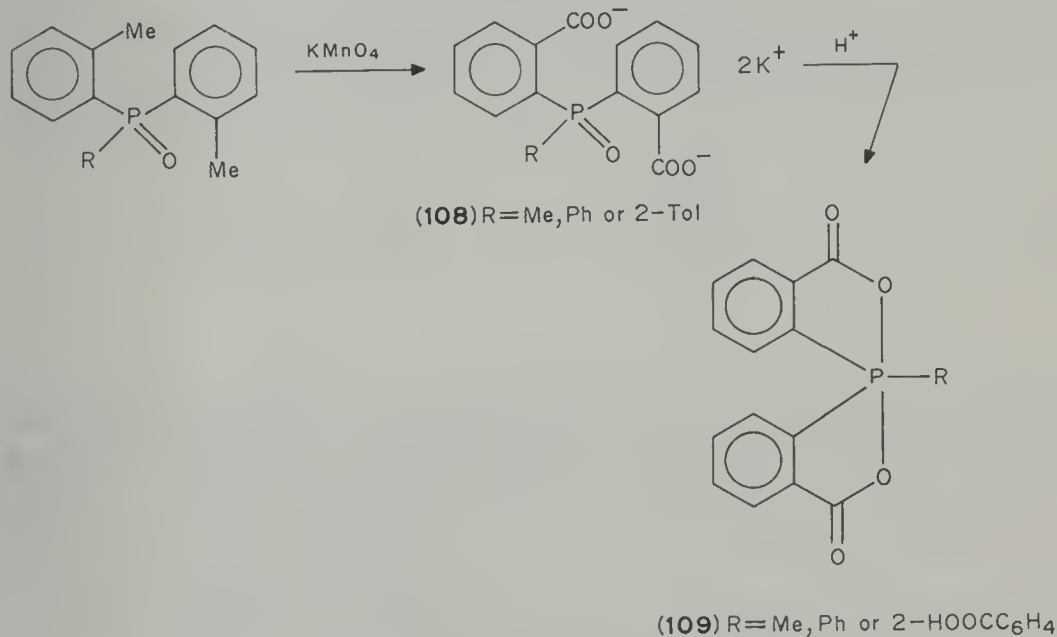


SCHEME 18

The formation of other oxyphosphoranes depends on the proximity of the phosphoryl bond to other oxygen-containing functions, generally carboxyl or hydroxyl. Such appropriate closeness can arise when suitable phosphines are oxidized, as in Scheme 19 where, for the phosphine **106**, *O*-protection in the aromatic substituents prevents the formation of a phosphorane, and in Scheme 20, where acidification of the salts **108** leads, by spontaneous dehydration of the liberated dicarboxylic acid, to the oxyphosphorane **109**¹⁶³⁻¹⁶⁵.



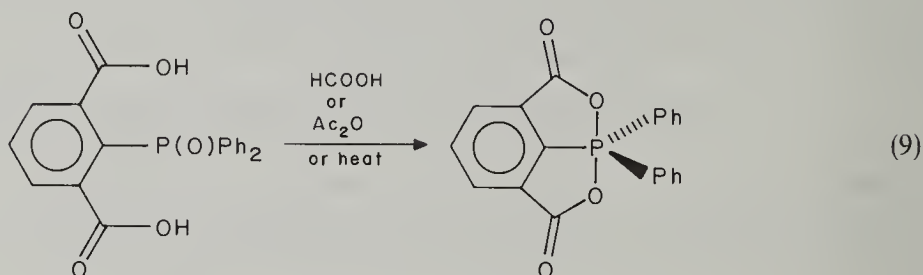
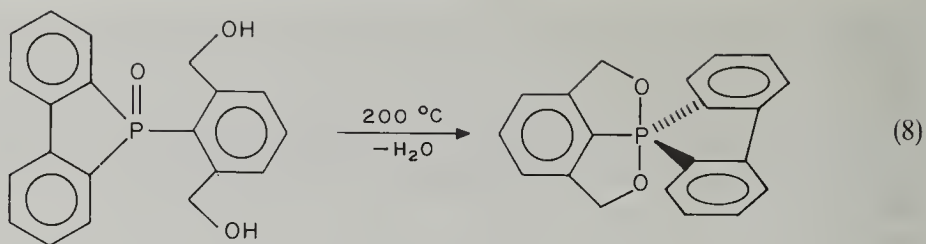
SCHEME 19

(109) R=Me, Ph or 2-HOOC₆H₄

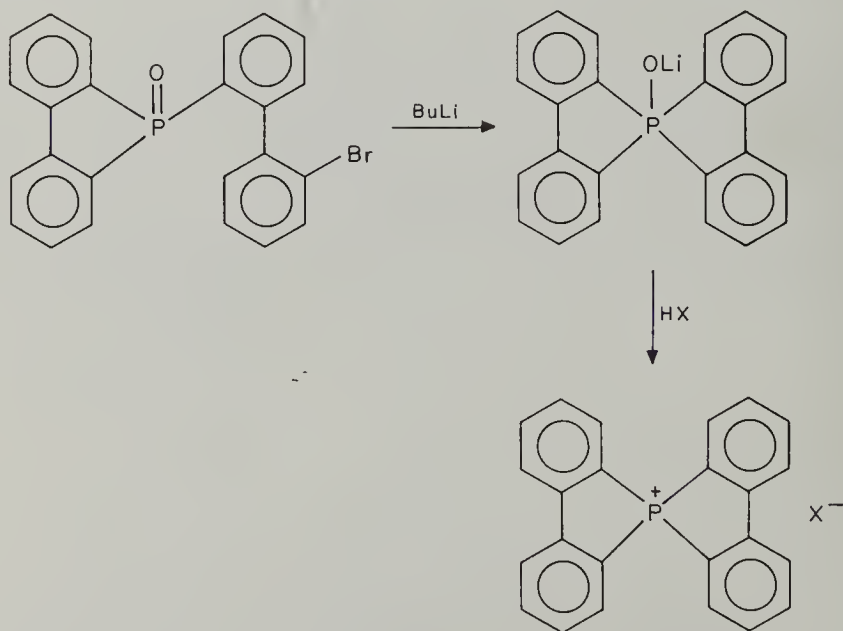
SCHEME 20

The conversion of a phosphine oxide into an oxyphosphorane by dehydration may be spontaneous, or it may be brought about in the ways shown in reactions 8¹⁶³ and 9¹⁶⁴.

The reaction between methyl 2-(diphenylphosphinoyl)benzoate and MeMgI (Scheme 2) yields the tertiary alcohol **6** which, when treated with NaH, yields the alkoxide **8**, which exists largely in the pentacoordinate form, **7**. On the other hand, the alcohol **6** is the main tautomer in the equilibration with the cyclic form **5**⁵.

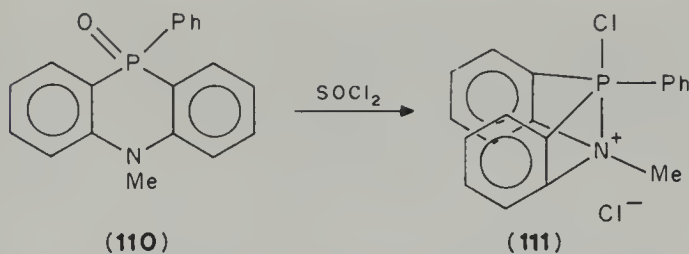


Acidification of the lithium salt obtained (Scheme 21) from the treatment of 5-(2'-bromobiphenyl)yl-5*H*-dibenzophosphole 5-oxide with BuLi fails to liberate a free hydroxyphosphorane, yielding instead a symmetrical phosphonium salt¹⁶⁶.



SCHEME 21

In an example of the formation of a pentacoordinate compound from a phosphine oxide, the oxide **110** when acted upon by SOCl_2 yields a mixed P^{V} -quaternary ammonium salt possessing a 'butterfly' structure (**111**)¹⁶⁷. Finally, the reader is reminded that pentacoordinate species based on the 1,3,2-oxaselenaphospholane system have been detected spectroscopically during the reactions between tertiary phosphine selenides and epoxides (Section II.B).

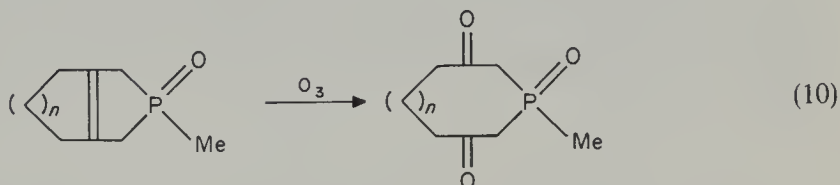


III. REACTIONS OF THE ORGANIC LIGANDS

A. Oxidation

Amongst the oxidation processes associated with the organic ligands of tertiary phosphine chalcogenides, four are recognized as being of significance. They are (1) oxidative cleavage of carbon—carbon multiple bonds, (2) oxidation of groups attached to aromatic nuclei, (3) epoxidation and (4) oxygen insertion.

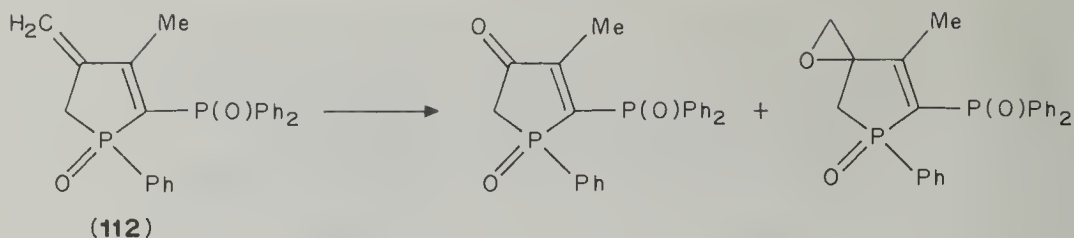
The oxidative cleavage of carbon—carbon multiple bonds is well illustrated by the use of $\text{KMnO}_4\text{--NaIO}_3$ to oxidize allyldiphenylphosphine oxide to diphenylphosphinoyl-acetic acid, and the use of ozone followed by H_2O_2 to cleave diallyldiphenylphosphine oxide to $\text{PhP(O)(CH}_2\text{COOH)}_2$ ¹⁶⁸. A similar oxidation of diphenyl(phenylethynyl)-phosphine oxide yields benzoic acid and diphenylphosphinoylformic acid, the latter then being rapidly cleaved to diphenylphosphinic acid¹⁶⁸. A useful extension in the process is the cleavage of carbon—carbon double bonds bridging large rings systems as represented in equation 10; in this way, derivatives of even larger phosphacycloalkanes can be obtained¹⁶⁹.



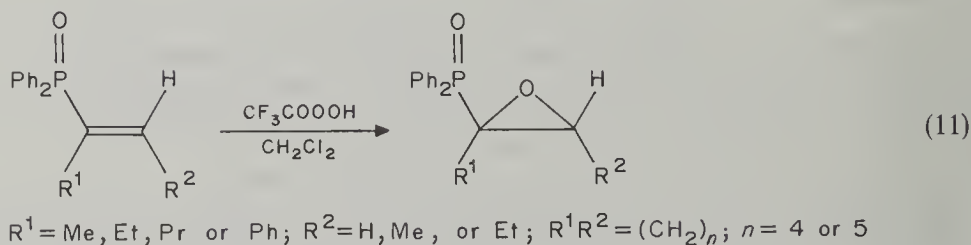
The oxidation of alkyl, and related, substituents on aromatic rings may be carried out successfully using $\text{KMnO}_4\text{--pyridine}$; when the resultant carboxyl groups are situated *ortho* to the phosphoryl group, mutual interaction might occur to afford products of a pentacoordinated nature (Scheme 20). When the substituents are situated *para* to a phosphoryl group, cyclization does not occur. Oxidation of alkyl substituents has also been carried out with derivatives of, for example, the 5*H*-dibenzophosphole and dibenzo[*b,e*]phosphorin systems.

Normally, when similar phosphine sulphides are so treated, the resultant products are essentially phosphine oxides, but one example, viz. 4-diphenylphosphinothiobenzyl alcohol, has been recorded for which oxidation by $\text{CrO}_3\text{--pyridine}$ afforded the aromatic aldehyde with no attack on the thiophosphoryl group¹⁷⁰.

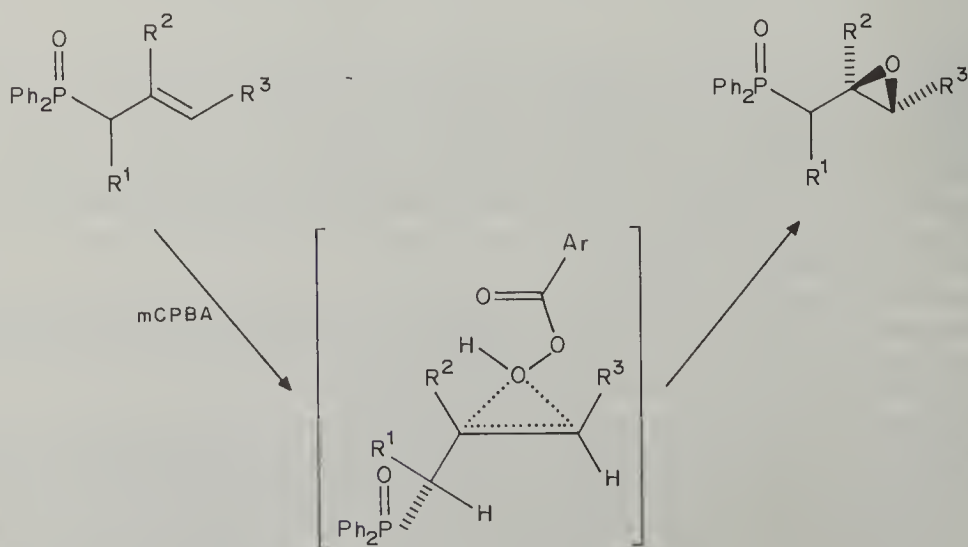
Epoxidation accompanies oxidative cleavage when the 2-(diphenylphosphinoyl)-phospholene 1-oxide **112** is treated with aibn⁶⁰. Some early observations on the epoxidation process itself are of interest. Initial success in the first reported epoxidation of a 3-phospholene, using peroxyacetic acid or monoperoxyphthalic acid, was not matched with examples of 2-phospholenes^{171,172}, although these findings have since been challenged³³. A possibly related phenomenon is the finding that diphenylvinyl-



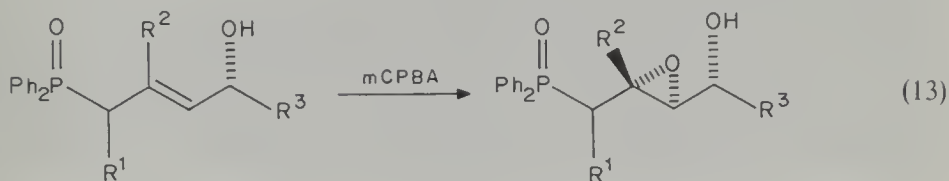
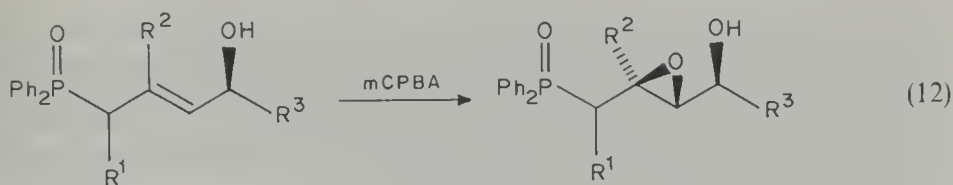
phosphine oxide is resistant to peroxy acids¹²⁶ whereas oxides substituted on the vinyl group are readily epoxidized (equation 11)¹⁷³.



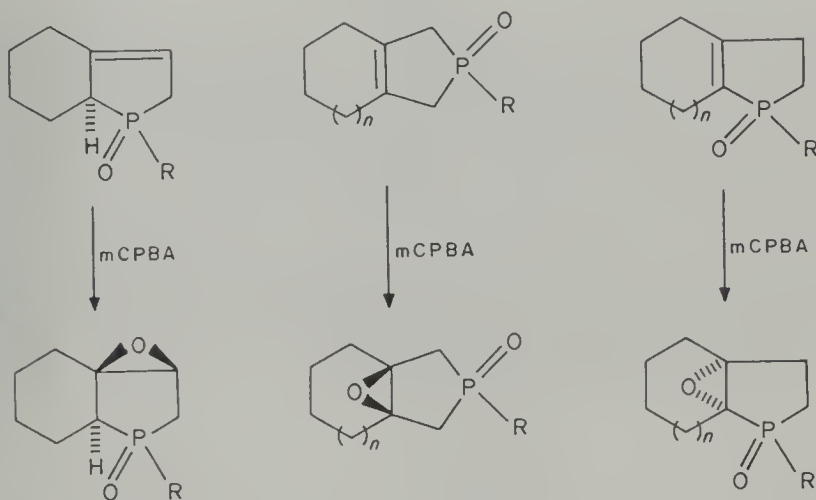
The epoxidation of allylic phosphine oxides by mCPBA is thought to proceed in a manner summarized in Scheme 22^{174,176}. The stereochemistry of the process is thought to be controlled by the chiral centre at the carbon α to phosphorus, and rationalized by the transition state; the yields are very high, with stereospecificities of from 4:1 to 10:1. For δ -OH homoallylic oxides, the stereochemical control originates in the hydroxyl group with the stereoisomeric ratios being greater for one diastereoisomer (10–13:1) as opposed to the other (1.3–2.7:1); equations 12 and 13 indicate the main products of the reactions. The stereochemistry of the epoxides has been confirmed by X-ray diffraction studies¹⁷⁵.



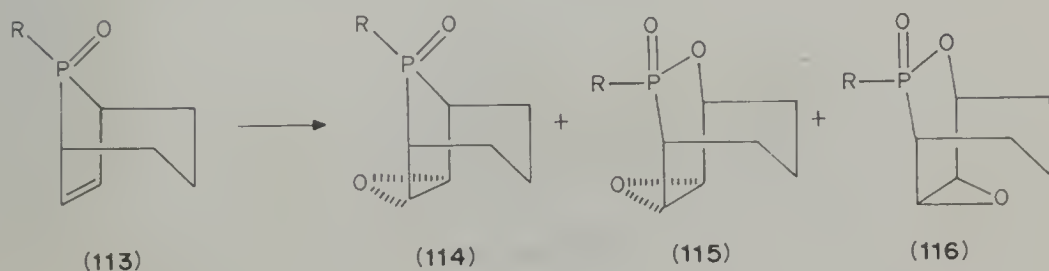
SCHEME 22



The stereochemistry of epoxidation has also been investigated using a series of 2- and 3-phospholenes³³. 3-Methyl-3-phospholene 1-oxide itself, and 3-phospholenes fused to cyclopentano or cyclohexano rings on the b or c bonds, are epoxidized with $mCPBA$ stereospecifically. When the cycloalkano group is fused to the b bond of a 2-phospholene, the epoxidation reaction also occurs readily but the orientation of the epoxide ring relative to the phosphoryl group is opposite to that experienced for the 3-phospholanes (Scheme 23).

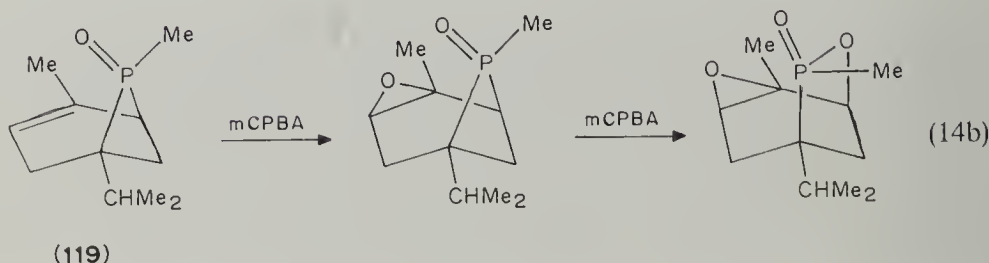
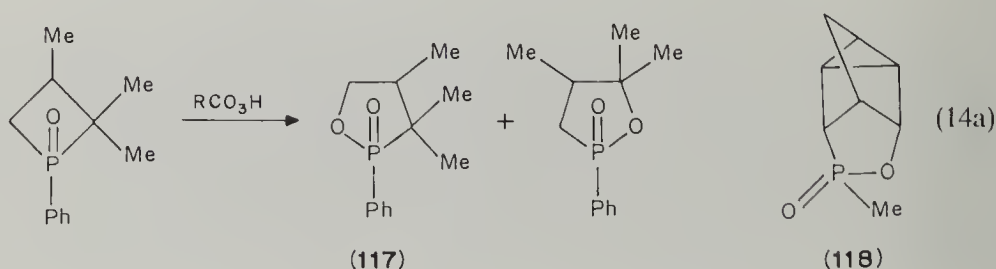


SCHEME 23

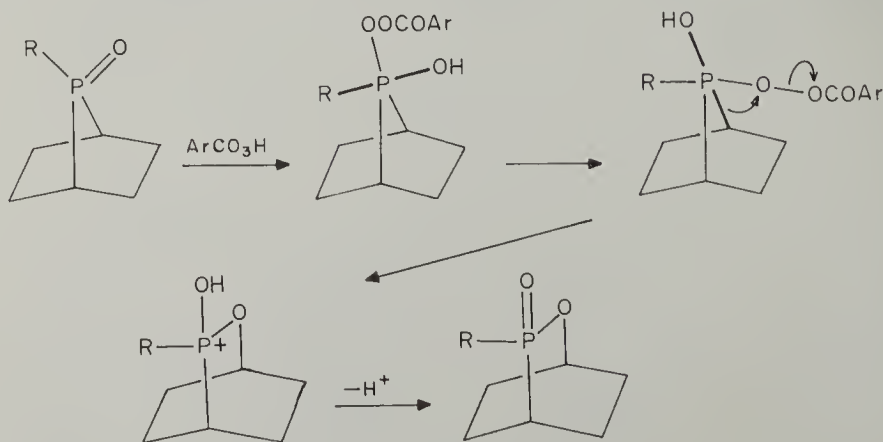


Epoxidation of the 8-phosphabicyclo[3.2.1]oct-6-enes (**113**) ($R = \text{Me}$ or Ph) with mCPBA is slow and yields the β -epoxides **114** accompanied by other products identified as oxygen insertion compounds (cyclic phosphinic esters) **115** and the α -epoxy compound **116** when $R = \text{Ph}$. Epoxidation of the phosphorus epimer of **113** ($R = \text{Me}$) is faster, taking place effectively at room temperature with an identical relationship between epoxide group and geometry of ring fusion^{117,178}.

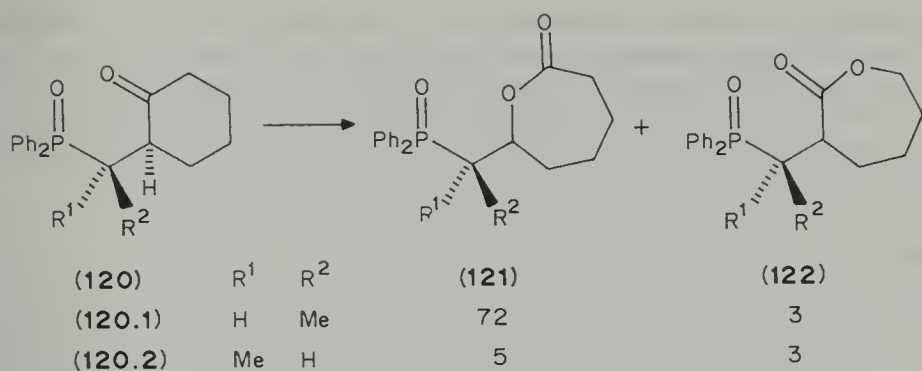
Phosphorus-containing ring systems in which the internal CCC angles are particularly constrained, e.g. the phosphetanes, undergo a Baeyer–Villiger-like insertion of oxygen between phosphorus and the carbon atom carrying fewer substituents (Equation 14a); here, **117** is the main product. The reaction occurs in the four-membered ring rather than in the less constrained five- or six-membered ring; thus **118** is obtained from **66**, and **119** reacts sequentially as indicated in equation 14b¹⁷⁹.



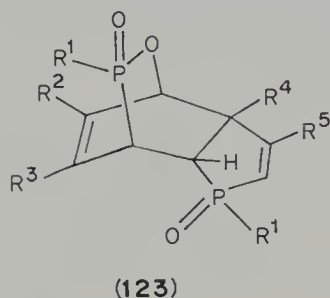
The oxygen insertion has been formulated mechanistically in Scheme 24¹⁷⁹. Scheme 25 outlines an application of the reaction which yields products having synthetic usefulness (Section V); cycloalkanones yield lactones and again the stereochemical control appears to depend on the stereochemistry at the α -carbon¹⁸⁰.



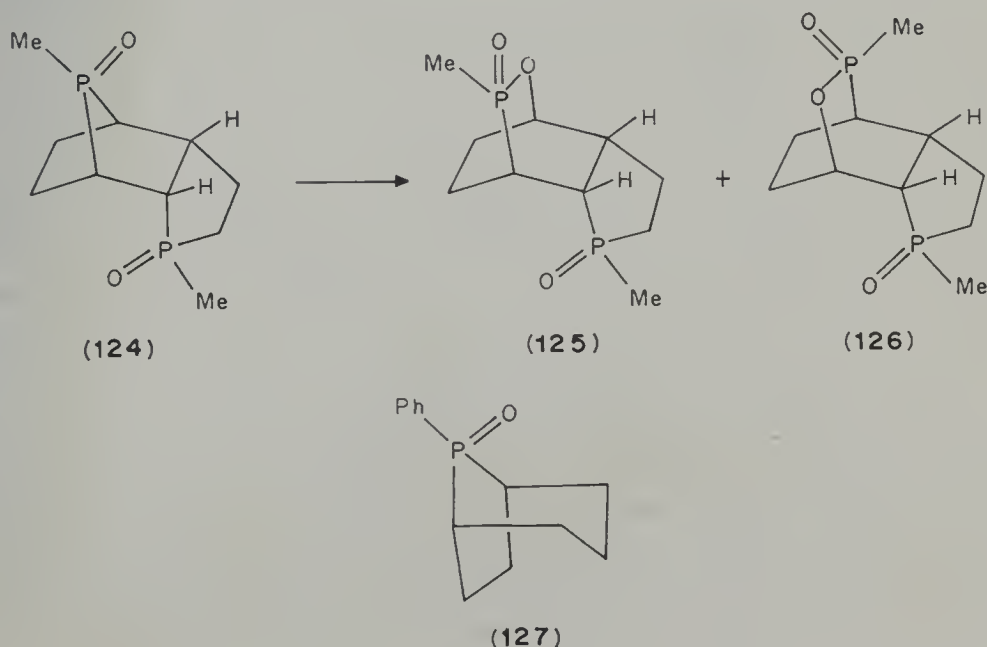
SCHEME 24



SCHEME 25



In the 7-phosphanorbornadiene system, oxygen insertion occurs readily and regiospecifically at the phosphorus bridge to give the compounds **123**. When the carbon skeleton is fully saturated, as in **124**, the insertion occurs non-regiospecifically to give a 1:1 mixture of the isomeric phosphinic ester **125** and **126**. Kashman and Averbouch¹⁷⁸ were unable to carry out the insertion reaction with the saturated compound **127** and they also failed with examples of the 8-phoshabicyclo[3.2.1]octane series. 4-Methyl-4-(diphenylphosphinoyl)pentan-2-one also fails in the Baeyer–Villiger process¹⁸¹.



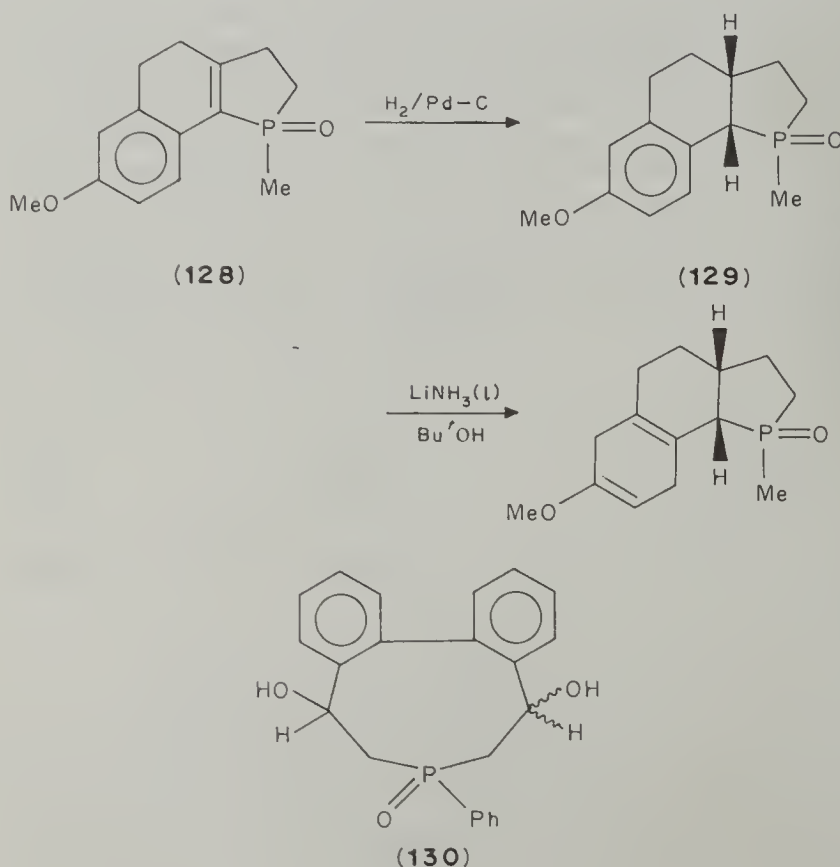
Other oxidation processes have received much less attention, but there are no apparent reasons why such processes should not occur in any manner other than that expected; thus, the secondary OH function in 3-hydroxy-2-phospholene 1-oxides is readily oxidised to the carbonyl group by CrO_3 -pyridine with retention of optical activity¹⁷², and the Jones reagent has been used for the same purpose for compounds in the 8-phosphabicyclo[3.2.1]octane series¹⁷⁷.

B. Reduction

Hydrogenation of isolated double bonds in acyclic compounds such as diphenyl-(2-phenylethenyl)phosphine oxide or in cyclic systems, e.g. 8-methyl-8-phosphabicyclo[3.2.1]octene 1-oxide¹⁷⁷, or in the tricyclic system **128**¹⁸² occurs readily in the presence of ruthenium, palladium or platinum catalysts. In the case of the last compound, the dihydro compound has *cis* geometry at the ring fusion; further reduction of the methoxyphenyl group in **129** is possible under Birch conditions, when the phosphoryl group remains unchanged.

Hydrogenolysis at 100–200 atm and 100°C in the presence of platinum reduces phenyl compounds to the cyclohexyl analogues, for example tribenzylphosphine oxide yields tris(cyclohexylmethyl)phosphine oxide^{45,183}; a potential drawback to the process is the possible elimination of halogen from the initial aromatic ring. Polarographic reduction of phosphorylvinyl groups is accompanied by dimerization, and diphenylvinylphosphine oxide itself afford 1,4-bis(diphenylphosphinoyl)butane.

Ketone groups in ring systems containing phosphorus atoms can be reduced by conventional means, e.g. through a dithioketal intermediate. Partial reduction of carbonyl



(ketone) groups to secondary alcohol functions is readily achieved using NaBH_4 and is of importance in the Horner reaction (Section V). The phosphoryl group is stable to the action of borohydride during the reduction of ring carbonyl groups in the preparation of the dialcohol **130**, which is of interest since it is a precursor to the unusual dibenzophosphonin ring system¹⁸⁴.

The widespread use of LiAlH_4 for the modification of organic ligands is rendered complicated by its ability to also remove the phosphoryl oxygen and give the parent phosphine although this could then be re-oxidized. The extent of its success in the reduction of the $\text{C}=\text{C}$ bond in 3-methyl-1-phenyl-2-phospholene 1-oxide without at the same time removing $\text{P}=\text{O}$ depends on the experimental conditions; relatively lower temperatures favour selective, but by no means specific, reduction of the $\text{C}=\text{C}$ bond¹⁸⁵.

When treated with LiAlH_4 , diaryl- and dialkyl-(alkynyl)phosphine sulphides yield the 1-alkenylphosphines in the *trans* form, which then undergo isomerization to the *cis* form. Deuteration experiments demonstrate the initial addition of H^- (or D^-) to $\text{C}_{(2)}$ in a normal Michael fashion. Such phosphine sulphides are stable to NaBH_4 , even in boiling thf, but the corresponding oxides are reduced to the *trans* olefinic phosphine oxide¹⁸⁶.

C. Dehydration: Phosphinoyl Carbocations

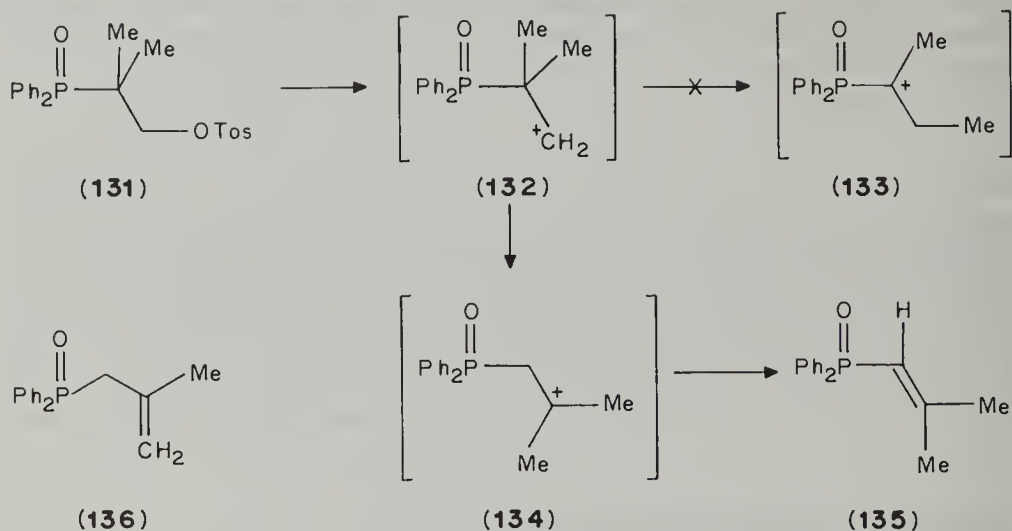
The diphenylphosphinoyl group appears to activate a process of spontaneous dehydration under appropriate conditions; thus the diketone $\text{Ph}_2\text{P}(\text{O})\text{CH}(\text{COPh})\text{CH}_2\text{COPh}$, presumably through its dienol, dehydrates to 2,5-diphenyl-3-diphenylphosphinoylfuran during crystallization. Dehydration of 1-(diethylphosphinothioyl)-1-hydroxycyclohexane has been reported to occur during its distillation¹⁸⁷. Powerful dehydrating agents such as KHSO_4 and P_4O_{10} fail to dehydrate $\text{Bu}_2\text{P}(\text{S})\text{C}(\text{OH})\text{Me}_2$, and the compound readily decomposes into its precursors, dibutylphosphine sulphide and acetone.

The diol **130** is dehydrated when treated with POCl_3 -pyridine and affords *cis*, *trans*-1-phenyldibenzophosphonin 1-oxide; although dehydration of the 1-methyl compound may similarly be achieved, the stereochemistry of the product appears, as yet, to be unknown¹⁸¹.

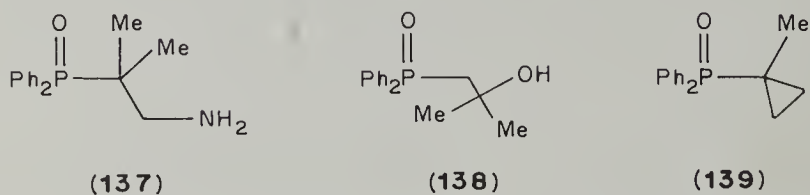
Extensive investigations have been carried out by Warren¹⁸⁸ into the dehydration of phosphinoylated alcohols in which the phosphinoyl group is placed β to the OH group, and hence to the site of cation formation under acidic conditions. One of the more important reactions accompanying the dehydration of the alcohol, or the solvolysis of an ester, e.g. a sulphonate, with tosOH or tfa in a solvent at either ambient temperature or at the boil, consists in the migration of the diphenylphosphinoyl group from the α -carbon atom (the migration origin) to an adjoining carbocationic site (the migration terminus). The roles of the two sites and their influence on the migrating ability of the phosphinoyl group, or indeed of any other nearby group, have been explored in a systematic manner. Although, in some cases, quenching of the reaction mixtures allows the isolation of an isomeric alcohol, the product(s) normally isolated consist of alkenes. Subject to the availability of an appropriately sited proton, these are either vinyl- or allyl-phosphine oxides; in practice the former are obtained comparatively rarely.

An example of the migration from a tertiary carbon origin to a primary carbocationic site occurs during the solvolysis, using formic acid at 120°C , of the tosylate **131** of a primary alcohol, and which proceeds through a 'low-energy' cation. Here, the unstable primary cation does not isomerize through methyl group migration (Scheme 26), (**132** to **133**), but rather by phosphinoyl migration, (**132** to **134**), the product being the vinylphosphine oxide **135**. On the other hand, presumably the same, or a very similar, carbocation is formed when the primary amine **137** is diazotized, but the eventual products then consist of mixtures of the vinyl- and allyl-phosphine oxides **135** and **136**,

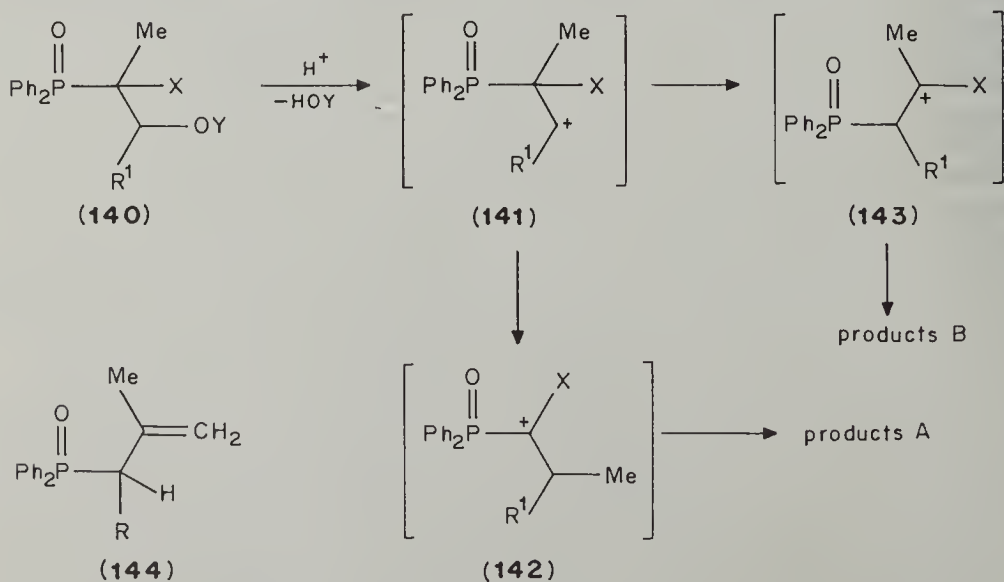
together with some of the alcohol **138** and traces of the cyclopropylphosphine oxide **139**¹⁸¹.



SCHEME 26



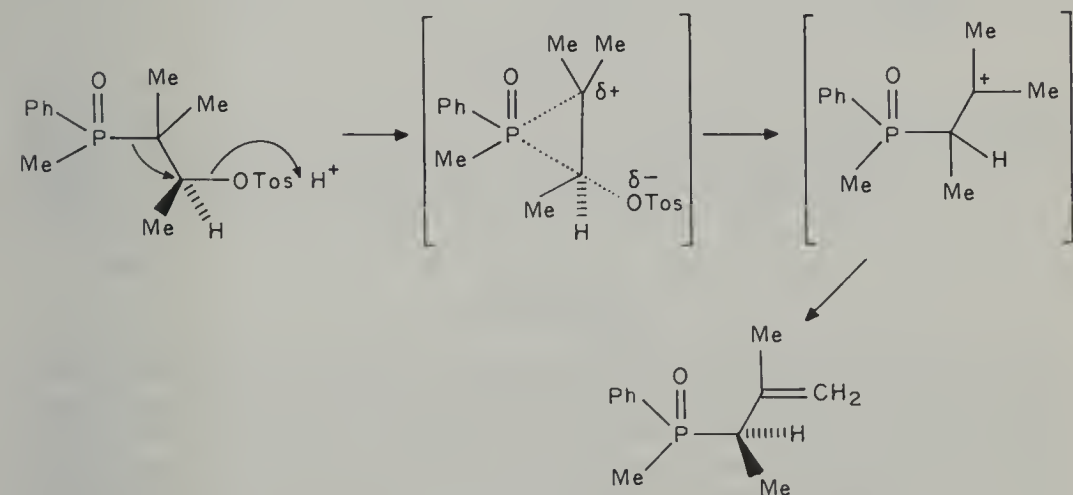
Scheme 27 depicts migrations from a substrate possessing a tertiary migration origin coupled with a secondary migration terminus. Essentially, dehydration or solvolysis of



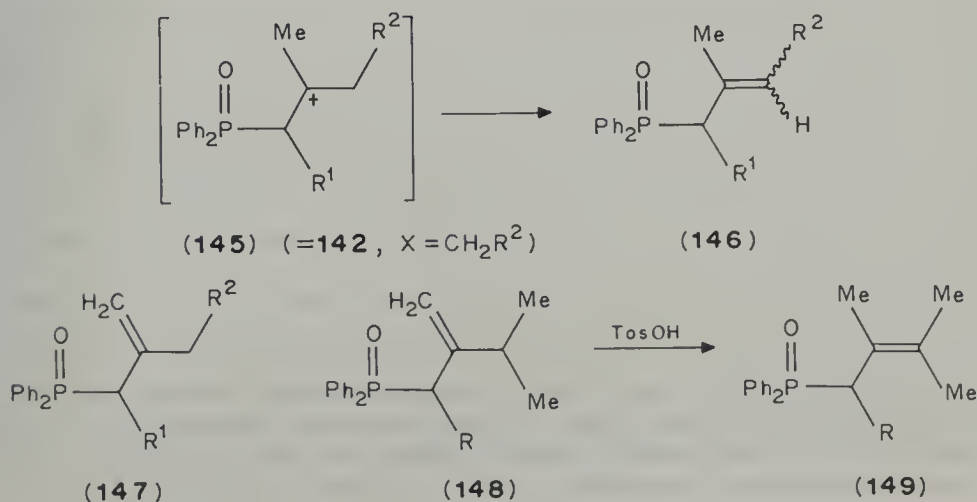
SCHEME 27

140 provides the initial carbocation **141**, which can isomerize by phosphinoyl migration to the relatively unstable carbocation **143** (positive charge adjacent to the electro-negative phosphinoyl group) leading to products B, or it can isomerize by methyl migration to the isomeric cation **142** to give products A.

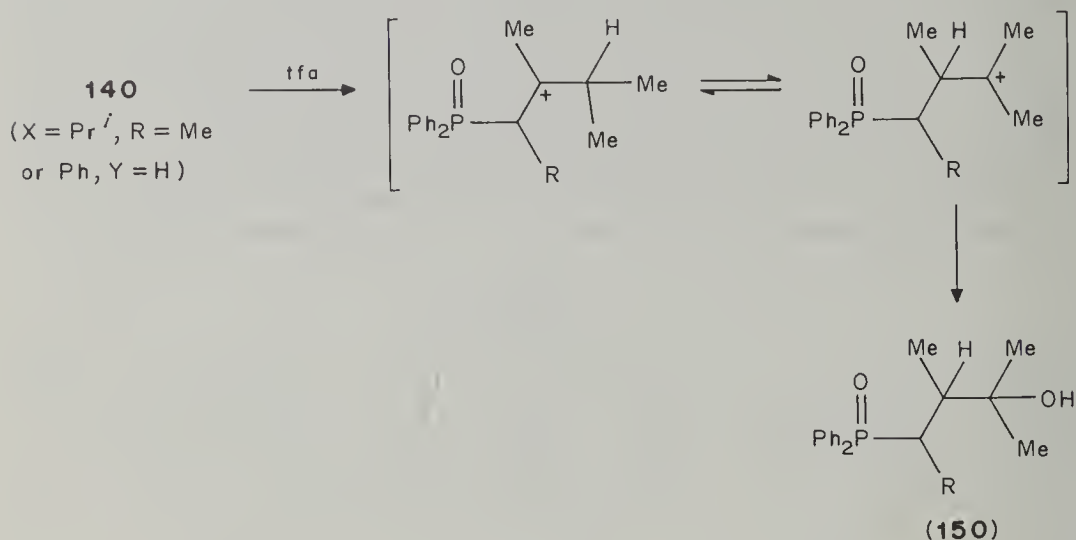
Not surprisingly, it has been argued that the choice, or balance, between the two routes represented in Scheme 27 will depend on electronic factors, in particular the relative stabilities of the carbocations **142** and **143** (and indeed **141**)¹⁸⁹. For the solvolysis of the ester **140** ($X = R^1 = \text{Me}$; $Y = \text{tos}$), the preferred choice is the formation of the cation **143**, with the observed formation of the allylic phosphine oxide **144** ($R = \text{Me}$) rather than a vinylic isomer. However, a conformational argument based on the preferred antiperiplanarity of the relatively large $\text{Ph}_2\text{P}(\text{O})$ and OTos groups in the most highly populated conformer (with a resultant boost to phosphinoyl migration) cannot be excluded. This latter argument has received some indirect support from the observation that the tosylate of 3-methyl-3-(methylphenylphosphinoyl)butan-2-ol undergoes solvolysis in acetic or formic acid with retention of configuration at phosphorus but with inversion of configuration at the migration terminus; the migration is thus pictured as a concerted process (Scheme 28) with very little epimerization¹⁹⁰. The structure of the final olefinic product was confirmed by an X-ray crystallographic investigation.



SCHEME 28



When, in **140**, $X = \text{CH}_2\text{R}^2$ ($\text{R}^2 = \text{Me}$ or Bu) and $\text{R}^1 = \text{Me}$ or Ph , acidolysis of the alcohol ($\text{Y} = \text{H}$) yields a mixture of the *E* and *Z* forms (in a ratio $>9:1$) of the allylic phosphine oxide **146** via the carbocation **145**, but none of the allylic isomer **147** nor of an isomeric vinylphosphine oxide, was obtained¹⁹¹. When, however, $X = \text{Pr}^i$, acidolysis then afforded the allylic phosphine oxide **148**, i.e. a phosphine oxide of type **147**, although for $\text{R}^1 = \text{Me}$ prolonged treatment with tosOH led to some isomerization to the more highly substituted alkene **149**¹⁹¹. However, when tfa was used as the acid catalyst, a further complicating feature then arose, viz. a double migration; this, consisting of a phosphinoyl migration followed by a hydride shift, led, following quenching, to the isomeric tertiary alcohol **150** (Scheme 29).

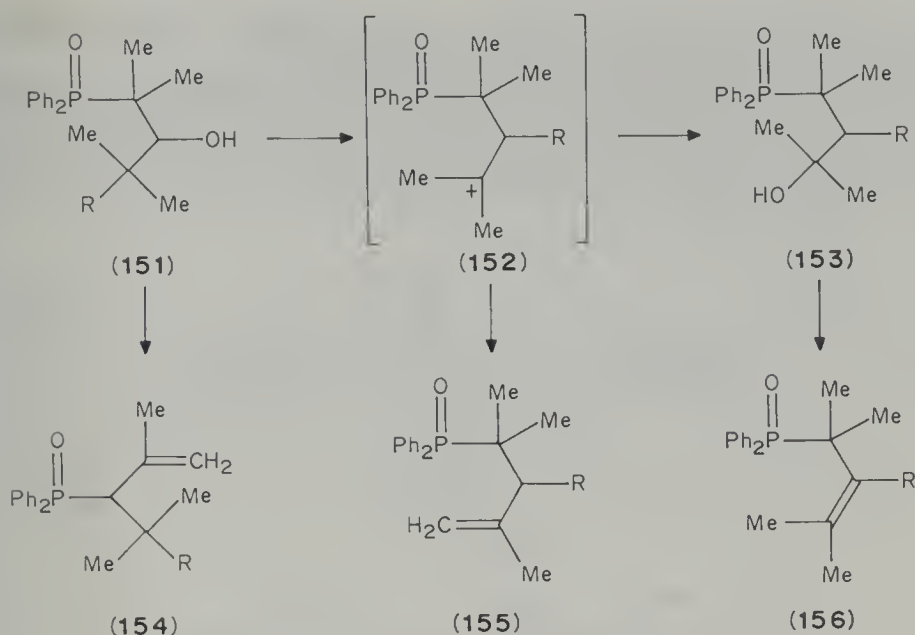


SCHEME 29

Tfa also brings about rapid dehydration of the secondary alcohols **140** ($X = \text{Me}$; $\text{Y} = \text{H}$) to give the allylic phosphine oxides **144**, which then isomerize to the more highly substituted alkene, in this case of the vinylic type. Dissolution of **140** ($X = \text{Me}$; $\text{R} = \text{Ph}$; $\text{Y} = \text{H}$) in 98% H_2SO_4 , followed by quenching, yields **150** ($\text{R} = \text{Ph}$). With a primary alkyl group at the migration terminus, as in **140** ($\text{R} = \text{Me}$, Et or Pr), tosOH yields **150** as the only products¹⁹².

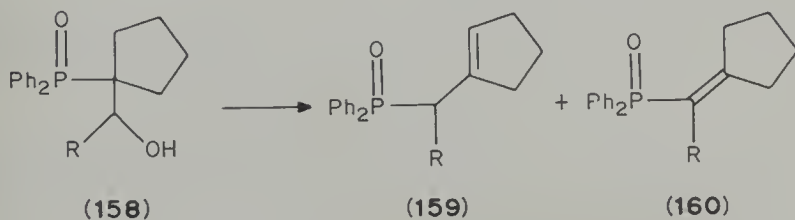
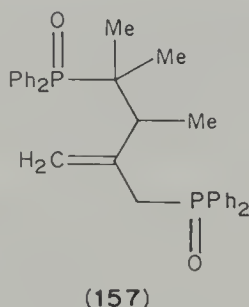
The picture regarding the migratory abilities of the diphenylphosphinoyl and alkyl(methyl) groups begins to change with an increase in the complexity of the alkyl group R^1 in **140** ($X = \text{Me}$; $\text{Y} = \text{H}$). Thus, acid-catalysed dehydration of **151** ($\text{R} = \text{H}$) (i.e. **140**, $\text{R}^1 = \text{Pr}^i$; $X = \text{Me}$; $\text{Y} = \text{H}$) yields only **154** (Scheme 30). Scheme 30 also indicates the various possible products which may be obtained from **151** ($\text{R} = \text{Me}$) (i.e. **140**; $\text{R}^1 = \text{Bu}^t$; $X = \text{Me}$; $\text{Y} = \text{H}$); treatment of the latter alcohol with H_3PO_4 at ambient temperature affords 90% of the isomeric alcohol **153** ($\text{R} = \text{Me}$)¹⁹³. When **151** ($\text{R} = \text{Me}$) is treated with tosOH in benzene, there are produced 50% **155** ($\text{R} = \text{Me}$) and 27% **153** ($\text{R} = \text{Me}$), both obtained through the carbocation **152** ($\text{R} = \text{Me}$) and Me migration, in addition to 18% of the alkene **154** ($\text{R} = \text{Me}$), the product of phosphinoyl migration. Thus, for the alcohol **140** ($\text{R}^1 = \text{Bu}^t$, $X = \text{Me}$, $\text{Y} = \text{H}$), Me migration more than satisfactorily competes with phosphorus migration¹⁹².

In an attempt to obtain a truer comparison of the migrating abilities of the Me and $\text{Ph}_2\text{P}(\text{O})$ groups, Howells and Warren¹⁹³ prepared the two bis(diphenylphosphinoyl) compounds **151** [$\text{R} = \text{Ph}_2\text{PO}$ or $\text{Ph}_2\text{P}(\text{O})\text{CH}_2$]. When acidolysed in buffered acetic acid, the mesylate of the former gave **155** ($\text{R} = \text{Ph}_2\text{PO}$) and **153** ($\text{R} = \text{Ph}_2\text{PO}$) in the ratio 9:1;



SCHEME 30

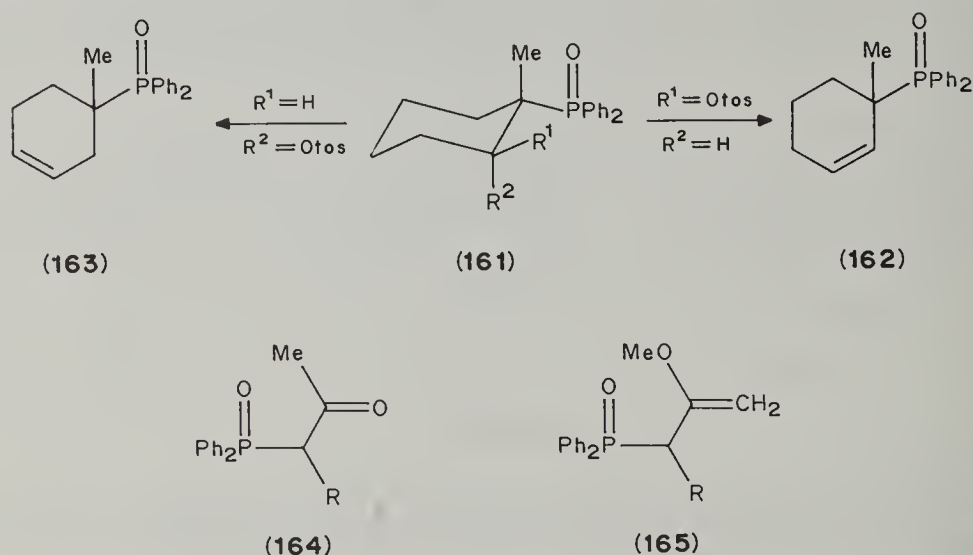
the latter alcohol dehydrates rapidly at ambient temperature to give the corresponding **156**. Under the same conditions, the second mesylate gave 70% of **154** ($\text{R} = \text{Ph}_2\text{PO}$) by phosphinoyl migration and 25% **157** ($\text{R} = \text{Ph}_2\text{PO}$) by Me migration¹⁹³.



Tfa dehydrates the alcohol **158** ($\text{R} = \text{Ph}$) to give only **159** ($\text{R} = \text{Ph}$), but with tosOH a 1:9 mixture of **159** and **160** ($\text{R} = \text{Ph}$) is formed. The alcohol **158** ($\text{R} = \text{Me}$) is similarly dehydrated to a mixture of **159** and **160** ($\text{R} = \text{Me}$) in the ratio 2.5:1. The formation of the compounds **160** represents one of the comparatively few examples of the formation of vinylphosphine oxides from β -hydroxyalkylphosphine oxides by dehydration. The

cyclobutane derivatives behave similarly, and the proportion of vinylphosphine oxide increases with the duration of the reaction contact time¹⁹².

Within this group of substrates in which phosphinoyl migration from a tertiary origin centre to a secondary site might occur, evidence has been obtained which certainly points to the existence of conformational control. The isomeric tosylates **161** when solvolysed yield the isomeric phosphinoyl cyclohexenes **162** and **163** with no evidence for either Me or Ph₂PO migration.



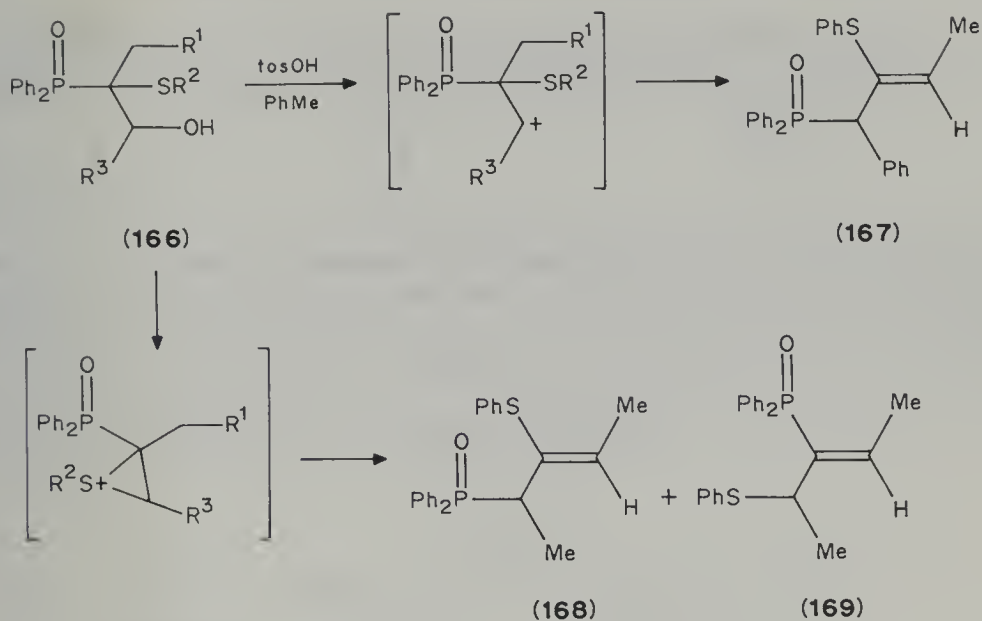
The presence of other functional groups is not restrictive to the migration of the diphenylphosphinoyl group. When treated with tfa, the alcohol **140** ($R^1 = \text{Ph}$; $X = \text{OMe}$; $Y = \text{H}$) yields the methyl ketone **164** ($R = \text{Ph}$) only. 3-(Diphenylphosphinoyl)butan-2-one (**164**; $R = \text{Me}$) is the only product obtained from **140** ($R^1 = \text{Me}$; $X = \text{OMe}$; $Y = \text{tos-}p$); on the other hand, when $R^1 = \text{Pr}^i$, both **164** and **165** ($R = \text{Pr}^i$) are formed in the reaction in buffered acetic acid¹⁹⁴.

Slight structural modifications also bring about changes to the dehydration reaction course for the sulphides **166** (Scheme 31). Phosphinoyl migration appears to be the sole pathway for **166** ($R^1 = \text{Me}$; $R^2 = R^3 = \text{Ph}$), with **167** being the product, whereas the allylic olefins **168** and **169** are obtained from **166** ($R^1 = R^3 = \text{Me}$; $R^2 = \text{Ph}$) through migration of the PhS group, a process which also has useful synthetic potential¹⁸⁸. Migrations of the MeS group have also been recorded^{188,194}.

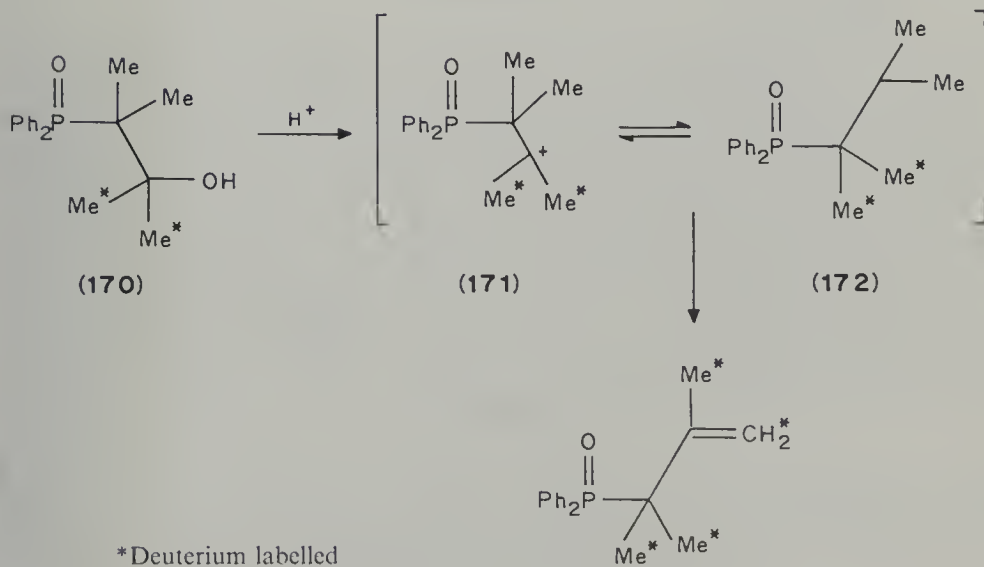
A special case exists when both migration origin and migration terminus are tertiary units (Scheme 32). The use of a deuterium-labelled substrate (**170**) has demonstrated equilibrium between the two carbocations **171** and **172**, and the overall reaction is very fast, occurring even during acylations under very mild conditions^{191,195}.

Reactions 15 and 16 exemplify phosphinoyl migrations from secondary carbon origins¹⁹¹. Here in reaction 15, the vinylphosphine oxide is not obtained when for **173** $R^1 = R^2 = \text{Me}$, but both vinyl- and allyl-phosphine oxides are obtained, in equal amounts, when $R^1 = \text{Et}$. A similar situation is found for reaction 16¹⁹⁶. In neither of these reaction systems is phosphinoyl migration observed.

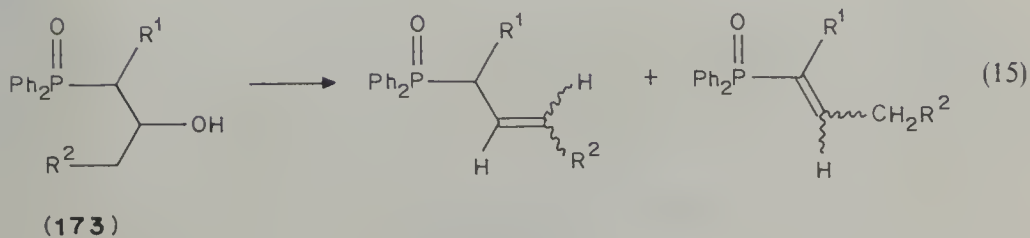
Warren's group also examined the behaviour of several silicon-containing phosphinoylated alcohols under acidolysis conditions; such substrates would be of interest since the silyl group can effectively act simply as a protecting group (Scheme 33)¹⁹¹. Following the action of tfa on the alcohol **174**, the nature of the product(s) is dependent on the reaction conditions. At ambient temperature phosphinoyl migration is followed

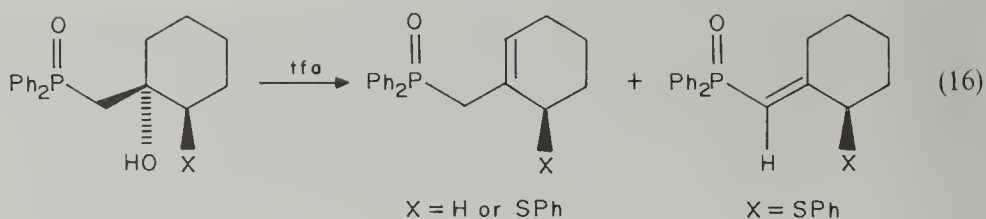


SCHEME 31

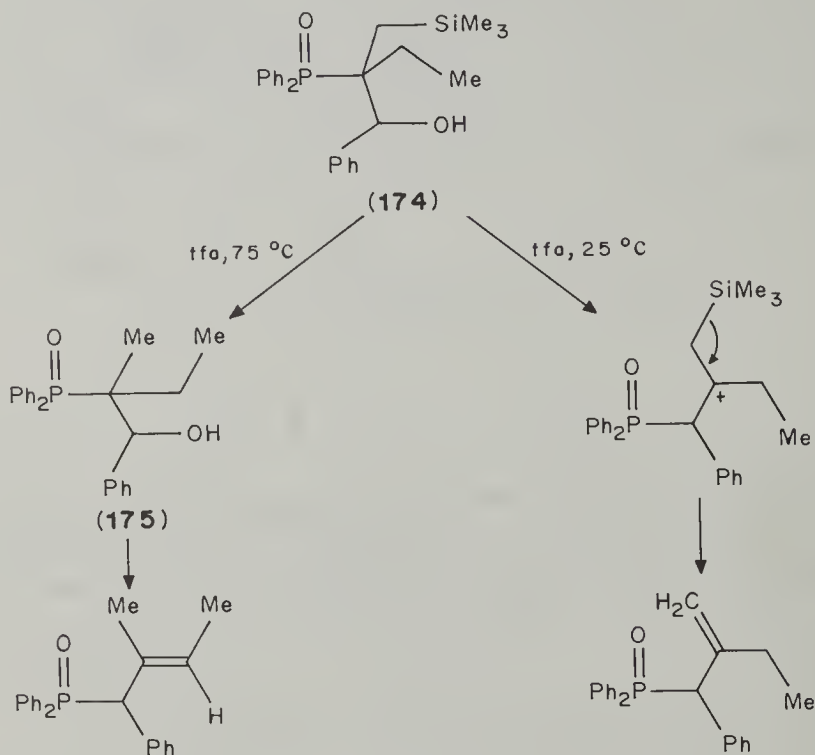


SCHEME 32

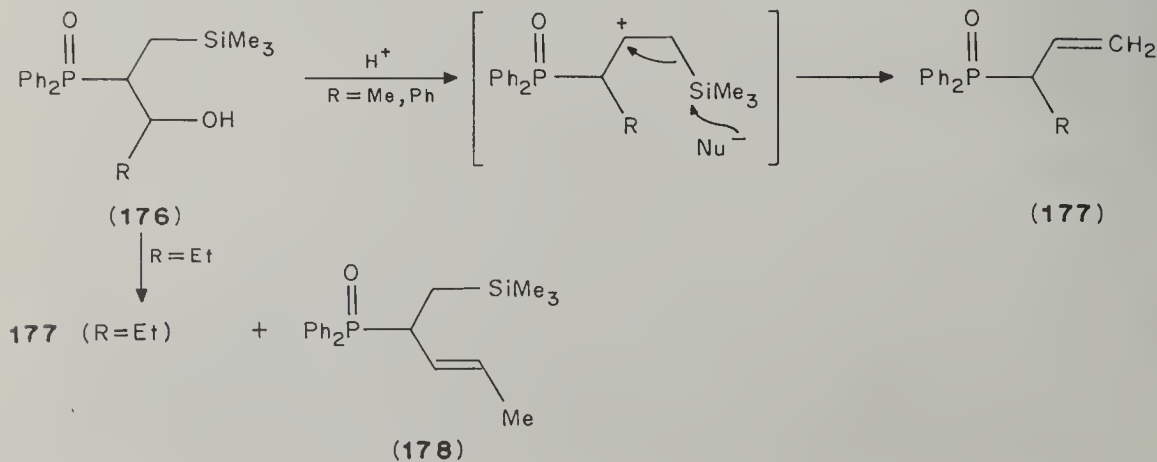




by desilylation, whereas at the higher temperature, desilylation to **175** evidently precedes phosphinoyl migration, and the product is an isomeric allylphosphine oxide (compare Scheme 27).



SCHEME 33

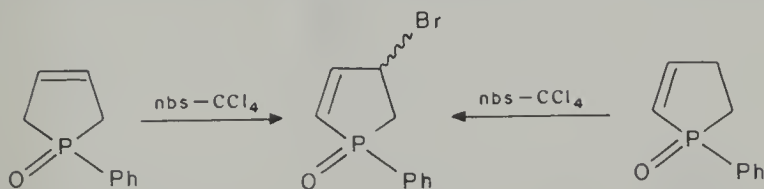


SCHEME 34

The group R in structure **176** is a controlling feature for the reactions of such compounds (Scheme 34), a single alkene being obtained when R = Me or Ph, but when R = Et a mixture of **177** (R = Et) and **178** is obtained in the ratio 2:1¹⁹¹.

D. Halogenation

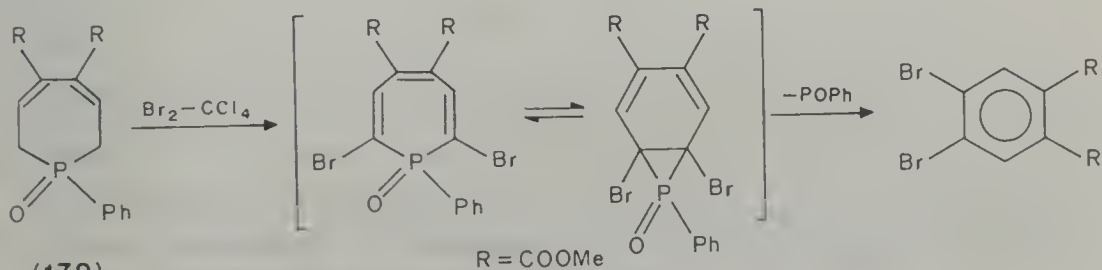
The reaction between benzyldiphenylphosphine oxide and *tert*-butyl hypochlorite affords 36% of the α -chlorobenzyldiphenylphosphine oxide in what is, presumably, a free-radical process; the α -bromo compound is similarly prepared and is also obtainable from α -diazobenzyldiphenylphosphine oxide and HBr in benzene. Other reported brominations of acyclic phosphine oxides using the same reagent include that of diphenyl-(2-phenylethyl)phosphine oxide in which substitution evidently occurs on C₍₂₎. The same mixture of stereoisomeric 4-bromo-1-phenyl-2-phospholene 1-oxides is obtained from isomeric 1-phenylphospholene 1-oxides (Scheme 35)¹⁹⁷.



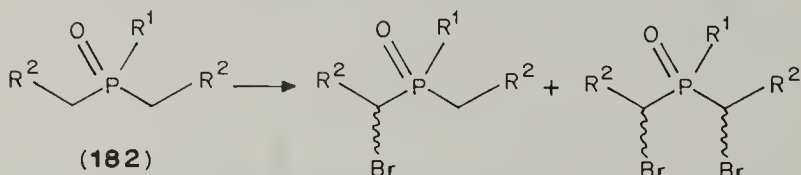
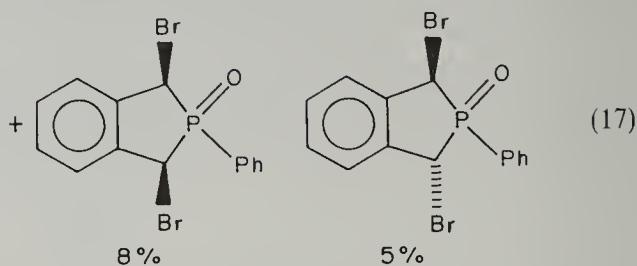
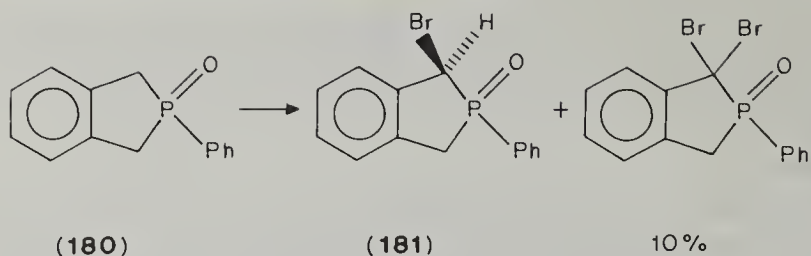
SCHEME 35

Direct bromination of the dihydrophosphepin 1-oxide **179** evidently occurs at the two allylic methylene positions to yield an unstable intermediate which extrudes phosphorus as PhPO and leaves dimethyl 3,4-dibromophthalate (Scheme 36)¹⁹⁸. In the presence of dibenzoyl peroxide, *nbs* brominates 2-phenylisophosphindoline 2-oxide (**180**); the products (equation 17) consist of a mixture of isomeric and stereoisomeric mono- and di-bromo derivatives of which the monobromo compound **181**, following dehydrobromination, serves as the precursor in the synthesis of bridged compounds in the 7-norbornene series by cycloaddition reactions (Section III.H.3)¹⁹⁹. Stereoisomeric α -mono- and α,α' -dibromo derivatives of dibenzylphenylphosphine oxide (**182**) (R¹ = R² = Ph)²⁰⁰ and of **182** (R¹ = Ph, R² = SOPh)²⁰¹ have been obtained following bromination with bromine/*nbs* in pyridine or with bromine in CCl₄ at 150 °C. Analogous chloro derivatives of the oxides **182** (R¹ = Bu^t or Ph, R² = Bu^t) may be prepared by reaction with BuLi followed by CCl₄^{200,202}.

3-Oxo-1-phenylphospholane 1-oxide is brominated by *nbs* in a process akin to that encountered for acetone, and the brominated enol form, 2-bromo-3-hydroxy-1-phenyl-2-phospholene 1-oxide, is obtained²⁰³. Other halogenation and related reactions occurring by addition mechanisms are described later (Section III.H).

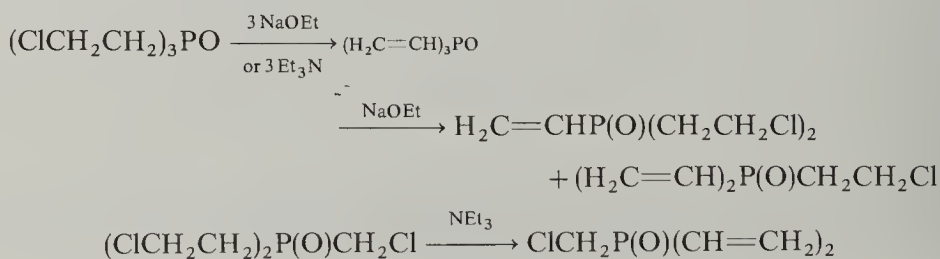


SCHEME 36

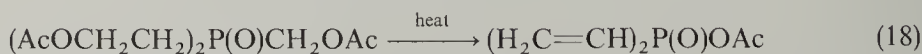


E. Dehydrohalogenation

Standard 1,2-elimination reactions have been performed on a variety of halogenated phosphine oxides using sodium alkoxides, thioalkoxides or, better, tertiary amines, to yield *trans*-alkenes (Scheme 37)²⁰⁴. Similar products have been obtained by the pyrolysis of acetate esters (equation 18).



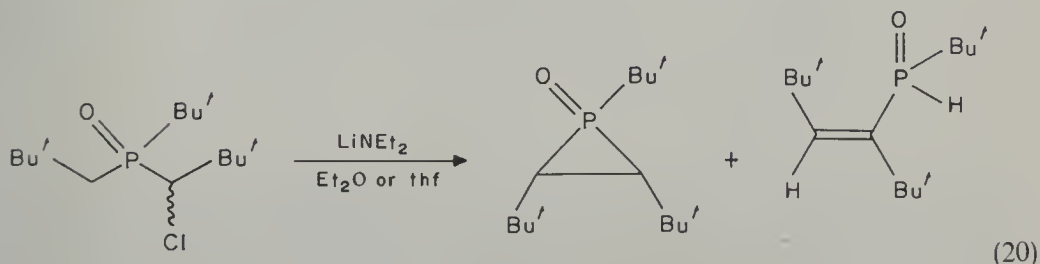
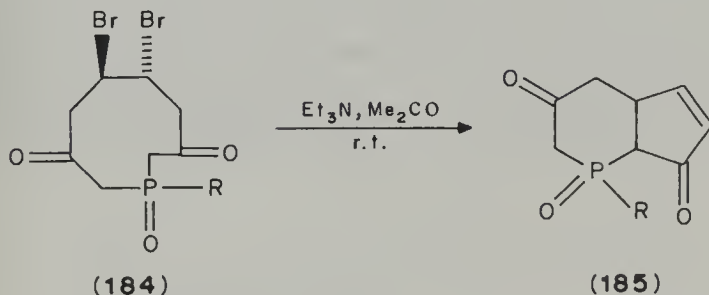
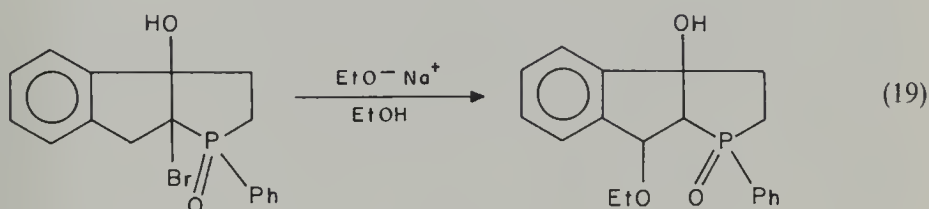
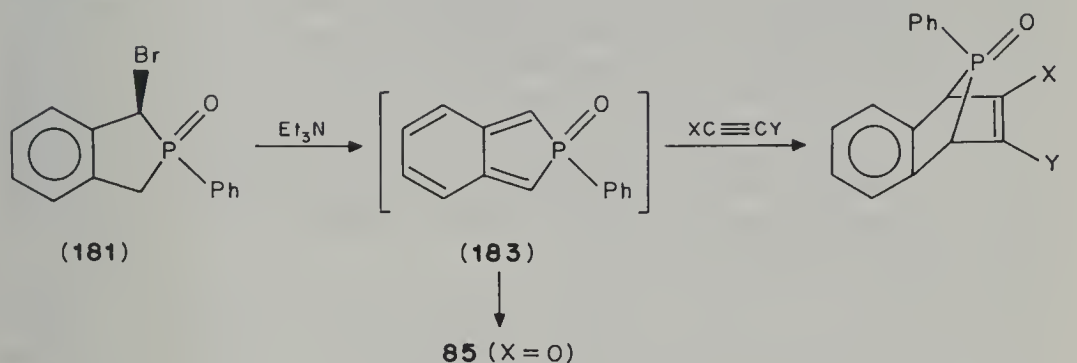
SCHEME 37



Other dehydrohalogenation reactions may be followed by rapid modification of the product, e.g. by the dimerization of the benzo[*c*]phosphole oxide (183) to give **85** (X = O), and the same reactive species can also be trapped by other dieneophiles^{84,159} or through non-cycloaddition processes (equation 19)⁷⁴.

In the dehydrobromination of the dibromophosphonanedione oxides **184** (R = Me or Ph) with Et₃N, a normal 1,2-elimination is accompanied by a transannular process to give the fused system **185**¹⁸¹. The elimination of hydrogen halide from monohalogenated

but otherwise symmetrical phosphine oxides leads to phosphiranes together with acyclic elimination products (equation 20)^{201,202}. Here, the choice of base is critical. The best yields in the cyclization are achieved by the use of LiNEt_2 in Et_2O at -60 to $+10^\circ\text{C}$, and with the minimum of elimination to alkenephosphine oxide and reductive dehalogenation. By contrast, little if any phosphirane is obtained when lithium 2,2,6,6-tetramethylpiperide in Et_2O or thf at -78 to $+35^\circ\text{C}$ is used, and when reductive dehalogenation is at a maximum.



F. Electrophilic Aromatic Substitution

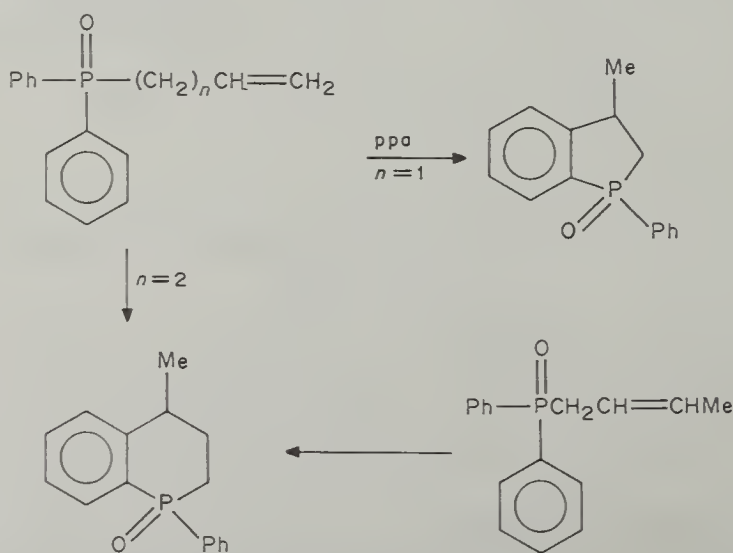
An early demonstration of the position that an electrophile occupies on entering an aromatic ring directly attached to the phosphoryl group in a phosphine oxide, was made

by Challenger and Wilkinson who, in 1924, showed that the product from the nitration of triphenylphosphine oxide was tris(3-nitrophenyl)phosphine oxide, obtained originally by the same process by Michaelis in 1885, although without characterization⁶⁻⁹. The later identification consisted of reduction to tris(3-aminophenyl)phosphine oxide followed by diazotization and a Sandmeyer conversion into tris(3-chlorophenyl)phosphine oxide, identified by alternative synthesis. We thus have an early indication of the electron-withdrawing activity of the phosphoryl group. Similar procedures have been followed to show the marked preponderance of *meta* substitution during the nitration of bis-(chloromethyl)phenylphosphine oxide and methyldiphenylphosphine oxide. Appreciable *ortho* substitution may also occur during conventional nitration. Thus, for the oxides $R_2P(O)Ph$, when $R = Me, Et$ or Pr^i , the ratios of *meta* to *ortho* substitution are 90:10, 93:7 and 99:1, respectively; when $R = CH_2Cl$, only *meta* substitution was observed (see above)²⁰⁵. Russian workers obtained similar results with other simple oxides and noted that the corresponding phosphine sulphides gave the same products and product ratios. However, as might be expected, nitration of dialkyl(benzyl)phosphine oxides gave the dialkyl(4-nitrobenzyl)phosphine oxides¹²⁴.

Elsewhere, *meta* substitution has been assumed in nitration, sulphonation²⁰⁶ and chloromethylation²⁰⁷. A recent study has demonstrated *meta*-sulphonation when triphenylphosphine oxide, or the sulphide, is dissolved in oleum, although in the case of the oxide the actual *meta*-directing group might then be $P^+ - OH$ ²⁰⁸.

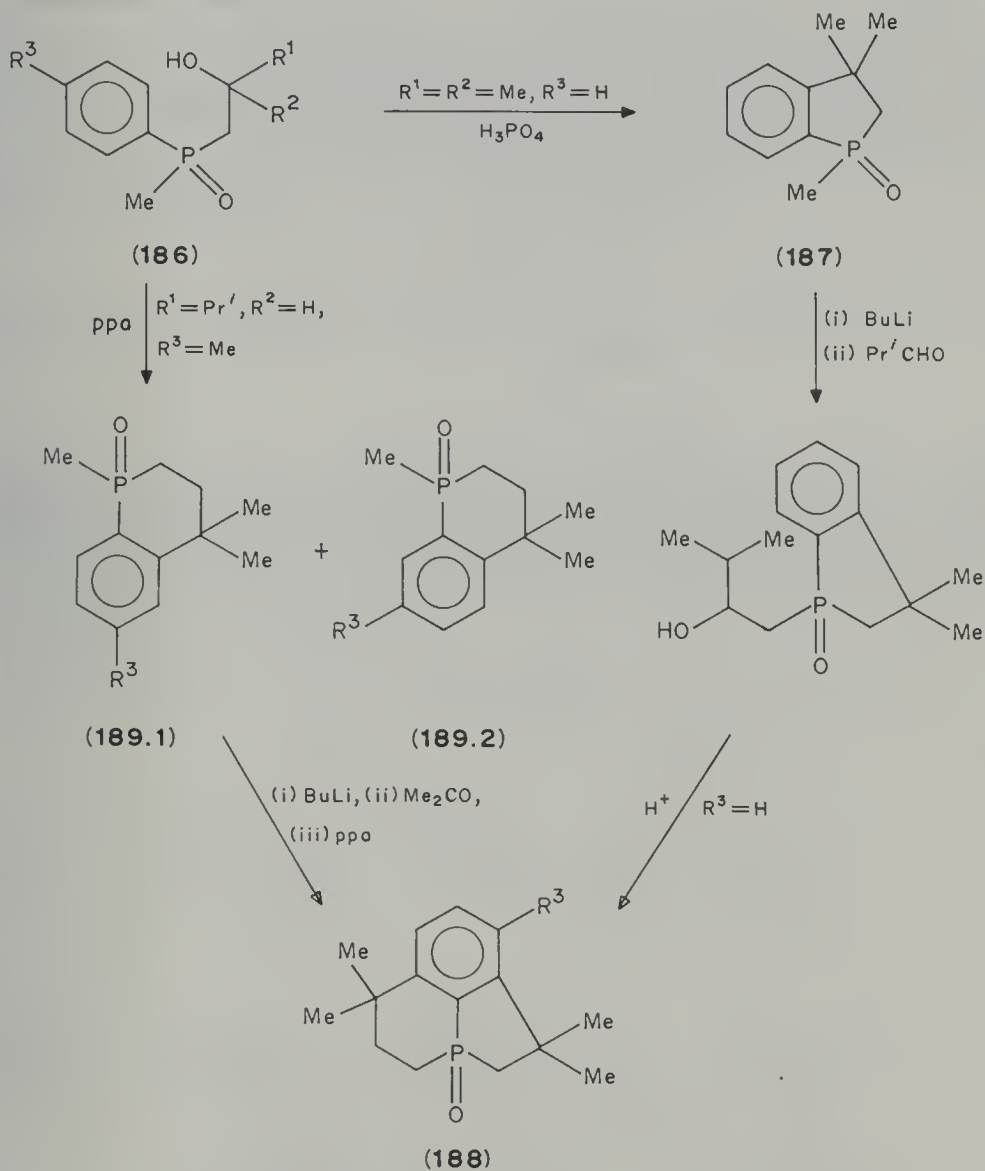
Although chloromethylation appears to be the only example thus far recorded of intermolecular alkylation of an aromatic ring directly attached to the phosphoryl group, and thus far to be of little interest, intramolecular alkylation is a process important in the synthesis of polycyclic phosphine oxides²⁰⁹. The alkylating function may consist, initially, of an olefinic bond or a hydroxyl group. In the reactions exemplified in Scheme 38 the cyclizations were achieved using polyphosphoric acid at 150–200 °C²¹⁰.

Two groups have synthesized tricyclic phosphine oxides using the methodology. Warren and coworkers started with **186** ($R^3 = H$), which yields the phosphindoline oxide **187** when treated with 98% H_3PO_4 ; further metallation, treatment with isobutyraldehyde and cyclization afforded **188** ($R^3 = H$)²¹¹. A similar sequence starting with **186** ($R^3 = Me$) proceeds through an inseparable mixture (**189**) of intermediates, although this provides no obstacle to the successful synthesis of **188** ($R^3 = Me$)⁵⁷.

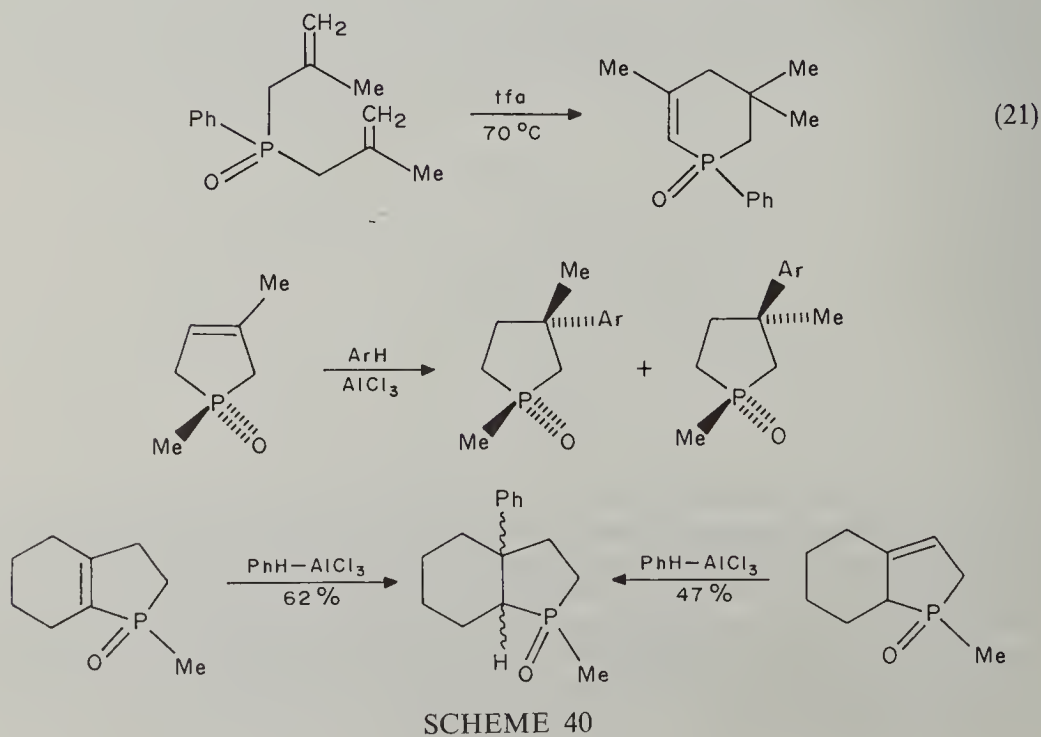
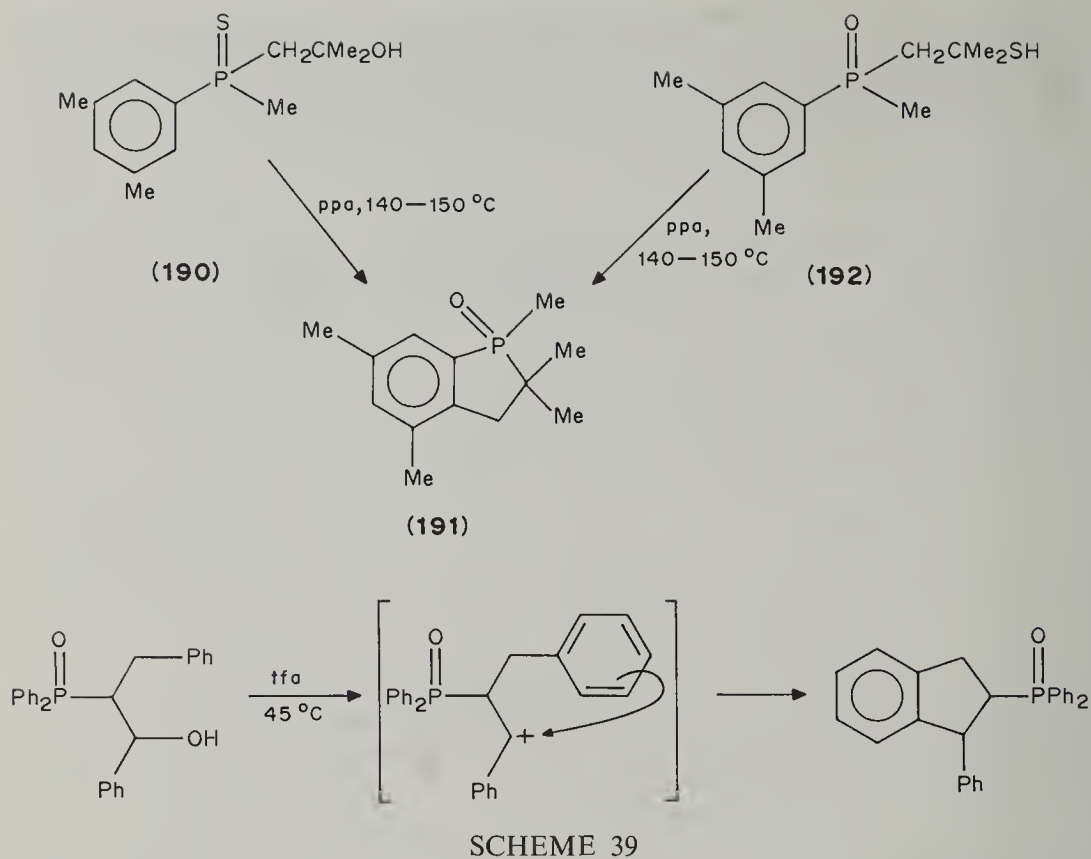


SCHEME 38

The phosphine sulphide **190** is acted on by ppa at 140–150 °C to give a 3:1 mixture of the phosphindoline oxide **191** and the corresponding sulphide. The phosphine oxide **192**, obtained through the isomerization of **190** with $\text{MeSO}_3\text{H}-\text{P}_4\text{O}_{10}$ at ambient temperature, loses H_2S when heated with ppa, and affords **191** only²¹².



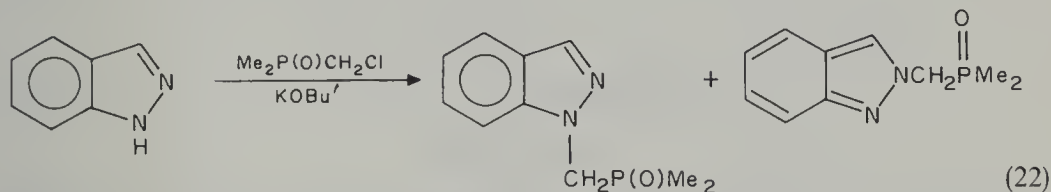
Acidity data for ω -phosphinoyl-alkanecarboxylic acids^{213–215} and -benzoic acids²¹⁶, and also for other compounds, demonstrate the strong electron-withdrawing ability of the $\text{R}_2\text{P(X)}$ group ($\text{X} = \text{O}$ or S), also proved by the course of electrophilic aromatic substitutions. If, in the latter, a carbocationic site is generated near to an aromatic ring distant from the phosphinoyl group, then it is that aromatic ring which will, in preference, react with the carbocation (Scheme 39)²¹¹. The deactivation is such that even an isolated carbon—carbon double bond will react in preference to the phosphinoyl-deactivated benzene ring (reaction 21).



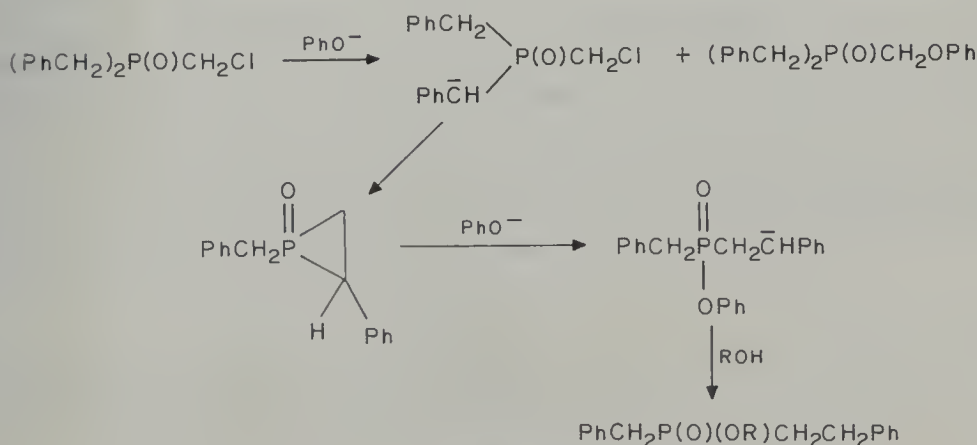
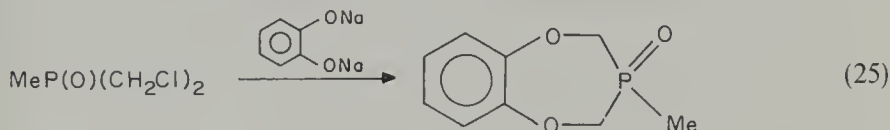
Friedel–Crafts arylation of phospholene derivatives has been accomplished readily (Scheme 40) using AlCl_3 as catalyst, although such reactions fail to occur in the presence of BF_3 , SnCl_4 , HCl or H_3PO_4 ²¹⁷.

G. Nucleophilic Substitution

Hydroxymethylphosphine oxides are converted into the corresponding chloromethyl compounds through reaction with SOCl_2 or PCl_5 . The chloromethyl group is then reactive towards a wide range of nucleophiles. Reaction with dialkylamines is straightforward²¹⁸, as is that with the sodium salt of imidazole, or other azoles in the presence of KO^tBu , although tautomerism may then be the cause of mixed product formation (reaction 22)²¹⁹.

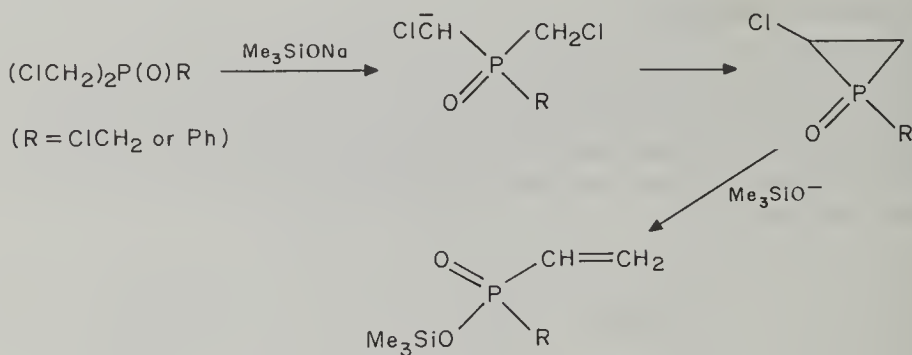


Reactions involving thiolate anions²¹⁸, alkoxide anions²¹⁸ or azides²²⁰ are also without apparent problems. The chloromethyl group undergoes Arbuzov reactions with suitable esters of trivalent phosphorus acids as exemplified by reaction 23²²¹; tertiary phosphines yield (phosphinoylmethyl)phosphonium salts²²². The chlorine is replaceable by certain carboxylate (generally aromatic) anions (reaction 24) and in some cases straightforwardly by aryloxy anions (equation 25)^{223,224}.



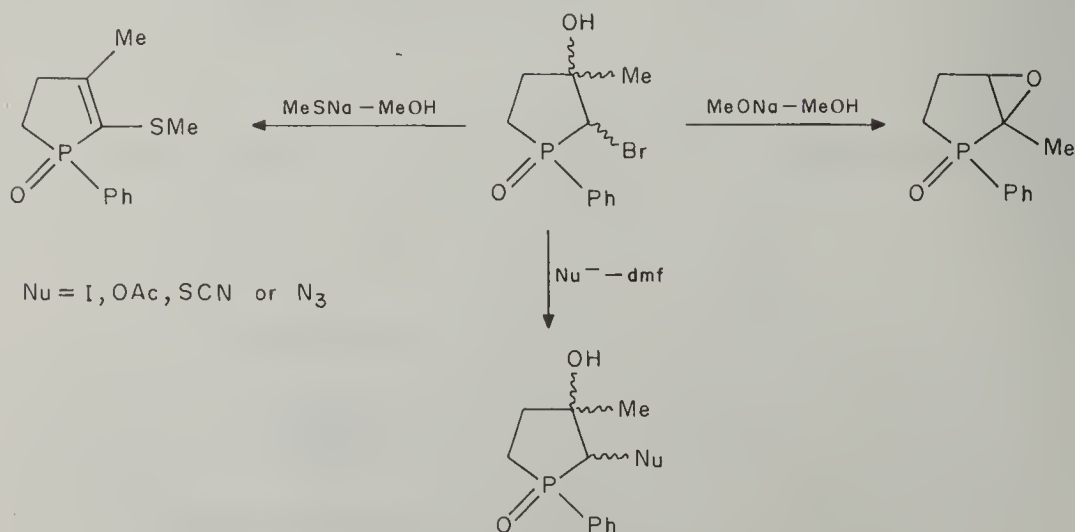
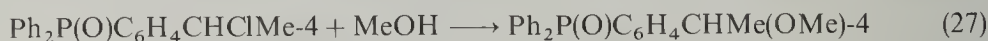
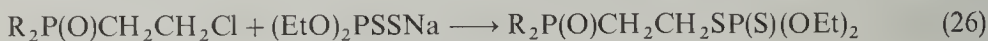
SCHEME 41

Other displacements by aryloxy anions may result in complications with the formation of 'normal' and rearranged products (Scheme 41)²¹⁸. A novel reaction between bis(chloromethyl)phosphine oxides and Me_3SiONa has been afforded a similar interpretation involving initial deprotonation (Scheme 42)²²⁵.



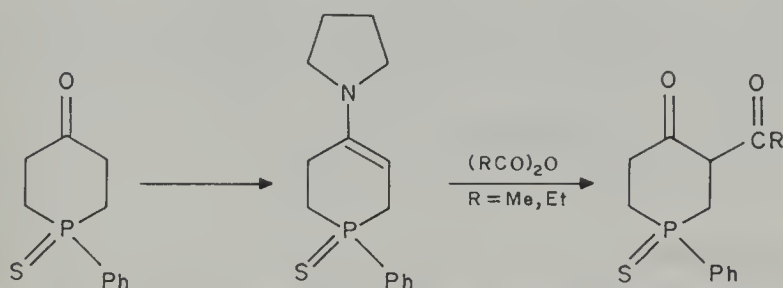
SCHEME 42

The halogen in 2- and 1-chloroethyl groups can be replaced directly (reaction 26)²²⁶ or by consecutive elimination–addition processes as in reactions 27²²² and 28²⁰⁴. The results of an investigation¹⁹⁷ into displacements of a halogen attached to a phospholane ring are summarized in Scheme 43; the type of product depended on the nature of the attacking nucleophile. Observed nucleophilic displacements have not been restricted to those of halogen from sp^3 carbon, but include those of other groups, e.g. sulphonate anions (reaction 29)²²⁷.



SCHEME 43

Reactions in which the functionalized phosphine oxide itself acts as the nucleophile include those reactions of hydroxyalkyl- and aminoalkyl-phosphine oxides towards acylating agents. Tris(hydroxymethyl)phosphine oxide is best acylated with the acyl chloride in PhNO_2 , and attempts to acetylate tris(2-hydroxyethyl)phosphine oxide with ketene, acetyl chloride or acetic acid all failed, although the use of acetic anhydride was successful²⁰⁴. Aminoalkylphosphine oxides form the customary derivatives in their interactions with acyl halides, ureas, isocyanates²²⁸ and ketenes²²⁹. Cyclic phosphaketones can be acylated on oxygen through their enol forms²⁰³ or on carbon through an enamine intermediate (Scheme 44)²³⁰.

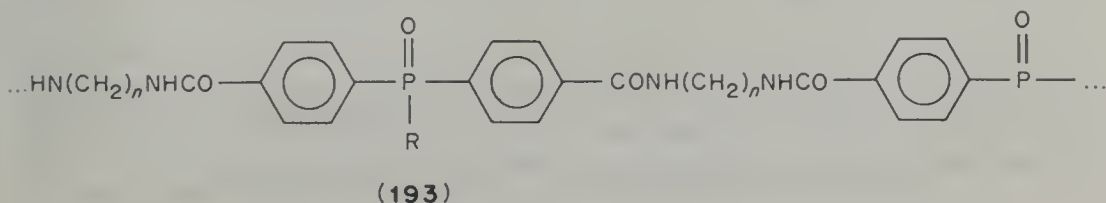


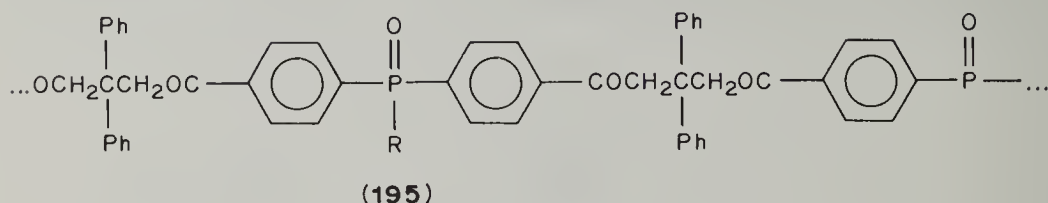
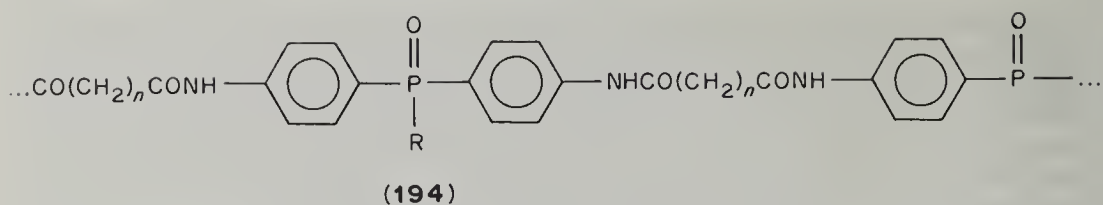
SCHEME 44

Tris(4-chlorophenyl)phosphine oxide is unreactive towards aqueous or ethanolic alkali, ammonia or aniline, but the positioning of NO_2 groups *ortho* to Cl renders the compounds increasingly reactive to these and similar nucleophiles^{206,231}. Aromatic halogen (Cl, F) *para* to a phosphinoyl group is displaceable by MeO^- and the kinetics of the process for a series of 4-(dialkylphosphinoyl)-1-halogenobenzenes have been determined^{222,232}. Methoxy groups in several 3- and 4-methoxyphenylphosphine oxides have been demethylated using 48% aqueous HBr, 50% aqueous HI or HBr in acetic acid.

MeNH_2 displaces only a *para* fluorine atom from either diphenylphosphinoyl- or diphenylphosphinothioyl-pentafluorobenzene in EtOH; in benzene, *ortho* substitution also occurs when, for the oxide, the *ortho:para* ratio is 46:54, whereas for the sulphide it occurs when the ratio is 82:18. With NaOMe in MeOH, *ortho* and *para* substitution again both occur for both oxide and sulphide; additionally, however, the sulphide undergoes phosphorus—carbon bond cleavage to give methyl diphenylphosphinothioate^{233,234}.

Phosphinoyl-substituted benzoic acids, conveniently obtained by the permanganate oxidation of tolylphosphine oxides, can be transformed via the acid chlorides into amides, aldehydes and alcohols¹⁷⁰. Phosphinoylarylamines provide phosphinoyl isocyanates and thus phosphinoyl-ureas and -urethanes²³⁵. Bis(carboxyphenyl)phosphine oxides in their reactions with α,ω -alkanediamines yield phosphine oxide-based polyamides of type **193**, and the related polyamides (**194**) are obtainable from bis(aminophenyl)phosphine oxides and dicarboxylic acids and their derivatives. The condensation of bis(chlorocarbonyl)-phenylphosphine oxide with diphenylolpropane yields a polymeric ester **195**⁶.



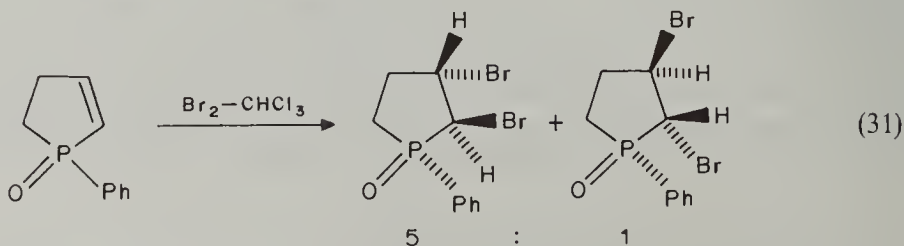
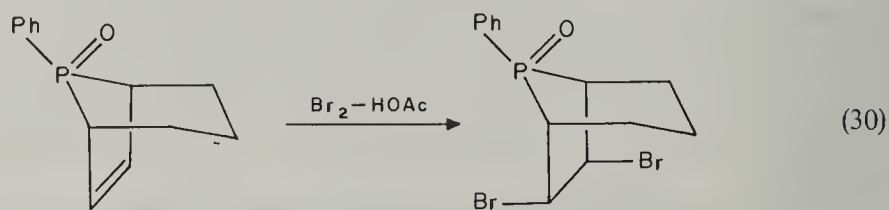


H. Addition Reactions

Unsaturated phosphine oxides undergo addition reactions with electrophiles, nucleophiles, free radicals and other species, with cycloaddition reactions playing a prominent role. Of particular interest is the involvement of the phosphinoyl group in such reactions, both indirect in its influence on the course of such reactions, but also by direct involvement in bond formation.

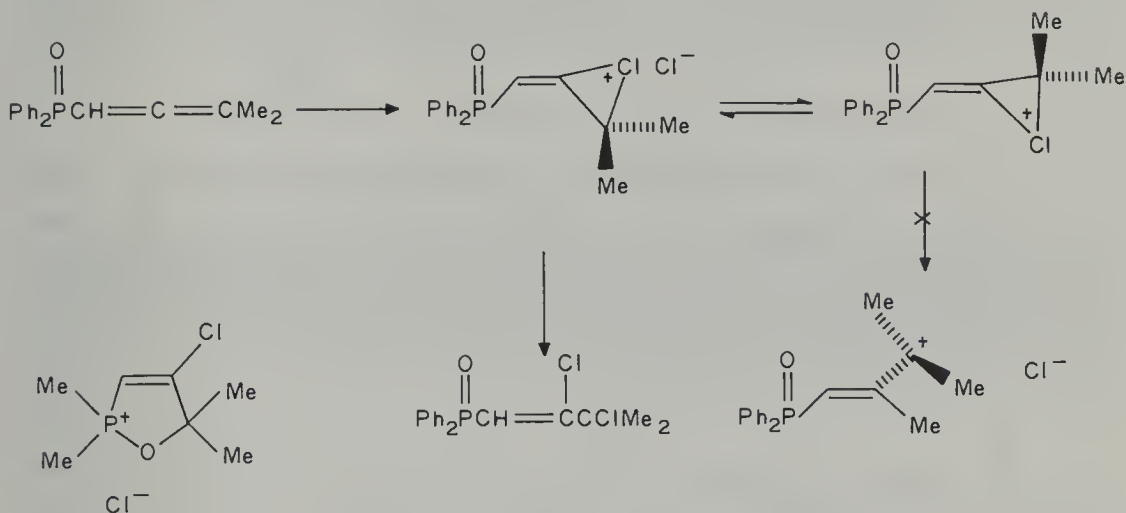
1. Electrophilic additions

The reaction of chlorine or bromine with either vinyl- or allyl-phosphine oxides yields products the natures of which are consistent with a *trans* addition shown for both acyclic and cyclic (phosphenes) phosphine oxides according to equations 30¹⁷⁷ and 31²³⁶.



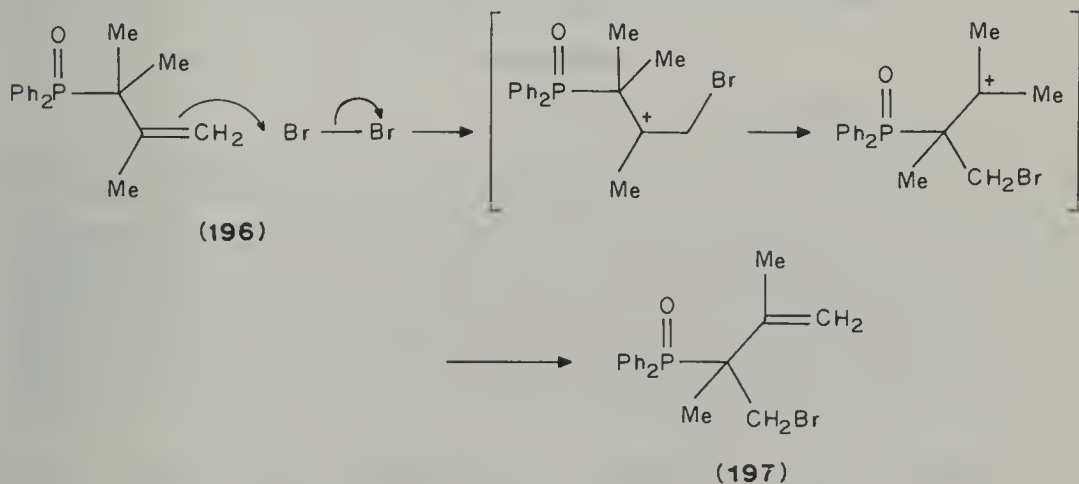
The addition of chlorine to allenephosphine oxides is a particularly interesting case of electrophilic addition. Although not so extensively examined as the additions of halogens and other electrophiles to structurally similar phosphonic esters, one notable feature is the fact that (3-methylbuta-1,2-dienyl)diphenylphosphine oxide adds the

halogen to the terminal double bond whereas (3-methylbuta-1,2-dienyl)dimethylphosphine oxide yields a cyclic phosphonium salt (Scheme 45)²³⁷.

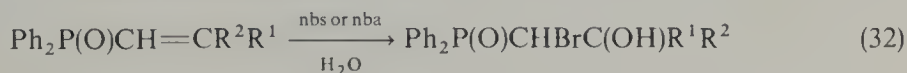


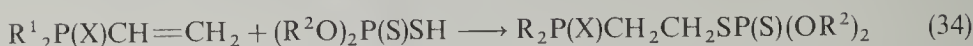
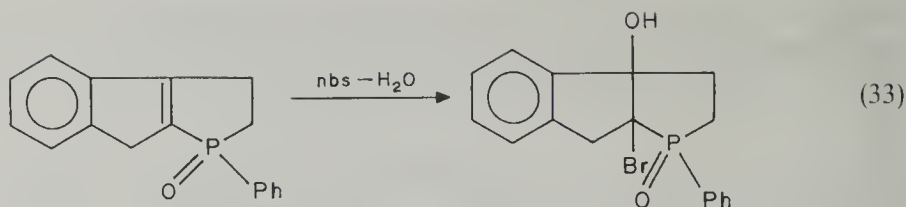
SCHEME 45

The addition of bromine to the phosphine oxide **196** is also unusual. Normal electrophilic attack is initiated but a faster phosphinoyl migration (Section III.C) occurs within the intermediate carbocation, and the product, isolated in quantitative yield is the monobromo compound **197**^{193,195}.

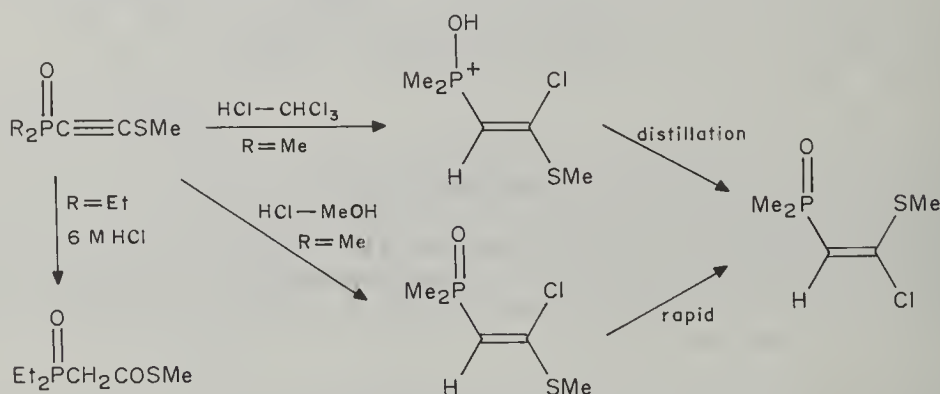


The formation of phosphinoylated bromohydrins when acyclic vinylphosphine oxides (equation 32)²³⁸ and 2-phospholenes (equation 33)⁷⁴ react with nbs under aqueous conditions is probably the result of nucleophilic participation by the solvent. Diphenylvinylphosphine oxide itself fails to react²³⁸. Addition of a phosphorodithioic acid to a vinylphosphine oxide takes place under moderate conditions of heat in a suitable solvent (equation 34). Additions to vinylphosphine sulphides occur more slowly and even then only under more forcing conditions²²⁶.





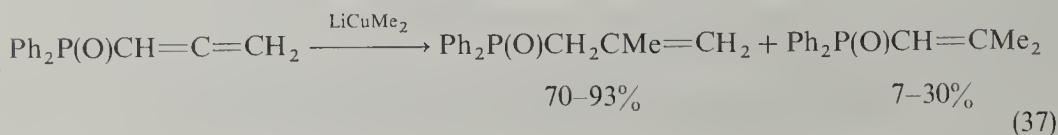
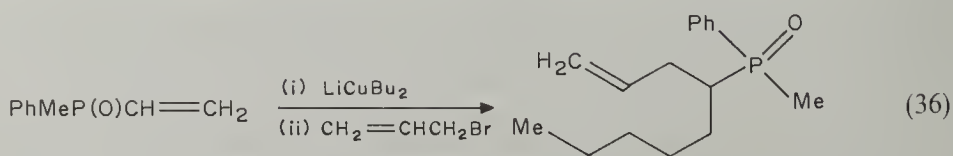
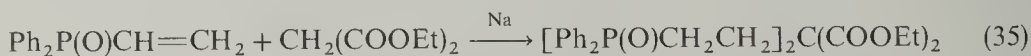
The addition of hydrogen halides to acetylenic phosphine oxides has also been investigated to only a limited extent, but agreement seems to have been reached that both HCl and HI react, the latter faster, in a *trans* fashion to yield a *cis*-olefinic phosphine oxide, through a pseudophosphonium intermediate (depending on reaction solvent), and that isomerization may occur during final distillation (Scheme 46)^{239,240}.



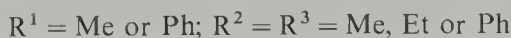
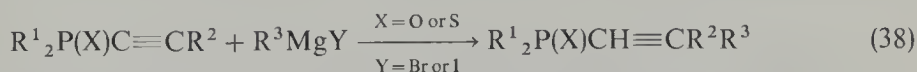
SCHEME 46

2. Nucleophilic additions

Reported Michael additions of carbanions to alkenephosphine chalcogenides include that of diethyl malonate (equation 35); equation 36 illustrates addition followed by alkylation with organolithium cuprates, LiCuR_2 ²⁴¹. A similar addition to an allenephosphine oxide affords a mixture of products (reaction 37)²⁴². Organometallic reagents have been used to effect anionic polymerization, with Grignard reagents acting on diphenylvinylphosphine oxide to obtain polymers with molecular weights of around 10 000. Zinc-copper couple promotes the addition of alkyl halides to vinylphosphine oxides in an aqueous ethanolic medium; the scope of the reaction includes the use of sterically hindered alkyl halides²⁴³.

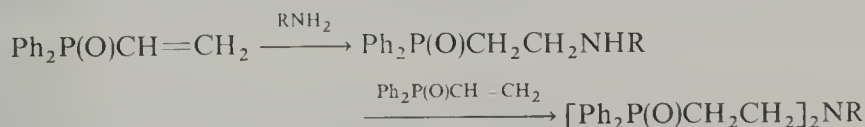


Acetylenic phosphines, $R^1_2PC\equiv CR^2$, cannot be alkylated by nucleophilic additions of Grignard reagents, whereas the corresponding reactions of the oxides and sulphides take place readily in the presence of a trace of copper(I) halide (equation 38) in high yields; the stereochemistry of addition appears, as yet, to be undecided. Further addition to the alkene products also does not take place²⁴⁴.



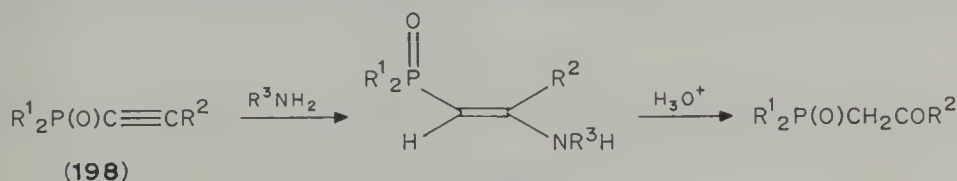
The additions of protic substances possessing the $X-H$ bond, where $X = N, O, S$ or P , have been investigated far more extensively than those of active methylene $C-H$ acids. In general, the additions reactions involving vinylphosphine oxides are much faster than those of the parent phosphines, if indeed the latter react at all, but they are slower than those same reactions of esters of vinyl-phosphonic or -phosphinic acids. The additions take place in a manner contrary to the Markownikoff rule and the heteroatom adds to the β -carbon atom. There is the direct analogy between the modes of additions to $C=CP=O$ and $C=CC=O$ ²⁴⁵.

Successful addition of an amine to a vinylphosphine oxide requires that for the amine pK_B be less than 3²⁴⁶ and in the case of primary amines a two-stage process is possible (Scheme 47). From the phosphorus reactant point of view, the addition of amines to vinylic or allylic diphenylphosphine oxides succeeds when substituents on the sp^2 carbon are lacking or when there is only one substituent on $C_{(2)}$, but the presence of one substituent α or two β to phosphorus prevents addition. Benzamide also adds to diphenylvinylphosphine oxide in the presence of NaH under thf ^{247,248}. Additions have been carried out with optically active chiral phosphine oxides²⁴⁹ and with optically active amines, e.g. L-prolinol²⁴⁶.



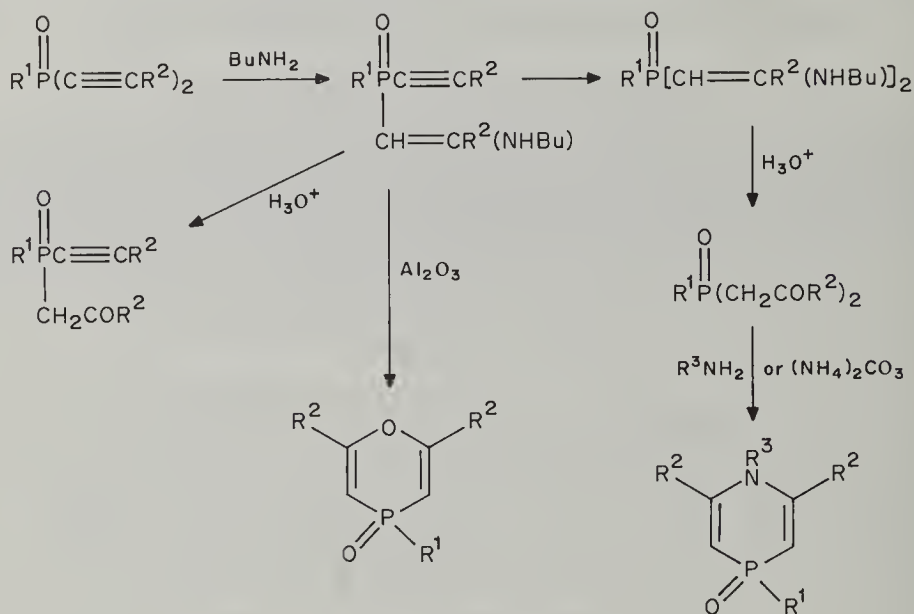
SCHEME 47

Conclusions differ as to the stereospecificity of additions of amines to acetylenic phosphine oxides (but again, additions to acetylenic phosphines do not occur), but do agree on regiospecificity. Additions to **198** ($R^1 = Ph$; $R^2 = H$, primary alkyl, cyclohexyl, Bu^t or Ph) have been stated to occur in a *cis* fashion to yield *trans*-enamine products which do not then isomerize to the *cis* forms (Scheme 48)^{250,251}. The enamines are hydrolysable (aqueous oxalic acid) to β -ketoalkylphosphine oxides. On the other hand, further studies using **198** ($R^1 = Me$ or Bu) have suggested that the stereospecificity of addition depends on the experimental conditions but appears to be initially *trans* followed by isomerization to the *cis* form: at $-20^\circ C$ Et_2NH adds to **198** ($R^1 = Bu$) to give the *cis*-enamine, but at $60^\circ C$ the product has *trans* geometry. When Me_2NH is used, a mixture of *cis* and *trans* products is formed even at $-20^\circ C$ ²³⁹.

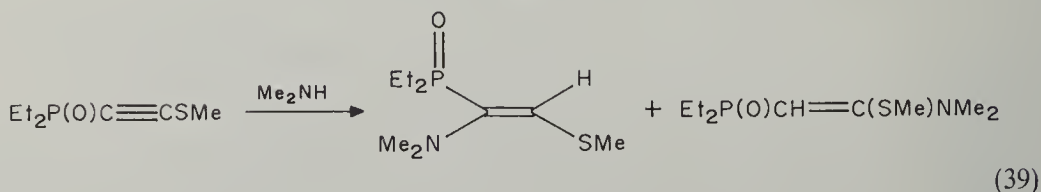


SCHEME 48

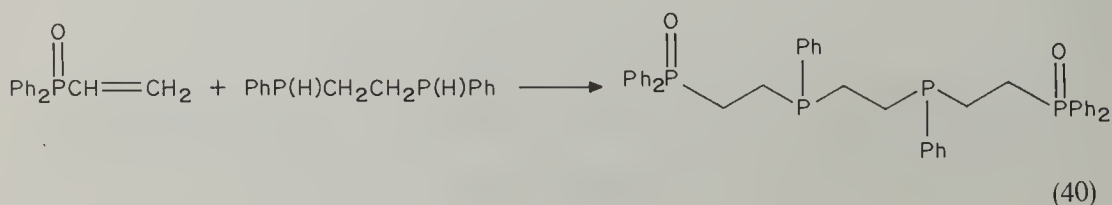
Additions to bis(acetylenic)phosphine oxides are of particular interest and value since they provide an acceptable route to several heterocyclic systems, as exemplified in Scheme 49^{252,253}. The regiospecificity of addition of amines can be modified by the presence of appropriate substituents at the acetylenic C₍₂₎ and also by change in experimental conditions (equation 39)²⁴⁰.

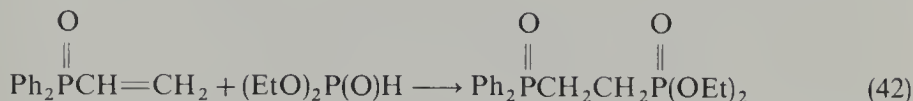
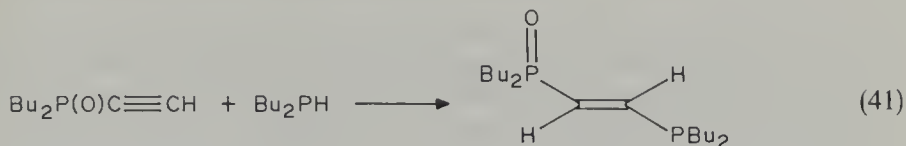


SCHEME 49



The additions of primary or secondary phosphines to vinylphosphine oxides or sulphides constitute well authenticated reactions for the synthesis of polyphosphine chalcogenides (e.g. reaction 40)²⁵⁴ and thus polyphosphines themselves following deoxygenation or desulphurization (Section II.A.1.2)^{90,91}. Phosphines which have been examined in connection with reaction 40 include phosphine itself, RPH_2 ($R = Me$ or Ph), R_2PH ($R = Me$ or Ph), $H_2PCH_2CH_2PH_2$ and $Ph(H)PCH_2CH_2P(H)R$ ($R = H$ or Ph). The additions of phosphines to acetylenic phosphine oxides (equation 41)²⁵⁵ and dialkyl phosphonates to unsaturated phosphine oxides (e.g. reaction 42) have also been recorded.



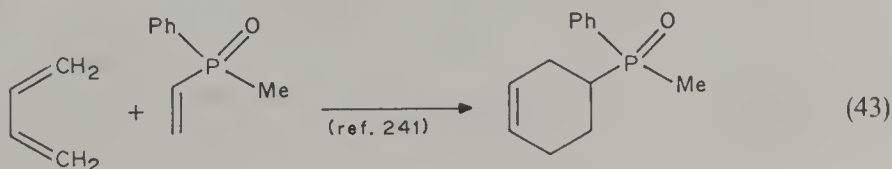


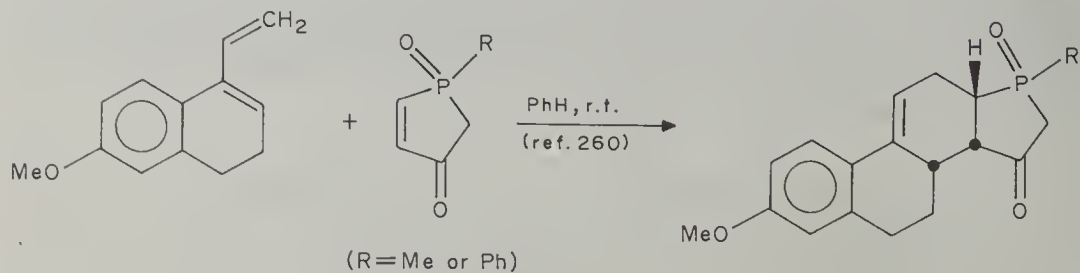
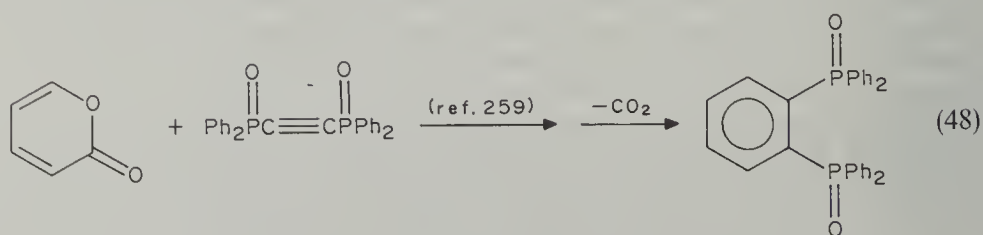
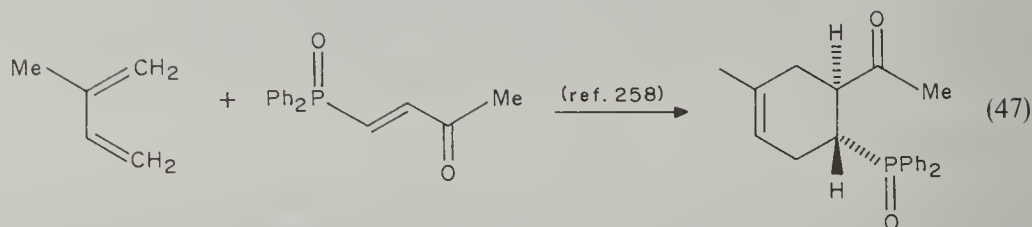
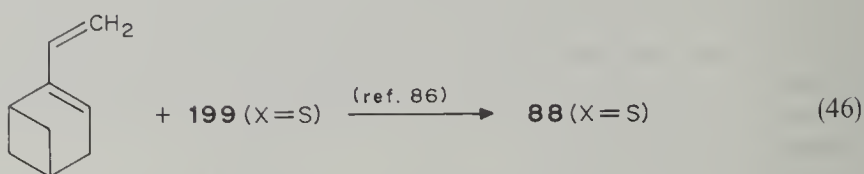
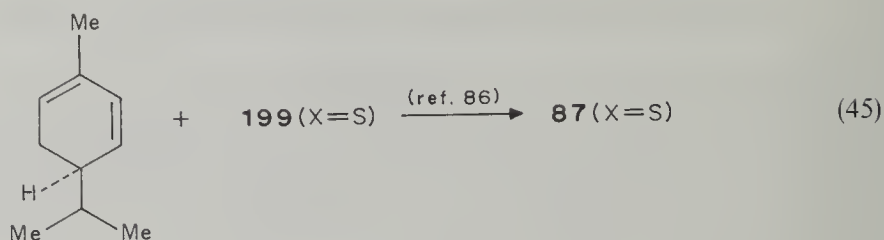
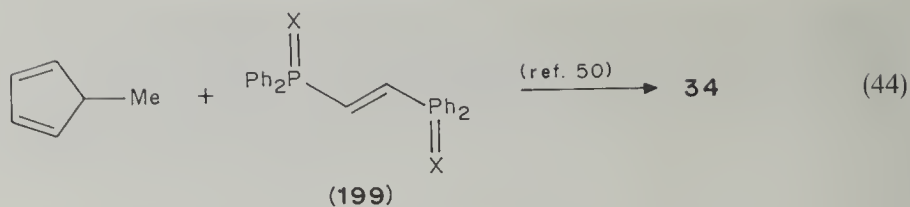
The addition of alcohols to vinylphosphine oxides and sulphides occurs regio-specifically with the RO group adding to C₍₂₎^{238,239}; reactions have been carried out with chiral phosphine oxides²⁷ and with optically active alcohols such as borneol and menthol²⁵⁶, but the reaction may be complicated by nucleophilic substitution at phosphorus. Thus, the products from the interaction of Bu₂P(O)C≡CH and NaOEt in EtOH for 2 h at 75 °C include both *cis*- and *trans*-Bu₂P(O)CH=CH(OEt) together with Bu₂P(O)CH₂CH(OEt)₂ (the total yield of the three products was 30%) and Bu₂P(O)OEt (47%) and acetylene²³⁹. Both mono- and bis-addition, as well as cleavage, have also been observed in the reaction between NaOMe and Me₂P(O)C≡CSMe²⁴⁰. Hydration of vinylphosphine oxides has been achieved by exploiting the hydroboration process; the stereochemistry of reaction for rigid cyclic systems is unaffected by the stereochemistry at phosphorus¹⁷⁷.

In competition experiments, thiols have been shown to be more selectively reactive in additions to diphenylvinylphosphine oxide than are either primary alcohols or amines²⁵⁷; the additions are regiospecific with the sulphur adding to C₍₂₎, but a mixture of (*E*)- and (*Z*)-vinyl thioethers results from acetylenic phosphine oxides^{239,240}. Additions have also been observed to occur slowly under free-radical conditions.

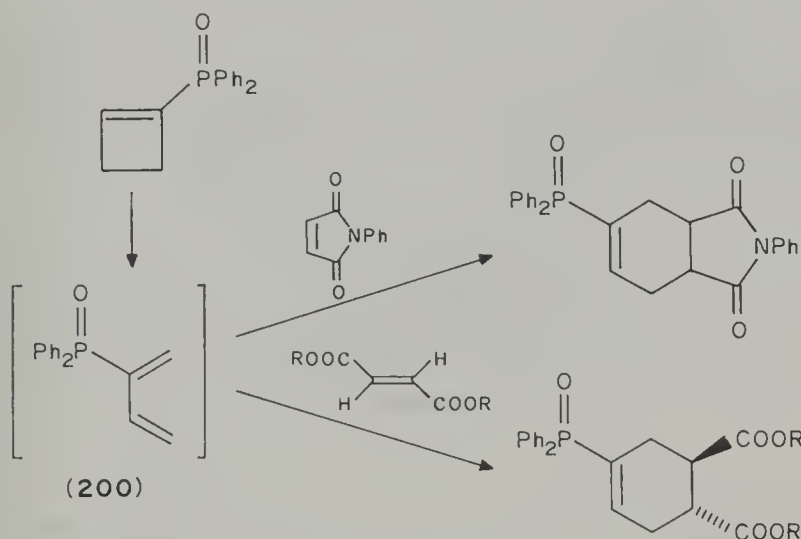
3. Cycloaddition reactions

Acyclic unsaturated phosphine oxides are able to react as either dienes or dieneophiles in intermolecular Diels–Alder reactions. The complexity of such reactions ranges from the very straightforward, such as the addition of diphenylvinylphosphine oxide to cyclopentadiene, through to reactions which build up phosphorus-containing analogues of well known natural product molecules. A selection of reactions which illustrate the dieneophilic behaviour of vinylphosphine oxides and sulphides is given in equations 43–49. Reference has already been made to the removal of the chalcogen from **34**, **87** (X = S) and **88** (X = S) to give the tervalent phosphorus compounds, useful as chiral ligands (Section II.1.2). The reaction represented by equation 47 is a complete reversal of the usual reaction direction, and is the result of the negation of the influence of the carbonyl group by the diphenylphosphinoyl group. Reaction 48 illustrates the instability of the initial Diels–Alder adduct, always a possibility, and which, by the rapid loss of CO₂ in a retro-reaction, affords ultimately 1,2-bis(diphenylphosphinoyl)benzene. Reaction 49 exemplifies the synthesis of a 17-phosphasteroid analogue; a similar reaction with 1-phenyl-2-phospholene 1-oxide and 2,3-disubstituted buta-1,3-dienes yields hexahydro-phosphindolines as their oxides⁷⁷.





Thermolysis of 1-(diphenylphosphinoyl)cyclobutene affords the very reactive 2-(diphenylphosphinoyl)buta-1,3-diene (**200**), which acts as an activated diene and can be trapped with the customary dieneophiles in reactions illustrated in Scheme 50²⁶¹. Monomeric phospholes can also act in the dual capacity as either dienes or dieneophiles. The 1-oxides and 1-sulphides of phospholes exhibit a marked propensity to dimerize, although there are some exceptions to such behaviour, and they include 1,2,5-triphenylphosphole 1-oxide, penta-substituted phosphole 1-oxides, including the pentaphenyl derivative, and 3,4-dimethyl-1-phenylphosphole 1-sulphide. When operational, the dimerization process yields the *endo* isomer products. Scheme 51 illustrates the ready formation and dimerization of a highly reactive phosphole, which can also be trapped by added dieneophiles^{262,263}.

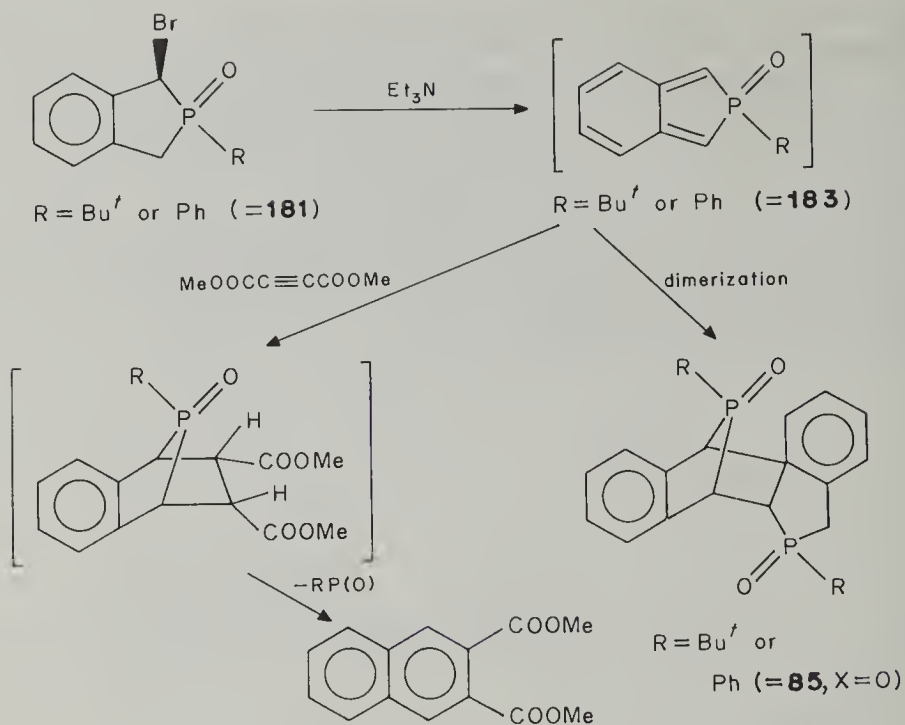


SCHEME 50

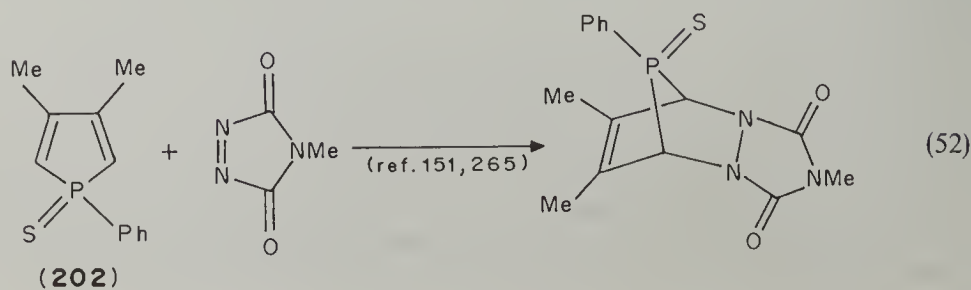
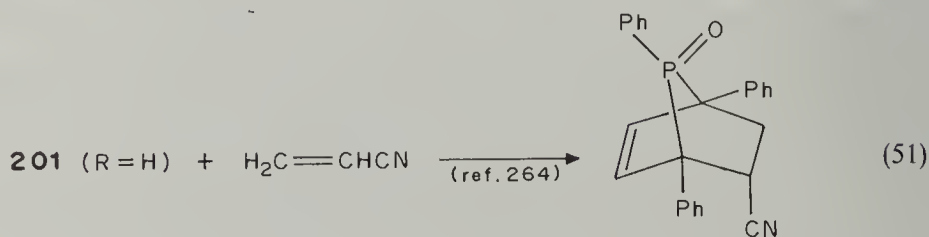
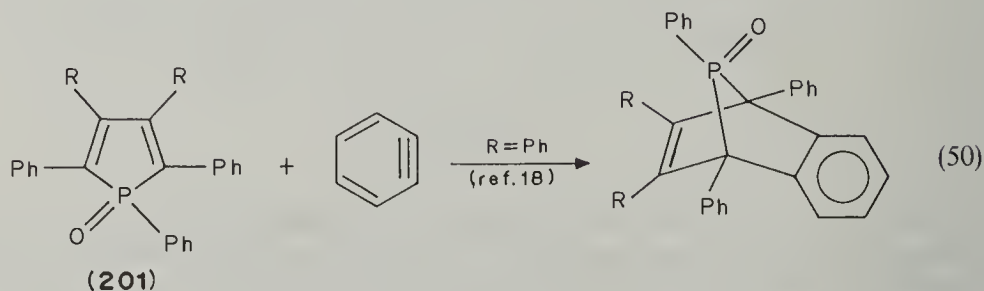
Reactions which illustrate the intermolecular diene behaviour of phosphine chalcogenides are illustrated in equations 50–53. The reactions indicated in Scheme 52 illustrate the diene behaviour of 1,2-dihydrophosphorin 1-oxides and their value in syntheses of 2-phosphabicyclo[2.2.2]oct-5-enes²⁶⁷ and -octa-5,7-dienes²⁶⁸. Once again, the initial [4 + 2] adducts often break down when heated gently.

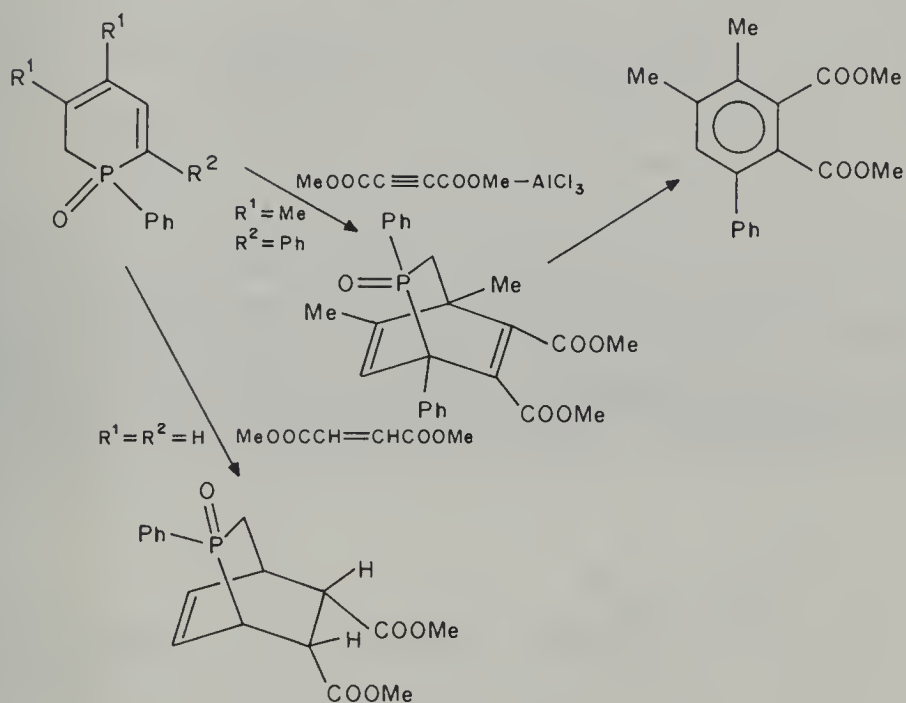
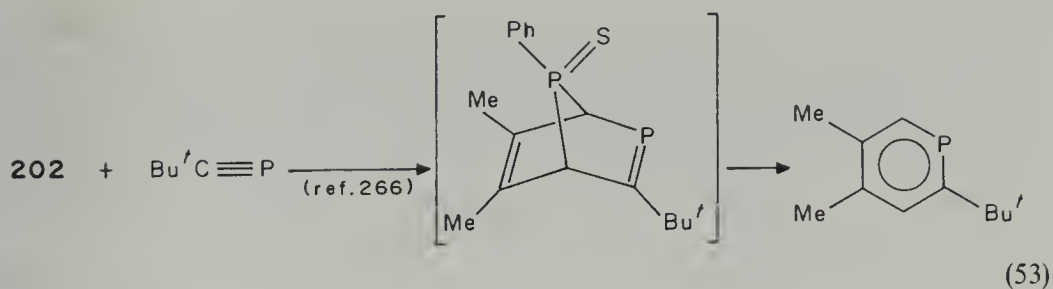
The capacity of phosphole 1-chalcogenides to act as dieneophiles is illustrated by reactions 54–56. Reaction 56 results in a 15-phosphasteroid analogue. The reaction with tropone should be considered as [2 + 4] rather than a [4 + 6] addition. Thioacetophenone undergoes a [4 + 2] cycloaddition to give **203**; other examples of compounds possessing the same bicyclic system have been obtained by the interaction of phosphole oxides or sulphides with oxyallyl cations, when the coproducts are 8-phosphabicyclo[3.2.1]octanes²⁶⁵.

A useful study²⁷¹ has demonstrated the catalytic activity of Lewis acids in reaction systems comprising vinylphosphine oxides and dienes. In the absence of catalyst, diphenylvinylphosphine oxide and cyclopentadiene react to give a 19% yield of a 42:58 mixture of *endo* and *exo* products. With the addition of 10 mol% of catalyst the yields of mixed adducts ranged from 23% (with SnCl_4) to 47% (using TiCl_4), but with generally little change in the stereochemical ratios, which ranged from 48:52 {for $[\text{Cl}_2\text{Ti}(\text{OPr}^i)_2]$ } to 60:40 (using TiCl_4), with AlCl_3 , FeCl_3 and SnCl_4 producing intermediate effects. More notable, however, were the significantly higher yields with *endo:exo* ratios of 3:1

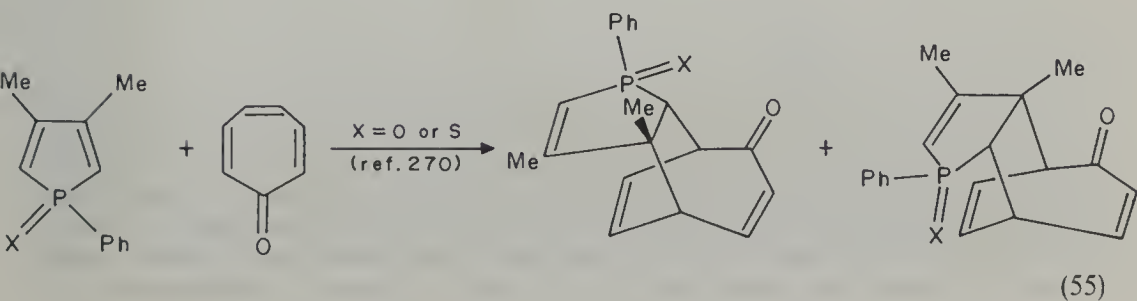
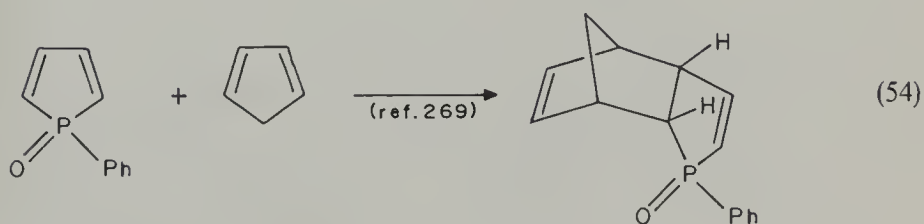


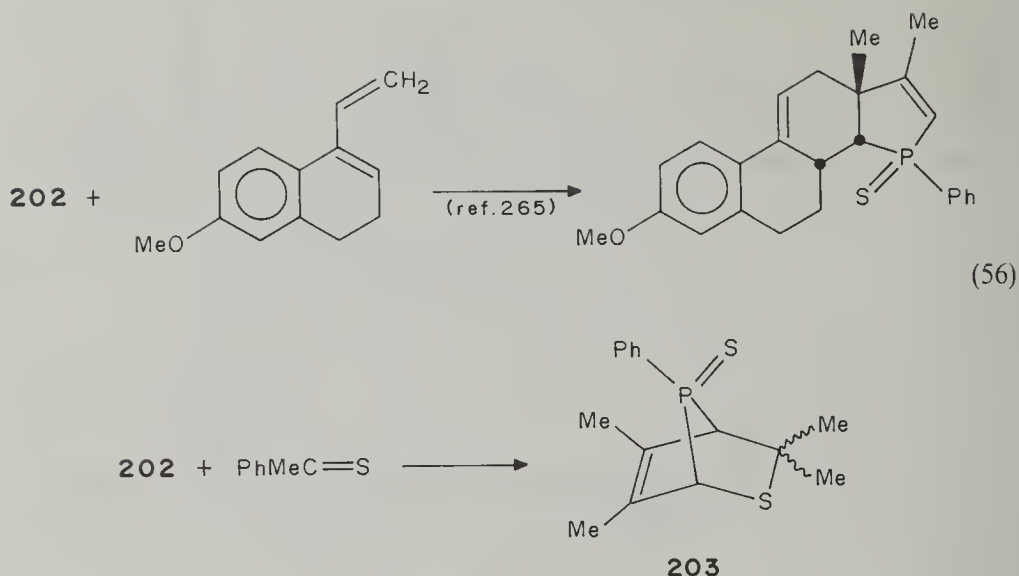
SCHEME 51



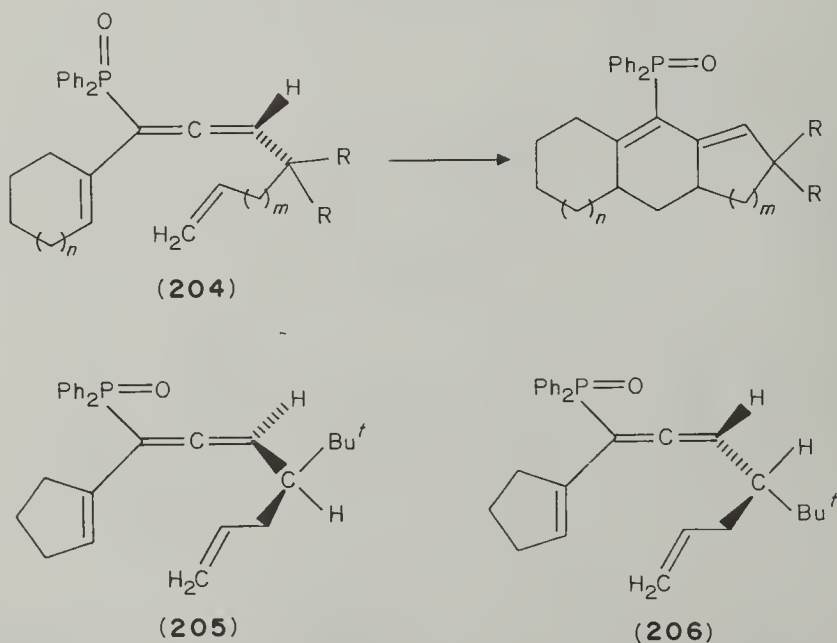


SCHEME 52



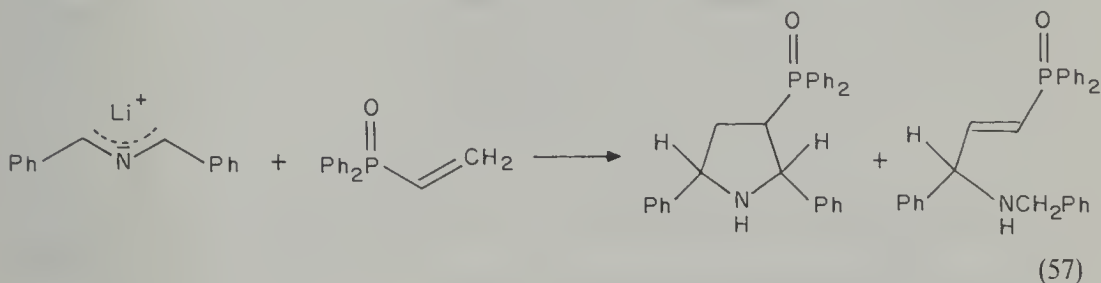


to 4:1 when 1 mol equiv. of catalyst (AlCl_3 , FeCl_3 or TiCl_4) was employed. The same Lewis acids also produced worthwhile changes in the diastereoisomer ratios for the products from (2-methoxyphenyl)phenylvinylphosphine oxide and cyclopentadiene, and for which titanium-containing reagents were particularly valuable for obtaining more of the *endo* products.



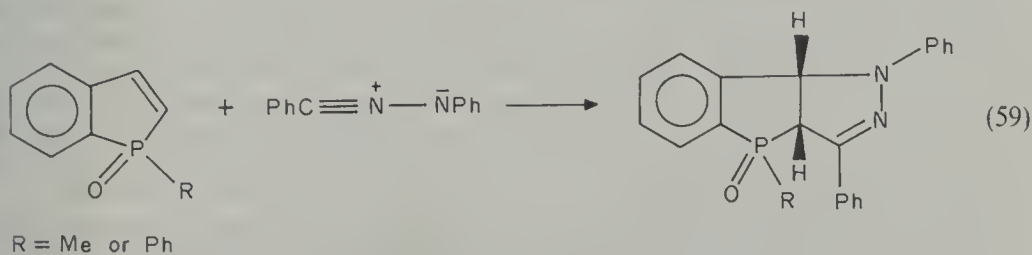
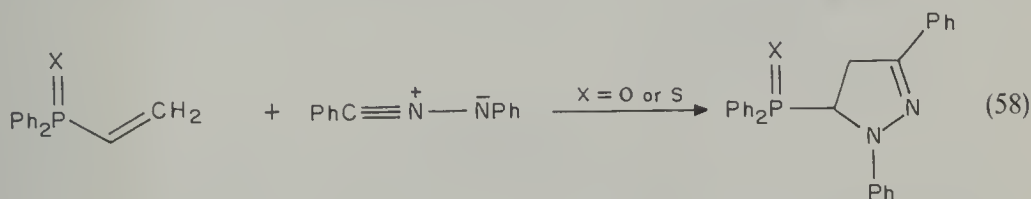
Some interesting activation effects have been found in connection with the unusual intramolecular Diels–Alder reaction of the allene phosphine oxides **204**²⁷². Relative to the reaction rate observed for **204** ($n = 0$; $m = 1$; $\text{R} = \text{H}$), substitution by alkyl groups increased reaction speeds by factors of 4.6 ($\text{R} = \text{Me}$), 21.1 ($\text{R} = \text{Et}$) and 27.8 ($\text{R} = \text{Pr}$). On the other hand, increasing n from 0 to 3 (with $m = 1$) produced relatively little change in reactivity. Much more pronounced was the effect of change in stereochemistry, as

demonstrated by **205** and **206**, which showed accelerations of 70 and 205 times that of **204** ($n = 0$; $m = 1$; $R = H$); increasing m from 1 to 2 in **204** ($n = 0$; $R = Me$) caused a decrease in the rate of cyclization by a factor of 850. The diphenylphosphinoyl group (and also the diphenylphosphino and analogous diphenylarsino and diphenylarsinoyl groups) activates ethene to cycloaddition with the lithium derivatives of Schiff bases as in reaction 57²⁷³.

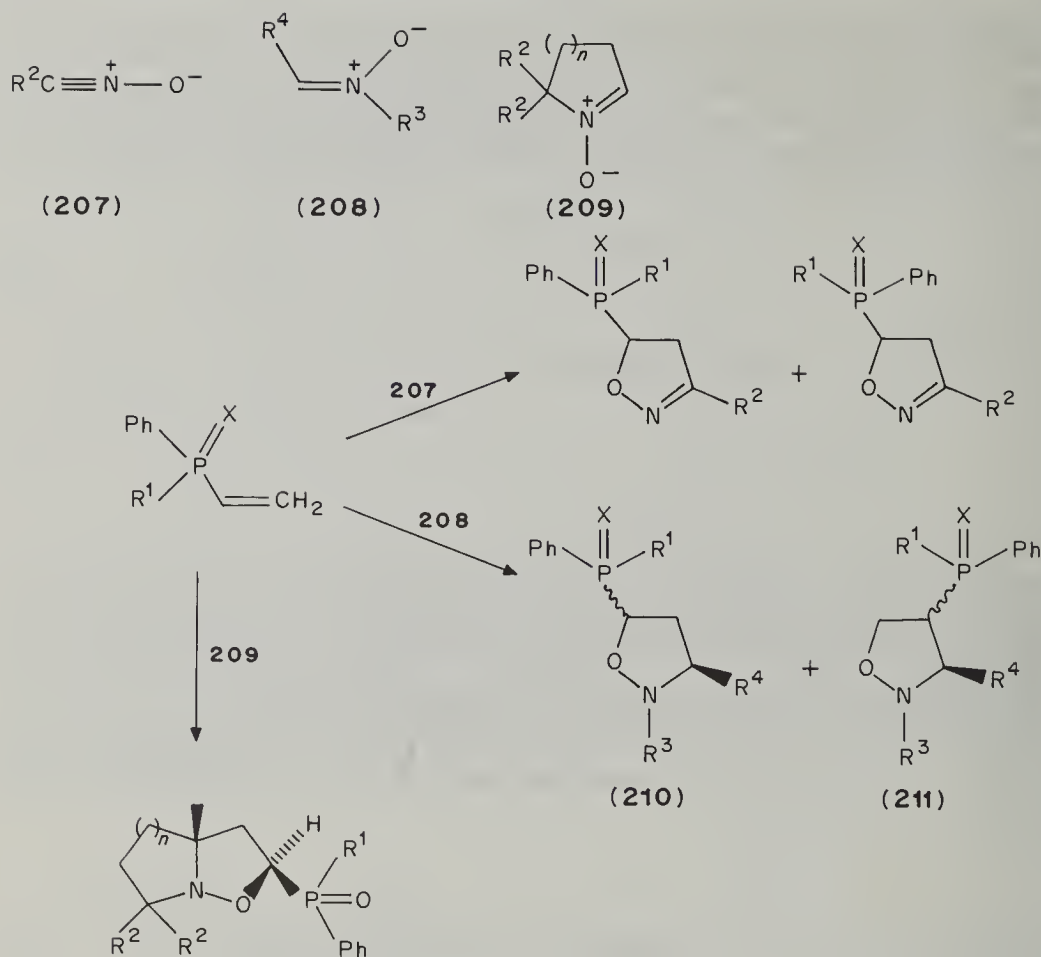


Vinylphosphine chalcogenides react with dipolarophiles in $[2 + 3]$ cycloadditions with nitrones, nitrilimines, nitrile oxides, azides and diazoalkanes; such reactions result in the synthesis of diphenylphosphinoylated heterocyclic systems, but they appear to take place more slowly than those reactions for similar vinylphosphinic and vinylphosphonic acid derivatives.

In the reactions of vinylphosphine oxides or sulphides with nitrilimines, Kolokol'tseva *et al.*²⁷⁴ have argued that the resultant pyrazolines are phosphinoylated at $C_{(2)}$ (equation 58) but this conclusion regarding regiospecificity has been disputed by other workers, e.g. for reaction 59²⁷⁵.



The same Russian authors have likewise described the formation of 5-phosphinoyl-1,2-oxazolines from vinylphosphinic oxides or sulphides and nitrile oxides (Scheme 53), with conclusions regarding regiospecificity not being disputed by others^{51,276}. Interestingly, the phosphine oxides are less reactive than the corresponding sulphides, and the 5-substituted regioisomers either prevail in the product mixtures or are the only products. Considerable diastereofacial selectivity is indicated by the dependence of the nature of the products on R^2 , the diastereoisomeric ratios being 2.6:1 for $R^2 = Me$ and 1.6:1 for $R^2 = Ph$.



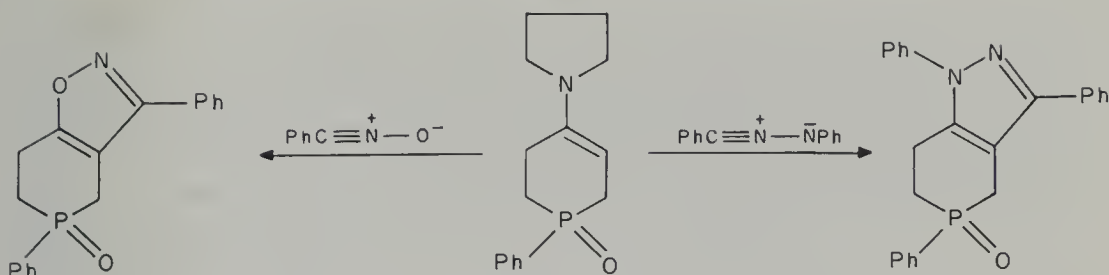
SCHEME 53

Reactions involving nitrones (**208**) yield the analogous 1,2-oxazolidines in non-regiospecific additions (Scheme 53)²⁷⁶⁻²⁷⁸. In all those cases examined, the composition of the product mixtures depended on the structure of the nitrone, but the reactions were highly specific for the cyclic nitrones **209** which produced regioisomer ratios of >95:5. When the nitrone **208** ($\text{R}^3 = \text{R}^4 = \text{Ph}$) reacts with diphenylvinylphosphine oxide, the regiospecificity is represented in a **210:211** ratio of ca 40:60, whereas for nitrone **208** ($\text{R}^3 = \text{Me}$; $\text{R}^4 = \text{Ph}$) the ratio is ca 60:40, both figures being in contrast to the ratio 86:14 obtained for **209** ($n = 1$; $\text{R}^2 = \text{Me}$).

The principal regioisomer obtained from diphenylnitrone and diphenylvinylphosphine oxide has been shown by X-ray diffraction experiments to have the *trans* arrangement between the phosphinoyl and $\text{C}_{(3)}$ phenyl groups²⁷⁸.

Cycloadditions of the same reagents to carbon—carbon double bonds which are not activated by adjacent phosphinoyl groups are but poorly exemplified (Scheme 54)²⁷⁹.

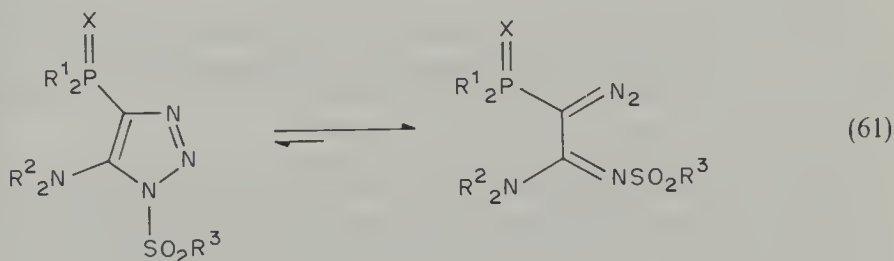
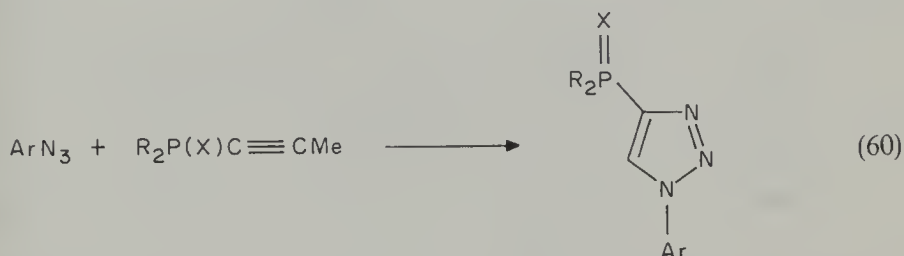
The influence of the chalcogen atom on the regio- and stereo-chemistry of addition of various nitrones to diphenylvinylphosphine chalcogenides has been examined in a recent study which showed that, for the acyclic nitrones **208** ($\text{R}^3 = \text{R}^4 = \text{Ph}$) undergoing reaction with $\text{Ph}_2\text{P}(\text{X})\text{CH}=\text{CH}_2$ in benzene at 80°C , a more equitable regioisomer distribution was obtained for $\text{X} = \text{O}$, but for $\text{X} = \text{S}$ or Se the regioisomer ratio was 10:90; the regiochemistry was reversed when $\text{R}^3 = \text{Me}$. When the cyclic nitrone **209** ($n = 1$;



SCHEME 54

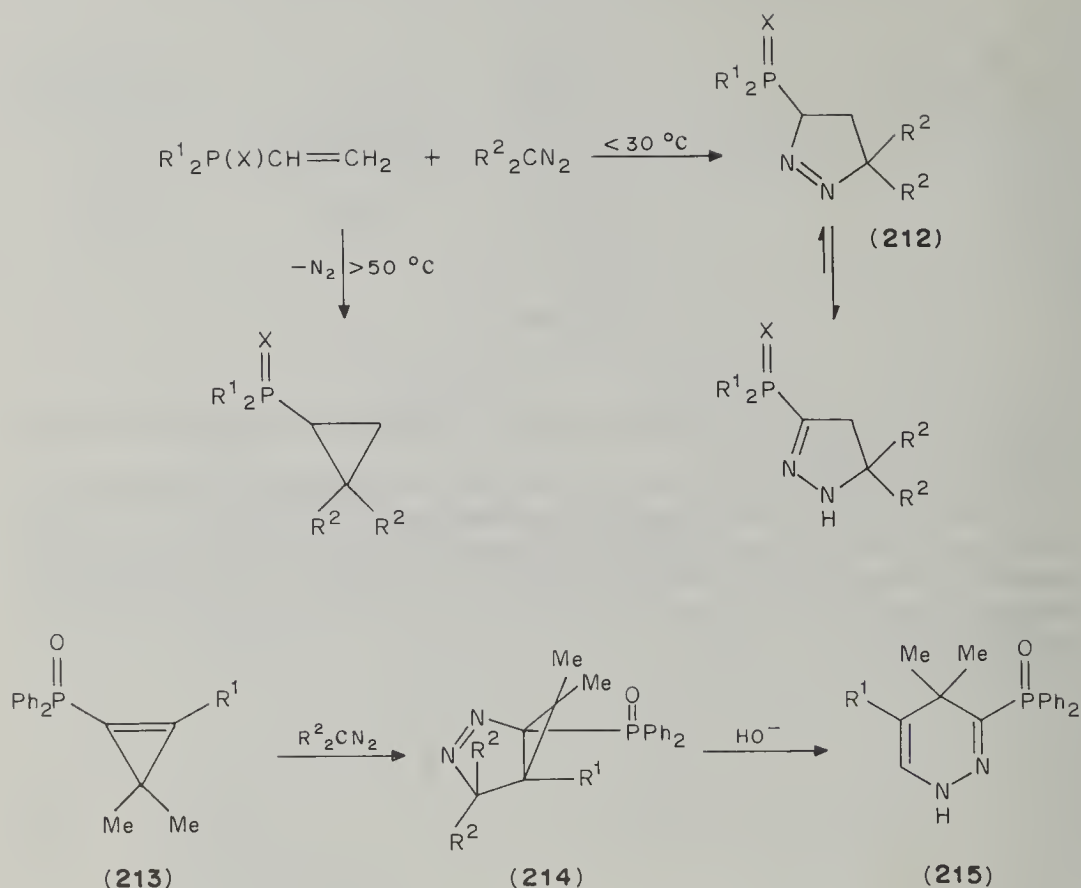
($R^2 = \text{Me}$) was employed in benzene at ambient temperature, the regiochemistry was unaffected by a change in X ²⁸⁰.

The addition of aryl azides to 1-propynylphosphine chalcogenides yields 4-phosphinoyl-1,2,3-triazoles (equation 60) in a process accelerated by either electron-donor or -acceptor substituents in the dipolarophile^{281,282}. In a similar reaction between (2-aminoethynyl)-phosphine chalcogenides and sulphonyl azides, the resultant 5-amino-4-sulphonyl-5-phosphinoyl-1,2,3-triazoles are tautomeric with the predominant linear 2-diazoalkyl from (equation 61)²⁸³.



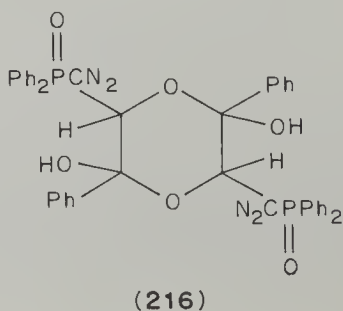
The addition of diazoalkanes R^1_2CN_2 ($\text{R}^1 = \text{H}$ or Ph) to olefinic phosphine oxides takes place under very mild conditions, and indeed needs to so as to prevent loss of nitrogen^{51,284} and allow the isolation of the pyrazolines (**211**) which readily isomerize, the tautomerism being faster in MeCN than in benzene²⁸⁵. At higher temperatures loss of nitrogen occurs during the initial reaction with the formation of phosphinoylcyclopropanes, a process for which a carbene mechanism has been excluded.

Reactions of a similar nature involving 1-alkynylphosphine oxides yield products which aromatize by prototropy when the diazoalkane is of the type RCHN_2 ²⁸⁶. The reactions between 1-(diphenylphosphinoyl)cyclopropenes (**213**) and diazoalkanes are generally regiospecific, and give the adducts **214** except when $\text{R}^1 = \text{Ph}$ and $\text{R}^2 = \text{H}$. The adducts **214** ($\text{R}^2 = \text{H}$) may be converted readily into the phosphinoylated 1,2-pyridazines **215**²⁸⁷.



That the phosphinoyl group has an activating effect on the cycloadditions to the vinyl group does not appear to be in doubt; thus, for example, diphenyldiazomethane does not react with allyldiethylphosphine oxide at lower temperatures, and at temperatures higher than 120°C yields only very small amounts of (cyclopropylmethyl)diethylphosphine oxide, probably through a carbene mechanism²⁸⁵.

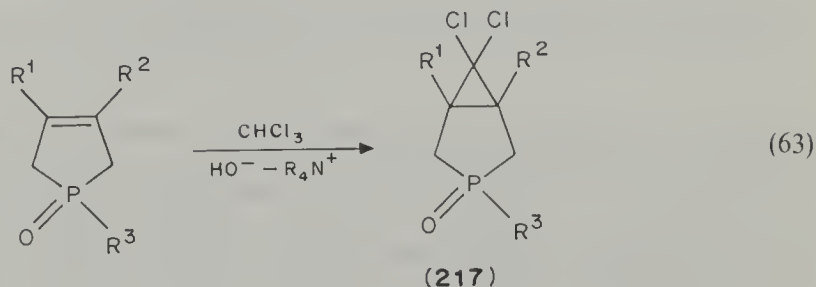
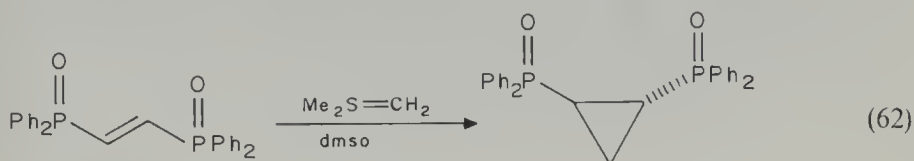
α -Diazo(diphenylphosphinoyl)alkanes undergo cycloadditions to α,β -unsaturated ketones²⁸⁸ and with acetylenes²⁸⁹. Reactions between α -diazobenzyl(diphenyl)phosphine oxide and aldehydes lead to (2-hydroxy-1-diazoalkyl)diphenylphosphine oxides (by aldol addition); in the case of glyoxal, the initial product dimerizes to give the 1,4-dioxan derivatives **216**²⁹⁰.



4. Reactions involving ylides or carbenes

Under thermal or photolytic conditions, (α -dialkoalkyl)diphenylphosphine oxides and sulphides are reactive and yield products suggestive of the formation of carbene intermediates; they are also subject to attack by nucleophiles, e.g. during their treatment with hydrogen halides with the formation of (α -halogenobenzyl)diphenylphosphine oxides, and also during hydrolysis. Similarly, when (α -diazobenzyl)diphenylphosphine oxide is heated in ethanol, (α -ethoxybenzyl)diphenylphosphine oxide and (benzhydryl)-phenylphosphinic acid result²⁹¹.

Representative examples of the additions of ylides or carbenes to unsaturated phosphine oxides are given in equations 62⁴⁸ and 63²⁹². The adducts **217** can be made to undergo rearrangement to 4-chloro-1,2-dihydrophosphorins through the action of heat, water or alcoholic AgNO_3 ²⁹³.



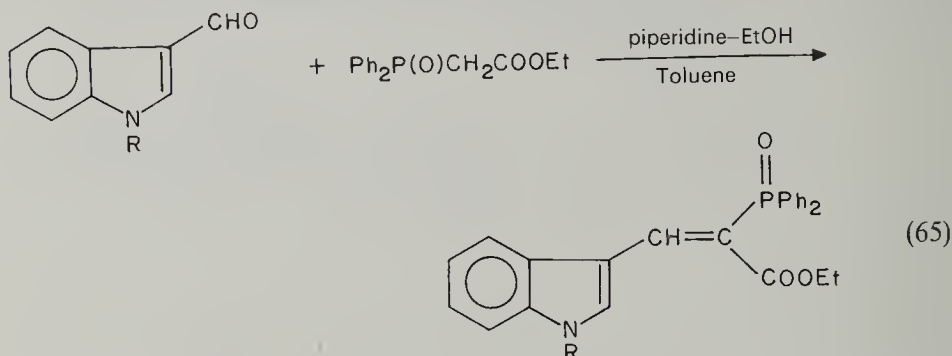
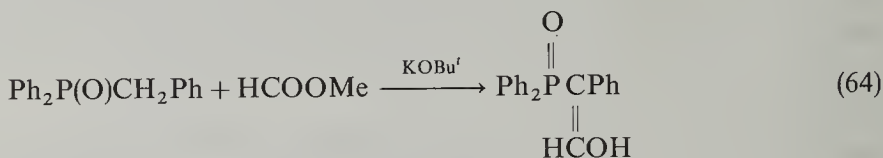
IV. PHOSPHINOYL CARBANIONS

A. Formation

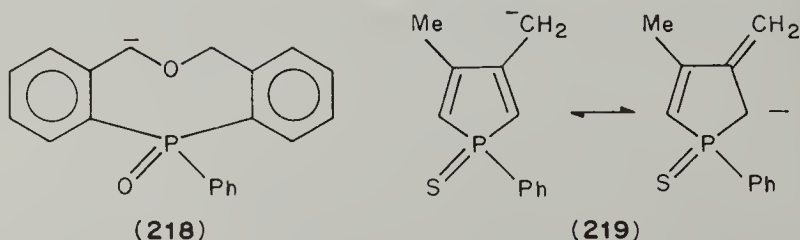
Data on the acidities of phosphine oxides, including (dialkylphosphino)alkane-carboxylates and (diarylphosphino)alkanecarboxylates^{214,215} and phosphinoyl-substituted benzoic acids²¹⁶ as well as other phosphinoylmethylene compounds^{213,294} demonstrate that the groups R_2PO and Ar_2PO are electronegative, with little difference between the electron attracting power of these and the corresponding phosphinothioyl groups. Their place in the general order of electron attracting power is $\text{Ph}_3\text{P}^+ > \text{PhCO} > \text{MeCO} > \text{CN} > \text{COOR} > \text{R}_2\text{P}(\text{S}) \approx \text{R}_2\text{P}(\text{O}) > \text{Ph}_2\text{P} > \text{Ph} > \text{H} > \text{Me}$.

Carbon—hydrogen bonds are thus activated towards proton removal by a suitable base. Bis(diphenylphosphino)l methane undergoes rapid exchange with deuterium but requires the presence of a weak base, and hence the use of a substance such as PhND_2 is satisfactory for the purpose. The introduction of a *p*-diphenylphosphino group into toluene raises the acidity in dmsO by ca 14 orders of magnitude; in other solvents the electronic effects of the diphenylphosphino group are similar to those displayed by a *p*-CN group. In the presence of KOBu^t , 4-diphenylphosphino toluene condenses with aromatic aldehydes (compare *p*-nitrotoluene) to give 4-diphenylphosphino-4'-substituted stilbenes²⁹⁵.

Activation of methylene groups has also been demonstrated by several condensation reactions such as those illustrated by equations 64²⁸⁸ and 65²⁹⁶. α -Phosphinoyl carbanions can be generated when phosphinoylalkanes or their derivatives are treated with an appropriate base; the more activated the methylene protons by the presence of

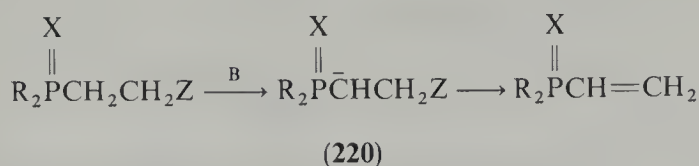


more than one phosphinoyl group attached to a common CH group, or alternatively aided by the presence of one of the common electron-attracting groups such as Ph, COOR, COR, CN or SO₂, the weaker the base needed, and a wide range of bases has been employed. For phosphine oxides, PhLi, NaNH₂, KOBu^t, PhNa, NaH (this has also been used to generate dianions from 2-oxoalkylphosphine oxides²⁹⁷), lithium diisopropylamide^{47,55,298} and, most commonly, BuLi, have all been used in combination with Et₂O or, better, thf. The same reagents are often satisfactory with mono- or di-methylphosphine oxides²⁹⁹ and even Et₃PO. The carbanion **218** has been generated by the use of NaN(SiMe₃)₂ or NaNHCH₂Ph⁶⁵. Bu^tLi was used to generate the mesomeric anion from [Me₂P(S)]₃CH³⁰⁰ and also the mesomerically stabilized anion **219**³⁰¹, although BuLi itself was sufficient for some mono- and di-methyl arylphosphine sulphides^{95,212}.



Two difficulties may arise during the generation of the carbanion. The first relates to the site of carbanion generation. Thus, with BuLi, EtMePhPO loses a proton from the Me group, whereas Me(Me₂NCH₂CH₂)PhPO loses a proton from the α -carbon of the substituted ethyl group³⁰². The second point arises from the stability of the generated carbanion; that of **220** depends on the leaving ability of the group Z, and fragmentation

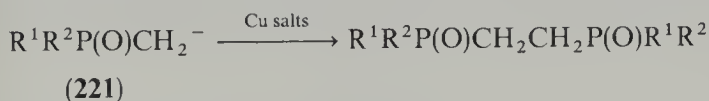
of the carbanion into the vinylphosphine oxide will be enhanced by a group Z easily stabilized as an anion.



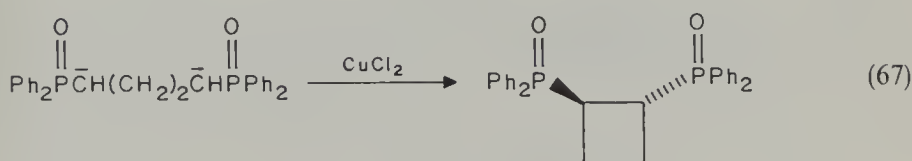
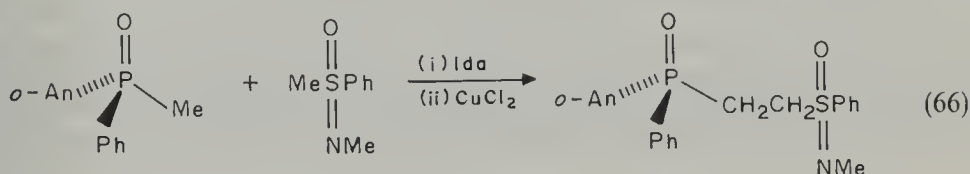
B. Reactions

1. Coupling

In the presence of CuCl_2 , phosphinoyl carbanions **221** couple ('dimerize') to give ethanebis(phosphine oxides)³⁰³. A mixture of diastereoisomers may result from appropriate starting materials; (*R*)-EtMePhPO affords a mixture of 3% *meso*-EtPhP(O)-CH₂CH₂P(O)PhEt together with 34% of the same dioxide in its (*S,S*)-form.



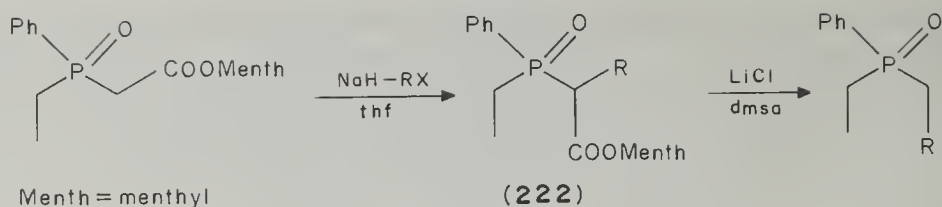
Interaction with other anions can take place (equation 66)⁵⁵ and an interesting application is the intramolecular coupling with the formation of cycloalkanebis(diphenylphosphine) dioxides as illustrated by equation 67⁴⁹.



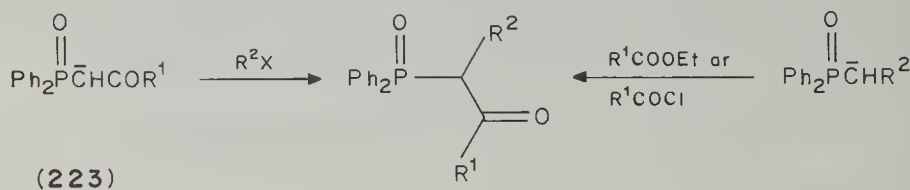
2. Alkylation

Alkylation of a phosphinoyl carbanion has been widely employed to build up more highly substituted alkyl groups attached to a diphenylphosphinoyl moiety, but such an apparently simple reaction may not always be so convenient from the practical standpoint. Thus, bis(diphenylphosphinoyl)methane, as its sodium salt, does not alkylate straightforwardly and, when acted upon by hexyl bromide in dmso, the salt affords a mixture of cleavage products, namely methyl diphenylphosphine oxide and hexyl diphenylphosphinate³⁰⁴. On the other hand, the corresponding potassium salt alkylates in the expected fashion.

L-Menthyl (*S*)_P-(ethylphenylphosphinoyl)acetate, when alkylated, gives the (*R*)_P product (**222**), from which the ester group is easily removable²⁴¹.



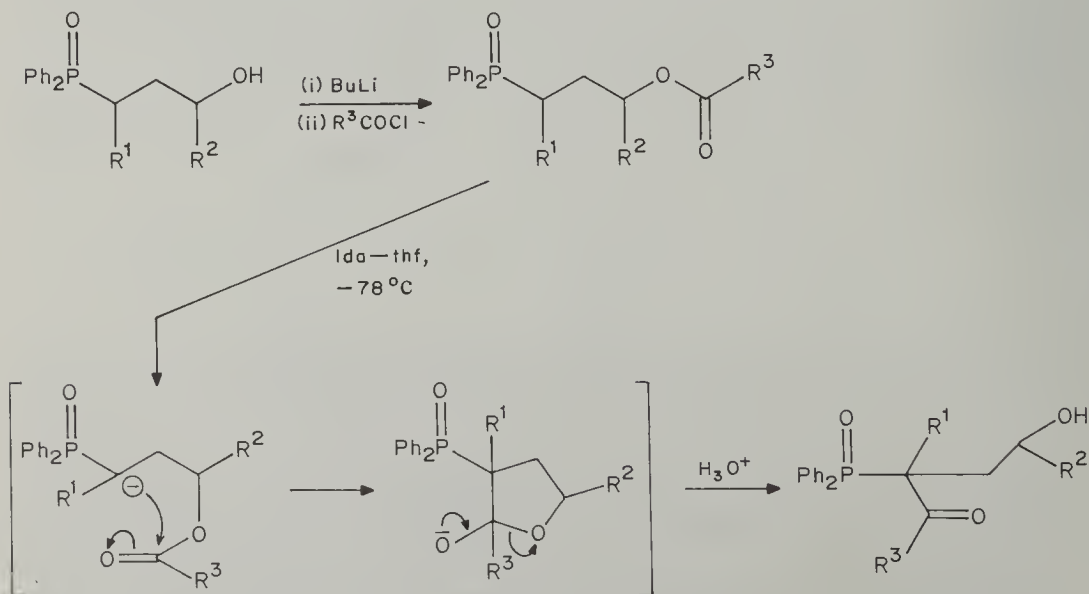
The carbanions from (2-oxoalkyl)phosphine oxides **223** ($R = \text{Me}$ or Ph) are readily alkylated by methyl, benzyl or prenyl halides, as well as by α -halogenocarbonyl compounds, but even a simple alkyl halide such as BuBr may fail to react, so that alkylation of an acylmethylphosphine oxide may only sometimes be an alternative to the acylation (see next section) of an alkylphosphine oxide (Scheme 55)²⁹⁷.



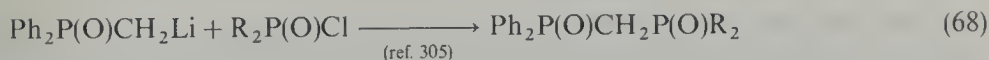
SCHEME 55

3. Acylation

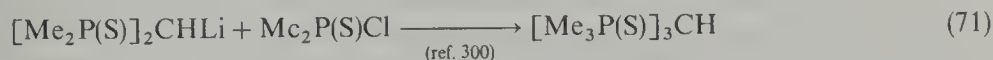
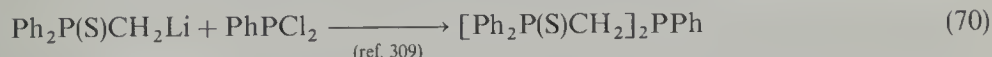
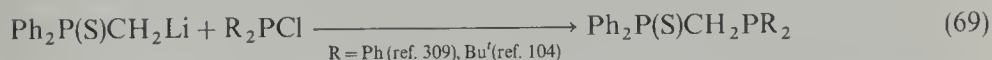
Acylation of phosphinoyl carbanions has normally been carried out using carboxylic esters (Scheme 55)^{292,305,306}, but lactones^{297,307} and carboxylic acid chlorides^{305,306} have also been employed. Acylation at the α -carbon atom can also be achieved through acyl transfer in an intramolecular process (Scheme 56), resulting from the influence of *Ida* at low temperature³⁰⁸. Other carbanions have been phosphorylated with a variety of halides of acids of either trivalent or quinquevalent phosphorus (reactions 68–71).



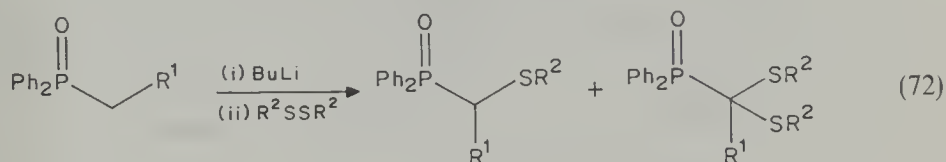
SCHEME 56



R = hex, oct, Ph

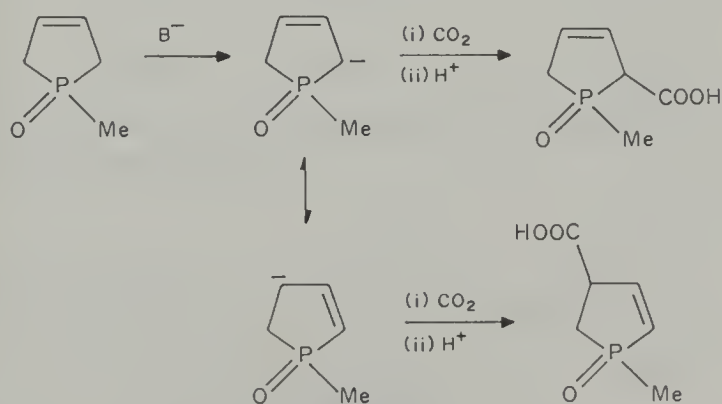


A widely exploited example of acylation is that of sulphenylation since this, through the Horner reaction (Section V), provides a route to vinyl sulphides and thence, through their hydrolysis, to ketones. Sulphenylation is achieved through reaction of the phosphinoylcarbanion with a disulphide (equation 72)^{306,310,311}; monosulphenylation may, under certain circumstances, be accompanied by disulphenylation. Oxidation of phosphinoylalkylsulphides with mCPBA yields the corresponding sulphinyl or sulphonyl derivatives³¹¹.

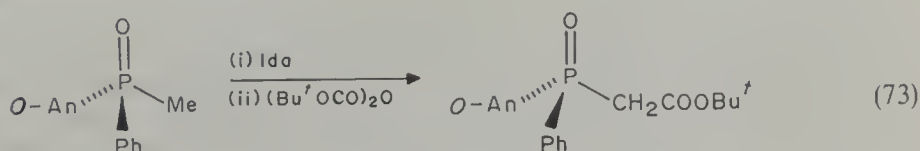


4. Carboxylation and decarboxylation

The treatment of the phosphinoyl or phosphinothioyl carbanions with an excess of CO_2 yields a carboxylic acid³⁰⁵. Those carbanions which are capable of resonance may yield mixtures of carboxylic acids (Scheme 57)⁶².



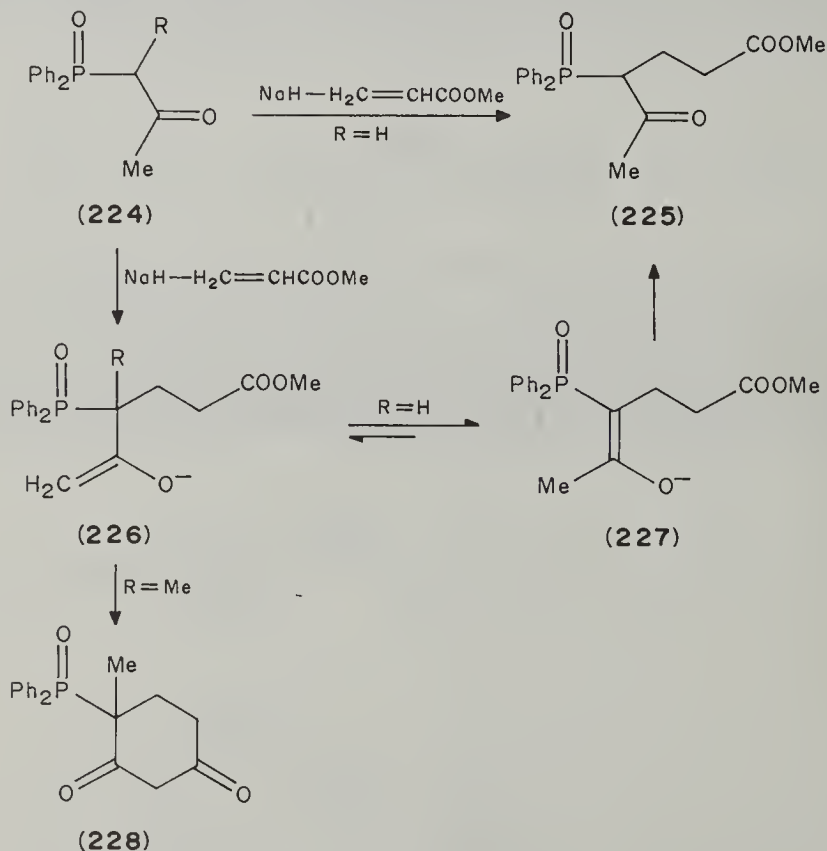
SCHEME 57



Reaction 73 illustrates a useful direct synthesis of the *tert*-butyl ester of a carboxylic acid; as in more conventional organic reactions, the *tert*-butyl group is a useful protecting group removable, after any further reaction at the active methylene group, with *p*-tosOH in xylene (see the next section)⁵⁵. The decarboxylation of (di)carboxylic acids follows the patterns observed for active methylene dicarboxylic acids and related compounds, e.g. $R_2P(O)CH(COOH)CH_2COOH$ is decarboxylated to $R_2P(O)CH_2CH_2COOH$.

5. Addition reactions

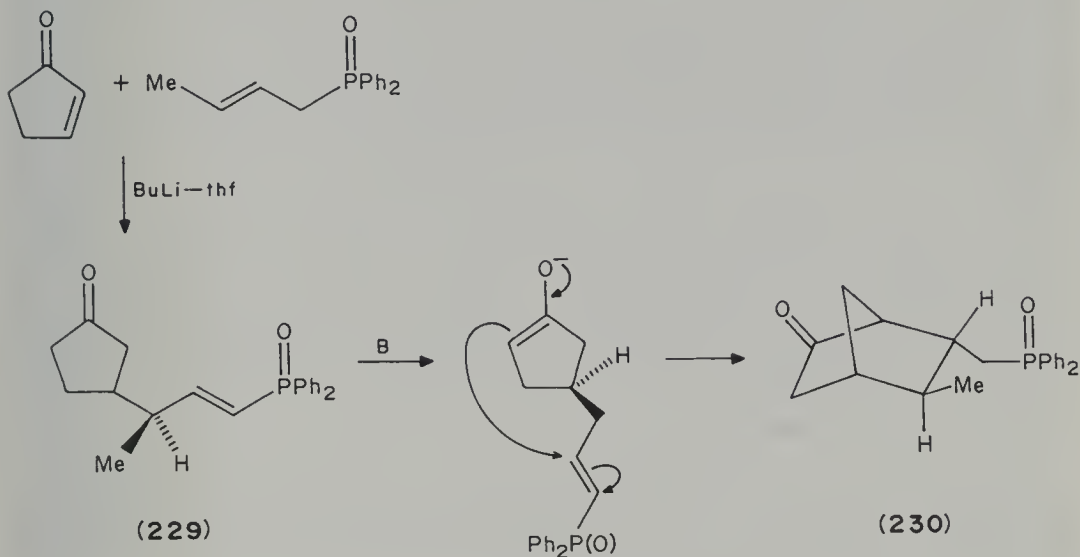
Torr and Warren²⁹⁷ have reported Michael additions of phosphinoyl carbanions to acrylic esters (Scheme 58). A base-catalysed reaction between the latter and the ketone **224** ($R = H$) gave the expected adduct **225**, whereas the product from the ketone **224** ($R = Me$) was the cyclohexadione **228**. The reason for this difference in behaviour resides in the anions **226** ($R = H$ or Me); when $R = H$, conversion to **227** occurs and hence formation of **225** is facile, but when $R = Me$ an equilibration occurs, resulting in cyclization to **228**²⁹⁷.



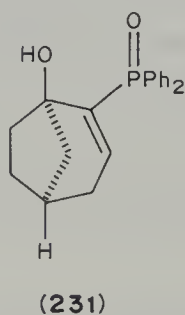
SCHEME 58

Haynes and coworkers^{312,313} exploited the already recorded Michael addition of the carbanions from (*E*)- and (*Z*)-but-2-enyldiphenylphosphine oxides to cyclopent-2-enone to yield the diastereoisomers of the vinyldiphenylphosphine oxide **229** in a route to diphenylphosphine oxides possessing the bicyclo[2.2.1]heptanone and bicyclo[3.2.1]octanol moieties through the intramolecular conjugate addition depicted in Scheme 59^{312,313}. Treatment of the oxide **229** with $KOBu^t$ in thf at room temperature gave **230** in 90% yield as a single diastereoisomer; similarly, the product from (*Z*)-but-2-

enyldiphenylphosphine oxide gave the diastereoisomer of **230** with *endo*-Me and *exo*-CH₂P(O)Ph₂ groups. Compound **231** was the product which resulted from the treatment of **229** with 2.5 equiv. of *l*da in thf at -78°C in a reaction which evidently involved the deprotonation of a vinylic phosphine oxide.

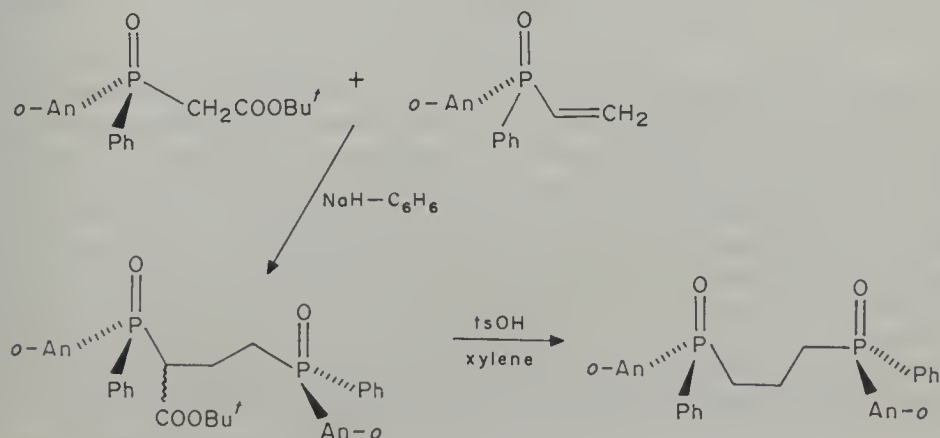


SCHEME 59



(231)

Scheme 60 exemplifies the potential of Michael addition reactions in the synthesis of precursors to valuable chiral ligands⁵⁵.



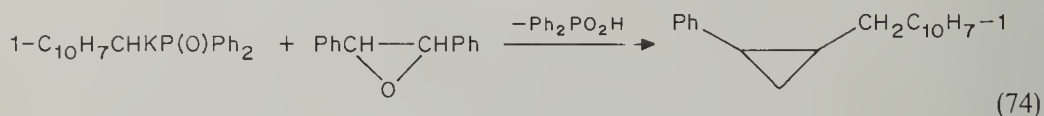
SCHEME 60

6. *Reactions with aldehydes, ketones and epoxides*

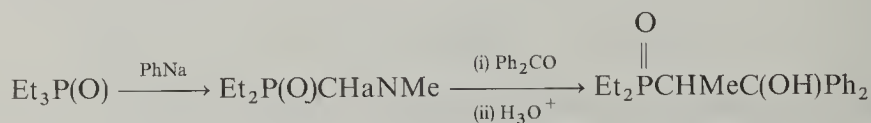
The original reports on the interaction of phosphinoyl carbanions with aldehydes or ketones were those given by Horner³¹⁴. Benzylidiphenylphosphine oxide, treated initially with NaNH_2 in benzene, reacted with benzophenone to give diphenylphosphinic acid and triphenylethene; a similar reaction took place between the potassium salt of the same phosphine oxide and benzaldehyde to give stilbene. The latter was also obtainable by oxygenation of the same potassium salt followed by acid hydrolysis, and by the decomposition of (α -hydroxybenzyl)diphenylphosphine oxide (obtainable from the lithium salt of benzylidiphenylphosphine oxide by oxygenation and acid hydrolysis) using KOBu^t .

In competition experiments involving benzylidiphenylphosphine oxide and benzyltriphenylphosphonium bromide (the latter acting as a source of the ylide $\text{Ph}_3\text{P}=\text{CHPh}$) in the presence of a base, phosphinoyl-activated olefination of benzaldehyde or benzophenone occurred preferentially. When both phosphorus-containing functions were present in the same substrate, loss of Ph_2PO (as diphenylphosphinic acid) always occurred in preference to loss of Ph_2PS or of Ph_2P . Unusually, α,α -bis(diphenylphosphinoyl)-toluene anion reacts with PhCHO , but affords $\text{Ph}_2\text{P}(\text{O})\text{CHPhCHPhP}(\text{O})\text{Ph}_2$ rather than a phosphinoylstilbene³¹⁵.

Coupled with the foregoing observations are those relating to the formation of cyclopropane derivatives from alkali metal salts of activated phosphine oxides through their reactions with epoxides, and again associated with the expulsion of phosphorus as diphenylphosphinic acid (e.g. reaction 74); such a reaction was thought to proceed through a β -hydroxyalkylphosphine oxide.



Other workers have observed that the use of phosphine oxides with less acidic α -hydrogen atoms coupled with the use of stronger bases allowed the actual isolation of β -hydroxyalkylphosphine oxides (Scheme 61).



SCHEME 61

The sequence phosphine oxide \rightarrow phosphine oxide carbanion \rightarrow phosphinic acid plus alkene bears a formal resemblance to the base-initiated reaction phosphonium salt \rightarrow ylide \rightarrow phosphine oxide plus alkene upon, in each case, the addition of an aldehyde or ketone at an intermediate stage. The second of these sequences is based on the work of Staudinger from the 1920s, but developed later by Wittig, under whose name it is now known; it was followed by still further developments using base-activated esters of phosphonic acids. Although in some ways not developed to the same extent as the original Wittig reaction or its later modifications for the convenient synthesis of alkenes, nevertheless, the reaction between phosphine oxide carbanions and aldehydes or ketones ('phosphine oxide olefination') offers considerable potential for future development. Because of both its present importance and the future potential in organic synthetic application, the reaction is considered in greater detail in a separate section.

V. REACTIONS BETWEEN PHOSPHINOYL CARBANIONS AND ALDEHYDES OR KETONES: THE HORNER REACTION

For the sake of clarity, the formation of alkenes through the interaction of aldehydes or ketones with carbanions from phosphine oxides is, in this chapter, referred to as the Horner reaction³¹⁶. In this way, it is clearly distinguishable from the parent Wittig reaction which employs phosphonium ylides, generally of the type $\text{Ph}_3\text{P}=\text{CR}^1\text{R}^2$, as the phosphorus-containing reactant, the Wadsworth–Emmons modifications, which uses phosphonic acid esters, $(\text{RO})_2\text{P}(\text{O})\text{CHR}^1\text{R}^2$, for the same purpose, and the Corey modification, which employs phosphonic acid bisamides, e.g. $(\text{Me}_2\text{N})_2\text{P}(\text{O})\text{CHR}^1\text{R}^2$ (ref. 316). In principle, all three of these series of compounds would interact with the carbonyl compound R^3COR^4 after suitable treatment with a base to yield the olefin $\text{R}^1\text{R}^2\text{C}=\text{CR}^3\text{R}^4$.

The Horner reaction uses phosphorus reactants of the general type $\text{R}_2\text{P}(\text{O})\text{CHR}^1\text{R}^2$, where, for convenience, R is nearly always Ph, and differs from the three other named reactions in allowing the use of reagents which afford, by the action of the base, a carbanion which need not necessarily be stabilized by the presence of a second electro-negative group on $\text{C}_{(1)}$. All four reactions have undoubted advantages over many more conventional alkene syntheses in being highly regiospecific.

Essentially, the Horner reaction consists in the generation of a phosphinoyl carbanion (Section IV.A) in a solvent and generally at low temperature (0 to -78°C) followed by the addition of the carbonyl reactant, again at fairly low temperature, although this might be allowed to rise during the course of the reaction. A metal salt (Li, Na or K) of the adduct is generated, and this may be allowed to decompose directly at a higher temperature; alternatively, an appropriate aqueous work-up often allows the isolation of a (β -hydroxyalkyl)phosphine oxide. The latter can then be made to decompose into the required alkene(s) by treatment with a strong base in a hot solvent; NaH in dmf or thf or KOBU^t in dmsO have been used extensively. The trimethylsilyl ethers of (β -hydroxyalkyl)diphenylphosphine oxides also decompose in the presence of sodamide-type bases to give alkenes²⁹⁹.

A. The Reactants

The general availability of the carbonyl reactants need not be discussed here, and it is sufficient to say at this stage that, generally, aldehydes tend to undergo the Horner reaction more readily than ketones, but this is a very broad generalization which may not necessarily hold in specific cases: thus, $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{OMe}$ reacts equally easily with aldehydes or ketones, whereas $\text{Ph}_2\text{P}(\text{O})\text{CHMe}(\text{OMe})$ is unreactive towards ketones³¹⁷. Enolizable ketones tend to afford poor yields of alkenes.

The phosphine oxide reactants are readily available by synthesis through the use of one of several fairly conventional reactions which include (i) application of the Arbuzov reaction between the ester Ph_2POR and an alkyl halide of a more reactive type, (ii) the alkylation of the anion Ph_2PO^- (generated from $\text{Ph}_2\text{P}(\text{O})\text{H}$ by the action of an alkali metal or organic base), (iii) the alkylation (Section IV.B.2) or acylation (Section IV.B.3) of the carbanions from simpler phosphine oxides, (iv) the alkaline hydrolysis of alkyltriphenylphosphonium salts, $\text{Ph}_3\text{PR}^+\text{X}^-$, and (v) the cleavage of Ph_3PO with alkylolithium reagents, e.g. RCH_2Li , when the products are PhH and $\text{Ph}_2\text{P}(\text{O})\text{CHLiR}$.

When the isolation of the intermediate (β -hydroxyalkyl)phosphine oxide is considered desirable, they can also be synthesized by other routes, more details of which will also be considered in a later section.

STATISTICAL DATA

B. Advantages of the Horner Reaction

The various modifications to the original Wittig reaction each have advantages over the latter and also over more conventional approaches to the synthesis of a particular alkene.

Unlike those reagents used in the Wadsworth–Emmons modification, Horner reagents are generally crystalline compounds and are relatively easily purifiable. Also of distinct practical significance is the relative ease of separation of the Horner reaction products—typically a liquid or solid water-insoluble alkene and the water-soluble metal diphenylphosphinate; in this respect, the Wadsworth–Emmons reaction is similar in that it generates a water-soluble salt of a phosphoric acid. The Wittig reaction can easily generate mixtures of products that are completely water insoluble.

The phosphinoyl carbanions in Horner reactions are capable of extensive modification through alkylation or acylation; they are considered to be non-nucleophilic, although allylic phosphine oxide carbanions have been reported to dealkylate phosphoryl chlorides³¹⁸. Such modifications may be further expanded through appropriate migration sequences involving Me, MeS, PhS or MeO groups, or even of the phosphinoyl group itself. The order of sequential modifications can be utilized to achieve desirable and specific results.

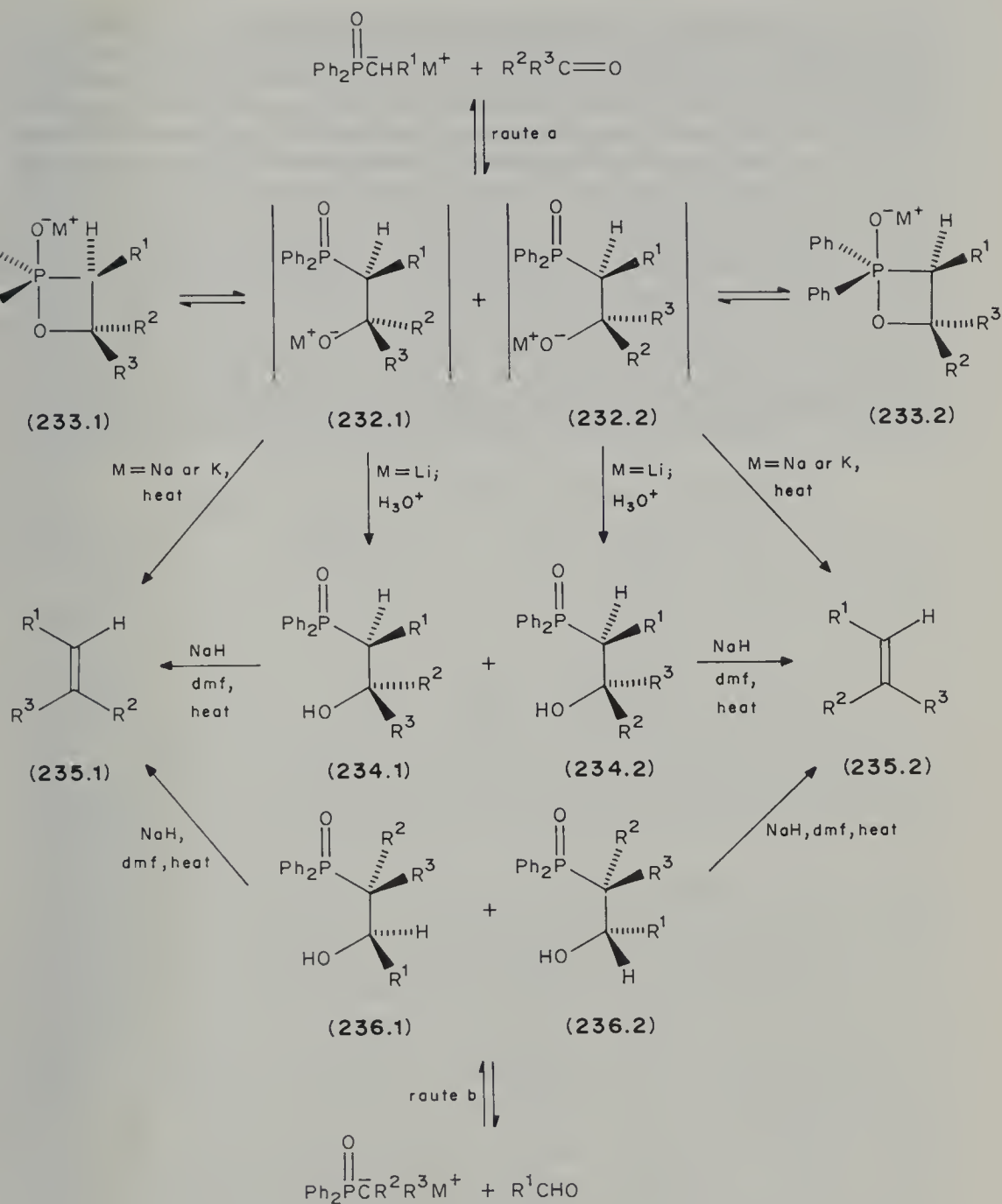
The very high regiospecificity of the Horner reaction, and of other Wittig modifications, and the consequent advantage over ‘non-phosphorus’ methodology, has already been commented upon. In many cases the Horner reaction also has advantages over the other Wittig modifications with regard to stereospecificity within a particular reaction. For example, the use of $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CN}$ rather than $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CN}$ in reactions with ArCHO or Pr^iCHO not only achieves higher yields of alkene, but also a much higher degree of stereoselectivity. In the reaction between $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{SMe}$ and PhCHO , the alkene *E/Z* ratio for the product is 20:1, whereas the use of the Wadsworth–Emmons reagent, $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{SMe}$, is stereochemically non-selective.

C. Mechanism, Stereochemistry and Regiochemistry

Scheme 62 outlines our present knowledge of the mechanism of the Horner reaction and its associated methodology, assembled, to some extent, through analogy with the original Wittig reaction and the Wadsworth–Emmons modification, but with additional evidence. The upper part of the Scheme (route a) indicates the mode of interaction of a phosphinoyl carbanion with a ketone to give, initially, a pair of diastereoisomeric salts (**232**); these may indeed exist in the acyclic form or they may exist as, or be in equilibrium with, pentacoordinate dioxaphosphorane species possessing oxaphosphetane rings (**233**); the latter feature would restrict the possibilities in isomerization.

The fate of either of the species **232** or **233** depends to a large extent on the metal counter ion. With care, appropriate work-up of the lithium salts can provide the free alcohols (**234**)^{192,193,211}, but the corresponding Na or K salts suffer ready *syn* elimination to give the product alkenes (**235**). Separation of the stereoisomeric alcohols **234** is often feasible, but the individual isomers can be recognized in mixtures by the application of ¹H NMR spectroscopy; individual diastereoisomers have also been structurally characterized using X-ray diffraction techniques, and they include *erythro*-(1*RS*,2*RS*)-2-diphenylphosphinoyl-1-phenylpropan-1-ol³¹⁹ and (2*RS*,3*RS*,4*RS*)-4-benzamido-3-diphenylphosphinoylpentan-2-ol²⁴⁸.

The lower part of Scheme 62 (route b) indicates how the same products (**235**) might be obtained using an aldehyde together with a branched-chain phosphine oxide through alcohols (**236**) isomeric with **234**. In the event of R^2 being hydrogen (route a), i.e. the carbonyl reactant being an aldehyde, then structures **234.1** and **234.2** are those of the



erythro and *threo* forms of the alcohol, and decomposition of the *erythro* alcohol or its salt would thus be expected to yield the (*Z*)-alkene with the (*E*)-alkene being obtainable from the *threo*-alcohol or its salt.

The question of stereoselectivity arises at two points in Scheme 62, namely with regard to the formation of the diastereoisomeric alkoxides **232** (and thus of the alcohols **234**, and also with the decomposition of these into the target alkenes.

In an extensive and systematic investigation into reactions summarized by equation 75, Buss and Warren³²⁰ showed that when R^2 was Ph or MeOC_6H_4 , a variation in R^1 maintained the *erythro:threo* ratio of alcohols at ca 6:1 unless there was branching at $C_{(1)}$, when the ratio could become 2:1. There was, however, a greater lack of diastereoselectivity when $R^2 = \text{Me}$. The stereoselectivity was sensitive to the size of R^2 when $R^1 = \text{Me}$ or an aromatic nucleus. No selectivity was observed when the size of the groups R^1 or R^2 , e.g. cyclohexyl, competed with that of the diphenylphosphinoyl group. No variation in the diastereoisomer ratio was observed when the position of the aromatic MeO substituent was changed³²⁰. For reaction 76³⁰⁶ a systematic decrease in the chain length of the group R from butyl to methyl caused an increase in the *erythro:threo* ratio from 1.7:1 to 3.2:1, but when R was branched at $C_{(1)}$, as in Pr^i or cyclohexyl, complete stereorandomness was observed. For $R = \text{Ph}$, the ratio was 3.8:1. Some additional data are given in Table 1. From the wealth of available data it would thus appear that reactions between unfunctionalized or simply functionalized phosphine oxide carbanions and aldehydes are either non-stereoselective or are biased towards the *erythro* product.

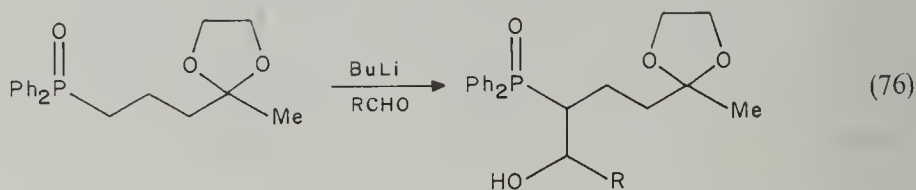
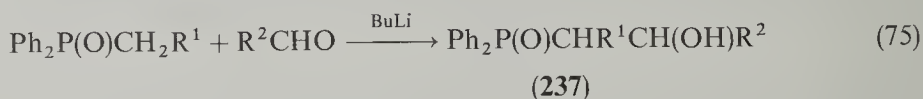

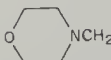
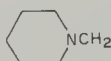
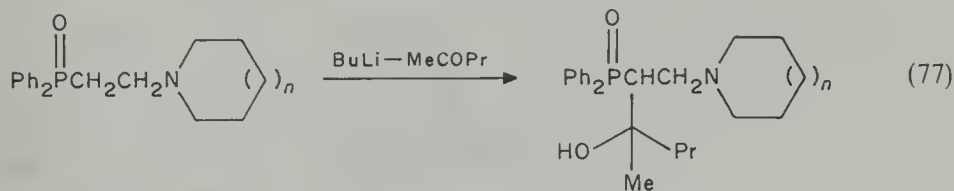


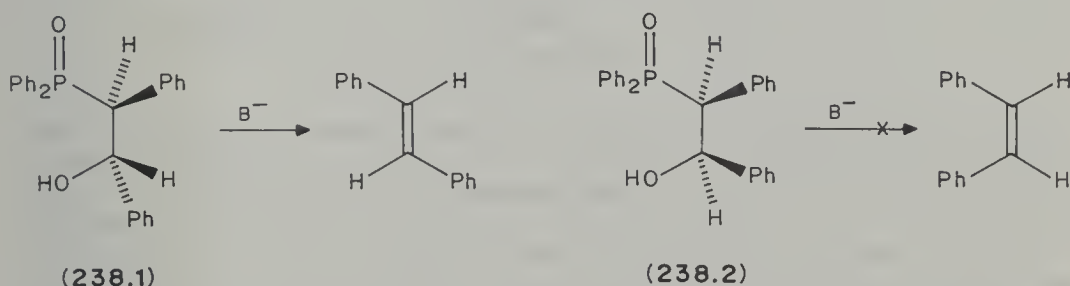
TABLE 1. Reaction 75: *erythro:threo* ratios for the products 237

$\text{Ph}_2\text{P(O)CH}_2\text{R}^1$ R^1	R^2CHO : R^2	<i>erythro:threo</i> ratio	Ref.
MeO	4-MeOC ₆ H ₄	45:55	317, 320
LiOCH ₂ CH ₂	Ph	75:25	321
Pr^iCH_2	Ph	80:20	320
	Me	51:49	248, 322
	Ph	52:48	322
	Me	50:50	248
	Ph	66:34	248
	Me	49:51	248
	Ph	48:52	248
PhCH_2CH_2	Me	58:42	320
$\text{Bu}^i\text{Me}_2\text{Si}(\text{CH}_2)_5$	Et	64:36	321

On the other hand, reactions involving ketones may be much more stereoselective and biased towards the *threo* product, as for reaction 77, when the *erythro:threo* product ratios are 28:72 and 20:80 for $n=0$ and 1, respectively²⁴⁸. The simple theoretical prediction that *erythro* intermediates lead to (*Z*)-alkenes and that *threo* intermediates afford (*E*)-alkenes is not always borne out in practice, and the question of reversibility of one or more of the steps in Scheme 62 must therefore be considered.



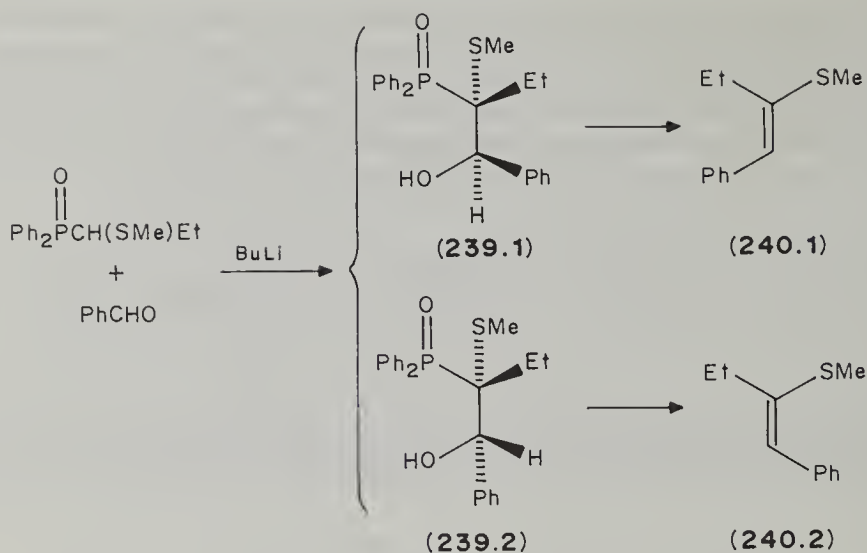
A simple case illustrates the nature of the problem. When treated with base, *threo*-1,2-diphenyl-2-(diphenylphosphinoyl)ethanol (**238.1**) yields only (*E*)-stilbene, the predicted



outcome. Under the same conditions, the *erythro* alcohol ought to give (*Z*)-stilbene but, although some of this is formed, the main products are (*E*)-stilbene and benzyldiphenylphosphine oxide. Warren and coworkers³²³ were unable to corroborate Horner's original report on the formation of (*Z*)-stilbene.

Exploratory decompositions of the *erythro* alcohol were performed with a variety of bases including PhLi in diethyl ether, BuLi in diethyl ether or thf [which at 0 °C afforded the highest yields of (*Z*)-stilbene] or thf-TMEDA [this solvent system gave the highest observed yield of (*E*)-stilbene], NaH-dmsO [no formation of (*Z*)-stilbene], Bu₄N⁺OH⁻ (benzyldiphenylphosphine oxide not formed), DBU in thf [which gave the lowest yield of (*E*)-stilbene but, at 66 °C the highest yield of benzyldiphenylphosphine oxide] and DBU-CaH₂ or KOH in dmsO³²³. These results were attributed to the known decomposition of **238** into PhCHO and the observed benzyldiphenylphosphine oxide. In the presence of base, interchange of benzaldehyde with *p*-chlorobenzaldehyde from **238** was possible, but only for the *erythro* isomer. Further evidence for equilibration in Horner reactions comes from reactions such as that depicted in Scheme 63. The lithium salt of [1-(methylthio)propyl]diphenylphosphine oxide and benzaldehyde react at -78 °C to give a mixture of diastereoisomeric alcohols **239.1** and **239.2** in the ratio 4:1, a value correlating well with the ratio of alkenes **240.1** and **240.2** when these were obtained in a one-step process. However, whereas **239.2** afforded only (*Z*)-alkene when decomposed by NaH, the isolated **239.1** gave a mixture of (*E*)- and (*Z*)-alkenes in the ratio 10:1.

In general, *threo* adducts tend to give (*E*)-alkenes with total stereospecificity and in high yields. For the *erythro* adducts, pure (*Z*)-alkenes may be obtained when R¹ and R² (equation 75) are both alkyl; adducts from aromatic aldehydes also tend to afford largely the *Z* hydrocarbon together with less than 5% of the *E* isomer, but when R¹ is aryl, both poor stereoselectivity and low yields are observed^{320,321,324}.

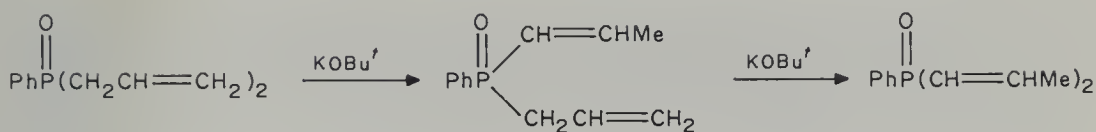


SCHEME 63

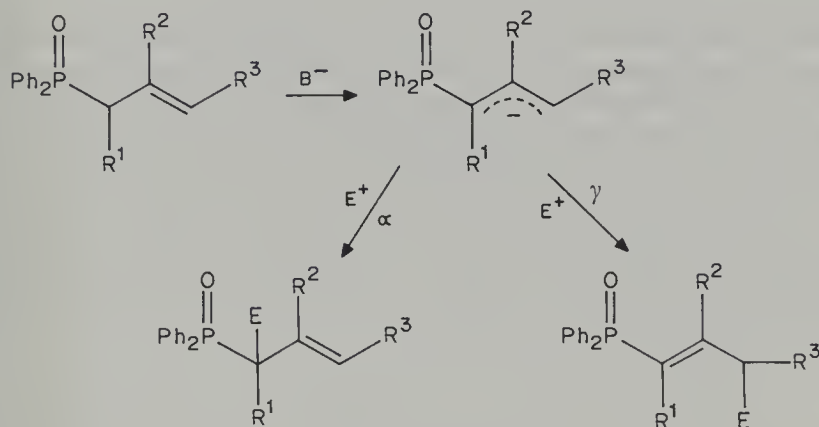
Route a (Scheme 62) has been employed to prepare alkenes with α -PhS or α -OMe substituents, β -Me₂N and γ -ketal substituents, all with poor stereoselectivity but which is generally in favour of the *threo* adducts. Treatment of the adducts **234** ($\text{R}^1 = \text{R}^3 = \text{Me}$, $\text{R}^2 = p\text{-Tol}$; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Et}$, $\text{R}^3 = \text{Me}$; $\text{R}^1 = \text{R}^3 = \text{Me}$, $\text{R}^2 = \text{PhCH}_2$) with NaH yields only traces of alkenes, the main products being the ketones $\text{R}^2\text{R}^3\text{CO}$. In addition, the adduct **234** ($\text{R}^1 = \text{PhCH}_2$; $\text{R}^2 = \text{Et}$; $\text{R}^3 = \text{Me}$) has been separated into its diastereoisomers but, when treated with NaH, each gives (E) -3,4-dimethyl-1-phenylpent-2-ene, presumably through reversion to the starting materials^{307,323}.

Route b (Scheme 62) has been employed for the synthesis of dienes, vinyl sulphides and unsaturated ketals with little stereoselectivity. For the particular case with $\text{R}^1 = \text{cyclopentyl}$, $\text{R}^2 = \text{Pr}^i$ and $\text{R}^3 = \text{Me}$, the bias towards the *threo* alcohol adduct is probably the result of equilibration.

Regiospecificity in the Horner reaction does not normally pose problems, but the problem does arise when the phosphine oxide is of the allylic type. Allylic phosphine oxides undergo prototropic rearrangement into 1-propenylphosphine oxides when acted on by strong bases (Scheme 64)^{247,325,326}. The reverse reaction (e.g. as in equation 78) has also been observed. Because of resonance, anions from allylic phosphine oxides can react with an electrophiles at either the α - or the γ -position (Scheme 65). Normally, reactions with electrophiles occur at the α -position³²⁷. Those between cyclohexanone and allylic phosphine oxide carbanions have demonstrated complete regiospecificity towards the α -position together with essentially complete retention of double bond stereochemistry (equation 79)³²⁸. However, there are many instances where the reaction takes place, at least partially, at the γ -position. Thus, the cyclohexenyl compound **241** reacts with PhCHO at the α -position whereas the analogous cyclopentenyl compound **242** reacts at the γ -position giving **243**. A lack of substituents at the γ -position renders the allylphosphine oxide particularly susceptible to attack at that position. Thus, reactions between **245** ($\text{R}^1 = \text{Me}$) and R^2CHO ($\text{R}^2 = \text{Me}$ or Ph) afford mixtures of α - and γ -adducts; when $\text{R}^1 = \text{Pr}^i$ virtually no γ -product is observed¹⁹². A series of (1-methoxyallyl)diphenylphosphine oxide carbanions (Scheme 65; $\text{R}^1 = \text{OMe}$) has been extensively investigated; here the carbon electrophiles PhCHO and MeCHO react at the γ -position to give the (E) -alkenes when R^2 and R^3 are either H or Me, or both are H, but when $\text{R}^1 = \text{H}$ and $\text{R}^2 = \text{Ph}$ the regiochemistry is a function of the electrophile, since MeCHO again reacts

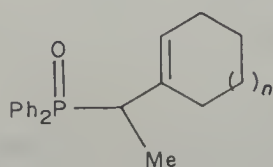
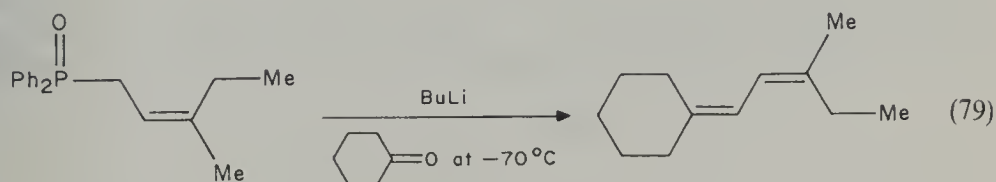
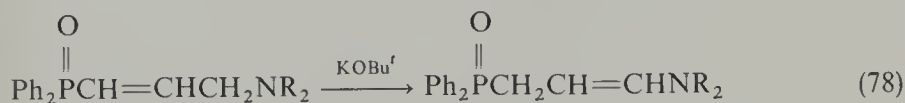
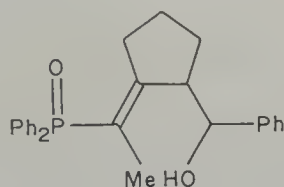


SCHEME 64



SCHEME 65

at the γ -position, but PhCHO gives a mixture of α -substituted stereoisomers^{311,329}. Other compounds which react as electrophiles at the γ -position include RSSO_2Me ($\text{R} = \text{Me}$ or Ph) and PhSSPh , as sulphenylating agents, and also Me_3SiCl and $\text{Ph}_2\text{P}(\text{O})\text{Cl}$ ³¹⁸.

(241) $n=1$; (242) $n=0$ 

(243)

Once again, substituents exert a pronounced effect on the course of the reactions; the carbanion from **251** ($R = \text{Me}$) is deuteriated or methylated at the α -carbon atom, but gives the γ -adduct with PhCHO , whereas the anion from **251** ($R = \text{Ph}$) fails to react with PhCHO , and gives mixtures of α - and γ -products when deuteriated or methylated³¹¹.

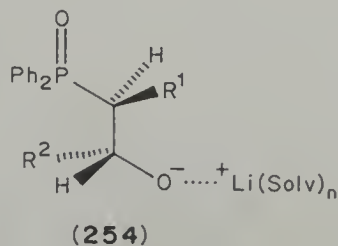
D. Control

Stereoselectivity in the Horner reaction depends on the rates of formation and decomposition (including, where appropriate, reversion to starting materials in equilibria) of alkoxides in Scheme 62. Attempts to control stereoselectivity, and so increase the potential synthetic value of the Horner reaction, have thus been partly concerned with those experimental factors which might govern the kinetics of such reactions.

One of the first systematic attempts to discern possible solvent effects on the course of the Horner reaction was a study³³⁰ of the reactions between benzyldiphenylphosphine oxide and PhCHO or EtCHO , and between diphenylpropylphosphine oxide and PhCHO in either dmf or cyclohexane; all these reactions, and also similar ones using diethyl benzylphosphonate, favour the formation of the (*E*)-alkene, by contrast to the use of Wittig reagents. Generally, the change from the polar to the non-polar solvent produced little change in the (*E*)-/(*Z*)-alkene ratio, but the more pronounced effects (but then only moderate) were found for the combinations $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{Ph}$ with EtCHO and $\text{Ph}_2\text{P}(\text{O})\text{Pr}$ with PhCHO , an increase in solvent polarity favouring the (*Z*)-alkene.

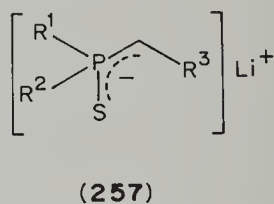
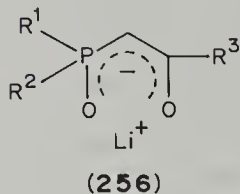
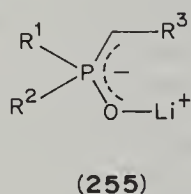
Poor stereoselectivity in the formation of the intermediate (β -hydroxyalkyl)phosphine oxide is often a result of the use of a non-polar solvent: thus, the reaction at -78°C between diphenylpropylphosphine oxide carbanion (Li^+ as counter ion) and PhCHO in hydrocarbon solvents is non-stereoselective. When Et_2O is used as the solvent, a 6:4 bias towards the *erythro* alcohol is observed, and an almost 6:1 bias towards the same diastereoisomer was found with the use of dme or thf ; the addition of tmeda still further increased the bias³²⁰.

It has been suggested that the nature and degree of solvation of the metal counter ion present in the alkoxide **232**, and its consequent size, are important factors in the control of the course of the Horner reaction³²⁰. Lithium is the counter ion commonly employed in the first stages of the Horner reaction; the use of thf saturated with LiBr or LiCl retards the final stages in the sequence (Scheme 62), and the use of lithium often allows the isolation of the intermediate β -alcohols^{194,320}. Even with the relatively small Li^+ ion (in contrast to Na^+ or K^+), conformational control within the complex **254** may well be governed by a tendency for the larger $\text{Ph}_2\text{P}(\text{O})$ and $\text{O}\cdots\text{Li}(\text{Solv})_n$ groups to position themselves antiperiplanar with respect to each other in the most highly populated conformer and hence govern the spatial relationship between R^1 and R^2 .

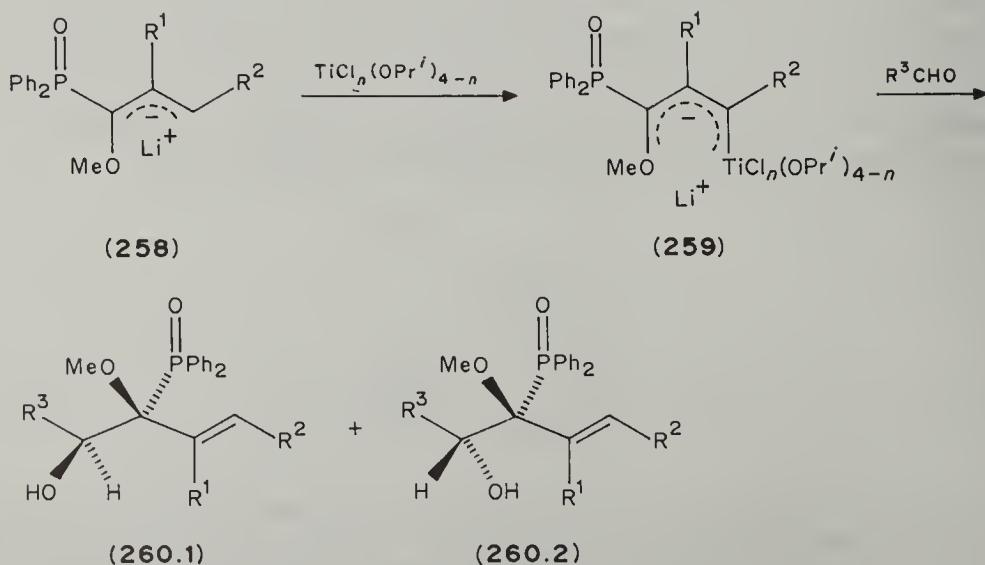


Irrespective of the degree of solvation, a further complicating feature is the nature of the bonding between metal and phosphine oxide ions. When basic groups other than the $\text{P}=\text{O}$ are absent from the phosphine oxide, bonding between Li^+ and phosphoryl oxygen possesses a high degree of covalence (as in **255**) and the cation may be

non-solvated, whereas in a more highly stabilized carbanion possessing a second electronegative group, the lithium cation might well be highly solvated, as in diglyme (structure **256**). In the case of phosphine sulphides, which lack both the more basic $\text{P}=\text{O}$ group and a second stabilizing group, the salt contains only contact ion pairs (**257**). Alkoxides containing other Group I metal counter ions decompose more readily, and in practice NaH is used widely to bring about the decomposition of isolated β -phosphinoylated alcohols to the alkenes. When the counter ion is K^+ or Cs^+ in dmso , there would appear to be no subdivision into the types **255**–**257**, regardless of the presence, or otherwise, of other groups present in the phosphine chalcogenide³³¹.



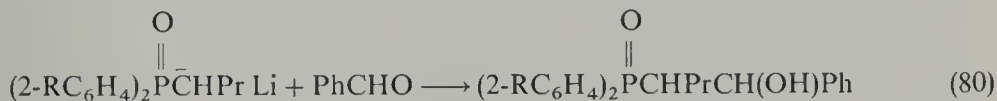
In reactions between the lithiated phosphine oxides **258** ($\text{R}^1, \text{R}^2 = \text{H}, \text{H}; \text{H}, \text{Me};$ or Me, H) and PhCHO ($\text{R}^3 = \text{Ph}$) (Scheme 67) only γ -products are obtained. A modification to the anion by its pretreatment with a titanium reagent $[\text{TiCl}_n(\text{OPr}^i)_{4-n}]$ resulted, in the case of **259** ($\text{R}^1 = \text{R}^2 = \text{H}; n = 0$) in mixed regiochemistry with a $\gamma:\alpha$ adduct ratio of 2:1 to 3:1, and with the (*S,R*)- and (*R,R*)- α -adducts **260.1** and **260.2** formed in the ratio 2.5:1. When $n = 1$ or 2, reaction occurs regiospecifically at the α -position, with the diastereoselectivity strongly biased towards the form **260.1**, although this is lower if R^3 is alkyl, and either or both R^1 and R^2 is (are) alkyl³³². Reactions of the anions of the phosphine oxides **251** in the presence of $[\text{Ti}(\text{OPr}^i)_4]$ are slow in comparison with those of the corresponding phosphines, although this effect can be overcome by incorporating hmpa into the solvent system, when the reaction becomes useful in the synthesis of alka-1,3-dienes³³³.



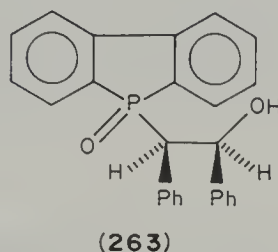
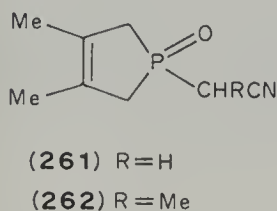
SCHEME 67

A lower reaction temperature not only disfavors the decomposition of an intermediate alkoxide to the alkene, thus making it easier to isolate the intermediate β -phosphinoyl alcohol, but it can also aid in controlling the diastereoisomeric composition thereof; for a reaction between $\text{Ph}_2\text{P}(\text{O})\text{Pr}$, BuLi and PhCHO , the *erythro:threo* ratios for the intermediate alcohol were 2:1, 6:1 and ca 11:1 at 10, -78 and -100°C respectively³²⁰.

Yet another factor capable of altering the rate of collapse of the intermediate alkoxide ions **232** with expulsion of diphenylphosphinic acid, and thus allowing for better equilibration between the individual diastereoisomeric ions and the starting materials, is the electronic charge distribution within the phosphoryl group. This effect has been explored, albeit to only a very limited extent, through reaction 80. As one ortho hydrogen is replaced successively with Me and MeO, the *erythro:threo* ratio, initially 74:26, is raised to 81:19, and then to 97:3³³⁴.

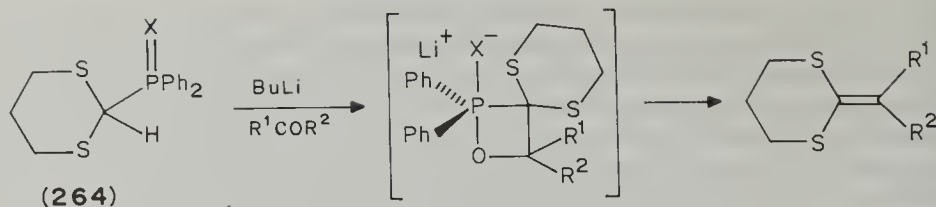


Phosphorus is also considered to be more electrophilic when present in a five-membered ring than in an analogous acyclic compound and hence, when in compounds such as **261** and **262**, should be capable of modifying the rate of collapse of the alkoxide ion resulting therefrom. The reaction between **261** (K^+ as counter ion) and PhCHO is stereoselective with a (*E*)-/(*Z*)-alkene product ratio of 80:20, but those reactions between **262** and either PhCHO or Pr^iCHO (and with Li^+ or K^+ as counter ions) are, unfortunately, completely non-stereoselective³³⁵.



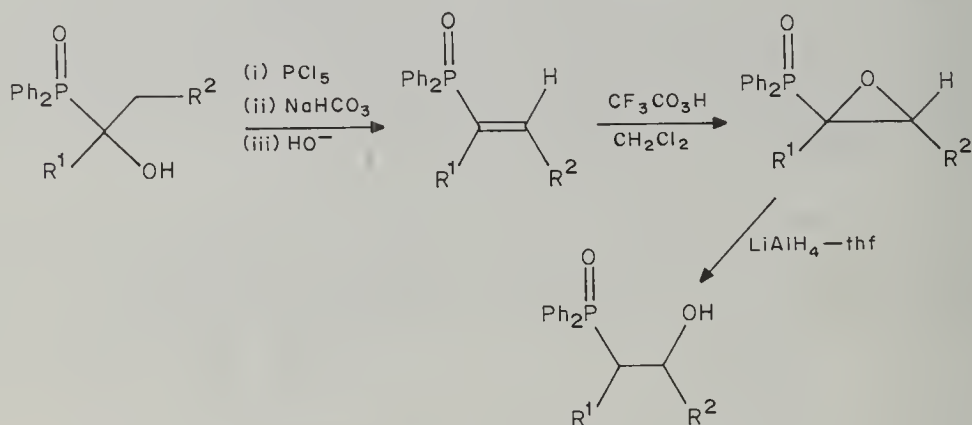
The failure of *erythro*-1,2-diphenyl-2-(diphenylphosphinoyl)ethanol to yield (*Z*)-stilbene on normal decomposition has been attributed to the combined influence of unfavourable Ph-Ph eclipsing interactions in a *syn*-elimination pathway from **238.2** and the relatively high acidity of benzyldiphenylphosphine oxide. Other *erythro* compounds afford (*Z*)-alkenes when acted on by base. When treated with NaH -dmsO under the same conditions as **238.2**, the *erythro* alcohol **263** gives a 91% yield of stilbene with a *Z/E* ratio of 89:11, modified only slightly by using DBU in dmsO at 60°C . Here the combined influence of using an organic base, rather than NaH , and a phosphole derivative completely reversed the normal stereoselectivity, a result considered as indirect evidence for the participation of an oxaphosph(V)etane intermediate³³⁶.

The role that diphenylphosphinothioyl derivatives take in the Horner reaction has been but little exploited. The diphenylphosphinothioyl-1,3-dithiane **264** ($\text{X}=\text{S}$) is unreactive to MeCHO , Ph_2CO and cyclohexanone, and is thus less reactive than the diphenylphosphinoyl analogue, a fact attributed to the relative stabilities of the penta-coordinate intermediates (Scheme 68) with their dependence on the relative apicophilicities when $\text{X}=\text{O}$ or S , rather than on an explanation based on steric crowding³³⁷.



SCHEME 68

In the second method of approach to the control of the stereochemical outcome of the Horner reaction, the importance of the intermediate (β -hydroxyalkyl)phosphine oxides is taken into consideration, and in particular their synthesis by other reactions. β -Phosphinoyl alcohols have been prepared by the regiospecific ring opening of epoxides with Ph_2PLi followed by treatment with acetic acid– H_2O_2 ^{189,338,340} or by treatment of the epoxide with $\text{Ph}_2\text{P}(\text{O})\text{K}$ ³⁴¹. In a second procedure, the readily obtainable (α -hydroxyalkyl)phosphine oxides are dehydrated, epoxidized and the β -alcohol obtained by ring opening with LiAlH_4 (Scheme 69)¹⁷³.



SCHEME 69

By far the most widely exploited synthesis of β -phosphinoyl alcohols by a different route consists in the reduction of (β -ketoalkyl)phosphine oxides. The latter can be obtained, in turn, by the oxidation of (β -hydroxyalkyl)phosphine oxides isolated from the Horner process, or by acylation of a phosphine oxide carbanion (Section IV.B.3). Other (β -ketoalkyl)phosphine oxides can be obtained by specific reactions, one example of which is illustrated in Scheme 70³²⁴.

The usefulness of the (β -ketoalkyl)phosphine oxides as precursors to the (β -hydroxyalkyl)phosphine oxides obviously depends on the stereospecificity with which they can be reduced. Unfortunately, high reaction stereospecificity tends to be associated with low reaction yields. Thus, in the reduction of $\text{Ph}_2\text{P}(\text{O})\text{CHMeCOPh}$, the use of H_2 – PtO_2 – MeOH or $\text{LiAlH}(\text{OBu}^t)_3$ – PhMe at 100°C gives only 40–50% yields of the alcohol but the *threo:erythro* ratio is 90–100:10–0. On the other hand, LiAlH_4 in thf at 0°C or B_2H_6 in thf at -78°C give 98% yields of the alcohol, with diastereoisomer ratios of ca 1:1 and 3:1, respectively. The reagent of choice for most reductions is NaBH_4 , which affords satisfactory yields and acceptable diastereoisomer ratios of ca 80–90:20–10³²⁰. Buss and Warren³²⁰ coworkers prefer to use the Felkin model³⁴² rather than Cram's rule to explain the stereoisomer ratios in borohydride reductions.

E. Applications

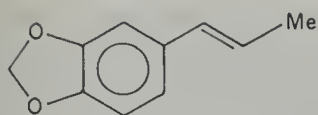
Table 2 lists many general types of compounds, other than simple alkenes, that have been synthesized using the Horner reaction, either directly, or indirectly through a single simple modification to the original Horner product. The list is not intended to be complete, but is intended to emphasize the broad scope of this versatile reaction.

The Wittig reaction between piperonal and an appropriate ethyltriphenylphosphonium salt provides a mixture of (*E*)-**266** and (*Z*)-isosafrole in 57% yield; the Horner reaction between ethyldiphenylphosphine oxide anion and piperonal gives a mixture (9:1) of *erythro* and *threo* β -alcohol adducts, the separated components of which provide *Z* and *E* isomers of isosafrole containing at most, only traces of the geometric isomers. A similar situation occurs in the synthesis of isomers of anethole (**267**)³⁰⁷. The same paper³⁰⁷ also reports the synthesis of (*E*)-feniculin (**268**), a constituent of fennel. (*Z*)- α -Bisabolene (**269**) has also been prepared, using the anion from $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CH}=\text{CMe}_2$, and also (*E*)-non-6-en-1-ol and (*E*)-dec-5-en-1-ol, insect pheromone constituents, from propyl- and pentyl-diphenylphosphine oxide anions, through acylation with lactones. Other applications in the natural product field include an approach to avermectin³⁷³ and a synthesis of the oudemansins A (**270**; $\text{R}^1 = \text{R}^2 = \text{H}$) and B (**270**; $\text{R}^1 = \text{OMe}$, $\text{R}^2 = \text{Cl}$)³⁷⁴.

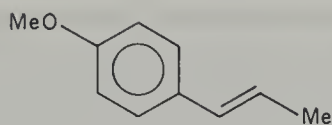
1,1-Difluoroalk-1-enes have been prepared from $\text{Ph}_2\text{P}(\text{O})\text{CHF}_2$ ³⁷⁵. A particularly interesting study concerns the syntheses of cyclic alkenes of medium ring size, prepared from phosphine oxides using the epoxide route. (*1R, 2R*)-2-Diphenylphosphinoylcyclooctanol (**271**) with NaH in dmf affords (*S*)-(+)-*trans*-cyclooctene (**272**), with the (*R*)-(–)-hydrocarbon being obtainable from the enantiomeric alcohol. (*S*)-(+)-*cis,trans*-Cycloocta-1,5-diene has the oxide **273** as its precursor³⁷⁶. (*1RS,4SR,5SR,8RS*)-5-Diphenylphosphinoylbicyclo[6.4.0]dodecan-4-ol (**274**) with KOBu^t in dmsO leads to the (*1RS,4RS,5RS,8RS*)-hydrocarbon **275**; the (*1RS,4RS,5RS,8RS*)-alcohol is converted into the (*1RS,4RS,5SR,8RS*)-alkene using NaH in dmf³³⁹. The bis(phosphine oxide) **276** is a source of (*E, E*)-cycloocta-1,5-diene (**277**)³⁴⁰. These various procedures have also been used in the preparation of cyclononadienes³⁷⁷. The phosphine oxide **278** has been used to prepare *trans*-cyclooctene by decomposition with NaH³³⁶.

TABLE 2. Types of compounds (other than monosubstituted ethene) preparable by the Horner reaction

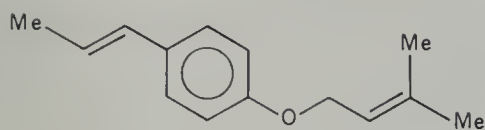
Compound type	Ref.
Di- and tri-substituted alkenes	307, 320
Dienes and polyenes	191, 320, 327–329, 345–351
Unsaturated acids and esters	324, 352
Unsaturated alcohols	176, 192, 307, 308, 321, 353–355
Unsaturated amines and amides	248, 322, 356
Unsaturated ketones	174, 306, 310, 357
Unsaturated keto esters	358
Vinyl ethers	194, 317, 359–361
Vinyl sulphides	196, 310, 311, 337, 362
Vinyl cyanides and isocyanides	363, 364
Vinyl amines (enamines)	365–367
Vinyl isoxazoles	368
Saturated ketones	353, 362, 365, 369
Saturated hydroxy ketones	308, 353
Saturated aminoketones	370
Ketals	306, 360, 371, 372



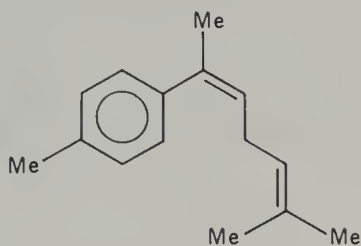
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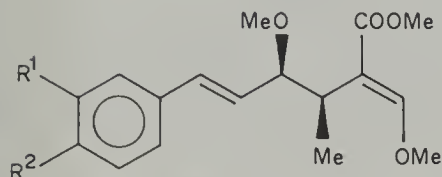
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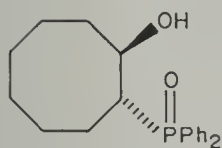
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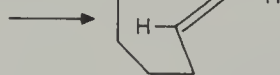
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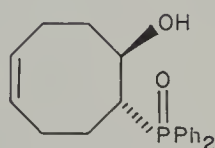
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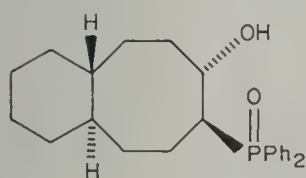
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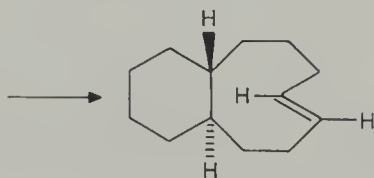
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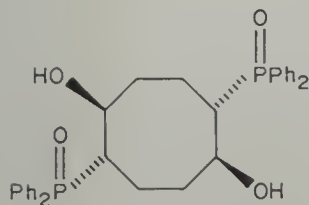
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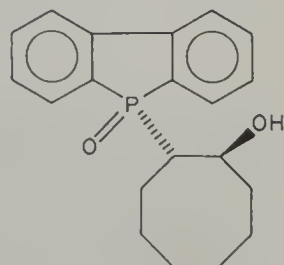
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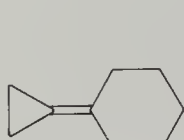


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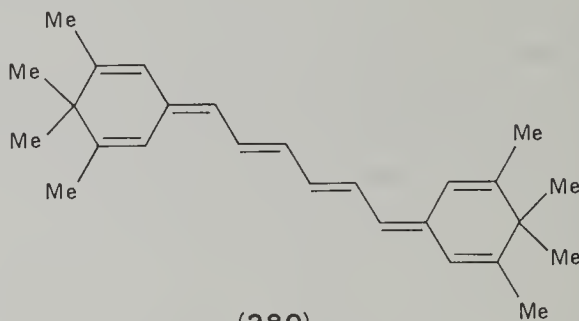


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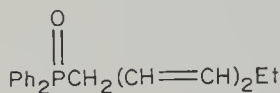
Treatment of the diphenylphosphinoicyclop propane anion with appropriate aldehydes or ketones yields hydrocarbons of the type **279**³⁷⁸; 1,2-bis(diphenylphosphino)ethane with KOBu^t and the appropriate dicarbonyl reactant yield the polyene **280**³⁵⁰. Other polyenes, e.g. **282**³⁴⁶ and **284**³⁴⁵, have been obtained from the anions of the phosphine oxides **281** and **283** using standard procedures. Syntheses of 25-keto-vitamin- D_3 have employed phosphine oxides such as **285**³⁴⁷⁻³⁴⁹.



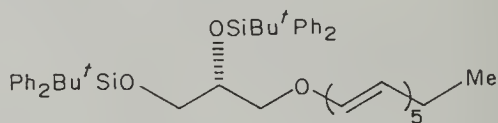
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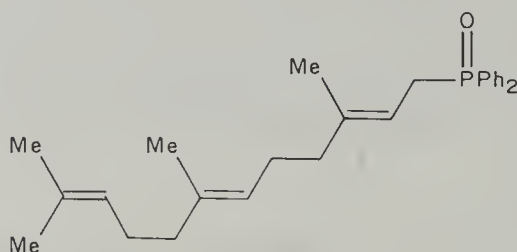
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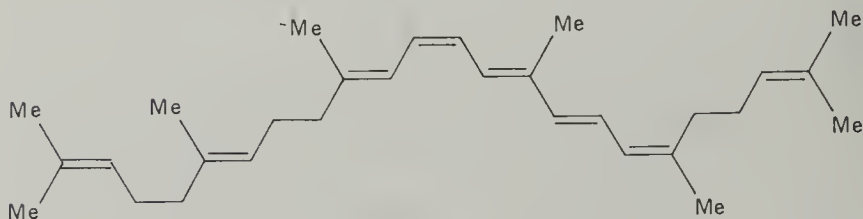
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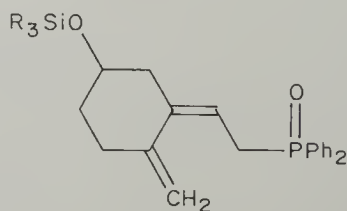
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(283)

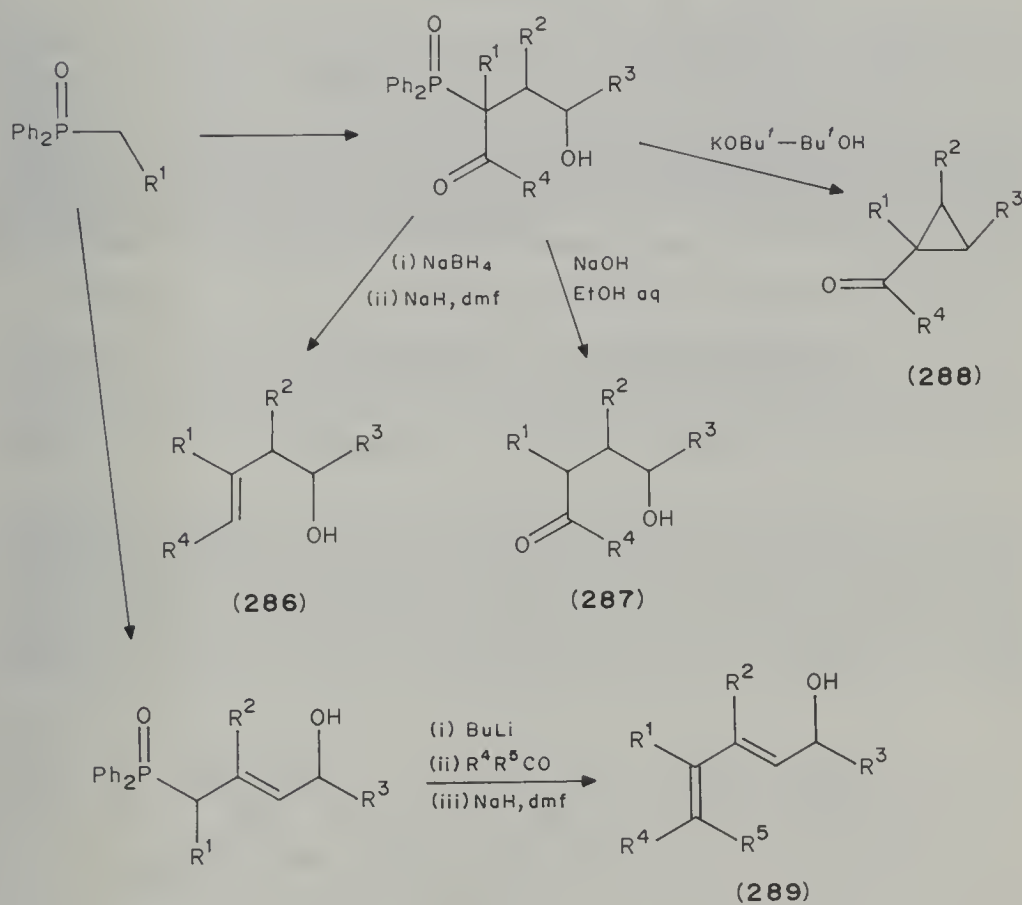
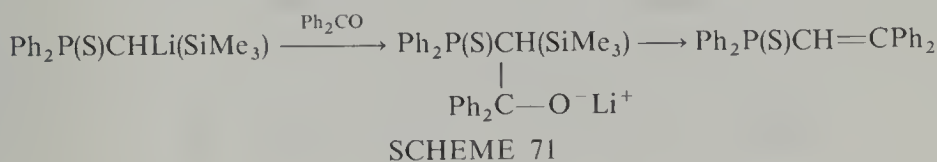


(284)



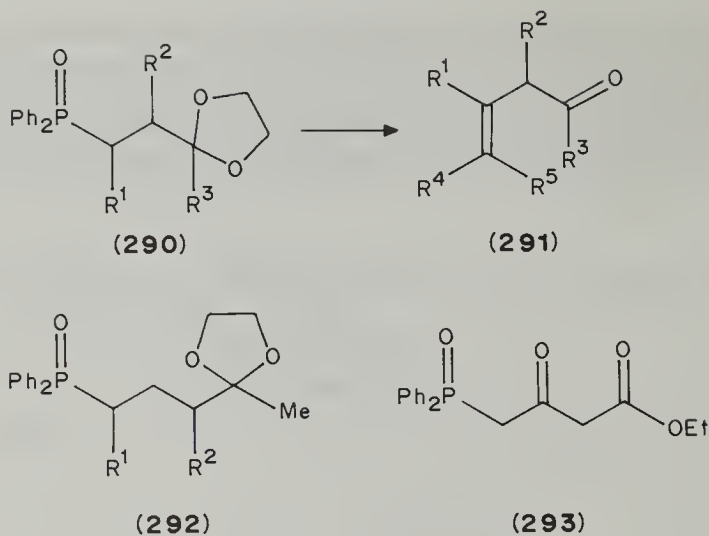
(285)

Returning to the possible use of phosphinothioyl compounds as intermediates in the Horner reaction, it is interesting to note an alternative reaction route (Scheme 71) for a silylated compound³⁷⁹. The versatility of the Horner reaction is well illustrated in Scheme 72, in which a single, simple, phosphine oxide as its anion acts as a source of unsaturated alcohols (**286**), hydroxy ketones (**287**) and cyclopropyl ketones (**288**)³⁵³, and also of hydroxydienes (**289**)³⁵⁴.

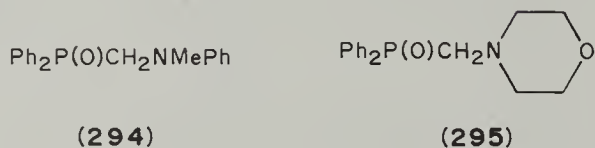


SCHEME 72

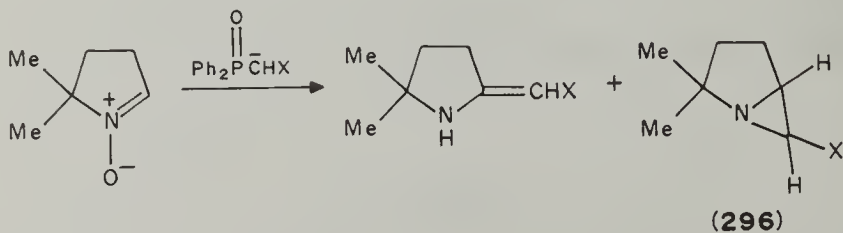
β,γ -Unsaturated ketones (**291**) are derived from the ketals **290**³⁷¹ and γ,δ -unsaturated ketones similarly from the ketals **292**³⁰⁶ in either *E* or *Z* forms. The use of **292** ($R^1 = \text{PhS}$) allows a synthesis of α,δ -diketones after hydrolysis of the initial Horner product³⁰⁶. β -Keto- γ,δ -unsaturated esters have been prepared from the oxide **293** using two equivalents of NaH in thf–hmpt with the high selectivity biased towards the *E* isomers³⁵⁸. The many reported syntheses of vinyl ethers and thio ethers allow, by hydrolysis of the



initial products, the preparation of a wide range of saturated ketones³¹⁰. Carbonyl compounds are also readily obtainable by the hydrolysis of enamines; the latter have been prepared with only poor to moderate stereoselectivity from the oxide **294** via the β -alcohol route^{365,366,368}; a similar reagent, **295**, is useful in the homologation of aldehydes³⁸⁰.



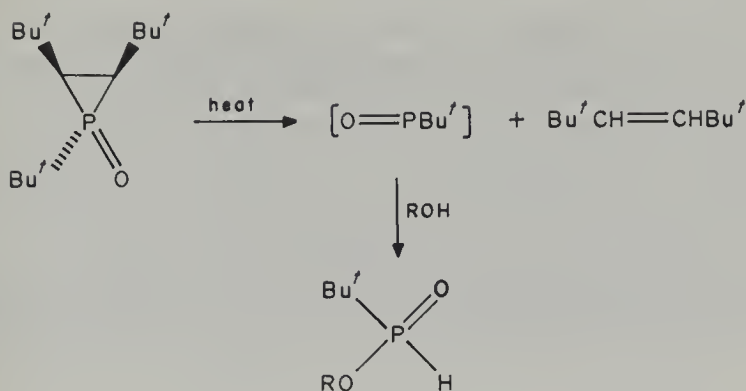
A modification to the normal Horner procedure involves the interaction of phosphine oxide carbanions with nitrones. In particular, the anions $\text{Ph}_2\text{P}(\text{O})\text{CHX}^-$ ($\text{X} = \text{CN}$ or COOR) have been made to react with 3,4-dihydroisoquinoline *N*-oxide to give 1-(substituted)methylene-1,2,3,4-tetrahydroisoquinolines, but the cyclic nitron **209** ($\text{R}^2 = \text{Me}$; $n = 1$) yields a mixture of 2-(substituted)methylenepyrrolidines and the bicyclic isomers **296**³⁸¹.



VI. PROPERTIES OF THE P—C (LIGAND) BOND

A. Thermal Stability

As might be expected, the thermal stability of tertiary phosphine chalcogenides depends on a number of structural features including the particular chalcogen atom and the

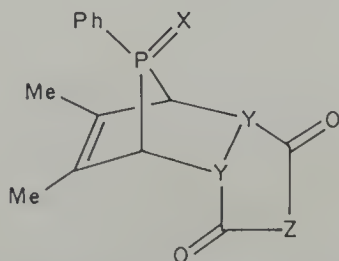
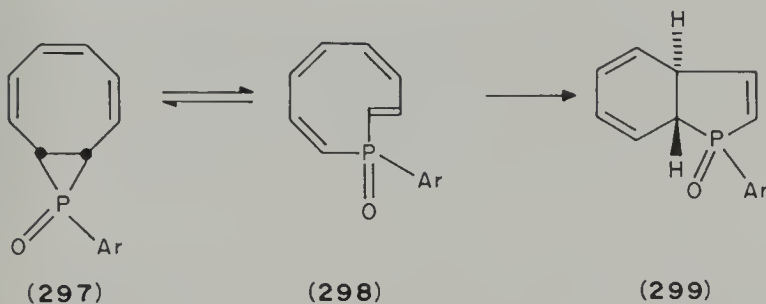


SCHEME 73

ligands, the general order of stability conferred by the chalcogen—phosphorus bond being oxide > sulphide > selenide > telluride. Ph_3PO decomposes at ca 450°C and the sulphide at ca 380°C . Trialkylphosphine oxides with no β -hydrogen atoms are even more stable, sometimes up to ca 600°C , and most tertiary phosphine oxides appear to decompose at temperatures higher than those of the corresponding amine oxides, often by as much as 300°C . When a β -hydrogen atom is available, elimination reactions may then occur during thermolysis (equation 81).



An important feature of the chemistry of smaller ring cyclic phosphine oxides is their tendency to fragment, particularly under thermolysis conditions. Thus, when heated, *r*-1,*t*-2,*t*-3-tri-*tert*-butylphosphirane 1-oxide eliminates *tert*-butylphosphinidene oxide, which can be trapped by reaction with alcohols or with a suitable *o*-benzoquinone



(300) $\text{X} = \text{S}$; $\text{Y} = \text{N}$; $\text{Z} = \text{NMe}$ or NPh

(301) $\text{X} = \text{Se}$; $\text{Y} = \text{CH}$; $\text{Z} = \text{O}$ or NPh

(Scheme 73)³⁸². The 1,8-bond in 9-phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene 9-oxide (**297**; Ar = Ph) is particularly susceptible to fission, and when the oxide is obtained by direct oxidation of the corresponding phosphine even at -20°C , it is accompanied by its valence tautomer **298**, which then rearranges to the dihydrophosphindole **299**³⁰. The analogous **297** (Ar = 2,4,6-Bu₃C₆H₂) readily decomposes in CHCl₃ to yield cyclooctatetraene and *P,P'*-bis[(2,4,6-*tert*-butyl)phenyl]phosphinic anhydride³⁸³. Extrusion of phenylphosphinidine oxide is assumed to account for the course of the bromination of the dihydroposphepins **179** (Scheme 36).

Elimination of the phosphinidene fragments $\text{RP}=\text{X}$ (X = O or S) occurs from bridging positions when phosphole dimers and other Diels–Alder adducts are heated, e.g. **300**^{384,385}, or photolysed, e.g. **301**³⁸⁴ (see also equations 52 and 53 and Schemes 51 and 52).

B. Cleavage by Metals

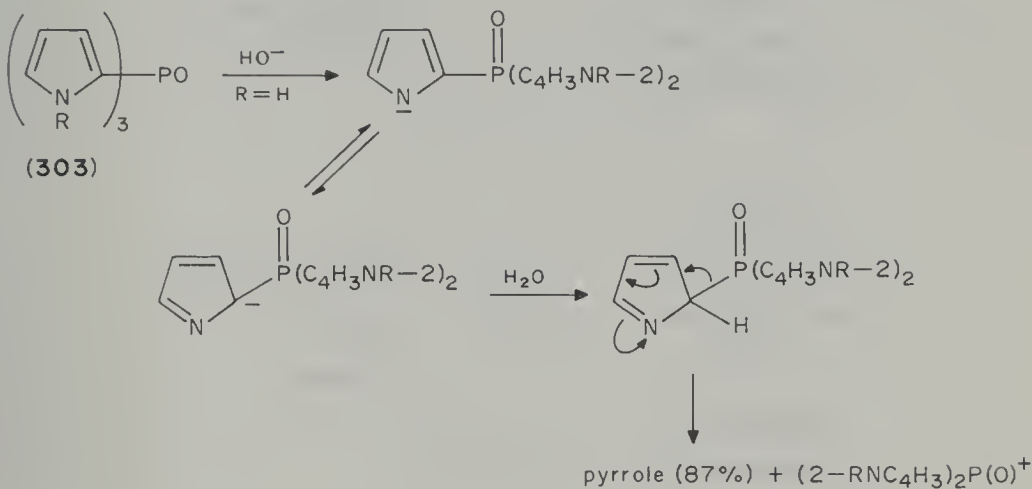
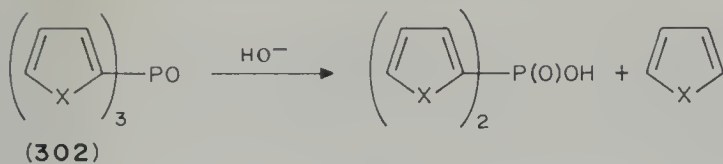
The older literature quotes several instances of the cleavage of P—C bonds by the action of metals, particularly the alkali metals. Trialkylphosphine oxides (butyl, octyl) and sodium have been shown to produce dialkylphosphines in ca 50% yields, but the oxide most widely investigated has been Ph₃PO. The latter is cleaved by two equivalents of sodium, and subsequent treatment with benzyl chloride gives benzyldiphenylphosphine oxide (77%); a similar reaction with potassium afforded [(3-benzyl)phenyl]diphenylphosphine oxide, probably through a biphenyl radical ion. The formation of a paramagnetic species is suspected as a result of the interaction of Ph₃PO and potassium or rubidium in ethereal solvents³⁸⁶. Benzyldiphenylphosphine oxide is also formed, together with benzene and diphenylphosphinic acid, from Ph₃PO and sodium under toluene, probably via PhCH₂Na.

C. Cleavage by Nucleophiles

Dialkylphosphine oxides are said to be formed when trialkylphosphine oxides interact with NaH; Ph₃PO and LiAlH₄ under thf or dioxane yield diphenylphosphine. The most widely studied examples of the cleavage of the phosphorus—carbon(ligand) bond by nucleophiles concern their behaviour towards alkali. The ready removal of a benzyl group from a benzylphosphine oxide is well authenticated. When fused with KOH, tribenzylphosphine oxide yields dibenzylphosphinic acid (about 10%), but higher yields of phosphinic acids are obtainable from substituted benzylphosphine oxides; under the same conditions the analogous tris(cyclohexylmethyl)phosphine oxides are unaffected³⁸⁷. Enantiomers of MePh(PhCH₂)PO with KOH in dmso yield racemic MePhP(O)OH³⁸⁸, and the same reagents remove the benzyl group from PhCH₂P(O)Ph₂³⁸⁹, but fusion with NaOH at 250° will remove *n*-alkyl groups from the oxides Ph₂P(O)R. Tris(3-nitrophenyl)phosphine oxide is hydrolysed to nitrobenzene by 50% aqueous KOH²³¹.

When heated with alkali in 50% dioxane³⁹⁰ or even with 10% aqueous NaOH solution³⁹¹, the oxides **302** (X = O or S) are cleaved to the free heterocycle and the phosphinic acid. Tris(2-pyrrolyl)phosphine oxide (**303**; R = H) was thought originally to hydrolyse to the pyrrolylphosphonic acid via the phosphinic acid, and ultimately to give pyrrole itself, following attack of HO[−] at phosphorus. The failure of **303** (R = Me) to undergo hydrolysis under the same conditions rules out a mechanism involving such a process, and the currently favoured mechanism involves deprotonation at nitrogen (Scheme 74)^{391,392}.

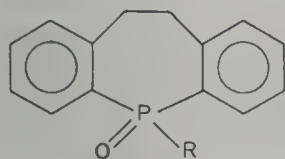
The attachment of strongly electronegative groups directly to phosphorus facilitates the fission of the phosphorus—carbon bond by nucleophiles. Tris(trifluoromethyl)phosphine oxide undergoes the fluoroform reaction with aqueous NaOH (and even with



SCHEME 74

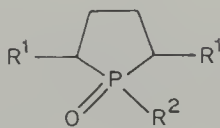
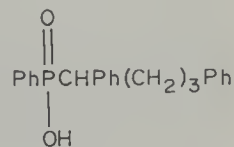
water only over an extended period); dimethylamine also removes one trifluoromethyl group very easily to give CHF_3 and $(\text{CF}_3)_2\text{P(O)NMe}_2$ ³⁹³. (Pentafluorophenyl)diphenylphosphine oxide loses the perfluorophenyl group by the action of NaOMe in MeOH; the corresponding sulphide behaves likewise^{233,234}. Acetylenic phosphine chalcogenides are cleaved by boiling aqueous KOH and by ethanolic AgNO_3 ³⁹⁴.

Some of the more interesting situations arise when the phosphorus atom is part of a ring system. The dihydrodibenzophosphepin **304** loses the exocyclic Ph group and gives the cyclic phosphinic acid **305** when acted upon by NaOH at 250°C ³⁹⁵; with LiAlH_4 or NaH, the principal reaction is one of ring fission, and with MeMgI both replacement of Ph by Me, and ring fission, occur³⁹⁶.



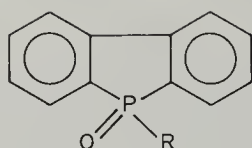
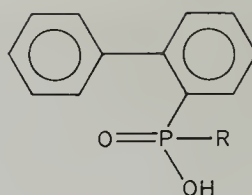
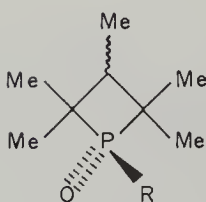
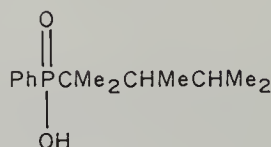
(304) R = Ph

(305) R = OH

(306) $\text{R}^1 = \text{Cy}$; $\text{R}^2 = \text{Ph}$ (307) $\text{R}^1 = \text{Cy}$; $\text{R}^2 = \text{OH}$ (308) $\text{R}^1 = \text{R}^2 = \text{Ph}$ 

(309)

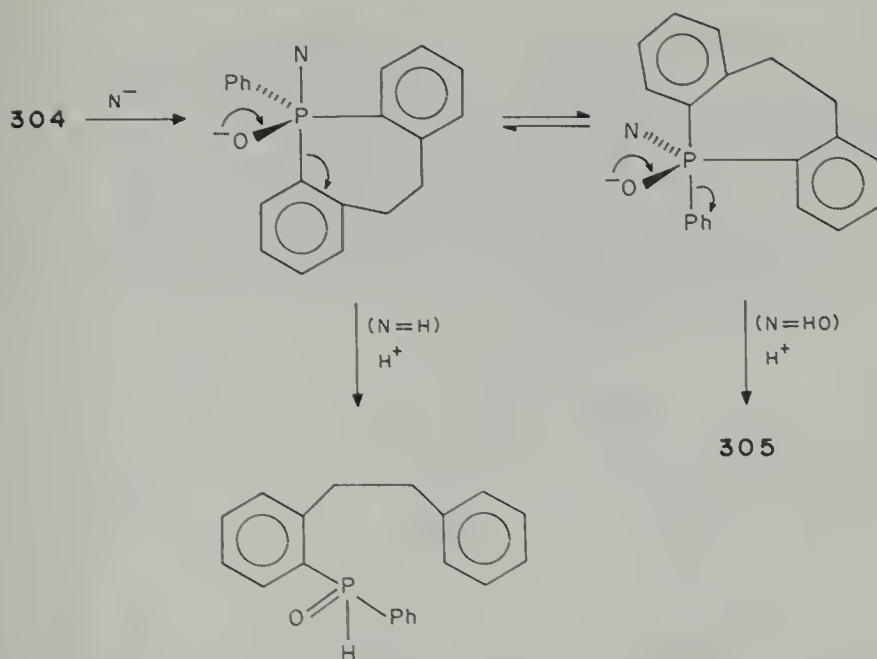
1-Methylphospholan-3-one 1-oxide is hydrolysed by NaOH solution to $\text{MeP(O)(OH)CH}_2\text{CH}_2\text{COMe}$ ²⁰³. The oxide **306** yields the phosphinic acid **307**, whereas **308** gives the acyclic phosphinic acid **309**³⁹⁷. The dibenzophosphole **310** suffers exclusive ring opening to **313** when fused with NaOH, but the benzyl analogue (**311**) preferentially ring opens to **314** (55%) but also affords 23% of the cyclic phosphinic acid **312**³⁹⁸.

(310) $R = \text{Ph}$ (311) $R = \text{PhCH}_2$ (312) $R = \text{OH}$ (313) $R = \text{Ph}$ (314) $R = \text{PhCH}_2$ (315) $R = \text{PhCH}_2$ (316) $R = \text{OH}$ (317) $R = \text{Ph}$ 

(318)

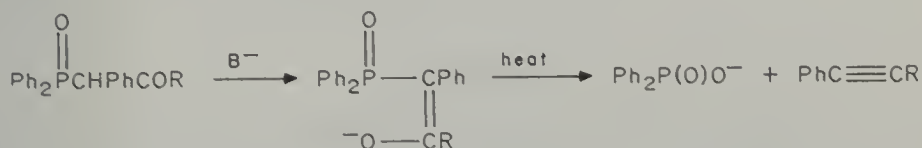
1-Benzyl-2,2,3,4,4-pentamethylphosphetane 1-oxide (315) is transformed exclusively into the phosphinic acid 316 with NaOH at 250 °C; the analogous 1-phenyl compound 317 yields both the cyclic phosphinic acid 316 and, preferentially, the acyclic phosphinic acid 318, in the ratio 1:4³⁹⁹; the oxide 317 is stable towards aqueous sodium hydroxide⁴⁰⁰.

It is apparent that the cleavage of acyclic phosphine oxides can generally occur when electronegative groups are attached directly to phosphorus, and the preferential site for fission can be predicted if there is a choice of leaving groups—that group forming the more stable anion will be expelled. Attempts have been made to explain the observed results in terms of pentacoordinate intermediates; the preferred choice between trigonal bipyramidal or square-planar intermediates seemed to be *tbp*³⁸⁹. The role that phosphorus(V) intermediates or transition states play in the chemistry of acyclic phosphine oxides is far from clearly understood, unlike their role for phosphate esters. The position is also unclear for cyclic phosphine oxides. The role of phosphorus(V) intermediates is well established in the chemistry of esters of cyclic phosphoric and phosphinic acids, and of cyclic phosphonium salts. In an attempt to discern a role for pentacoordinate intermediates in the chemistry of cyclic phosphine oxides, Gorenstein⁴⁰¹ examined the pH–rate profile for the epimerization and ¹⁸O incorporation for 1-phenyl-2,2,3-trimethylphosphetane 1-oxide, but was unable to provide conclusive positive evidence. On the other hand, other workers have explained the behaviour of 304 towards nucleophiles in terms of phosphorus(V) intermediates (Scheme 75)^{396,397}, employing the concept of relative apicophilicities. The latter concept, in conjunction with the feature(s) of the cyclic phosphine oxide which controls the siting of the ring in the phosphorus(V) intermediate, i.e. ring size (a four-membered ring is likely to be restricted to an apical–equatorial position), together with the question of stability of the leaving group as an anion, will all contribute to the final outcome of the reaction of a phosphine oxide with a nucleophile.



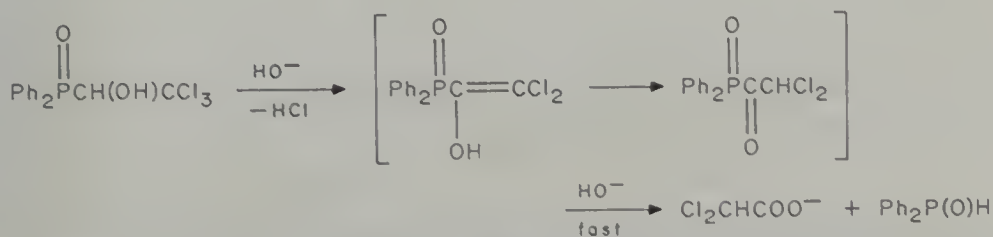
SCHEME 75

The Horner reaction is yet another example of a reaction in which the P—C (ligand) bond is cleaved, probably at some stage through the breakdown of a tbp intermediate formed by nucleophilic attack of O^- at electrophilic phosphorus. A similar breakdown accounts for the formation of acetylenes from the thermolysis of (2-ketoalkyl)phosphine oxides under basic conditions (Scheme 76)⁴⁰².

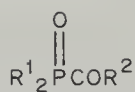


SCHEME 76

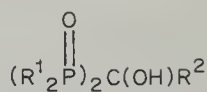
α -Hydroxyalkylphosphine oxides are particularly susceptible to degradation under alkaline conditions (Scheme 77)⁴⁰³. (1-Oxoalkyl)phosphine oxides (319) hydrolyse under even milder conditions to the secondary phosphine oxides $R^1_2P(O)H$, which then react with the starting material to give (hydroxyalkyl)bis(phosphine oxides) (320)⁴⁰⁴.



SCHEME 77

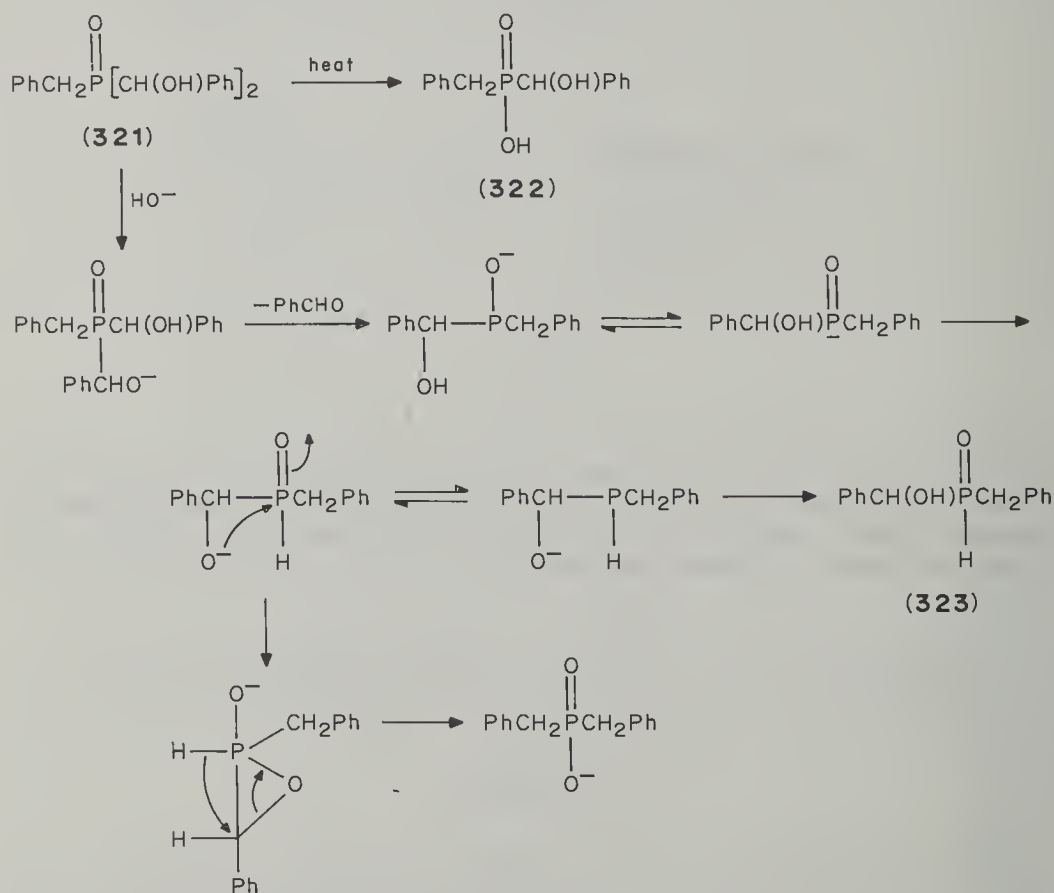


(319)

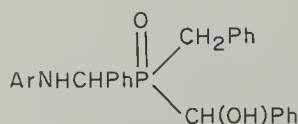


(320)

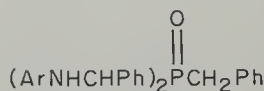
The phosphine oxide **321** decomposes in boiling benzene and benzyl(α -hydroxybenzyl)phosphinic acid (**322**) can be isolated. In the presence of 1 M NaOH solution, the oxide **321** yields dibenzylphosphinic acid; a mechanism for this reaction has been postulated (Scheme 78)⁴⁰⁵.



SCHEME 78



(324)

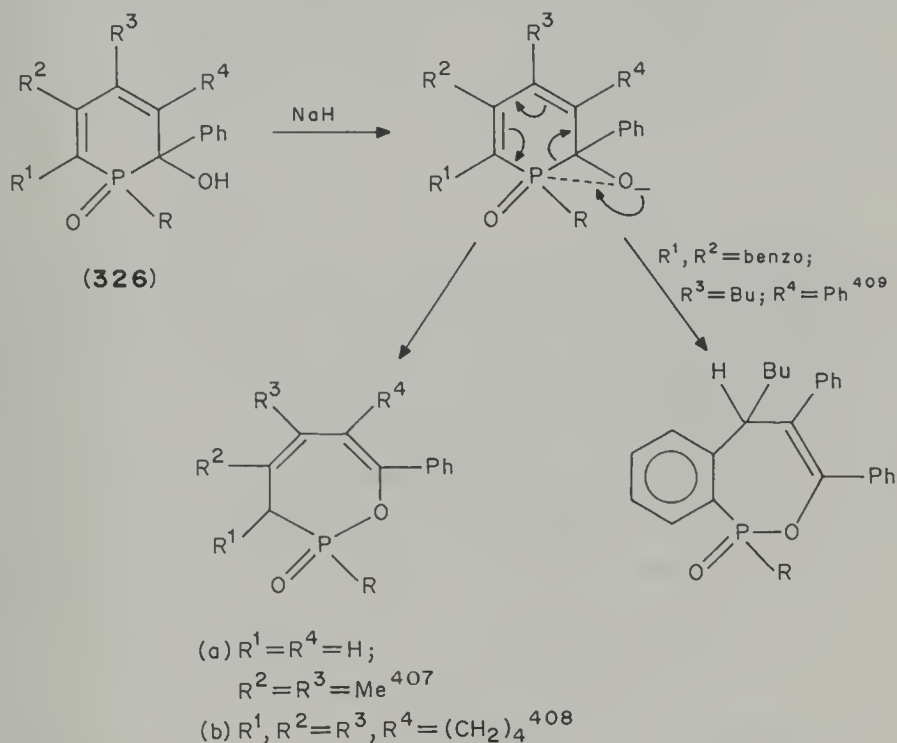


(325)

The same oxide (**321**), when heated with aromatic amines, yields first the monoamino compounds **324**, probably via the secondary phosphine oxide **323**; the final products

are bis(α -aminobenzyl)benzylphosphine oxides (325). No such reaction occurs with branched-chain aliphatic amines⁴⁰⁶.

In another rearrangement proceeding through nucleophilic intramolecular attack and of high synthetic potential, 2-hydroxy-2-aryl-1,2-dihydrophosphorins (326) are treated with NaH; the intermediate anion can furnish tautomeric-like products depending on the nature of the original substituents (Scheme 79)⁴⁰⁷⁻⁴⁰⁹.

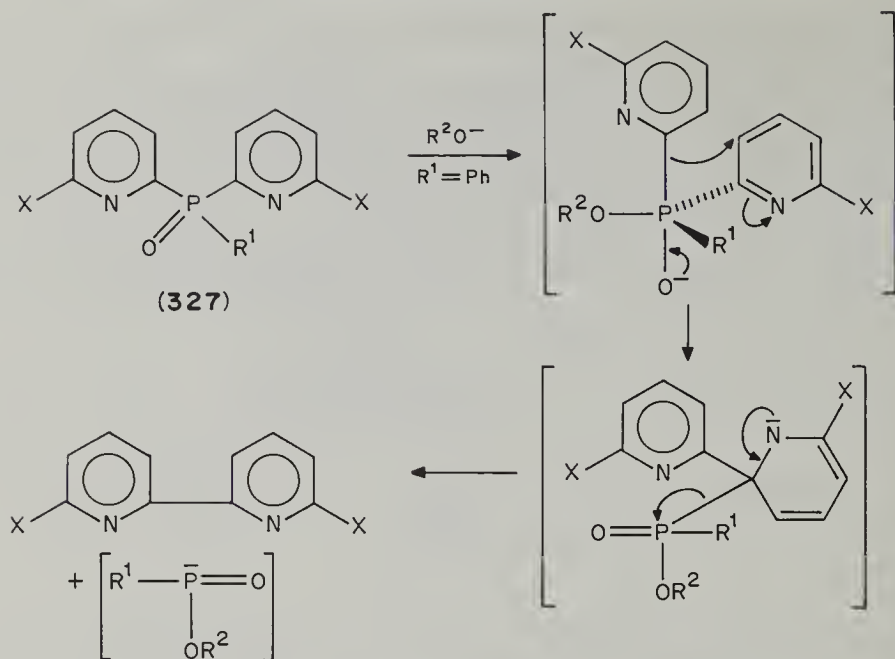


SCHEME 79

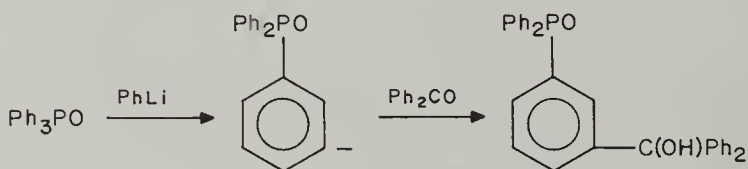
One of the more unusual examples of the fission of the P—C(ligand) bond is that depicted in Scheme 80, in which di-2-pyridinylphosphine oxides (327; X = H or Br, or XX = a polyether chain) are treated with NaOEt in toluene at 100°C when the main reaction products are the 2,2'-bipyridinyl⁴¹⁰. Carbon nucleophiles (MeMgI, PhMgBr, PhCH₂MgCl, PhLi, 2-pyrLi, etc.) yield additionally simple 2-substituted pyridines, and pyridine itself⁴¹¹, also produced by the action of acidic reagents⁴¹². The phosphorus—carbon bond in tri-*tert*-butylphosphirane 1-oxide is cleaved by nitrogen nucleophiles, in particular the bases LiNR₂; fission also occurs to some extent at the C—C bond, and the relative extents of these reactions depend on R and the solvent²⁰².

Wittig and Cristau⁴¹³ were unable to corroborate earlier observations (Wittig and Rieber, 1949)⁶⁻⁹ of the formation of tetraphenylphosphonium salts from Ph₃PO and PhLi, and instead showed that carbanions were formed which could be trapped in a reaction with benzophenone (Scheme 81). According to Schaub *et al.*⁴¹⁴, metallation of Ph₃PO with PhLi or BuLi occurs at the (mono)*ortho* positions⁴¹⁴. Exchange of organic groups when Ph₃PO was treated with RCH₂Li (R = H or Me) had already been demonstrated by Seyferth *et al.*⁴¹⁵.

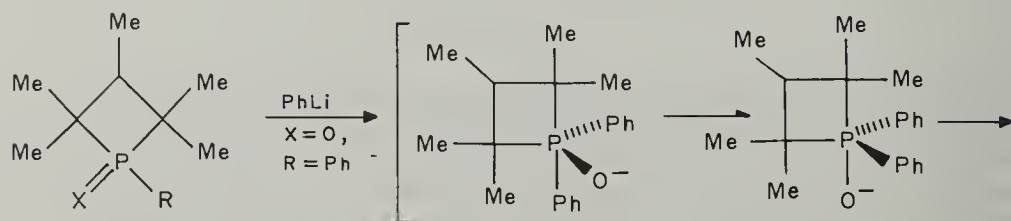
The fission of the P—C(sp) bond in diphenyl(phenylethynyl)phosphine oxide under the influence of PhLi to give Ph₃PO and the lithium salt of phenylacetylene has been formulated as occurring via a pentacoordinate intermediate⁴¹⁶.



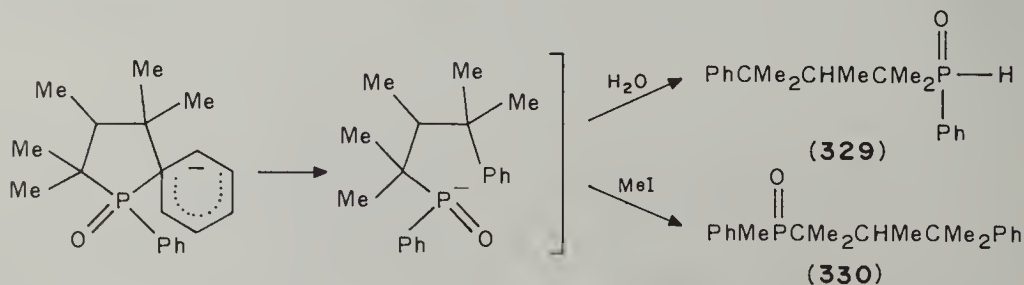
SCHEME 80



SCHEME 81



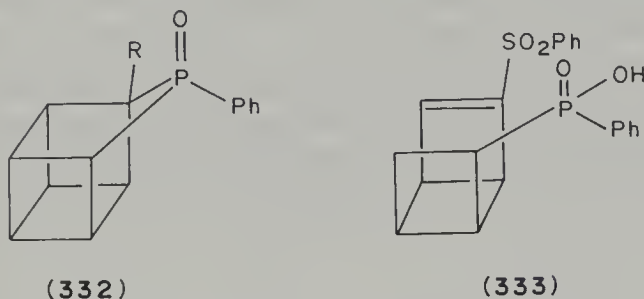
(328)

 $Ph_2PCMe_2CHMe_2Ph$

(331)

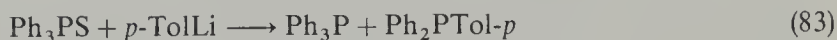
SCHEME 82

Ring cleavage occurs when the phosphetane 1-oxide **328** ($X = O$; $R = Ph$) is acted upon by $PhLi$ (Scheme 82), as evidenced by subsequent methylation of the intermediate(s) to give the phosphine oxide **330**, and treatment with water when the secondary phosphine oxide **329** was obtained^{417,418}.



The phosphahomocubane **332** ($R = H$) is lithiated with $PhLi$ in thf without ring opening; deuteration or methylation gives **332** ($R = D$ or Me), and $PhSSPh$ gives *inter alia* the sulphide **332** ($R = SPh$). Oxidation of the latter with $mCPBA$ and treatment of the sulphone with $NaN(SiMe_3)_2$ resulted in ring opening to the phosphinic acid **333**⁴¹⁹.

As in the case of the oxide, Seyferth and Welch⁴²⁰ demonstrated exchange between Ph_3PS and RCH_2Li to give $Ph_2P(S)CHRLi$, and with $PhLi$, triphenylphosphine sulphide gives Ph_3P and $PhSH$ (Wittig, 1969, unpublished results). In the latter example, the loss of sulphur and valence contraction are also to be found in reactions 82 and 83, and also occur when the sulphide **328** ($X = S$, $R = Ph$) is treated with one equivalent of $PhLi$ when half the starting amount of starting sulphide is recovered and the phosphine (**331**) is obtained concurrently.



It appears that, to some extent at least, attack occurs at sulphur in addition to phosphorus⁴¹⁷.

VII. REACTIONS OF PRIMARY AND SECONDARY PHOSPHINE CHALCOGENIDES

As indicated at the beginning of this chapter, the chalcogenide derivatives of primary and secondary phosphines are tautomeric substances with the phosphorus capable of existence in both the tricoordinate tervalent (**2.2**) and tetracoordinate quinquivalent (**2.1**) states. In practice the phosphorus adopts, almost exclusively (with two known exceptions), the latter state. Secondary phosphine oxides are not particularly stable substances with regard to heat. Thus, dimethylphosphine oxide begins to disproportionate to Me_2PH and $Me_2P(O)OH$ at ca $100^\circ C$; the diethyl compound decomposes at $180\text{--}200^\circ C$ ⁴²¹.

Chiral secondary phosphine oxides have been prepared in optically active forms: $Ph(PhCH_2)P(O)H$ is configurationally stable in $MeOH$ at room temperature, but rapidly racemizes in the presence of a trace of mineral acid; it also undergoes rapid deuterium exchange at ambient temperature⁴²². On the other hand, $Ph(PhCHMe)P(O)H$ does not undergo stereomutation in $MeOH$ containing $NaOMe$ or 0.05 M HCl , but does epimerize in the presence of $LiAlH_4$ ⁴²³.

The chalcogenides of primary phosphines, $RP(X)H_2$, are also tautomeric, and are relatively inaccessible substances and have been studied only poorly (see, e.g., ref. 424). The derivatives of secondary phosphines have now been well characterized and their

reactions studied to a much greater extent. Their nucleophilic character in the presence of a base, reacting at either the chalcogen or phosphorus to give tervalent or quinquivalent phosphorus derivatives, has been recognized for some time. Their duality of behaviour is also to be noted, since not only can they react as nucleophiles in the absence of a base, as in the conversion of diarylphosphine oxides into diarylphosphinous chlorides (diarylchlorophosphines) by the action of PCl_3 ⁴²⁵, but they can also behave as electrophiles towards bases. Thus, a rapid evolution of hydrogen occurs when secondary phosphine oxides are treated with an excess of NaOEt or NaOH in EtOH ; the main phosphorus-containing product is a phosphinic acid. Thiophenoxide behaves in a similar fashion, e.g. with $\text{Ph}_2\text{P}(\text{O})\text{H}$, when the phosphorus-containing product is *S*-phenyl diphenylphosphinothioate. This observation explains the formation of hydrogen when (α -hydroxyalkyl)phosphine oxides are in contact with alkaline reagents⁴²⁶.

The reactions considered in this section are those in which the quinquovalency of the phosphorus is maintained.

A. Oxidation and Reduction Reactions

The oxidation (addition of chalcogen) of secondary phosphine chalcogenides may be represented simply by the general equation 84. Secondary phosphine oxides are readily oxidized to phosphinic acids by means of hydrogen peroxide^{427,428}; diarylphosphine oxides have also been oxidized with *tert*-butyl hydroperoxide or *p*-nitroperoxybenzoic acid and the kinetics of the reactions studied⁴²⁷.



The analogous conversion of secondary phosphine sulphides into phosphinodithioic acids by the addition of elemental sulphur is also known. The addition of oxygen to a phosphine sulphide appears to be less satisfactory for those very few examples reported⁴²⁹; on the other hand, the successful addition of sulphur to *tert*-butylphenylphosphine oxide to give the corresponding phosphinothioic acid has been recorded, whilst the treatment of diarylphosphine oxides with diphenyl disulphide leads to *S*-phenyl esters of diarylphosphinothioic acids⁴³⁰.

Iron powder has been used successfully in the desulphurization of secondary phosphine sulphides (diisobutyl, diphenyl) to the parent phosphines (Maier, 1964)⁶⁻⁹.

B. Replacement Reactions

The simplest of these is that of the phosphine hydrogen by a metal when the chalcogenide is treated with the metal itself, or with a metal alkoxide or organometallic reagent such as an organolithium or Grignard reagent.

The replacement of hydrogen by a halogen, although well established, is not a reaction which always lends itself to synthetic utility since there are easier ways to prepare the products. $\text{Ph}_2\text{P}(\text{O})\text{H}$ with SOCl_2 yields diphenylphosphinic chloride, $\text{Ph}_2\text{P}(\text{O})\text{Cl}$. The interaction of $\text{Et}_2\text{P}(\text{O})\text{H}$ and SOCl_2 initially affords $\text{Et}_2\text{P}(\text{O})\text{Cl}$, but this reacts further with the starting oxide, and a sequence of steps leads eventually to Et_2PCl , Et_2PH and ultimately to Et_2PCl_3 ⁴³¹. The direct thiocyanation of *tert*-butylphenylphosphine oxide yields the relatively stable $\text{Bu}^i\text{PhP}(\text{O})\text{SCN}$ [compounds possessing the $\text{P}(\text{O})\text{SCN}$ grouping tend to be unstable], which then rearranges to $\text{Bu}^i\text{PhP}(\text{O})\text{NCS}$ ⁴³².

Secondary phosphine oxides have been alkylated with reactive, e.g. benzylic, halides to give tertiary phosphine oxides^{428,433}, and a recently reported procedure for this same conversion involves the treatment of a secondary phosphine oxide with an alcohol (secondary and tertiary alcohols react more slowly than do primary alcohols) in the presence of 5–10 mol% of an alkyl chloride, bromide or iodide (equation 85)⁴³⁴. Benzylic

halides, α -bromo ketones and methylolamines⁴³⁵ have been used to alkylate secondary phosphine sulphides, either in the free state or as a metal derivative⁴²⁹ (see also Section VII.C.3).



C. Addition Reactions

Additions to systems possessing sp^2 or sp carbon form by far the most widely investigated and synthetically important group of reactions of secondary phosphine chalcogenides⁴³⁶.

1. Additions to $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ bonds

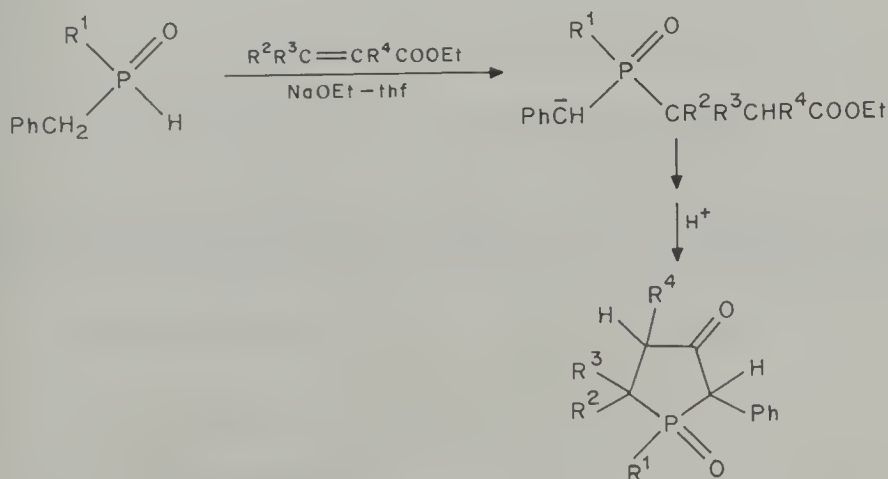
The general mode of addition of secondary phosphine chalcogenides to activated olefinic compounds is illustrated in equation 86.



(334)

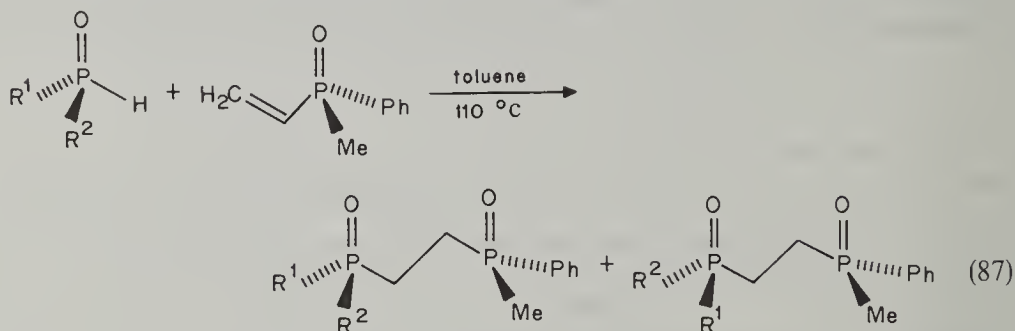
Additions of secondary phosphine oxides to derivatives of propenoic acid and those of homologous acids and other carbonyl compounds are well known, and including additions to **334** ($\text{R}^2 = \text{H}, \text{Me}, \text{Ph}$ or COOEt ; $\text{R}^3 = \text{H}$ or Me ; $\text{Y} = \text{CN}, \text{COOEt}, \text{CONH}_2, \text{COMe}$ or COPh) for $\text{R}^1 = \text{PhCH}_2$ or Oct ⁴³⁷ and $\text{R}^1_2 = \text{Ph}(\text{PhCH}_2)$ ⁴³⁸. A series of similar additions have been reported for the phenophosphazine system⁴²⁸ and for vinylsilanes⁴³⁹.

The initial addition of secondary phosphine oxides to unsaturated carboxylic esters provides a route to phospholane oxides (Scheme 83). The yields of initial adducts are generally low for derivatives of propenoic acid but are greater (45–75%) for those of homologues and for cinnamic acid esters⁴⁴⁰ (see also Scheme 90). Although addition reactions of secondary phosphine sulphides have been recorded^{429,435,441}, the general outcome is less successful than for the phosphine oxides.

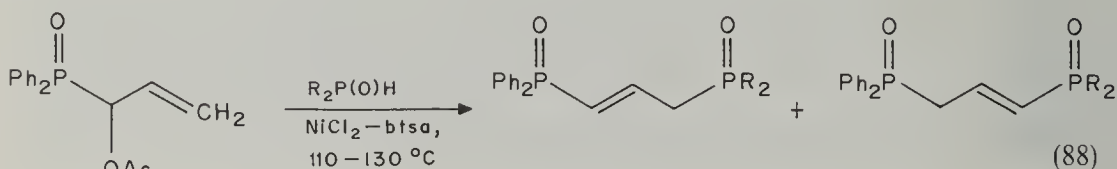


SCHEME 83

Recently studied examples of the addition of secondary phosphine oxides to tertiary vinylphosphine oxides include those of $R\text{PhP(O)H}$ ($R = \text{Me}$ or Bu^t) to (*S*)-methylphenylvinylphosphine oxide in boiling toluene, from which a mixture of diastereoisomeric products was obtained (equation 87)^{298,442}. Assignment of configurations to separated compounds was sometimes made on the basis of optical rotation measurements (R^1 or $R^2 = \text{Me}$ or Ph) or X-ray crystallography ($R^1 = \text{Bu}^t$, $R^2 = \text{Ph}$) but was not always possible, e.g. when R^1 or R^2 is benzyl. The same compounds are obtainable in an addition-elimination sequence when chiral α -bromo- or α -chloro-vinylmethylphenylphosphine oxides are treated with secondary phosphine oxides in the presence of Et_3N ⁴⁴³.

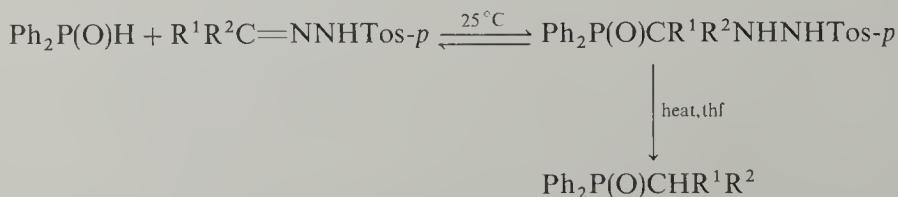


In the presence of nickel(II) and bis(trimethylsilyl)acetamide secondary phosphine oxides do not add to (1-acetoxyallyl)diphenylphosphine oxide, but rather displace the acetoxy group with the formation of a mixture of isomeric [hydrogenolysed to the same 1,3-bis(diphenylphosphinoyl)propane] 1,3-bis(diphenylphosphinoyl)propenes (equation 88)⁴⁴⁴.



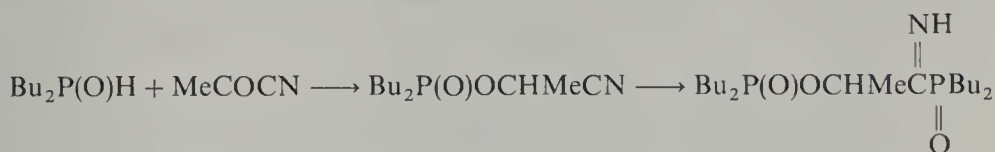
2. Additions to $\text{C}=\text{N}$ and $\text{C}\equiv\text{N}$ bonds

The addition of diphenylphosphine oxide to the imino bond of the hydrazones of aldehydes or ketones, was reported in 1960 by Kreutzkamp⁶⁻⁹; it is a reaction which is easily reversible, particularly in the presence of traces of acid or base. Thermolytic cleavage of the products of addition leads to branched-chain tertiary phosphine oxides (Scheme 84), but the scope of this preparative process appears not to have been examined to any great extent⁴⁴⁵.



SCHEME 84

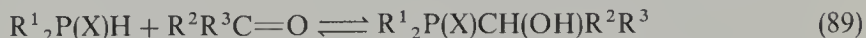
Diphenylphosphine oxide adds to the nitriles RCN (R = Ph, PhCH₂ or CN) when heated in the presence of EtO⁻ to give the phosphinoylaldimines Ph₂P(O)CR=NH, and the kinetics of the reaction have been studied⁴⁴⁶. For α-ketonitriles, the initial reaction to give a 1:1 adduct occurs at the carbonyl group, but further reaction to give the 2:1 adduct involves the nitrile group (Scheme 85)⁴⁴⁷.



SCHEME 85

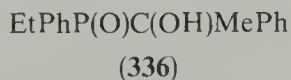
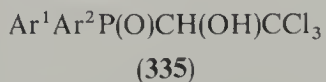
3. Additions to C=O and C=S bonds

Numerous examples exist of the interaction of aldehydes or ketones with secondary phosphine chalcogenides. Until fairly recently, these consisted only of the intermolecular type (equation 89). More recently, however, examples of intramolecular reaction have been forthcoming, leading usefully to the synthesis of phosphorus-containing ring systems.

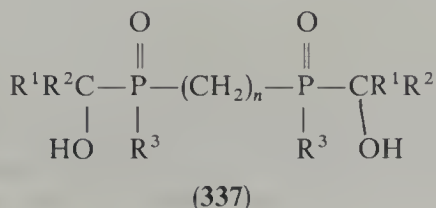


Within the grouping of intermolecular reactions, additions occur to saturated carbonyl compounds (1,2-additions), and also to conjugated systems, in which both 1,4- and 1,6-additions have been observed.

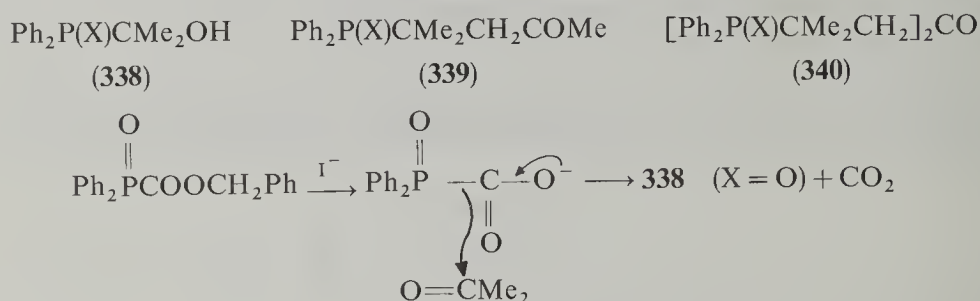
In contrast to the similar interactions between dialkyl hydrogen phosphonates and aldehydes or ketones which require a basic catalyst, those involving secondary phosphine oxides may not require such a catalyst. Reactions between dibutyl- or dioctyl-phosphine oxide and activated carbonyl compounds, e.g. R² = H, Me, Et or Ph, R³ = COMe, COOalkyl or P(O)(OEt)₂ (equation 89) occur exothermically and are complete within a few days⁴⁴⁸⁻⁴⁵⁰. Mixtures of diastereoisomeric products (**335**) have been obtained from unsymmetric diarylphosphine oxides and chloral⁴⁵¹ and from ethylphenylphosphine oxide and acetophenone. The latter, at 25 °C, yielded a 70:30 mixture of the *erythro* and *threo* forms of the 1:1 adduct **336**, a result explained in terms of the preferred mutual transoidal approach of C=O and P=O⁴⁵². Alkanebis(phosphine oxide)s react in the expected manner to give the adduct **337**⁴⁵³. Steric interference in reaction 89 has been observed; thus, di-*tert*-butylphosphine oxide fails to add to simple aldehydes or ketones even in the presence of a basic catalyst⁴⁵⁴.



The reaction between acetone and the magnesium salt of diphenylphosphine oxide yields a mixture of the expected 1:1 adduct **338** (X = O) together with **339** (X = O) and **340** (X = O), the latter adducts being derived from mesityl oxide and phorone, the source



of which was the acetone and base⁴⁸⁵. The adduct **338** ($X = O$) has also been obtained, in an interesting manner, following the debenzoylation of benzyl diphenylphosphinoylformate by NaI in acetone; evidently, under the experimental conditions, the diphenylphosphinoylcarboxyl anion decarboxylates very readily (Scheme 86)⁴⁵⁶.



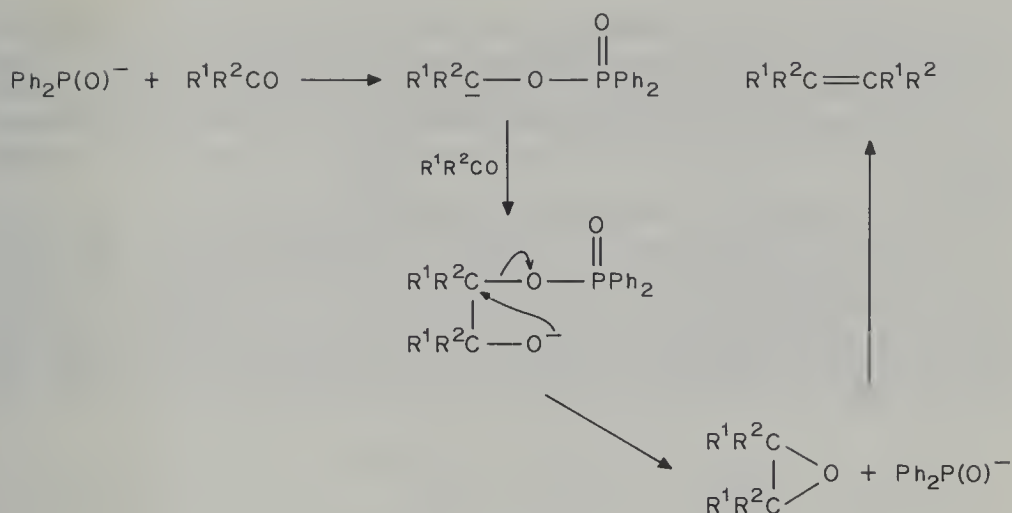
SCHEME 86

Additions to secondary phosphine sulphides are much slower and need to be base catalysed, but they are also reversible so as to make satisfactory characterization of the products impossible, or at least very difficult⁴²⁹. Combinations of the adducts **338–340** ($X = S$) are obtainable from diphenylphosphine sulphide and acetone under neutral to basic conditions⁴⁵⁴.

The possible role of the carbonyl–phosphine oxide condensation in the aminomethylation of secondary phosphine oxides using mixtures of carbonyl reactant and amines has been discussed by Petrov *et al.*⁴⁵⁷. In the case of the $(\text{PhCH}_2)_2\text{P}(\text{O})\text{H} - \text{HCHO} - \text{Et}_2\text{NH}$ system, the two main constituents in the product are $(\text{PhCH}_2)_2\text{P}(\text{O})\text{CH}_2\text{NEt}_2$ and $(\text{PhCH}_2)_2\text{P}(\text{O})\text{CH}_2\text{OH}$; both are produced at 60–110°C, but at 140–150°C only the former is present, and the former is not obtained from the phosphinoylmethanol and amine at the lower temperatures. The reaction is therefore considered to proceed through an initial hydroxymethylation of the amine. The formation of the aminomethylphosphine oxide at higher temperatures may well proceed through dissociation of the hydroxymethylphosphine oxide into secondary phosphine oxide and HCHO followed by hydroxymethylation of the amine to $\text{Et}_2\text{NCH}_2\text{OH}$ and its subsequent reaction; it is worth noting that the oxide $(\text{PhCH}_2)_2\text{P}(\text{O})\text{CH}_2\text{OMe}$ does not dissociate when heated, nor does it exchange MeO for NEt_2 even at 180–190°C⁴⁵⁷. Some comparison may be made between these results and those embodied in Scheme 78.

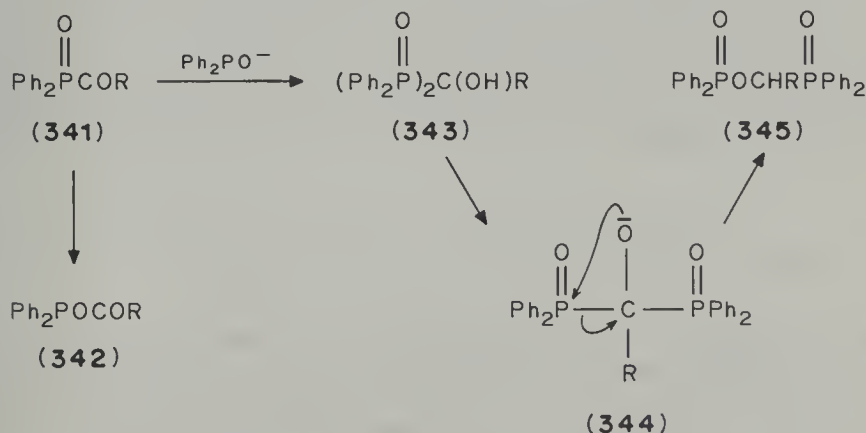
Following his original (1961) observations on the formation of *trans*-stilbene when benzaldehyde and diphenylphosphine oxide anion were heated together at 200°C, Horner^{6–9} suggested that the reaction might proceed via (α -hydroxybenzyl)diphenylphosphine oxide. However, it is now known that the latter is unstable to base, and even at 100°C reverts to PhCHO and the secondary phosphine oxide anion in the presence of NaH. Moreover, it has now been demonstrated that $\text{Ph}_2\text{P}(\text{O})^-$ with two equivalents of PhCHO at 180°C yields *trans*-stilbene together with a mixture of *trans*- (45%) and *cis*- (40%) stilbene epoxides, a result similar to that produced when (α -hydroxybenzyl)diphenylphosphine oxide is heated with one equivalent of PhCHO and NaH at 180°C. Further, when heated with $\text{Ph}_2\text{P}(\text{O})^-$ at 180°C, *trans*-stilbene epoxide gives a quantitative yield of *trans*-stilbene. The formation of symmetrical alkenes from phosphine oxide anions and (aromatic) aldehydes or ketones is formulated as in Scheme 87⁴⁵⁸.

The acylation of secondary phosphine oxides yields (1-oxoalkyl)phosphine oxides; thus, di-*tert*-butylphosphine oxide, as its lithium salt, affords $\text{Bu}^t_2\text{P}(\text{O})\text{COPh}$ in 27% yield when treated with benzoyl chloride⁴⁵². The acetylation of diphenylphosphine oxide at 55°C with acetic anhydride leads to acetyldiphenylphosphine oxide (**341**; $R = \text{Me}$), which slowly isomerizes into diphenylphosphinous acetic anhydride (**342**; $R = \text{Me}$)



SCHEME 87

(Scheme 88). With more diphenylphosphine oxide anion, acetyldiphenylphosphine oxide yields the bis(diphenylphosphinoyl) compound **343**, rearrangement of which through the three-centre process indicated in **344** results in the formation of the phosphinic ester **345** ($\text{R} = \text{Me}$)^{456,459}. The phosphine oxides $\text{PhRP}(\text{O})\text{COMe}$ ($\text{R} = \text{PhCH}_2$, Cy, Bu^t or Ar), when heated with the oxides $\text{PhRP}(\text{O})\text{H}$ also furnish compounds of types **343** and **345**^{460,461}. The reported formation of tetraphenyldiphosphine monoxide from diphenylphosphine oxide and acetic anhydride in the presence of pyridine has been attributed to reaction between the anhydride **342** ($\text{R} = \text{Me}$) and the $\text{Ph}_2\text{P}(\text{O})\text{H}$ ⁴⁶².

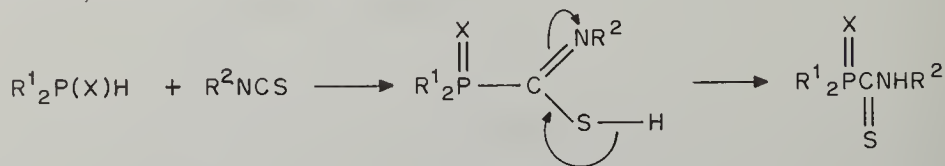


SCHEME 88

Benzoyldiphenylphosphine oxide (**341**; $\text{R} = \text{Ph}$), obtained from tetraphenyldiphosphine and benzoic acid, is rapidly converted into **345** ($\text{R} = \text{Ph}$); following a similar reaction with certain aliphatic acids, e.g. phenylacetic acid, phenoxyacetic acid and 3-phenylpropanoic acid, compounds of type **343** were isolable because of the slowness of the rearrangement steps. Other acids, e.g. di- and tri-phenylacetic acids, were converted into hydrocarbons⁴⁶³. The same products (Scheme 88; $\text{R} = \text{Me}$) have been observed following an Arbuzov reaction between the appropriate RCOCl and methyl diphenylphosphinite Ph_2POMe ⁴⁶⁴.

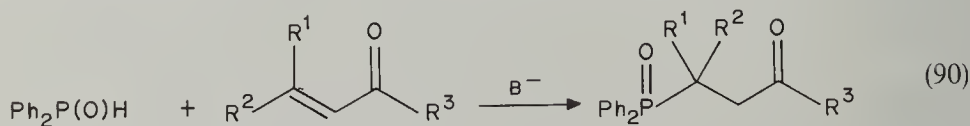
The nucleophilic activity of secondary phosphine oxides, already referred to, accounts for the formation of chlorodiphenylphosphine and acetic acid from a reaction between diphenylphosphine oxide and MeCOCl ⁴⁶⁵; $\text{Ph}_2\text{P}(\text{O})\text{H}$ and Ph_2PCl then react further in a stepwise sequence involving tetraphenyldiphosphine and its monoxide, diphenylphosphinic chloride and, ultimately, diphenylphosphinic acid and chlorodiphenylphosphine⁴⁶⁶.

The addition of MeMgI to benzoylethylphenylphosphine oxide affords a mixture of *erythro* and *threo* diastereoisomers of (1-hydroxy-1-phenylethyl)ethylphenylphosphine oxide (336), the proportions of which (7:3) are essentially independent of reaction temperature, and are explicable in terms of a Cram model⁴⁵². The additions of secondary phosphine oxides or sulphides to isothiocyanates requires basic catalysis and probably proceeds through an addition across the $\text{C}=\text{S}$ bond followed by a prototropic shift (Scheme 89)^{453,467}.



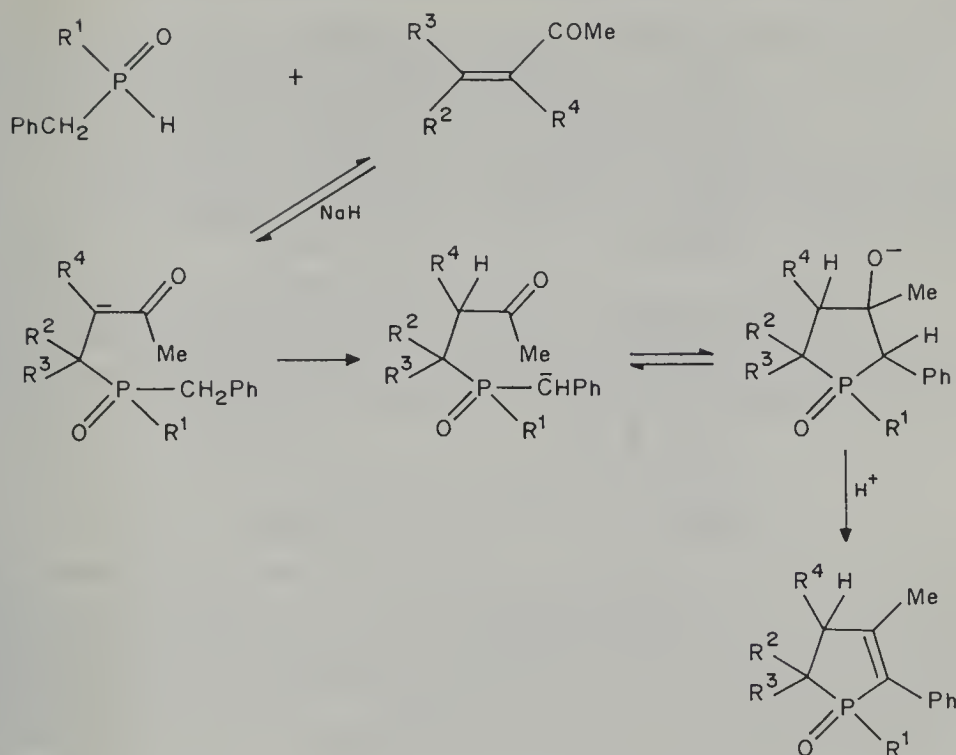
SCHEME 89

The conjugate (Michael) addition of, e.g., diphenylphosphine oxide anion to an unsaturated carbonyl compound is generalized in equation 90, and several examples of these and similar additions have been reported^{181,433,456}. The failure of diphenylphosphine oxide to add in this manner to but-2-enal is rather unexpected; the product is, instead, 2-(diphenylphosphinoyl)pent-3-en-2-ol, formed by normal 1,2-addition⁴⁵⁶. An earlier recorded example of a 1,4-addition to a conjugated carbonyl system is to be found in the ready addition, in the absence of a catalyst, of diphenylphosphine oxide to *p*-benzoquinone; the phenolic product was thought to be diphenyl(2,5-dihydroxyphenyl)phosphine oxide^{426,468,469}. A sequence potentially useful for the synthesis of phospholes or dihydrophospholes (Scheme 90) is initiated by the Michael addition of a secondary benzylphosphine oxide to an unsaturated methyl ketone (compare Scheme 83)⁴⁷⁰.

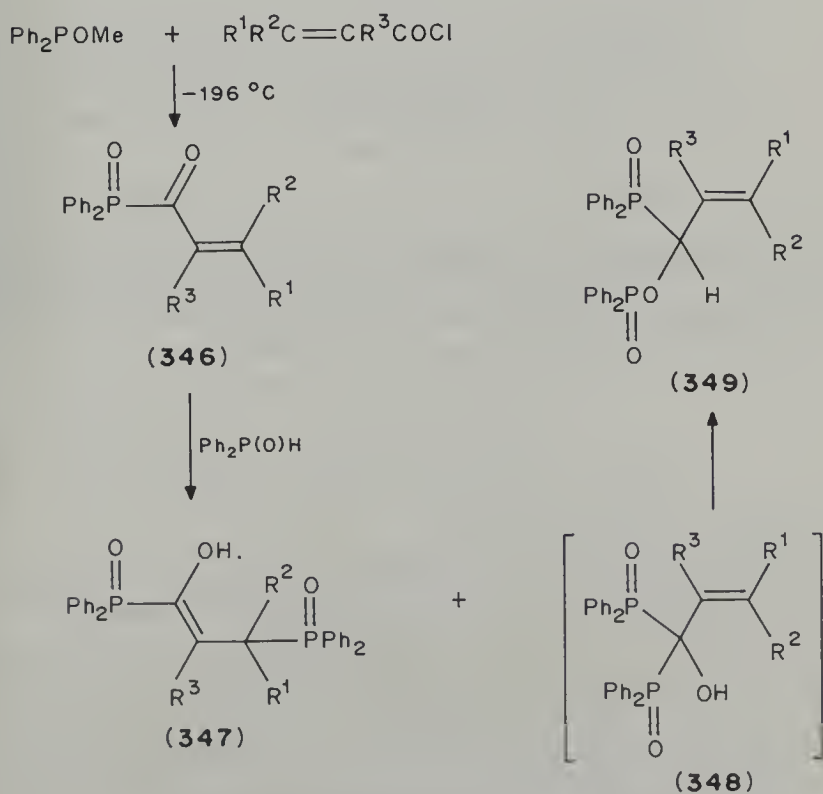


Diphenylphosphine oxide adds conjugatively to the unsaturated ketophosphine oxide 346 to give the enol 347, and also non-conjugatively to give the adduct 348; the latter compounds evidently rearrange to the isolable phosphinic esters 349 (Scheme 91)⁴⁷¹. When the depicted synthesis of the oxides 346 is carried out using diethyl ether as solvent, the products also contain the appropriately *O*-acylated derivatives of 347⁴⁷². The structure of the compounds (*E*)-347 ($\text{R}^1 = \text{R}^2 = \text{Me}$; $\text{R}^3 = \text{H}$) and 349 ($\text{R}^1 = \text{R}^2 = \text{Me}$; $\text{R}^3 = \text{H}$) were confirmed by X-ray crystallographic analysis.

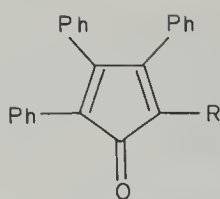
A particularly interesting case of conjugate addition is that of secondary phosphine oxides to cyclopentadienones leading to 1:1 adducts. The mixing of solutions of diphenylphosphine oxide and the cyclopentadienones 350 ($\text{R} = \text{Me}$ or Ph) in the presence of dimethylamine results in a series of colour changes suggestive of reversibility of addition⁴⁷³. The adducts are thought to be formed by nucleophilic attack of phosphorus(III) on the carbon sited adjacent to the carbonyl group, the final site of protonation being dependent on the experimental conditions. The main product from 350 ($\text{R} = \text{Ph}$) was 351. This compound is unstable to heat and to strong bases, being



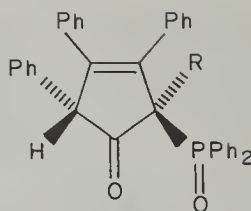
SCHEME 90



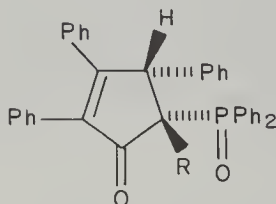
SCHEME 91



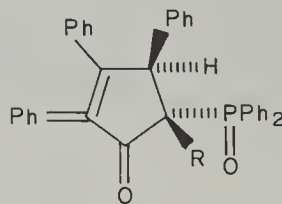
(350)



(351)

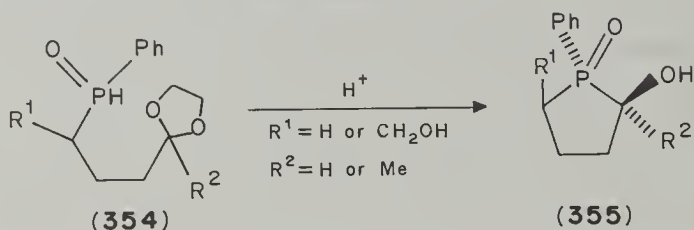


(352)



(353)

rapidly decomposed on alumina and silica; **351** was also the main product when $\text{Ph}_2\text{P}(\text{O})\text{Na}$ reacted with tetraphenylcyclone, or when the addition was carried out in the presence of a very weak base⁴⁷⁴. When the addition was carried out in the presence of HCl , the products included tetraphenyldiphosphine dioxide, the three adducts **352–354** and the *trans*-2,3-dihydro derivative of the starting material. Of the diastereoisomers **352** and **353** ($\text{R} = \text{Me}$ or Ph), the additions proceed with a bias towards **352**. This system thus presents evidence for conjugate 1:4 and 1:6 additions.



(354)

(355)

The addition reactions thus far considered have all been of the intermolecular type. As an example of an intramolecular 1:2 addition, the conversion of **354** into the 2-hydroxyphospholane 1-oxide **355** following liberation of the δ -carbonyl group (by acidolytic removal of the protecting group) may be cited⁴⁷⁵.

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IX. ADDENDA

Some aspects of the chemistry of phosphine chalcogenides have been considered, of necessity, in a recent volume on phosphorus chemistry⁴⁷⁶.

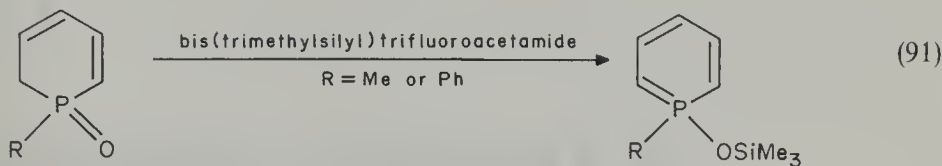
Section II.A.1.

The transfer of phosphoryl oxygen from a phosphine oxide to a metal centre represents a unique approach to the deoxygenation of a phosphine oxide. The transfer occurs when the initial adduct from a tungsten(II) complex, $WCl_2(PMeR_2)_4$ ($R = Me$ or Ph), and the phosphine oxide, e.g. $Ph_2P(O)CH_2CH_2PPh_2$, is heated. The products of the reaction include the complexes $W(O)Cl_2(diphos)(PMeR_2)_2$ and $W(O)Cl_2(PMeR_2)_3$. One serious limitation to the scope of the procedure is the lack of reactivity shown by non-chelating phosphine oxides⁴⁷⁷.

Section II.D.

The treatment of 1,2-dihydrophosphorin 1-oxides with bis(trimethylsilyl)trifluoroacetamide at room temperature results in their rapid and quantitative conversion into cyclic silyoxyphosphoranes, as indicated in equation (91). The reaction proceeds in a like manner with 1,4-dihydro-4-azaphosphorine 1-oxides. More forcing conditions are required with 2,5-dihydrophosphole 1-oxide, and a quaternary phosphonium structure has been tentatively assigned to the product⁴⁷⁸. The high reactivity in the case of the six-membered ring compounds is connected, ultimately, with the generation of the

relatively stabilized phosphabenzene ring⁴⁷⁷, either by rapid initial prototropy and nucleophilic attack on the silylating reagent by OH, or nucleophilic attack on the latter by the phosphoryl group and subsequent rapid loss of H from the adjacent ring CH₂ group.

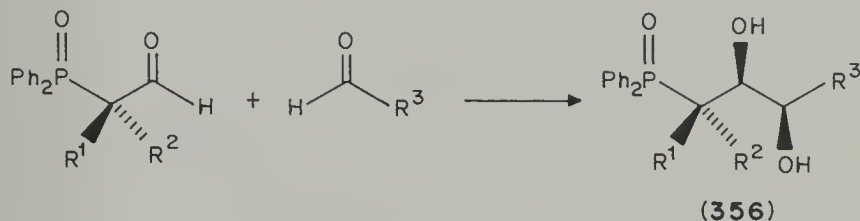


Section II.H.4.

The adduct 217 ($R^1 = \text{H}$, $R^2 = \text{Me}$, $R^3 = \text{Ph}$, $X = \text{O}$), obtained by the addition of dichlorocarbene to 2,5-dihydro-3-methyl-1-phenylphosphole, has been shown by X-ray analysis to have the cyclopropane ring *trans* to the phosphoryl bond⁴⁷⁹.

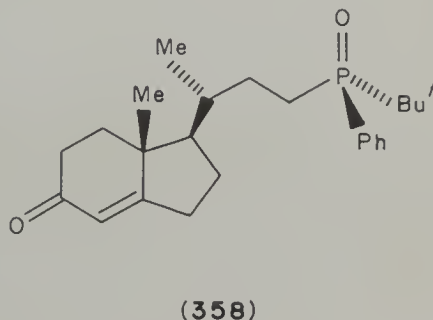
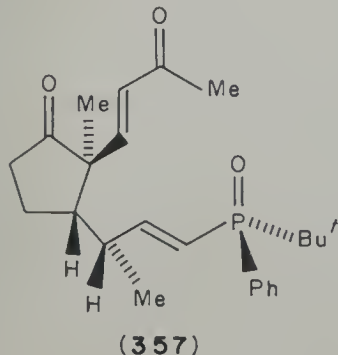
Section IV.B.6.

A cross-coupling reaction between α,α -disubstituted α -diphenylphosphinoyl acet-aldehydes and saturated aldehydes occurs in the presence of a vanadium-containing catalyst formulated as $[\text{V}_2\text{Cl}_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$, to give the *threo* diols (356) with excellent diastereospecificity within the range 7.5:1 to > 99:1 depending on R^1 and R^2 ⁴⁸⁰.



Section V.E.6.

In an application of some of the chemistry indicated in Scheme 59, lithiated (\pm)-(*E*)-but-2-enyl (*tert*-butyl)phenylphosphine oxide has been treated with 2-methylcyclopent-2-enone, and the product acted upon by 4-chlorobut-3-en-2-one, to give the (\pm)-phosphine oxide (357); the Ph and Bu^t groups are sufficiently dissimilar sterically to ensure that the product is obtained in only one diastereoisomeric form. Hydrogenolysis of 357 in the presence of Pd/C gives a tetrahydro derivative which, when acted upon by 2% aqueous KOH solution cyclizes to the (\pm)-phosphine oxide (358), useful in the synthesis of analogues of vitamin D⁴⁸¹.



Coordination chemistry of phosphine chalcogenides and their analytical and catalytic applications

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^aThis chapter is dedicated to my mother, the late Mrs. Vidya Kaur, wife of S. Harnam Singh of Village Gado Majra, Rajpura (Patiala).

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I. INTRODUCTION

A. History, Previous Reviews and Scope

Tertiary phosphine oxides, sulphides, selenides and tellurides constitute an important class of ligands after tertiary phosphines¹⁻¹⁵. The former ligands contain pentavalent phosphorus with O, S, Se or Te as the donor atoms, while the latter type have P as the donor atom.

The first tertiary phosphine oxide complexes, namely $[MX_2L_2]$ ($M = Zn, Cd, Hg$; $X = Cl, I$; $L = Ph_3PO$), were reported in 1906¹⁶, but the first significant studies on the coordination chemistry of tertiary phosphine oxides were carried out only during the late 1950s and 1960s. Similarly, the first complex of a phosphine sulphide, $[(HgCl_2)_2Et_3PS]$, was reported in 1947 by Malatesta¹⁷, but 1960 is often considered as the first year of the coordination chemistry of phosphine chalcogenides when Bannister and Cotton¹⁸ reported a few metal complexes, $[PdCl_2L_2]$ and $[SnCl_4L_2]$ ($L = Ph_3PS$ or Ph_3PSe). The first stable complexes of any phosphine telluride, $[M(CO)_5(TePR_3)]$ ($M = Cr, Mo, W$; $R = Me_3C$), were reported only recently¹⁹.

The coordination chemistry of monotertiary phosphine oxides, sulphides, selenides or tellurides has been extensively studied, particularly of first three types of ligands; corresponding studies with di- or poly-tertiary phosphine oxides and chalcogenides are much fewer. However, multidentate tertiary phosphine derivatives have attracted considerable interest, particularly recently for several reasons. For instance, the anionic derivatives of $\{Ph_2PE\}_2CH_2$ and $\{Ph_2PE\}_3CH$ namely, $\{Ph_2PE\}_2CH^-$ and $\{Ph_2PE\}_3C^-$ ($E = O, S, Se$), and unsymmetrical phosphorus ligands such as $R_2P(E)CH_2PR_2$ and $R_2P(S)(CH_2)_nP(Se)Ph_2$ ($n = 1, 2$) provide an interesting set of ligands whose coordination chemistry is rich from the structural bonding and spectroscopic points of view. The anionic ligands, e.g. $\{Ph_2P(E)\}_2CH^-$, can bind to a metal via (a) methine carbon, (b) C and one E donor atom with a second E donor atom being uncoordinated

or (c) E donor atoms. The free E donor atom [case (b)] can be made to coordinate to another metal ion, forming homo- or hetero-polymetallic complexes. Also, the coordinated and free E donor atoms show exchange behaviour with one another. Similarly, $\{\text{Ph}_2\text{P}(\text{E})\}_3\text{C}^-$ -type ligands form interesting cage compounds such as $[\text{HgClL}]$ ($\text{L} = \{\text{Ph}_2\text{PE}\}_3\text{C}^-$)²⁰. The unsymmetrical ligands mentioned above and also the anionic ligands provide very interesting systems for ^{31}P NMR study.

Tertiary phosphine oxides have been applied in a number of areas. The most notable

TABLE 1. Previous reviews on metal-phosphine oxide, chalcogenide and telluride chemistry

Topic	Year of publication	Ref.
<i>Phosphine oxides</i>		
1 Properties and applications of uranium(IV) and uranium(VI) complexes with phosphines, phosphonium salts, tertiary phosphine oxides and tetracoordinated phosphorus compounds	1968	22
2 Bibliographic revision of the coordination chemistry of phosphine oxides	1976	23
3 Some considerations on coordination compounds of phosphine oxides with lanthanide perchlorates	1976	24
4 Actinide nitrate complexes	1981	25
5 Fluoro complexes of silicon(IV) with oxygen-containing donor ligands	1983	26
6 Transition metal chemistry review, 1981, Part B	1984	27
7 Preparation and stereochemistry of rare earth phosphine oxide complexes	1984	28
8 Coordination compounds of phosphine oxides	1975	29
9 Coordination chemistry of metal ions with bidentate di-tertiary phosphine and arsine dioxides	1979	30
<i>Phosphine sulphides, selenides or tellurides</i>		
10 Interaction of organophosphine oxides, sulphides selenides and tellurides with metal salts and formation of complexes	1971	31
11 Preparation, chemistry and physical properties of phosphine sulphides, selenides and tellurides	1972	32
12 Oxidation and other products from the reaction of thiones and phosphine sulphides with metal salts and halogens	1976	33
13 Phosphine sulphides and their complexes with metals: carbon-13 NMR spectroscopy	1977	34
14 Coordination compounds of metal ions with tertiary phosphine and arsine sulphides or selenides	1978	35
15 Structure and bonding of metal complexes of tertiary phosphine and arsine chalcogenides including analytical, catalytic and other applications of the complexes	1989	21
<i>Extraction area</i>		
16 Solvent extraction properties of di-tertiary phosphine dioxides	1982	36
17 Extraction of mineral acids, actinides and lanthanides by diphosphine dioxides	1986	37
18 Recovery of uranium using di(2-ethylhexyl)phosphoric acid-trioctylphosphine oxide	1987	38
19 Solvent extraction with organophosphines—Commercial and potential applications	1988	39

are liquid-liquid extraction chemistry of metals, reversed-phase chromatography, ion-selective electrodes, extractive metal determinations and catalysis. Analogous studies on phosphine chalcogenides are limited²¹.

Table 1 gives a list of previous reviews on phosphine oxides or chalcogenides. Although the area of phosphine chalcogenides has been well reviewed²¹, a similar recent or authoritative coverage of phosphine oxides could not be found in any commonly available international journals or series. A similar situation prevails for the extraction chemistry, particularly of mono-tertiary phosphine oxides. The work on phosphine tellurides is very limited however.

The coverage of the literature in this review is up to November 5, 1990, based on *Chemical Abstracts* and on leading and available international journals. Efforts have been made to cover almost every significant investigation, although the possibility of a few omissions cannot be ruled out. This review incorporates the complexes formed by the common metal salts, and also by all other metal compounds with anions derived from carboxylic acids, β -diketones, pyrazolones, Schiff bases, thio ligands, etc. Complexes formed by the organometallic moieties including metal carbonyls are also discussed. In brief, the review provides detailed coverage of the coordination chemistry of tertiary phosphine oxides, sulphides, selenides and tellurides, with the incorporation of significant applications of the ligands.

B. Types of Ligands

The ligands whose coordination chemistry is described in this review are essentially tertiary phosphine derivatives. The primary or secondary phosphine oxides or chalcogenides are not included and may form the basis for a future review, although not much work on the coordination chemistry of primary or secondary phosphine oxides has been reported. However, Walther⁴⁰ reviewed the coordination chemistry of secondary phosphine chalcogenides in 1984.

Among the tertiary phosphine oxides and chalcogenides, the ligands having the formula R_3PE (R = alkyl or aryl group with or without one or more substituent; $E = O, S, Se, Te$) are discussed. Thus ligands of the type $(Me_2N)_3PE$ with $P-N$ and not $P-C$ bonds and those of the type $(R'O)R_2PE$, $(R'O)_2RPE$ and $(R'O)_3PE$ having $P-R$ bonds replaced with $P-OR'$ bonds (where R and R' may be the same or different) are mentioned in the review, particularly in the section on extraction chemistry, but their coordination chemistry is again excluded. Otherwise, the review would have become unmanageable. However, future reviews may cover the coordination chemistry of $(R'O)R_2PE$ -type ligands, etc., which has been significantly studied. The same applied to di- and poly-tertiary phosphine oxides and chalcogenides.

Some of the important types of ligands whose coordination chemistry is discussed in this review are as follows:

- (a) R_3PE [$R = Ph, Bu^n$ etc.; $E = O, S, Se$ or Te];
- (b) $Ph_2P(E)(CH_2)_nP(E)Ph_2$ [$n = 1, 2$, etc.; $E = O, S, Se$];
- (c) $\{Ph_2P(O)CH_2\}_2P(O)Ph$, $\{Ph_2P(O)CH_2CH_2\}_2P(O)Ph$;
- (d) *cis*- $Ph_2P(O)CH=CHP(O)Ph_2$;
- (e) $\{Ph_2P(E)\}_2CH^-$, $\{Ph_2P(E)\}_3C^-$;
- (f) $Ph_2P(E)CH_2PR^1R^2$ [$R^1, R^2 = Ph, Ph$, etc.];
- (g) $Ph_2P(S)(CH_2)_nP(Se)Ph_2$ ($n = 1, 2$);
- (h) $\{Ph_2P(E)\}_3CH$.

Ligands having PO substituents in the *ortho* position of the benzene ring and a few

II. TERTIARY PHOSPHINE OXIDES

A. Mono-tertiary Phosphine Oxides

For simplicity, the work reported is divided into sections devoted to transition elements, Main Group elements and alkali and alkaline earth elements.

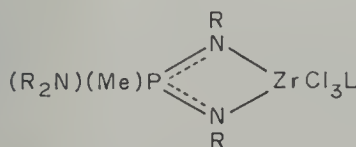
1. Transition elements

Both d- and f-block elements are discussed here.

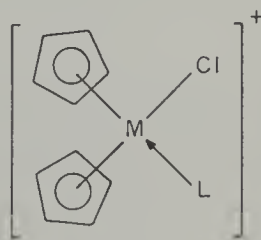
a. Complexes of the scandium Group (IIIB). Scandium(III) and yttrium(III) form several complexes with R_3PO ligands of the type (A) $[ScCl_3L_3]$ and $[ScCl_{6-n}L_n]^{n-3}$ (^{45}Sc NMR study)⁴⁷, (B) $[Sc(NCS)_3L_3]$ ⁴⁸ ($L = Ph_3PO$), (C) $[Sc(TTA)_3L_2]$ ($L = topo, Ph_3PO$)⁴⁹⁻⁵¹, (D) $[MA_3L]$ [$HA = 2,2,6,6$ -tetramethylheptane-3,5-dione (HPVA)^{52,53}, (E) $[M(OR)_3L]$ ($R = 2,6$ -di-*tert*-butyl-4-methylphenoxo, $L = Ph_3PO$)⁵⁴, (F) $[ScL_4(EtOH)_2](ClO_4)_3$ ($L = Me_3PO, Ph_3PO$)^{55,56}, (G) $[YCl_3L_n]$ ($n = 3,4$) and $[YCl_3L_3]$. Me_2CO ($L = Ph_3PO$)⁵⁷. Whereas the formation of complexes A was revealed by ^{45}Sc NMR, the other complexes were formed from direct reaction of a metal salt with ligand. The coordination number of the complexes A–D and G varied from 4, 6 to 8. Finally, the phenoxo complexes $[M(OR)_3L]$ (E)⁵⁴ represent unique examples of four-coordinated compounds with high solubility in hydrocarbons [see Section II.A.1.i for more complexes of yttrium (III)].

b. Complexes of the titanium Group (IVB). Various titanium and zirconium complexes are listed in Table 2. Titanium(IV) formed adducts with 1:1 or 1:2 M:L ratios whereas zirconium(IV) adducts have 1:1, 1:2, 1:4 or 1:6 M:L ratios. Alkoxytitanium(IV) complexes were hygroscopic. Peroxyzirconium(IV) complexes (G) $[ZrO_2Al_n]$ ($n = 1,2$) with chelating bi- or tri-dentate anions are very stable. ^{19}F NMR studies suggested a *cis*-octahedral structure for complexes $[TiF_4L_2]$ ($L = Ph_3PO, Bu^t_3PO$)⁶⁵. The 1:1 adducts $[MCl_4(OPPh_3)]$ are likely to have halogen-bridged dimeric structures.

A 1:1 adduct of Ph_3PO with $\{N,N'$ -bis(trimethylsilyl)diamido- N'' -bis(trimethylsilyl)-*P*-methylphosphonoimidato}-trichlorozirconium(IV) (I)⁸²



(1)



(2)

Organozirconium and-hafnium dimers, $[(\eta^5-cp)_2M(\mu-Cl)]_2(BF_4)_2$ formed complex 2 with Ph_3PO ⁸³. Similarly, $[(\eta^5-cp)_2MCl]I_3$ was obtained from $[(\eta^5-cp)_2M(\mu-Cl)]_2$ and Ph_3PO followed by treatment with excess of iodine.

c. Complexes of the vanadium Group (VB). Reaction of $[V(CO)_6]$ with Ph_3PO did not give a substituted product, but rather an ionic complex, viz. $[VL_4][V(CO)_6]_2$ ⁸⁴, was obtained. Numerous other vanadium complexes have been reported, although an X-ray analysis has only been reported for one complex. The complexes are of the formulations $[VCl_3L_2]$ ($L = R_3PO$; $R = Et, Pr, Cy, Ph$)⁸⁵; $[VCl_4(OPPh_3)]$ ⁵⁸; $[VOX_2(OPPh_3)_2]$ ($X = Cl,$

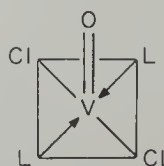
TABLE 2. Complexes of the titanium Group (IVB)

Complex		X	L	Ref.
A	[TiX ₄ L _n]	Cl	Ph ₃ PO(<i>n</i> = 1)	58-61
		F, Cl, Br	R ₃ PO(<i>n</i> = 2) (R = Ph, Bu ⁿ , etc.)	62-65
B	(i) [TiX _m A _{4-m} L ₂] ^a (<i>m</i> = 2,3)	Cl	Ph ₂ P(O)CH=CH ₂	66
		Cl	Ph ₃ PO	67
C	(ii) [TiA ₄ L] ^a	—	Ph ₃ PO	67
			Ph ₃ PO	68, 69
D	(i) [Ti(OR)X ₃ L] ^b (R = Me, Et, ClC ₂ H ₄ , F ₃ C ₂ H ₂ O)	Cl	Ph ₃ PO	70
		NCS	Ph ₃ PO	70
E	(ii) [Ti(OR)X ₃ L ₂] (R = Me, Et)	(i) Cl	Ph ₃ PO(<i>n</i> = 1)	60
		(ii) Cl, NO ₃	R ₃ PO(R = Me, Bu, Bz, Ph) (<i>n</i> = 2)	71-75
F	[ZrOX ₂ L ₂]	Cl, Br, NCS, SeCN, NO ₃	Ph ₃ PO	76, 77
		—	Ph ₃ PO	76
G	(i) [ZrOL ₄ L ₂] (ii) [ZrOL ₄](BPh ₄) ₂ (iii) [ZrOL ₆](ClO ₄) ₂	—	Ph ₃ PO	78
		—	Ph ₃ PO	76
H	(i) [ZrO ₂ AL ₂] ^c (ii) [ZrO ₂ AL] ^d	—	Ph ₃ PO	79
		—	Ph ₃ PO	80
I	[Zr(OAc) _m (SO ₃ F) _{4-m} L _n] (<i>m</i> = 0,2,3)	—	Ph ₃ PO	81
		—	Ph ₃ PO	81

^aHA = 1-naphthol.^bClC₂H₄O = 2-chloroethoxy; F₃C₂H₂O = 2,2,2-trifluoroethoxy.^cH₂A = succinic acid.^dH₂A = pyridine-2,6-dicarboxylic acid and salicylideneaminobenzoic acid.

Br)⁸⁶⁻⁹⁴; [VOCl(OH)(topo)₂]⁹⁵; [VOL_nX₂] (*n* = 2 for X = BPh₄, *n* = 4 for X = ClO₄, L = Ph₃PO)^{90,96}; [VO(acac)₂(OPBu₃)₃]⁹⁷; [V(NO)Cl₂(OPPh₃)₄]⁹³; [V(NO)₂L₄]Br (L = R₃PO; R = Me, Ph)⁹⁸; [V(OR)₃L] (R = ClC₂H₄; L = Ph₃PO)⁹⁹; [V(SO₃CF₃)₃L], [VO(SO₃CF₃)_nL] (*n* = 2, 3; L = Ph₃PO)¹⁰⁰; and [V(SO₃F)₃(OPPh₃)₃]¹⁰¹. The hydroxy complex [VOCl(OH)(topo)₂]⁹⁵ was obtained by an extractive method, whereas the other complexes were obtained by normal direct reactions.

Monomeric vanadyl halide complexes, [VOX₂L₂]⁸⁶⁻⁹⁴, have been well studied. An X-ray study of [VOCl₂(OPPh₃)₂] showed a square-pyramidal structure with *trans*-Ph₃PO ligand (3)⁸⁹. For the other complexes, namely [VOL₄](ClO₄)₂ and VOL₂(BPh₄)₂, square-pyramidal structures are suggested, but need to be confirmed from X-ray analysis, particularly the latter, which would shed light on possible coordination



(3)

by BPh_4 anion^{90,96}. Similarly, in vanadium-alkoxide complexes, $[\text{V}(\text{OR})_3\text{L}]$, bridging by OR groups is suggested⁹⁹. Finally, the SO_3CF_3 groups in $[\text{V}(\text{SO}_3\text{CF}_3)_3\text{L}]$, $[\text{VO}(\text{SO}_3\text{CF}_3)_n\text{L}]$ and $[\text{V}(\text{SO}_3\text{F})_3\text{L}]$ act as chelating agents^{100,101}.

Niobium(V) and tantalum(V) form complexes of the type $[\text{MX}_5\text{L}]$ ($\text{X} = \text{Cl}, \text{Br}; \text{L} = \text{Ph}_3\text{PO}$ ^{60,102-104}; $\text{Ta}, \text{Cl}, \text{BzPh}_2\text{PO}$ ¹⁰²); $[\text{NbOX}_3\text{L}_2]$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}; \text{L} = \text{Ph}_3\text{PO}$)^{102,105-108}; $[\text{NbCl}_4(\text{NO})(\text{MeCN})(\text{OPPh}_3)]$ ¹⁰⁹; $[\text{M}(\text{OR})_2\text{X}_3\text{L}]$ ($\text{X} = \text{Cl}, \text{Br}; \text{R} = \text{Me}, \text{Et}; \text{L} = \text{Ph}_3\text{PO}$)^{110,111}; $[\text{M}(\text{OMe})_5(\text{OPMe}_3)]$ ¹¹²; $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2\text{L}_4]$ ($\text{L} = \text{Ph}_3\text{PO}$)¹¹³; $\text{M}[\text{NbO}(\text{C}_2\text{O}_4)_2\text{L}_2]$ ($\text{M} = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}; \text{L} = \text{Me}_3\text{PO}, \text{Ph}_3\text{PO}$)^{114,115}; $[\text{Me}_2\text{MCl}_3\text{L}]$ ^{116,117}; $[\text{Me}_3\text{MCl}_2\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$)¹¹⁸; $[\text{MeMOC}_2\text{L}_2]$ ($\text{L} = \text{Me}_3\text{PO}, \text{Ph}_3\text{PO}$); and $[\text{MeNbOBr}_2\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$)¹¹⁹. Similarly, a few niobium(III) and niobium(IV) complexes, $[(\eta^5\text{-cp})_2\text{Nb}(\text{PMe}_3)\text{L}]$ (BF_4) and $[(\eta^5\text{-cp})_2\text{NbClL}]$ (BF_4) ($\text{L} = \text{Ph}_3\text{PO}$)¹²⁰, are known.

The complexes $[\text{MX}_5\text{L}]$ and $[\text{NbOX}_3\text{L}_2]$ were obtained from reaction of $[\text{MX}_5]$ or $[\text{NbOX}_3]$ with L. In the reaction of $[\text{NbX}_5]$ with L, the abstraction of oxygen from the ligand takes place, forming $[\text{NbOX}_3\text{L}_2]$ -type complexes. Similarly, the oxygen abstraction phenomenon was also observed when $[\text{MeNbX}_4]$ was reacted with R_3PO ¹¹⁹. Metal-alkoxide complexes, e.g. $[\text{M}(\text{OR})_2\text{X}_3\text{L}]$ ^{110,111}, were obtained by the reaction of $[\text{MX}_5]$ with ROH in the presence of the ligand L. The formation of $[\text{M}(\text{OMe})_5\text{L}]$ was detected in solution by ^1H NMR spectrometry and was in equilibrium:



^{19}F NMR studies revealed the formation of a number of unusual species. For instance, reaction of $[\text{MF}_5]$ with Ph_3PO in CH_2Cl_2 or PhMe gave *cis*- and *trans*- $[\text{MF}_4\text{L}_2]^+\text{F}^-$ and small amounts of the dimers $[\text{M}_2\text{F}_{10}\text{L}]$ ¹²¹⁻¹²³. When acetonitrile was the solvent, only $[\text{MF}_5\text{L}]$ complexes were formed. Similarly, the formation of $[\text{MF}_5\text{L}]$ and also *cis*- and *trans*- $[\text{MF}_4\text{L}_2]\text{F}$ ($\text{L} = \text{Bu}_3\text{PO}$) was observed when the solvent was toluene^{124,125}. Ageing of a solution of *trans*- $[\text{TaF}_4(\text{PBu}_3)_2]\text{F}$ ¹²⁴ gave the same products. The addition of BF_3 led to the disappearance of the above-mentioned species and instead BF_3L , $\text{B}_2\text{F}_6\text{L}$, BF_4^- , etc., were formed¹²⁶. This demonstrates the greater affinity of BF_3 for Bu_3PO than that of $[\text{MF}_5]$ ($\text{M} = \text{Nb}, \text{Ta}$). Mixed halide complex species, namely, two *trans* forms of $[\text{TaF}_3\text{Cl}_2\text{L}]$, *trans*- $[\text{TaE}_2\text{Cl}_3\text{L}]$ and two *cis*-forms of $[\text{TaF}_2\text{Cl}_3\text{L}]$ were detected by ^{19}F NMR in a 1:1:1 solution of TaF_5 , PCl_5 and R_3PO ($\text{R} = \text{Bu}^n, \text{Ph}$) in PhMe ¹²⁷. An increase in the basicity of the ligand shifted the ^{19}F NMR signal to high field when MF_5 was reacted with $(\text{RC}_6\text{H}_4)_3\text{PO}$ and $\text{Me}_2\text{P}(\text{O})(\text{RC}_6\text{H}_4)$ ($\text{R} = \text{H}, p\text{-Me}, \text{MeO}, \text{Cl}, \text{Me}_2\text{N}, m\text{-Cl}, \text{NO}_2, \text{Me}$)¹²⁸⁻¹³⁰.

d. Complexes of the chromium Group (VIB). Various complexes of this group are given in Tables 3-5. Reaction of chromium(II) halides with the ligand L in organic solvents gave moisture- and air-sensitive complexes, $[\text{CrX}_2\text{L}_2]$ ^{131,132}, which on reaction with NO gave the nitrosyl complexes $[\text{Cr}(\text{NO})_2\text{X}_2\text{L}_2]$ ¹³⁵. The bromo complexes $[\text{CrBr}_2\text{L}_2]$ exist in two forms. The green forms of $[\text{CrBr}_2\text{L}_2]$ and $[\text{CrCl}_2\text{L}_2]$ possess halogen-bridged dimeric structures. Formation of $[\text{CrI}_2\text{L}_2(\text{thf})_2]$ ¹³¹ was detected by electronic absorption spectroscopy (Table 3).

The dimeric chromium(II) trifluoroacetate complex $[\text{Cr}_2(\text{O}_2\text{CCF}_3)_4\text{L}_2]$ ($\text{L} = \text{Me}_3\text{PO}$), obtained from $[\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{ether})_2]$ and Me_3PO , showed a normal μ value of 3.06 BM¹³⁶ compared with a value of 0.89 BM for the ether solvate. X-ray analysis showed a dimeric structure (4) with a weak Cr—Cr bond.

The chromium(III) complexes, $[\text{CrX}_3\text{L}_3]$ $[\text{Cr}(\text{O}_2\text{NO})_2\text{L}_2](\text{NO}_3)$, $[\text{CrX}_3\text{L}(\text{bipy})]$ and $[\text{CrL}_4(\text{OCIO}_3)_2](\text{ClO}_4)$ ^{132-134,136,137} are assigned octahedral structures having bidentate NO_3 and unidentate ClO_4 groups. Thiosemicarbazone in $[\text{CrAA}'\text{L}]$ complexes is tridentate¹³⁹ (O, N, S), whereas salen in $[(\text{C}_6\text{F}_5)\text{Cr}(\text{salen})\text{L}]$ is tetradentate¹⁴⁰ (O_2N_2); both of these complexes are octahedral (Table 3).

Reaction of CrO_3 with glycol and R_3PO ($\text{R} = \text{Et}, \text{Ph}$) gave the chromium(V) complexes

TABLE 3. Complexes of chromium

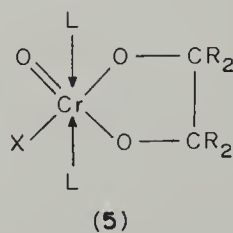
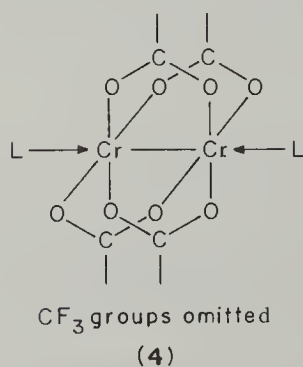
	Complex	X	L	Ref.
A	(i) $[\text{CrX}_2\text{L}_2]$	Cl, Br, I	Ph_3PO	131
			$\text{R}_3\text{PO}(\text{R} = \text{Et, Pr, Cy, Ph})$	132
	(ii) $[\text{CrX}_2(\text{NO})_2\text{L}_2]$	Cl, Br, I	Ph_3PO	135
	(iii) $[\text{Cr}_2\text{X}_4\text{L}_2]$	CF_3COO	Me_3PO	136a
B	(i) $[\text{CrX}_3\text{L}_3]$	Cl, NCS, ClO_4	Ph_3PO	133, 134
		NCS	$\text{R}_3\text{PO}(\text{R} = \text{Et, Bu, Cy})$	132
	(ii) $[\text{CrX}_2\text{L}_2]\text{X}$	NO_3	Ph_3PO	133
	(iii) $[\text{CrX}_3\text{L}(\text{bipy})]$	Cl	Ph_3PO	136b
	(iv) $[\text{CrL}_4\text{X}_2]\text{X}$	ClO_4	Bu_3PO	137
C	$(\text{L}_n\text{H})[\text{CrX}_4(\text{NH}_3)_2]$	NCS	$\text{R}_3\text{PO}(\text{R} = \text{Et, Pr, Bu, Cy, } n = 1, 2)$	138
D	(i) $[\text{CrAA}'\text{L}]^a$	—	Ph_3PO	139
	(ii) $[(\text{C}_6\text{F}_5)\text{Cr}(\text{salen})\text{L}]^b$	—	Ph_3PO	140
	(iii) $[\text{CrOAL}](\text{SO}_3\text{CF}_3)^c$	—	Ph_3PO	141

^a H_2A = salicylaldehyde thiosemicarbazone; HA' = quinolin-8-ol.

^bsalen = *N,N'*-ethylenebis(salicylaldimine).

^c H_2A = 5,5'-dichloro-8,8,8',8'-tetramethylbis(salicylidene)ethylenediamine.

$[\text{Cr}(\text{O})\text{XL}_2(\text{O}_2\text{C}_2\text{R}_4)]$ ($\text{R} = \text{H, Me, X} = \text{Cl}$)¹⁴² with the proposed structure 5. X-ray study of another chromium(V) complex, $[\text{CrOAL}](\text{SO}_3\text{CF}_3)$ ¹⁴¹ (Table 3), showed octahedral geometry with *trans* L and O groups with the Schiff base occupying the equatorial plane. The $(\text{L}_n\text{H})[\text{CrX}_4(\text{NH}_3)_2]$ complexes have hydrogen-bonded L_nH^+ cations with no Cr–ligand interaction. Finally, reaction of the unsymmetrical phosphine ligand $\text{Ph}_2\text{P}(\text{O})\text{CH}(\text{R})\text{PPh}_2$ ($\text{R} = \text{Pr}$) with $[\text{Cr}(\text{CO})_6]$ gave $[\text{Cr}(\text{CO})_4\text{L}]$ with *cis*-octahedral geometry¹⁴³.



A wide variety of molybdenum and tungsten complexes have been reported (Tables 4 and 5). $[\text{MoOX}_3\text{L}_2]$ complexes¹⁵⁰ were obtained from MoX_3 or $\text{K}_3[\text{MoCl}_6]$ and molten Ph_3PO involving oxidation of Mo^{III} to Mo^{V} . Reaction of MoCl_5 with Ph_3PO gave $[\text{MoOCl}_3\text{L}_2]$ and $[\text{MoO}_2\text{Cl}_2\text{L}_2]$ ¹⁵⁷ and when dioxane ($\text{C}_4\text{H}_8\text{O}_2$) was the solvent, $[\text{MoOCl}_3\text{L}(\text{C}_4\text{H}_8\text{O}_2)]$ ¹⁵¹ was obtained. Oxidation of $[\text{M}(\text{CO})_4\text{L}_2]$ and $[\text{M}(\text{CO})_3\text{L}_3]$ ($\text{L} = \text{Ph}_3\text{PO}$) by Cl_2 or Br_2 gave $[\text{MoX}_3\text{L}_2]$ and $[\text{Mo}_2\text{X}_2\text{L}_2]$ complexes¹⁴⁶. Interestingly, reaction of $[\text{MoSCl}_3]$ with Ph_3PO in MeCN gave three products: $[\text{MoOCl}_3\text{L}_2]$, $[\text{MoO}_2\text{Cl}_2\text{L}_2]$ and $[\text{MoO}(\text{S})\text{Cl}_2\text{L}_2]$ ¹⁴⁷. The complex $(\text{HPPH}_3)[\text{WOCl}_4\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$)¹⁶⁷ was obtained by the partial hydrolysis of $[\text{WCl}_4(\text{PhC}\equiv\text{CPh})_2]$ in the presence of Ph_3PO .

TABLE 4. Complexes of molybdenum and tungsten

	Complex	L	Ref.
A	(i) $[\text{MoI}_3\text{L}(\text{PMe}_2\text{Ph})]$	Me_2PhPO	168
	(ii) $[\text{Mo}_2\text{Cl}_6\text{L}_3]$	Ph_3PO	169
	(iii) $[\text{MoCl}_4\text{L}_2]$	Ph_3PO	170
	(iv) $[\text{MoCl}_5\text{L}]$	Ph_3PO	64
	(v) $[\text{WCl}_4(\text{PPh}_3)\text{L}]$	Ph_3PO	171
B	(i) $[\text{MoOX}_3\text{L}_2](\text{X} = \text{Cl}, \text{Br})$	Ph_3PO	144–150
	(ii) $[\text{MoOX}_3\text{L}(\text{C}_4\text{H}_8\text{O}_2)_2]^a$ ($\text{X} = \text{Cl}, \text{Br}$)	Ph_3PO	151, 152
	(iii) $[\text{MoOCl}_3\text{L}]$	Ph_3PO $\text{Et}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{PEt}_2$	153 154
	(iv) $[\text{WOCl}_3\text{L}_2]$	Ph_3PO	155, 156
C	(i) $[\text{MO}_2\text{X}_2\text{L}_2](\text{X} = \text{Cl}, \text{Br})$	Ph_3PO	144, 146, 147, 152 155, 157–161
	$[\text{MoO}_2\text{F}_2\text{L}_2]$	Ph_3PO	158, 162
	(ii) $[\text{MoO}_2(\text{ONO}_2)_2\text{L}_2]$	Ph_3PO	160, 161
	(iii) $[\text{MoO}_2\text{Cl}_2\text{L}(\text{C}_4\text{H}_8\text{O}_2)]^a$	Ph_3PO	152
	(iv) $[\text{MoO}(\text{S})\text{Cl}_2\text{L}_2]$	Ph_3PO	147
	(v) $(\text{Et}_4\text{N})[\text{WO}_2\text{F}_3\text{L}]$	Me_3PO	163
D	(i) $\text{MoOF}_4\text{L}]$	Ph_3PO	164a
	(ii) $[\text{WOX}_4\text{L}_n](\text{X} = \text{F}, \text{Cl})$	$\text{R}_3\text{PO}(n = 1, 2)$ ($\text{R} = \text{Ph}, \text{Bu}^n$, etc.)	106, 164a 165, 166
	(iii) $(\text{HPPH}_3)[\text{WOC}_4\text{L}]$	Ph_3PO	167
E	(i) $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_4\text{L}_2]$	Ph_3PO	172
	(ii) $(\text{L}_n\text{H})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$	Ph_3PO	172
F	(i) $[\text{Mo}(\text{O}_2)_2\text{L}_2](\text{M} = \text{Mo}, \text{W})$	$\text{Ph}_3\text{PO}, \text{Pr}_3^n\text{PO},$ Bu_3^nPO	173–175
	(ii) $[\text{W}(\text{O}_2)_2\text{A}_2\text{L}]^b$	Ph_3PO	176
G	(i) $[\text{MoCl}_4(\text{NO})\text{L}]$	Ph_3PO	177
	(ii) $(\text{Et}_4\text{N})[\text{MoCl}_4(\text{NO})\text{L}]$	$\text{Ph}_2\text{MePO}, \text{Ph}_2\text{EtPO}$	178
	(iii) $[\text{MCl}_3(\text{NO})\text{L}_2](\text{M} = \text{Mo}, \text{W})$	$\text{Ph}_2\text{MePO}, \text{Ph}_2\text{EtPO},$ Ph_3PO	161, 178–179
	(iv) $[\text{MoCl}_3(\text{NO})\text{L}'_2\text{L}]$ ($\text{L}' = \text{PhMe}_2\text{P}, \text{Ph}_2\text{Pr}^n\text{P}$)	$\text{MePh}_2\text{PO}, \text{Ph}_2\text{Pr}^n\text{PO}$	178
	(v) $[\text{M}(\text{NO})_2\text{Cl}_2\text{L}_2]$	$\text{Ph}_3\text{PO}, \text{EtPh}_2\text{PO},$ $\text{Et}_2\text{PhPO}, \text{Cy}_3\text{PO},$ $\text{Ph}_2(\text{R})\text{PO}$ ($\text{R} = \text{neomenthyl}$)	182–184
	(vi) $[\text{Mo}(\text{NO})_2\text{Cl}_2\text{L}_2] \cdot \text{C}_6\text{H}_6$	Ph_3PO	183
	(vii) $[\text{Mo}(\text{NO})_2(\text{OEt})_2\text{L}_2]$	Ph_3PO	185
	(viii) $[\text{Mo}(\text{NO})(\text{S}_2\text{CNR}_2)_2\text{L}]$ ($\text{R} = \text{Me}, \text{Et}$)	Ph_3PO	186
H	(i) $[\text{MoCl}_4(\text{NPR}_3)(\text{OPR}_3)]$	L^c	178, 187, 188
	(ii) $[\text{MoCl}_2(=\text{NH})\text{OL}_2]$	$\text{R}_3\text{PO} (\text{R}_3 = \text{Ph}_3, \text{Ph}_2\text{Et},$ $\text{PhEt}_2)$	189
	(iii) $[\text{WCl}_3(=\text{NPh})\text{L}_2]$	Me_3PO	190
	(iv) $[\text{WCl}_4(=\text{NC}_2\text{Cl}_5)]\text{L}$	Ph_3PO	151
	(v) $[\text{MoCl}_3(=\text{N})\text{L}_n]$	$\text{Ph}_3\text{PO} (n = 1, 2)$	191–193
	(vi) $[\text{MoCl}_3(\text{NH}_2)\text{L}_2]\text{Cl}$	$\text{Ph}_2\text{MePO}, \text{Ph}_2\text{EtPO}$	178

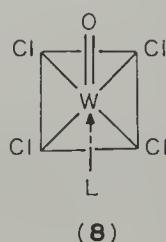
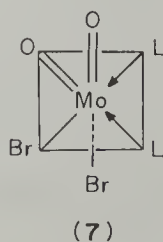
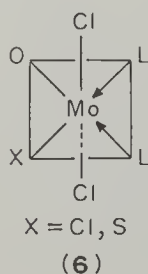
^a $\text{C}_4\text{H}_8\text{O}_2 = \text{dioxane}.$ ^b $\text{HA} = S\text{-benzylidithiocarbazate}.$ ^c $\text{PR}_3 = \text{Ph}_2\text{PrP}, \text{Ph}_3\text{P}, \text{Ph}_2\text{EtP}, \text{PhMe}_2\text{P}, \text{Et}_3\text{P}, \frac{1}{2}\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2.$

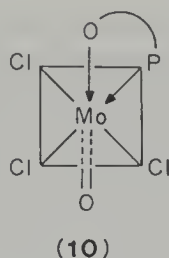
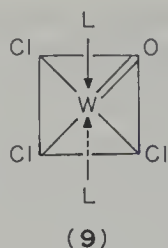
TABLE 5. Complexes of organo-molybdenum and tungsten

	Complex	L	Ref.
A.	(i) $cis-[M(CO)_4L_n]$ (M = Mo, W)	$Ph_3PO (n = 2)$	194,195
		$Ph_2P(O)CH(R)PPh_2$ (R = Pr)	143
	(ii) $[W(CO)_5L]$	$Ph_2P(O)CH_2CH_2PPh_2$	196
		$R_3PO (R = Me, Ph)$	197
		$Ph_2P(O)NPh_3$	197
		$Ph_2P(O)(CHPh_3)$	198
	(iii) $[M(CO)_3L_3]$	$Ph_3PO, Bu_3PO,$ $EtPh_2PO, Et_2PhPO,$ Et_3PO	195,199–201
	(iv) $[M(CO)_nCl_2L_2]$ (M = Mo, W; $n = 2, 3$).	Ph_3PO	202,203
	(v) $[M(CO)_3I_2L_2]$	Ph_3PO	204
B.	(i) $[M(CO)_3L(OH)]_2$	$Ph_3PO, Ph_2EtPO,$ $PhEt_2PO, Et_3PO$	205
		Ph_3PO, Et_3PO	205
C.	$[M(S_2CNEt_2)_2(CO)_2L]$	Ph_3PO	206
D.	(i) $[Mo(Me)(cp)(NO)XL]$ (X = Cl, Br)	Ph_3PO	207
	(ii) $[MeWCl_3EL] (E = O, S, Se)$	Ph_3PO	208
	(iii) $[Me_3CC \equiv WCl_3L]$ $[Me_3CC \equiv WCl_3LL']$ ($L' = Et_3P$)	Et_3PO	209
	(iv) $[MeWOCl_3L]$	R_3PO	210
	(iv) $[MeWO_2ClL]$ $[MeWO_2ClL_2]$	R_3PO Ph_3PO	210 211

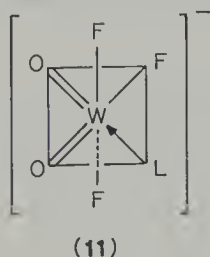
and CH_2Cl_2 . From solution-phase ^{19}F NMR studies, several type of species such as $trans-[WOF_4L]$, $[MO_2F_2L_2]$, $[M_2O_2F_8L]$ and $[W_2O_2F_9L_2]^-$ (M = Mo, W; L = Ph_3PO)^{164b} were detected, depending on the ligand concentration. The complex species $[MoOCl_3L]$ and $[MoOCl_4]^-$ also reacted with Ph_3PO to form $[MoOCl_3L_2]$ and $[MoOCl_4L]^-$ and it was found that the ability to form the complexes varied in the order $C_5H_5N > Ph_3PO \approx H_2O > thf$.

X-ray studies of $[MoOCl_3L_2]$ ¹⁴⁷, $[MoO(S)Cl_2L_2]$ ¹⁴⁷, $cis-[MoCl_2BrL_2]$ ¹⁵⁸, $(HPPH_3)-[WOCl_4L]$ ¹⁶⁷, $[WOCl_3L_2]$ ¹⁵⁶ (L = Ph_3PO) and $[MoOCl_3L]$ [L = $Et_2P(O)CH_2CH_2PEt_2]$ ¹⁵⁴ have shown them all to involve octahedral structures (6–10). The moiety MO_2^{2+} is non-linear^{158,160–163}, unlike UO_2^{2+} , which is linear (cf. Section II.A.1.j)





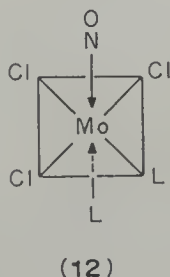
NMR studies (^1H , ^{19}F and ^{31}P) of $(\text{Et}_4\text{N})[\text{WO}_2\text{F}_3\text{L}]$ ($\text{L} = \text{Me}_3\text{PO}$)¹⁶³ reveal a *trans*-labilizing affect of the oxo ligand as the fluoride ligand in the *trans* position is readily dissociated. Structure 11 is suggested as the basis of NMR data. Further, the *trans* influence of the ligand L on the $\text{W}=\text{O}$ bond ($\text{L} = \text{R}_3\text{PO}$) in WOF_4L varies as $\text{R} = \text{amyl} > n\text{-butyl} > n\text{-octyl} > \text{phenyl}$ ¹⁶⁶.



Only a few diperoxo complexes $[\text{MO}(\text{O}_2)_2\text{L}_2]$ are known (Table 4). The activation energies for the loss of dioxygen from the dry or the dissolved complexes are independent of whether the ligand is a phosphine oxide or an arsine oxide. In the tungsten thiocarbazate complex $[\text{W}(\text{O}_2)_2\text{A}_2\text{L}]$ ¹⁷⁶, the *S*-benzylthiocarbazate $\text{H}_2\text{NN}=\text{C}(\text{SH})\text{SCH}_2\text{Ph}$ acts as a uni-negative bidentate ligand. Further X-ray analyses of peroxo complexes would be very valuable.

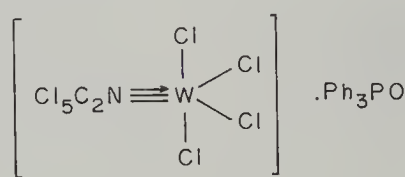
The nitrosyl complexes G (Table 4) have been obtained by a number of different routes: (a) $[\text{MoCl}_3(\text{NO})\text{L}_2]$ from $[\text{MoCl}_3(\text{NO})]$ and Ph_3PO ¹⁸¹ or from $[\text{MoO}_2(\text{OAc})_4]$ and NOCl in the presence of Ph_3PO ¹⁶¹; (b) $[\text{Mo}(\text{NO})_2\text{Cl}_2\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$)¹⁷¹ by reductive nitrosation of $[\text{MoCl}_5]$ with NO in the presence of Ph_3P in CH_2Cl_2 ; (c) $[\text{Mo}(\text{NO})_2(\text{OEt})_2\text{L}]$ from $[\text{Mo}(\text{NO})_2(\text{MeNO}_2)_4](\text{BF}_4)_2$, Ph_3PO and MOEt ($\text{M} = \text{Li}, \text{Na}$) in MeNO_2 ¹⁸⁵; and (d) $[\text{W}(\text{NO})_2\text{Cl}_2\text{L}_2]$ from $[\text{W}(\text{NO})_2\text{Cl}_2]$ and L ¹⁸⁴. Reaction of $[\text{Mo}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2\text{L}]$ with NOBr gave $[\text{Mo}(\text{NO})_2\text{Br}_2\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$)¹⁸⁶.

It was noted that the coordinated NO in these complexes¹⁷⁸ showed no sign of reactivity with nucleophiles or electrophiles. Further, on heating $[\text{M}(\text{NO})_2\text{Cl}_2\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$)¹⁸³ at 300°C , $[\text{MOC}_2\text{L}_2]$ and N_2O were formed, implying an intramolecular redox reaction in the halonitrosyl complexes. Nitric oxide oxidizes M^{II} to the M^{IV} state. In the complex $[\text{Mo}(\text{NO})_2\text{Cl}_2\text{L}_2]$, C_6H_6 ¹⁸³, benzene was lost at 100°C . No X-ray study has been reported for any nitrosyl complex. However, for $[\text{MCl}_3(\text{NO})\text{L}_2]$, structure 12 was suggested^{161,178,180,181}.

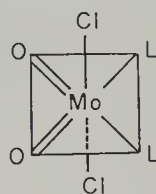


Complexes H(i-vi) (Table 4) represent respectively phosphineiminato, imido, phenylimido pentachloroethylimido, nitrido and amido complexes of molybdenum and tungsten. Phosphineimine derivatives H(i) were formed by the oxidation of $[\text{MoCl}_4\text{L}_2]$ ($\text{L} = \text{Ph}_2\text{PrP}$) by sulphonylazide, $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{N}_3$ ^{178,188}. Similarly, the reaction of $[\text{MoOCl}_3]$ with Me_3SiN_3 in thf and R_3PO gave the imido complexes $[\text{MoCl}_2(\text{NH})\text{O}(\text{OPR}_3)_2]$ ¹⁸⁹. The nitrido complexes $[\text{MoCl}_3(\text{:N})\text{L}_n]$ were obtained by the addition of Ph_3PO to a molybdenum(II) nitrido species formed from $[\text{MoCl}_4\text{L}_2]$ ($\text{L} = \text{thf}, \text{MeCN}$) and trimethylsilylazide¹⁹². An interesting observation is that reductive hydrolysis of $[\text{MoCl}_3(\text{:N})\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$)¹⁹³ gave 11–13% NH_3 under mild conditions whereas only a trace of NH_3 was formed from hydrolysis of $(\text{Et}_4\text{N})[\text{Mo}(\text{N})\text{Cl}_4]$ ¹⁹³.

ESR and magnetic moment studies suggest that the phosphineiminato complexes are mononuclear¹⁸⁷. Complex H(iv) showed no ligand coordination (13). For complexes H(i, iii, v, vi), octahedral structures have been suggested. The X-ray analysis of $[\text{MoCl}_2(=\text{NH})\text{O}(\text{OEtPh}_2)_2]$ ¹⁸⁹ has shown a distorted octahedral structure, 14.



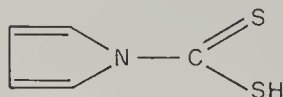
(13)



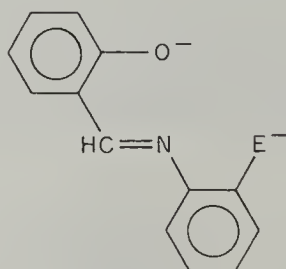
(14)

Dimeric molybdenum(II) acetate, $[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4]$, forms a 1:2 adduct with Me_3PO ²¹². NMR studies (¹⁹F, ³¹P) reveal extensive dissociation of the adduct $[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4\text{L}_2]$. Other analogous molybdenum(II) derivatives, $[\text{Mo}_2\text{A}_2(\text{OAc})_2\text{L}]$ $\{\text{L} = \text{Ph}_3\text{PO}, \text{HA} = \text{pyrrolyldithiocarboxylate (15)}\}$ ²¹³ and $[\text{Mo}_2(\text{S}_2\text{PET}_2)(\text{OAc})_3\text{L}](\text{BF}_4)$ ($\text{L} = \text{Et}_3\text{PO}$)²¹³, are also known.

A tridentate dianionic Schiff base 16 gave a complex $[\text{MoO}_2\text{AL}]$ ($\text{L} = \text{Ph}_3\text{PO}$; $\text{H}_2\text{A} = 16$)²¹⁴ with a *cis*- MoO_2 moiety (17). An oxotungsten(V) dimer with unusual stereochemistry, namely, *anti*-bis (μ -isobutylthiolato)bis{oxodichloro(triphenylphosphine oxide)}tungsten(V), *anti*- $[\text{Cl}_2(\text{O})\text{LW}(\mu\text{-SBu}^t)_2\text{W}(\text{O})\text{Cl}_2\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$) has been reported²¹⁵. The molecule has a crystallographically imposed centre of symmetry and therefore possesses the very unusual feature of terminal oxo ligands lying in an *anti* disposition to one another. Similarly, an adduct of Ph_3PO with the arylazomolybdenum cluster is also known²¹⁶.

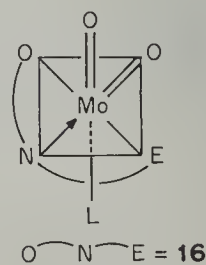


(15)



E = O, S

(16)



(17)

Table 5 contains a number of organo-molybdenum and-tungsten complexes obtained by different methods of preparation. $[\text{M}(\text{CO})_4\text{L}_4]$ complexes were obtained by the

reaction of $[\text{M}(\text{CO})_6]$ with Ph_3PO in toluene¹⁹⁴. The monosubstituted complex, $[\text{W}(\text{CO})_5\text{L}]$ [$\text{L} = \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{PPh}_2$] was obtained from the filtrate of the reaction of $[\text{W}(\text{CO})_5(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$ with $\text{K}_2[\text{PtCl}_4]$ ¹⁹⁶. However, this complex has no $\text{W}-\text{O}$ bond; the ligand binds through the Ph_2P group. Trisubstituted $[\text{M}(\text{CO})_3\text{L}_3]$ complexes were obtained either from the reaction of $[(\text{C}_7\text{H}_8)\text{Mo}(\text{CO})_3]$ with Ph_3PO under a nitrogen atmosphere or from $[\text{M}(\text{CO})_6]$ and L in a light petroleum–benzene mixture²⁰¹. The reaction of $[\text{Mo}_2(\text{CO})_6(\text{OH})_3\text{H}_3]$ with Ph_3PO gave $[\text{Mo}(\text{CO})_3\text{L}_3]$ ²⁰⁰. These trisubstituted derivatives, being unstable to air, must be kept under a nitrogen atmosphere^{195,199}.

The X-ray analysis of octahedral $[\text{W}(\text{CO})_5\text{L}]$ [$\text{L} = \text{Ph}_2\text{P}(\text{O})(\text{CHPPh}_3)$] showed that the $\text{W}-\text{C}$ bond *trans* to $\text{W}-\text{O}$ was shorter than the other $\text{W}-\text{C}$ bonds (1.949 Å versus average 2.025 Å)¹⁹⁸. Similarly, an X-ray study of $[\text{W}(\text{CO})_5\text{L}]$ [$\text{L} = \text{Ph}_2\text{P}(\text{O})\text{NPPH}_3$] showed $\text{W}-\text{O}$ rather than $\text{W}-\text{P}$ bonding¹⁹⁷. Kinetic studies of ligand substitution (L by CO) revealed the high *trans* effect of $\text{Ph}_2\text{P}(\text{O})\text{NPPH}_3$, which was similar to an anionic oxygen donor atom.

Thermal studies of $[\text{M}(\text{CO})_n\text{Cl}_2\text{L}_2]$ ^{202,203} have shown that the carbonyl groups are lost in one step, unlike the multiple steps required for the ligand L . Tungsten complexes showed higher thermal stability than molybdenum complexes. Further, the stability based on the nature of the ligand was found to decrease in the order $\text{L} = \text{Ph}_3\text{P} > \text{Ph}_3\text{As} > \text{Ph}_3\text{PO}$ ²⁰². Methyltungsten(V) complexes were stable²¹⁰ and ^1H NMR revealed that the Me group was never *trans* to a $\text{W}=\text{E}$ bond ($\text{E} = \text{O}, \text{S}, \text{Se}$)²⁰⁸. ^{95}Mo and ^{183}W NMR studies of $[\text{M}(\text{S}_2\text{CNEt}_2)_2(\text{CO})_2\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$) showed that the adduct participates in a dynamic equilibrium with $[\text{Mo}(\text{S}_2\text{CNEt}_2)(\text{CO})_2]$ ²⁰⁶.

e. Complexes of the manganese Group (VIIB). Several complexes of manganese(II) are known, some of which are listed in Table 6. Although the complexes can be formed by direct reaction of a phosphine oxide with a manganese salt, the higher thermodynamic stability of the $\text{Mn}-\text{O}$ bond results in phosphine complexes such as $[\text{MnX}_2(\text{PR}_3)]$ ($\text{R}_3 = \text{Et}_3, \text{Me}_3, \text{Ph}_3$) being converted into the corresponding phosphine oxide complexes in the presence of air^{240,241}. The existence of a dioxygen complex, namely $[\text{MnBr}_2(\text{O}_2)\text{L}]$ ($\text{L} = \text{Me}_3\text{P}$), was detected in the solid state, but it undergoes irreversible transformation to $[\text{MnBr}_2(\text{OPMe}_3)]$ ²⁴². Interestingly, the air oxidation of an ethanol

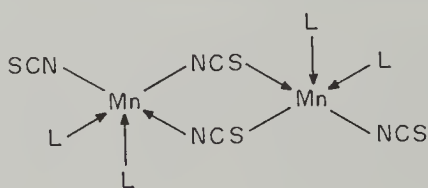
TABLE 6. Complexes of the manganese Group (VIIB)

Complex		L	Ref.
A	(i) $[\text{MnX}_2\text{L}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3$)	$\text{Ph}_3\text{PO}, p\text{-Tol}_3\text{PO},$ $\text{Bz}_2\text{PhPO}, \text{Bz}_3\text{PO}$	217–226
	(ii) $[\text{MnCl}_2\text{L}_2]$	$\text{RCH}_2\text{P}(\text{O})\text{Me}_2$ ($\text{R} = \text{Cl}, \text{MeO}, \text{PhO}$)	227
B	(i) $[\text{MnL}_4](\text{ClO}_4)_2$	Bu_3PO	137
	(ii) $[\text{MnI}_2\text{L}_4]$	Ph_3PO	228
	(iii) $[\text{MnL}_4(\text{OCIO}_3)](\text{ClO}_4)$	$\text{Ph}_3\text{PO}, \text{Ph}_2\text{MePO}, \text{Me}_3\text{PO}$	228–232
	(iv) $[\text{MnL}_4(\text{BF}_4)_2]$	Ph_3PO	233
	(v) $[\text{MnL}_5](\text{BF}_4)_2$	Me_3PO	234
	(vi) $[\text{MnL}_n(\text{NCS})_2]$	$\text{Ph}_3\text{PO}, \text{PhMe}_2\text{PO}, \text{Pr}_3\text{PO},$ $\text{Bu}_3\text{PO}(n = 1-4)$	228, 235–237
	(vii) $[\text{MnA}_2\text{L}_2]^a$	Bu_3PO	238
	(viii) $[\text{Mn}(\text{NCSe})_2\text{L}_4]$	Ph_3PO	239

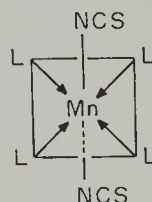
^aHA = Hhfa.

solution of $[\text{Mn}(\text{CNR})_4\text{L}_2][\text{MnBr}]$ ($\text{R} = \text{Bu}^t$, $\text{L} = \text{Me}_2\text{PhP}$) gave a mixed phosphine-phosphine oxide complex, $[\text{Mn}(\text{CNR})_4\text{L}_2][\text{MnBr}_3\text{L}']_2$ ($\text{L}' = \text{Me}_2\text{PhPO}$) with a *trans*-octahedral cation and a tetrahedral anion²⁴³. X-ray diffraction showed distorted tetrahedral structures for $[\text{MnX}_2(\text{OPPh}_3)_2]$ ($\text{X} = \text{Cl}, \text{I}$) complexes^{217,223}.

X-ray analyses of $[\text{Mn}(\text{NCS})_2\text{L}_2]$ (**18**) and $[\text{Mn}(\text{NCS})_2\text{L}_4]$ (**19**) ($\text{L} = \text{Ph}_3\text{PO}$) have been reported²³⁵. In complex **18** the geometry about manganese is square-pyramidal with Ph_3PO in the axial positions. Complex **19** has a *trans*-octahedral structure. The magnetic moments suggest polymeric structures for $[\text{MnL}_n(\text{NCS})_2]$ ($n = 1, 3$) complexes with antiferromagnetic interactions. An interesting feature of thiocyanate complexes of manganese(II) is that when $n = 3$ or 4, the complexes react reversibly with SO_2 forming $[\text{MnL}_n(\text{NCS})_2(\text{SO}_2)]$, whereas there is no similar reaction for $n = 1$ or 2. Dilute solutions of $[\text{MnL}_4(\text{NCS})_2(\text{SO}_2)]$ effect the air oxidation of SO_2 to H_2SO_4 , which was confirmed by X-ray analysis of the isolated product, $(\text{Ph}_3\text{PO})(\text{Ph}_3\text{POH})(\text{HSO}_4)$.



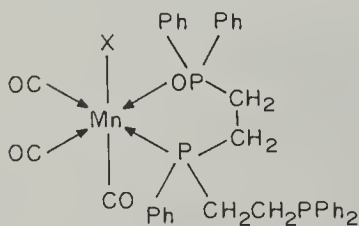
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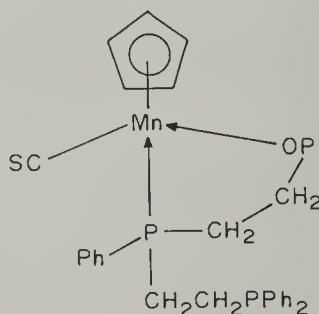
(19)

Like the thiocyanate complexes, manganese(II) iodide also formed an SO_2 complex, *trans*- $[\text{MnL}_4(\text{SO}_2)_2]\text{I}_2$ ($\text{L} = \text{Ph}_3\text{PO}$), with $\text{Mn}-\text{OSO}$ bonding²⁴⁴. It displayed reversible loss of SO_2 to form $[\text{MnL}_4(\text{SO}_2)\text{I}_2]$.

Ultraviolet irradiation of an equimolar mixture of $[(\text{cp})\text{Mn}(\text{CO})_3]$ and $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ in benzene or cyclohexane gave $[(\text{cp})\text{Mn}(\text{CO})_2\text{L}]$ ($\text{L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$)²⁴⁵. Similarly, oxidation of $[\text{Mn}(\text{CO})_3\text{LX}]$ ($\text{X} = \text{Br}, \text{I}$; $\text{L} = \text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$) with O_2 gave *fac*- $[\text{Mn}(\text{CO})_3\text{L}'\text{X}]$ (**20**)²⁴⁶; photochemical reaction of $[(\text{cp})\text{Mn}(\text{CS})\text{L}]$ with ozone gave $[(\text{cp})\text{Mn}(\text{CS})\text{L}']$ (**21**)²⁴⁷. It may be noted that $\text{Mn}-\text{CS}$ bonding is stronger than $\text{Mn}-\text{CO}$ bonding since reaction of $[(\text{cp})\text{Mn}(\text{CO})_2(\text{CS})]$ with L gave $[(\text{cp})\text{Mn}(\text{CS})\text{L}]$ and not $[(\text{cp})\text{Mn}(\text{CO})\text{L}]$.



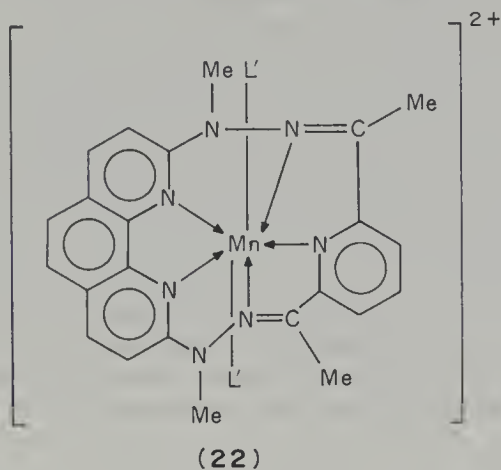
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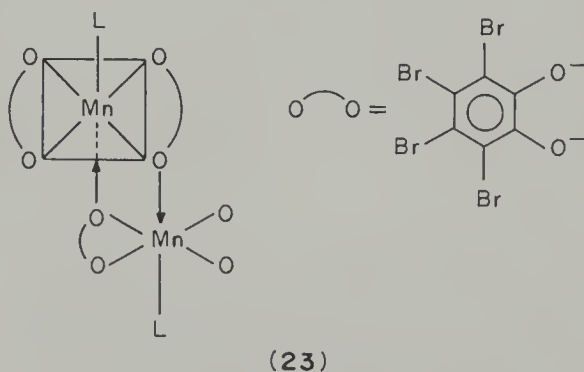
(21)

Salt-like mixed-valence complexes of manganese carbonyls of the type $[\text{Mn}^{\text{II}}\text{LX}][\text{cis-Mn}^{\text{I}}(\text{CO})_4\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} = \text{Ph}_3\text{PO}$) have been reported^{248,249}. X-ray study of the iodo complex showed a square-pyramidal cation and a *cis*-octahedral anion²⁴⁸. In $[\text{Mn}(\text{CO})_5(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]$ there was no coordination by the PO group^{250a} but the possibility of intermolecular coordination by PO when a carbonyl group is replaced

promises further activity in this type of complex. A seven-coordinate complex, $[\text{MnLL}'_2](\text{BF}_4)_2$ (**22**) ($\text{L}' = \text{Ph}_3\text{PO}$; $\text{L} =$ quinquedentate macrocycle), has been reported^{250b}.



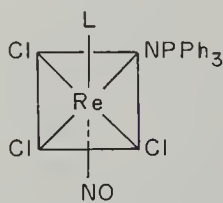
Manganese(III) chloride and nitrate form air-stable 1:2 and 1:3 complexes, MnX_3L_n ($\text{X} = \text{Cl}$, $n = 2, 3$; $\text{X} = \text{NO}_3$, $n = 2$)²⁵¹⁻⁵³. Similarly, the manganese(III) tetrabromocatecholate complex $\text{K}[\text{Mn}(\text{Br}_4\text{C}_6\text{O}_2)_2\text{L}]\text{H}_2\text{O} \cdot \text{Me}_2\text{CO}$ ($\text{L} = \text{Ph}_3\text{PO}$) has been reported²⁵⁴ and X-ray analysis showed that the dianion $\text{Br}_4\text{C}_6\text{O}_2^{2-}$ chelates to manganese in a planar arrangement with Ph_3PO bonded to the apical site. The sixth site of the octahedron is occupied by the catecholate oxygen of an adjacent complex, leading to the formation of a dimer (23).



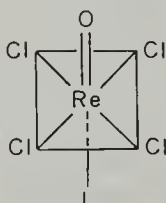
Rhenium(III) halides gave $[\text{ReX}_3\text{L}_n]$ ($\text{X} = \text{Cl}, \text{Br}$; $n = 2, 3$; $\text{L} = \text{Ph}_3\text{PO}$) complexes²⁵⁵⁻²⁵⁷. The complexes with $\text{Re}=\text{O}$ bonds, such as $[\text{ReOX}_3\text{L}_2]$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{Ph}_3\text{PO}$, Et_2PhPO , Ph_2EtPO) and $[\text{ReO}(\text{OEt})\text{Cl}_2\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$)^{258,259} were obtained via inner-sphere oxidation of the coordinated phosphine ligands on thermal heating. However, direct reaction of K_2ReOX_5 with Ph_3PO also gave the same products^{259a}. Air oxidation of the monomers $[\text{ReX}_3(\text{NCR})(\text{PPh}_3)_2]$ ($\text{R} = \text{alkyl}$; $\text{X} = \text{Cl}, \text{Br}$) gave $[\text{ReOCl}_3\text{L}(\text{Ph}_3\text{P})]$ ($\text{L} = \text{Ph}_3\text{PO}$)²⁶⁰. Similarly, reaction of the dimer $[\text{ReCl}_3(\text{NR})(\text{OPPh}_3)]_2$ ($\text{L} = \text{Ph}_3\text{P}$; $\text{R} = \text{arylimido}$) with O_2 gave $[\text{ReCl}_3(\text{ONR})(\text{OPPh}_3)]$ and $[\text{ReCl}_4(\text{NR})(\text{OPPh}_3)]$ as a side-product. It required milder conditions than those needed for the reaction of $[\text{ReCl}_3(\text{NR})(\text{PPh}_3)_2]$ with O_2 ($\text{R} = p\text{-MeC}_6\text{H}_4$)²⁶¹.

The complexes $(\text{HPPH}_3)_2[\text{ReX}_6]$ ($\text{X} = \text{Cl}, \text{Br}$) lost HX on heating and formed $[\text{ReCl}_4\text{L}_2]$ and $(\text{HPPH}_3)[\text{ReLBr}_5]$ ($\text{L} = \text{Ph}_3\text{PO}$)^{262a}. Similarly, $[\text{ReCl}_4\text{L}_2]$ was formed on heating a solution of $(\text{HPPH}_3)_2[\text{ReCl}_6]$ in acetone in the presence of HCl ^{262b}. Further,

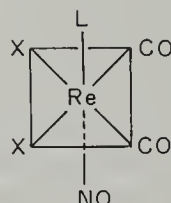
the inner-sphere oxidation of $[\text{Re}(\text{PPhEt}_2)_4\text{Cl}_4]$ gave $[\text{Re}(\text{OPPhEt}_2)_2\text{Cl}_4]^{263}$. Several other rhenium complexes reported are as follows: (a) $[\text{ReCl}_3(\text{OPPh}_3)_2(\text{ONAr})]$ formed by the oxidation of $[\text{ReCl}_3(\text{PPh}_3)_2(\text{ArN})]$ with O_2 in boiling toluene²⁶⁴; (b) $[\text{ReCl}_3(\text{NO})(\text{NPPh}_3)(\text{OPPh}_3)]$ (**24**) prepared by the reaction of $[\text{ReCl}_3(\text{NO})_2]$ and Ph_3PO in CH_2Cl_2 (³¹P, X-ray)²⁶⁵; (c) $[(\text{cp})\text{Re}(\text{NO})(\text{PPh}_3)(\text{OPPh}_3)]\text{X}$ ($\text{X} = \text{BF}_4, \text{PF}_6$) formed from $[(\text{cp})\text{Re}(\text{NO})(\text{PPh}_3)\text{ClCH}_2\text{Cl}]^+$ and Ph_3PO (here CH_2Cl_2 is coordinated)²⁶⁶; (d) $[\text{ReOCl}_4(\text{OPPh}_3)]$ (**25**) formed from $[\text{ReOCl}_4]$ and Ph_3PO ²⁶⁷; (e) $[\text{Re}(\text{CO})_3\text{L}_2\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)²⁶⁸; (f) $[\text{Re}(\text{CO})_2(\text{NO})\text{X}_2(\text{OPPh}_3)]$ ($\text{X} = \text{Br}, \text{I}$) (**26**) prepared by the reaction of the halogen-bridged dimer, $[\text{Re}(\text{CO})_2(\text{NO})\text{X}_2]_2$ and Ph_3PO ²⁶⁹; (g) $[\text{Re}_2\text{X}_4(\text{OAc})_2\text{L}_2]$ ($\text{X} = \text{Cl}, \text{Br}$) (**27**) formed from $[\text{ReX}_2(\text{OAc})]$, H_2O and Ph_3PO ²⁷⁰⁻²⁷²; (h) deoxygenation of $[\text{MeReO}_3]$ with Ph_3P in the presence of Me_3SiCl gave a 70% yield of the oxygen bridged complex, $[\text{MeCl}_2\text{L}(\text{O})\text{Re}-\text{O}-\text{Re}(\text{O})\text{Cl}_2\text{LMe}]$ (**28**)^{273a}, and (i) $[\text{ReCl}_4(\text{NO})(\text{OPPh}_3)(\text{NO})(\text{MeCN})]$ was prepared from $[\text{ReCl}_5(\text{NO})]$ and Ph_3P in acetonitrile^{273b}. Structures **24** and **28** were confirmed by X-ray analysis^{265,273}. The Re—N and P—N bond distances suggested double bond character in the Re—NPPh₃ bond in **24**. The Re—Re bond in **27** is fairly strong and dissociates above 320 °C. No loss of ligand takes place below 300 °C.



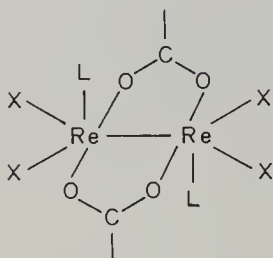
(24)



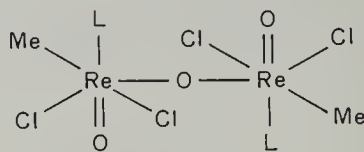
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(26)



(27)



(28)

f. Complexes of the iron, cobalt and nickel Group (VIII)

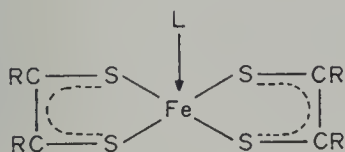
i. Iron sub-Group. Several iron(II) complexes have been reported; $[\text{FeLX}_2]$ ($\text{X} = \text{Br}, \text{SO}_3\text{F}, \text{L} = \text{Ph}_3\text{PO}$)^{63,274}; $[\text{FeL}_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}; \text{L} = \text{Ph}_3\text{PO}, \text{Me}_2\text{P}(\text{O})\text{CH}_2\text{R}$ ($\text{R} = \text{Cl}, \text{OMe}, \text{OPh}$), HFA , Bu_3PO , SO_4 , Ph_3PO)^{227,238,275,276}; $[\text{FeL}_4\text{X}]\text{X}$ ($\text{X} = \text{OCIO}_3$; $\text{L} = \text{Me}_3\text{PO}, \text{Ph}_3\text{PO}, \text{MePh}_2\text{PO}$)^{231,232}; $[\text{FeL}_4\text{X}_2]$ ($\text{X} = \text{OCIO}_3$; $\text{L} = \text{Bu}_3\text{PO}, \text{Ph}_3\text{PO}, \text{BF}_4, \text{I}_3, \text{Ph}_3\text{PO}$)^{137,230,233,277-279}; $[\text{FeL}_n][\text{Fe}_2(\text{CO})_8]$ ($n = 2, 3$; $\text{L} = \text{Ph}_3\text{PO}$)²⁸⁰. A number of complexes have been obtained indirectly: $[\text{Fe}(\text{OPPh}_3)_4](\text{ClO}_4)_2$ was obtained from the reaction of iron(III) perchlorate with Ph_3P , which involved reduction of Fe^{III} to Fe^{II} and oxidation of Ph_3P to Ph_3PO ²⁷⁹; similarly, $[\text{Fe}(\text{OPPh}_3)_4(\text{I}_3)_2]$ was obtained²⁷⁸ from the reaction of either as iron(II) or an iron(III) salt with iodide ions and Ph_3P in the presence of O_2 .

X-ray studies have not been reported for any of the above complexes. However, based on Mössbauer studies, distorted tetrahedral structures were suggested for the complexes

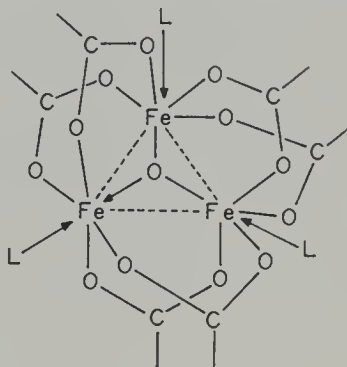
$[\text{FeL}_2\text{X}_2]^{275}$. For complexes $[\text{FeL}_4\text{X}]\text{X}$ square-pyramidal and for $[\text{FeL}_2(\text{hfa})_2]$ ($\text{L} = \text{Bu}_3\text{PO}$)²³⁸ and $[\text{FeL}_4\text{X}_2]^{137,230,233,277-279}$ octahedral structures have been suggested. A thermal study of $[\text{FeL}_2(\text{hfa})_2]^{238}$ revealed that the chelate ring formed by the hfa^- anion is stable in the gas phase. However, hfa^- changes to the mononuclear mode and at higher temperatures loss of Bu_3PO takes place with rupture of the $\text{M}-\text{O}$ bonds. From Mössbauer studies²⁷⁵, an interesting observation is that Cl^- and Ph_3PO have a similar ligand field effect.

Two iron(II)-phthalocyanine(HPc) complexes, $[\text{Fe}(\text{Pc})(\text{CO})\text{L}]$ and $[\text{Fe}(\text{Pc})(\text{L}_2)]$ ($\text{L} = \text{Ph}_3\text{PO}$), are known²⁸¹. The replacement of Ph_3PO in $[\text{Fe}(\text{Pc})(\text{Ph}_3\text{PO})_2]$ by CO led to a decrease in the quadrupole splitting and isomer shift values, consistent with a decrease in the main axial bond distances on carbonylation and a concomitant increase in s-electron density along the z-axis. Similarly, a high-spin iron(III)-porphyrin complex, $[\text{FeL}_2(\text{A})](\text{ClO}_4)(\text{H}_2\text{A} = \text{tetraphenylporphyrin})$, has been reported; it exhibited certain properties similar to those of aquomethaemoglobin²⁸².

A few square-pyramidal iron-dithiolene complexes such as $(\text{Bu}_4\text{N})[\text{Fe}(\text{S}_2\text{C}_2\text{R}_2)_2\text{L}]$ ($\text{R} = \text{CN}, \text{CF}_3$; $\text{L} = \text{Ph}_3\text{PO}$; **29**) have been reported²⁸³⁻²⁸⁵. Reaction of $(\text{Bu}_4\text{N})_2[\text{Fe}_2(\text{S}_2\text{C}_2\text{R}_2)_4]$ with Ph_3P in the presence of O_2 gave the same product. Here activation of molecular oxygen by the iron-dithiolene complex takes place. In contrast, cobalt-dithiolene complexes were not effective in activating the oxidation of Ph_3P .

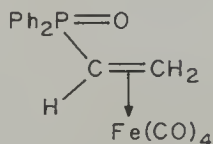


(29)



(30)

A trinuclear mixed-valence complex, $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2(\text{O})(\text{O}_2\text{CCF}_3)_6(\text{OPPh}_3)_3]$ (**30**) is known²⁸⁶; Mössbauer study revealed octahedral environments about each iron centre. An oxo complex, $[\text{L}_4\text{FeOOFeL}_4 \cdot 2\text{H}_2\text{O}]\text{X}_4$ ($\text{X} = \text{ClO}_4$; $\text{L} = \text{Ph}_3\text{PO}$) was obtained when $[\text{FeL}_4](\text{ClO}_4)_2$ was reacted with H_2O_2 , *m*- $\text{C}_6\text{H}_4\text{C}(\text{O})\text{OOH}$ or other oxidants in acetonitrile²⁸⁷. The same material was obtained by the addition of H_2O_2 and two molar hydroxide ions to $[\text{FeL}_4](\text{ClO}_4)_3$ in acetonitrile. Reaction of vinyl-diphenylphosphine oxide with $[\text{Fe}_3(\text{CO})_{12}]$ did not give substituted products like those formed with Ph_3P ; instead, a π -bonded complex (**31**) was obtained³¹⁵.



(31)

Several other complexes of iron(III) are known: $[\text{FeCl}_3\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁶⁰, $[\text{FeX}_3\text{L}_2]$ $\{\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{NCS}; \text{L} = \text{Ph}_3\text{PO}, \text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CH}_2, \text{Bz}_2\text{PhPO}, \text{Bz}_3\text{PO}\}^{66,289-292}$,

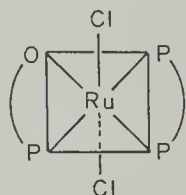
$[\text{FeL}_4](\text{ClO}_4)_3$ ($\text{L} = \text{Ph}_3\text{PO}$, Me_3PO , Bz_2PhPO , Bz_3PO)^{229,232,292,293}, $[\text{Fe}(\text{NCS})_3\text{L}_3]$ ($\text{L} = \text{Ph}_3\text{PO}$, Cy_3PO , Bu_3PO)²⁹⁴, $[\text{Fe}(\text{NCS})_3(\text{OPPh}_3)_2]$ ²⁹¹, $[(\text{FeCl}_2\text{L})_2\text{O}]$ ($\text{L} = \text{Ph}_3\text{PO}$)²⁹⁵, $[\text{Fe}(\text{OR})_3\text{L}]$ ($\text{R} = \text{Me}_3\text{Si}$, ClCHCH_2 , Cl_3CCH_2 ; $\text{L} = \text{Ph}_3\text{PO}$)²⁹⁶⁻²⁹⁹, $[\text{Fe}(\text{NCS})_3\text{L}_2(\text{HgCl}_2)_3]$ ³⁰⁰ and $[\text{Fe}(\text{NO}_3)_2\text{XL}_2]$ ($\text{X} = \text{Cl}$, I ; $\text{L} = \text{Ph}_3\text{PO}$)³⁰¹.

In general, these complexes were obtained by the direct reaction of the metal salt with the ligand, but some complexes were obtained indirectly. For example, reaction of FeBr_2 with Ph_3P in acetonitrile at 80°C in the presence of O_2 gave $[\text{FeBr}_3(\text{OPPh}_3)_2]$ ²⁸⁹. Similarly, oxidation of iron with Ph_3PO and CCl_4 in MeCOEt gave $[\text{Fe}(\text{Ph}_3\text{PO})_2\text{Cl}_3]$ ²⁹⁰. Passing O_2 through a solution or suspension of FeCl_2 , FeSO_4 , etc., or iron powder in acetonitrile containing KCl or HCl , etc., in the presence of Ph_3P gave $[\text{FeX}_3(\text{OPPh}_3)_2]$ ($\text{X} = \text{Cl}$, Br , NCS)^{302,303}.

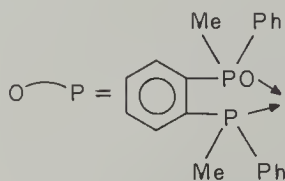
The binuclear complex $[(\text{FeCl}_2\text{L})_2\text{O}]$ ($\text{L} = \text{Ph}_3\text{PO}$)²⁹⁵ was obtained from the reaction of either $[\text{FeCl}_2(\text{OPPh}_3)_2]$ or $[\text{FeCl}_2(\text{PPh}_3)_2]$ with O_2 in benzene²⁹⁵. Mixed anion complexes, $[\text{Fe}(\text{NO}_3)_2\text{XL}_2]$ ³⁰¹ were obtained from the reaction of $[\text{Fe}(\text{NO}_3)_2\text{X}]_2$ ($\text{X} = \text{Cl}$, I) with PPh_3 and O_2 or Ph_3PO ; these represent the first examples of transfer of 'O' from NO_3 to Ph_3P in cyclohexane³⁰¹. X-ray analysis for $\text{X} = \text{Cl}$ has shown that the NO_3^- is asymmetrically bonded³⁰¹. The reaction of $[\text{Fe}(\text{NCS})_3(\text{OPPh}_3)_2]$ with HgCl_2 gave $[\text{Fe}(\text{NCS})_3(\text{OPPh}_3)_2(\text{HgCl}_2)_3]$ involving an $\text{Fe}-\text{NCS}-\text{Hg}$ linkage. Each of the three NCS groups bonds to an HgCl_2 molecule³⁰⁰.

Iron(III) halide complexes, $[\text{FeX}_3\text{L}_2]$ ($\text{X} = \text{Cl}$, Br ; $\text{L} = \text{Ph}_3\text{PO}$, etc.), have been shown to exist as ionic complexes, $[\text{FeL}_4\text{X}_2][\text{FeX}_4]$, with a *trans*-octahedral cation and a tetrahedral anion^{291,292,304}, as confirmed by X-ray analysis³⁰⁴ of $[\text{FeCl}_2(\text{OPPh}_3)_4][\text{FeCl}_4]$.

Reaction of $[\text{Ru}(\text{CO})_4\text{X}_2]$ with Ph_3PO formed monosubstituted octahedral complexes, $[\text{Ru}(\text{CO})_3\text{X}_2\text{L}]$ ³⁰⁵. Inner-sphere oxidation of the coordinated Ph_3P in $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ gave $[\text{Ru}(\text{OPPh}_3)_3\text{Cl}_2]$ ³⁰⁶. Some mixed-ligand complexes of ruthenium(II) that have been reported are $[\text{RuCl}_2\text{LL}']$ ($\text{L} = o\text{-C}_6\text{H}_4\{\text{PMePh}\}_2$; $\text{L}' = o\text{-C}_6\text{H}_4\{\text{PMePh}\}\{\text{OPMePh}\}$)³⁰⁷, $[\text{Ru}(\text{NO}_3)_3(\text{NO})(\text{OPPh}_3)(\text{PPh}_3)]$ ³⁰⁸ and $[(\text{bipy})(\text{py})\text{Ru}(\text{OPPh}_3)]^{2+}$ ³⁰⁹. X-ray analysis of $[\text{RuCl}_2\text{LL}']$ has shown a *trans*-octahedral geometry³⁰⁷ with an unusually short $\text{Ru}-\text{P}$ distance *trans* to O (2.219 versus 2.310–2.346 Å for $\text{Ru}-\text{P}$ *trans* to one another (32a). In the bipyridyl complex, transfer of oxygen from $[(\text{bipy})_2(\text{py})\text{RuO}]^{2+}$ to Ph_3P takes place³⁰⁹. In the nitrosyl complex $[\text{Ru}(\text{NO})(\text{NO}_2)_2\text{L}_2(\text{OH})]$ ($\text{L} = n\text{-Bu}_3\text{PO}$)³¹⁰, L lies *trans* to NO and the *trans* effect of L decreases in the order $\text{L}-\text{Bu}_3\text{PO} > \text{py} > \text{NH}_3 > \text{H}_2\text{O}$. A mixed-valence complex, $[\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}(\mu\text{-OAc})_4(\text{OPPh}_3)_2](\text{BF}_4)_2$ was obtained from the reaction of $[\text{Ru}_2(\mu\text{-OAc})_4(\text{thf})\text{BF}_4]$ and Ph_3PO ^{311a}. Other mixed-valence complexes that have been reported include $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{OPR}_3)_2](\text{PF}_6)_2$ ($\text{R} = \text{H}$, F , Cl , etc.). X-ray analysis of $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{OPPh}_3)_2]$ has shown a dimeric structure (32b) with $\text{Ru}-\text{Ru}$ bonding and Ph_3PO in the terminal positions^{311b}.



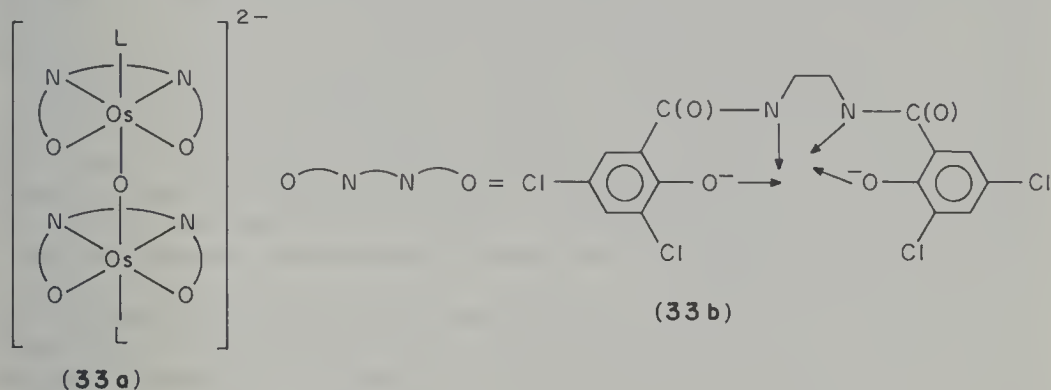
(32a)



(32b)

Reduction of $[\text{Os}(\text{OEP})\text{O}_2]$ by Ph_3P in CH_2Cl_2 gave $[\text{Os}(\text{OEP})\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$, $\text{H}_2\text{OEP} = \text{octaethylporphyrin}$)³¹². An X-ray study has shown a *trans*-octahedral structure with normal $\text{Os}-\text{O}$ (from Ph_3PO) bonding (2.036 Å). Similarly, *cis* and *trans*

isomers of $[\text{Os}(\text{bipy})_2\text{L}_2]^{2+}$ ³¹³ and $[\text{Os}(\eta^4\text{-CHBA-DCB})\text{L}]$ $\{\text{L} = \text{Ph}_3\text{PO}, \text{H}_4\text{CHBA-DCB} = 1,2\text{-bis}(3,5\text{-dichloro-2-hydroxybenzamido})\text{-4,5-dichlorobenzene}\}$ ³¹⁴ have been reported. In the latter complex, the *trans* isomer contains planar amido-N-ligands and the *cis-α*-isomer contains non-planar amido-N-ligands. Finally, treatment of $\text{K}_2[\text{OsO}_2(\text{OH})_4]$ with $[2\text{-OH-3,5-Cl}_2\text{C}_6\text{H}_2\text{CONHCH}_2]_2$ in methanol followed by reduction with Ph_3P in thf gave complex **33**³¹⁵.



ii. Cobalt sub-Group. Table 7 contains a number of complexes of cobalt(II) halides (or other anions). Generally, the complexes involve 1:2 metal: ligand ratios. A few 1:4 complexes, *trans*- $[\text{CoL}_4\text{X}_2]$ ($\text{X} = \text{Cl}, \text{ONO}_2$; $\text{L} = \text{R}_3\text{PO}$; $\text{R} = \text{Bu}^n, \text{CH}_2\text{OH}$) are also known²³⁴. A number of different routes have been reported for their preparation: (a) direct reaction of metal salt with a ligand; (b) reaction of a metal salt with a phosphine oxide ligand in the molten state, e.g. $[\text{CoCl}_2(\text{OPPh}_3)_2]$ ^{351,352}; (c) autoxidation of cobalt(II)-alkylphosphine complexes, $[\text{CoX}_2\text{L}_2]$ ($\text{L} = \text{Et}_3\text{P}$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} = \text{Ph}_3\text{PO}$, $\text{X} = \text{Cl}$ in an organic solvent³⁴⁷; (d) inner-sphere oxidation of the complexes using H_2O_2 , e.g. $[\text{CoBr}_2(\text{PPh}_3)_2]$ ³⁴⁸, or by thermal heating, e.g. $[\text{Co}(\text{PPhR}_2)_2\text{X}_2]$ $[\text{Co}(\text{PPh}_2\text{R})_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{R} = \text{Et}, \text{Pr}, \text{Bu}$)³⁴⁹ and $[\text{Co}(\text{PPh}_3)_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)³⁵⁰; (e) oxidation of

TABLE 7. Complexes of the cobalt sub-Group

Complex	X	L	Ref.
A $[\text{CoX}_2\text{L}_2]$	Cl, Br, I, NCS, NO_3 Cl, I, NCS	L^a RPh_2PO^b	73, 230, 234, 316–336 337
B $[\text{CoX}_2\text{L}(\text{PPh}_3)]$	Cl, Br, I, NCS	Ph_3PO	326, 328, 338–341
C $[\text{CoX}_2\text{L}_n]$	(i) $(\text{NC})_2\text{CC}(\text{O})\text{NH}_2^c$, $\text{NCNC}(\text{O})\text{NH}_2^d$ (ii) hfa (iii) tta (iv) CN	$\text{Ph}_3\text{PO}(n = 2)$ $\text{Bu}_3\text{PO}(n = 2)$ $\text{R}_3\text{PO}(n = 1)$ $\text{Me}_3\text{PO}(n = 1)$ $\text{R}_3\text{PO}(\text{R} = \text{Et}, \text{Bu}, \text{Ph}; n = 0.5)$	341 238, 342 343 344 344
	(v) SO_3CF_3	$\text{Bu}_3\text{PO}, \text{Ph}_3\text{PO}$ $(n = 4-6)$	\propto 345
	(vi) $\text{CF}_3\text{CH}_2\text{O}$	$\text{Ph}_3\text{PO}(n = 1)$	346
D $[\text{CoClXL}]$	$\text{CF}_3\text{CH}_2\text{O}$	Ph_3PO	346

^a $\text{L} = \text{Me}_3\text{PO}, \text{Et}_3\text{PO}, \text{Pr}_3\text{PO}, \text{Bu}_3\text{PO}, \text{Ph}_3\text{PO}, \text{Cy}_3\text{PO}, (p\text{-MeC}_6\text{H}_4)_3\text{PO}, \text{Bz}_3\text{PO}.$

^b $\text{R} = 2\text{-pyridylmethyl}.$

^cCarbamylidicyanomethanide.

^dCarbamylcyanamide.

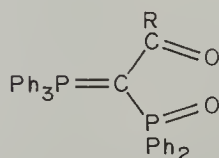
cobalt metal with Ph_3PO in a mixture of CCl_4 and MeCOEt , e.g. preparation of $[\text{CoCl}_2(\text{OPPh}_3)_2]^{290}$; and (f) replacement of Ph_3P from its complexes of Ph_3PO , e.g. $[\text{CoX}_2(\text{OPPh}_3)_2]$ obtained from $[\text{CoX}_2(\text{PPh}_3)_2]$ and Ph_3PO ($\text{X} = \text{I}, \text{NCS}$)^{338,340}. Routes b–f are less common, although interest persists in route d.

X-ray analyses of $[\text{CoCl}_2(\text{OPMe}_3)_2]^{319}$ and $[\text{Co}(\text{O}_2\text{NO})_2\text{L}_2]$ ($\text{L} = \text{Me}_3\text{PO}, \text{Ph}_3\text{PO}$)^{353,354a} have shown them to involve distorted tetrahedral and *trans*-octahedral structures, respectively. The angles at oxygen, i.e. P—O—Co lie between 133 and 140° ^{353a}. A nitro complex, $[\text{CoL}_2(\text{NO}_2)_2]$ ($\text{L} = \text{Ph}_3\text{PO}$), presumably has a similar structure³⁵⁵. Powder X-ray data have been reported for some cobalt(II) complexes, viz. $[\text{CoCl}_2\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}, \text{BzPh}_2\text{PO}, \text{Bz}_2\text{PhPO}, \text{Bz}_3\text{PO}$)^{320,328} and $[\text{Co}(\text{NCS})_2\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}, \text{Ph}_2\text{BzPO}$)³⁵⁶. The nitrate complexes $[\text{M}(\text{O}_2\text{NO})_2(\text{OPPh}_3)_2]$ ($\text{M} = \text{Co}, \text{Zn}$) are isomorphous³⁵⁷. The single-crystal ESR and polarized electronic spectra of $[\text{CoCl}_2(\text{OPPh}_3)_2]$ have shown highly distorted tetrahedral geometry about the cobalt centre (g values: $g_1 = 5.67, g_2 = 3.59$ and $g_3 = 2.16$)³¹⁸. The X-ray analysis of $[\text{CoCl}_2\text{L}_2]$ $\{\text{L} = \text{Ph}_2\text{P}(\text{O})\text{py}, \text{py} = 2\text{-pyridyl}\}$ has shown a distorted octahedral structure with ligand L chelating via O and N ^{354b}.

A 3:4 and 1:1 complex of cobalt(II), viz. $[\text{CoL}_2\text{X}]_2[\text{CoX}_4]$ $\{\text{X} = \text{Cl}, \text{Br}; \text{L} = \text{Me}_2\text{NCH}_2\text{P}(\text{O})\text{Ph}_2\}$ and $[\text{Co}(\text{LH})\text{Cl}_3]$ $\{\text{LH}^+ = \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{N}^+\text{Me}_2(\text{H})\}$, have also been reported³⁵⁸. The cation $[\text{CoL}_2\text{X}]^+$ is 5-coordinate and the anion tetrahedral. The latter complex was obtained from CoCl_2 and $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{NMe}_2$ and the origin of the protonation of NMe_2 is not known. $[\text{CoCl}_3(\text{LH})]$ has a tetrahedral structure with LH coordinating via its PO group. Reaction of CoCl_2 with $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{NMe}_2$ in the presence of HCl gave $[(\text{LH})_2\text{CoCl}_4]$. Similarly, $[\text{Co}(\text{NCS})_2\text{L}_2]$ $\{\text{L} = \text{Me}_2\text{N}(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2; n = 1, 2\}$ are also known. For $n = 1$ a distorted octahedral structure and for $n = 2$ tetrahedral geometry have been suggested. In the latter complex there was no coordination by PO groups³⁵⁸.

The mixed-ligand complexes $[\text{CoX}_2\text{LL}']$ (Table 7) were obtained from the reaction of $[\text{CoX}_2(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$) and Ph_3PO . The lability of the Co—PPh_3 bond was high for $\text{X} = \text{NCS}$. Complexes C and D (Table 7) have been poorly studied so only a few comments can be made. Thermal studies on $[\text{Co}(\text{hfa})_2(\text{OPBu}_3)_2]^{238,342}$ have shown that it is stable in the gas phase. Before decomposition on heating, the anion hfa first changes from the bidentate to the monodentate form. In the solution phase three forms of the hfa complex were identified³⁴².

The interaction of CoCl_2 with L ($\text{L} = \text{Ph}_3\text{PO}, \text{Ph}_2\text{Bu}^n\text{PO}, \text{topo}, \text{etc.}$) was studied in solution phase^{227,359–363}. Although normally the complexes formed had a 1:2 stoichiometry, complexes with other stoichiometries, viz. 1:1, 1:3 and 1:4, were also formed in some cases, for example in the CoCl_2 –*topo* system^{360,364}. Some other observations that have been noted include the following: (a) Co—O bonds were more covalent when R was alkyl than when R was an aryl group^{359,362,363}; (b) the ligand-field effects of various ligands were similar³⁵⁹; and (c) the complex-forming tendency in different solvents was in the order $\text{MeNO}_2 > (\text{thf} + \text{CCl}_4) > \text{acetate ester} > \text{BuOH} > \text{Me}_2\text{CO} > \text{MeCN}$. Finally, the formation of $[\text{CoLCl}_2]$ ($\text{L} = \mathbf{34}$) was also established from solution-phase studies³⁶⁵.

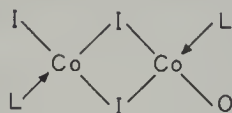


(34)

Cobalt(II) perchlorate and fluoroborate also form several complexes of the type $[\text{CoL}_4](\text{ClO}_4)_2$ ($\text{L} = \text{Bz}_3\text{PO}, \text{Bz}_2\text{PhPO}, \text{BzPh}_2\text{PO}, \text{Bu}_3\text{PO}, \text{Ph}_3\text{PO}$)^{137,327,331,334},

$[\text{CoL}_4](\text{BF}_4)_2$ ($\text{L} = \text{R}_3\text{PO}$; $\text{R} = \text{Et}, \text{Pr}, \text{Bu}$)²³⁴, $[\text{CoL}_6](\text{ClO}_4)_2$ ($\text{L} = \text{Cy}_3\text{PO}$)^{229,230}, $[\text{CoL}_4\text{X}_2]$ ($\text{L} = \text{Ph}_3\text{PO}, \text{BF}_4, \text{Me}_3\text{PO}, \text{Ph}_3\text{PO}$ ^{230,232,233,366} ($p\text{-Me}_2\text{NC}_6\text{H}_4$)₃ PO ; $\text{X} = \text{ClO}_4$ ²²⁹) and $[\text{CoL}_4\text{X}]\text{X}$ ($\text{X} = \text{BF}_4, \text{ClO}_4$; $\text{L} = \text{Me}_3\text{PO}, \text{MePh}_2\text{PO}$)^{231,234}. The complexes $[\text{CoL}_4]^{2+}$, $[\text{CoL}_4\text{X}]^+$ and $[\text{CoL}_4\text{X}_2]$ have been assigned tetrahedral, square-pyramidal and octahedral geometries respectively, but an X-ray study is needed to confirm coordination by either the BF_4^- or ClO_4^- anions. Reaction of $[\text{Co}(\text{PMe}_3)_4](\text{Ph}_4\text{B})_2$ in acetonitrile gave $[\text{Co}(\text{NCCH}_3)_2(\text{OPMe}_3)_4](\text{Ph}_4\text{B})_2$ and its X-ray analysis showed a *trans*-octahedral cation³⁶⁷. An intermediate $[\text{Co}(\text{PMe}_3)_4(\text{O}_2)](\text{Ph}_4\text{B})_2$ was also detected.

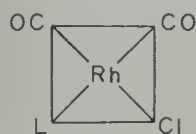
Dimeric cobalt(II) complexes, $[\text{Co}_2\text{I}_4\text{L}_2] \cdot 2\text{C}_6\text{H}_6$ ($\text{L} = \text{Ph}_3\text{PO}$) and $[\text{Co}_2(\text{CO})_6(\text{R}^1\text{R}^2\text{P}(\text{O})(\text{C}\equiv\text{CR}^3))]^+$ ($\text{R}^1 = \text{R}^2 = \text{Ph}$; $\text{R}^3 = \text{Me}_3\text{C}, \text{Ph}$)^{368,369} have been reported. The iodo complex was obtained from CoI_2 and Ph_3PO in O_2 -free benzene. The same product was obtained from the reaction of the phosphine complex $[\text{CoI}_4(\text{PPh}_3)_2]$ with Ph_3PO . X-ray analysis of the iodo complex confirmed the dimeric structure **35** with C_6H_6 molecules lying in the lattice. There is antiferromagnetic coupling between the cobalt centres³⁶⁸. In the alkynephosphine oxide complexes, there is $\text{Co}-\text{O}$ bonding and the alkyne groups are uncoordinated. Similarly, complexes of the type $[\text{Co}(\text{OPBu}_3)_4][\text{Co}(\text{CO})_4]_2$, $[\text{Co}(\text{OPMe}_3)_6][\text{Co}(\text{CO})_4]_2$ ³⁷⁰ and $[\text{Co}_4(\text{SPh})_6\text{Cl}_2(\text{PPh}_3)(\text{OPPh}_3)]$ ³⁷¹ have been reported. X-ray analysis of the Ph_3PO complex³⁷¹ showed that the $\text{Co}_4\text{S}_6\text{Cl}_2$ core is that of a nearly regular Co_4 tetrahedron inscribed in an irregular octahedron of bridging sulphur atoms, resulting in an adamantane-type cage. Cobalt(III) complexes, $[\text{CoCl}_3(\text{OPPh}_3)]$ ⁶⁰ and $[\text{CoI}_2\text{L}_2]\text{I}$ ($\text{L} = \text{Cy}_3\text{PO}$)²²⁹ are also known. The iodo complex was obtained by oxidation of $[\text{CoI}_2\text{L}_2]$ with I_2 in ethanol.



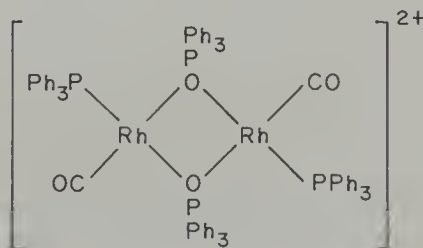
(35)

A number of rhodium(III) complexes have been reported: $[\text{RhLCl}]_n$, $[\text{Rh}(\text{CO})_2\text{LCl}]$ ($\text{L} = \text{Ph}_3\text{PO}$)³⁷²; *cis*- $[\text{RhCl}(\text{CO})_2\text{L}]$ ($\text{L} = \text{topo}$)³⁷³; *cis*- $[\text{RhCl}(\text{CO})_2\text{L}]$ ($\text{L} = \text{cy}_3\text{PO}$)³⁷⁴ [$\{\text{Rh}(\text{HDMG})\text{L}\}_2\text{O}_2$]³⁷⁵, $[\text{Rh}(\text{cod})(\text{OPR}_3)(\text{PPh}_3)](\text{ClO}_4)$ ($\text{R} = \text{Ph}, \text{substituted phenyl}$), $[\text{Rh}(\text{cod})(\text{OPR}_3)_2](\text{ClO}_4)$, $[\text{Rh}(\text{CO})_2(\text{OPR}_3)_2](\text{ClO}_4)$, $[\text{Rh}(\text{CO})(\text{OPR}_3)_2(\text{PPh}_3)](\text{ClO}_4)$, $[\text{Rh}(\text{CO})(\text{OPR}_3)(\text{PPh}_3)_2](\text{ClO}_4)$ ³⁷⁶, $[\text{Rh}_2(\mu\text{-OPR}_3)_2(\text{CO})_2(\text{PPh}_3)_2](\text{ClO}_4)_2$ and $[\text{Rh}_2(\mu\text{-OPR}_3)_2(\text{cod})_2](\text{ClO}_4)_2$ ³⁷⁶.

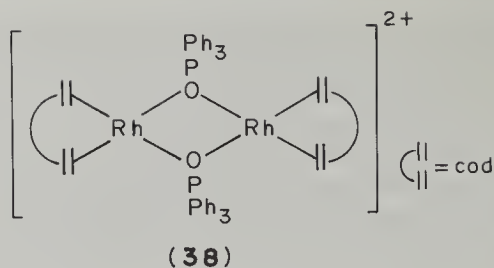
An X-ray study of *cis*- $[\text{RhCl}(\text{CO})_2\text{L}]$ ($\text{L} = \text{cy}_3\text{PO}$)³⁷⁴ has shown a *cis*-square planar structure about rhodium (**36**). Other complexes with same stoichiometry are believed to possess similar structures. $[\text{Rh}_2(\mu\text{-OPR}_3)_2(\text{CO})_2(\text{PPh}_3)_2](\text{ClO}_4)_2$ and $[\text{Rh}_2(\mu\text{-OPR}_3)_2(\text{cod})_2](\text{ClO}_4)_2$ complexes³⁷⁶ are thought to possess bridging ligands (**37** and **38**).



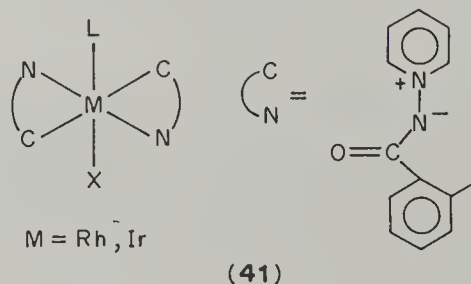
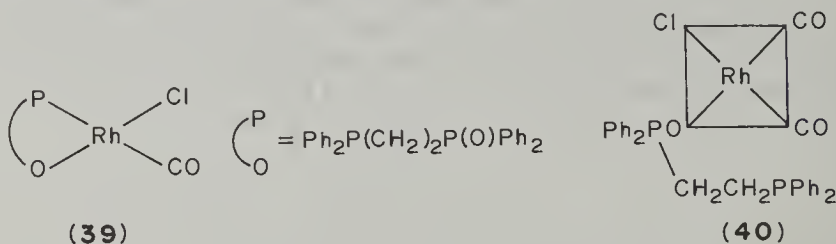
(36)



(37)



Thermal heating of solid samples of $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$, $[\text{Rh}(\text{PPh}_3)_3\text{NO}]$ ³⁷⁷, $[\text{RhL}_3\text{Cl}_3]$ $\{\text{L} = \text{Ph}_2\text{P}(\text{CF}_3)$, $\text{Ph}_2\text{PC}_2\text{F}_5\}$ ³⁷⁸ and $[\text{Rh}(\text{CO})\text{L}(\text{PPh}_3)_2(\text{ClO}_4)]$ ($\text{L} = \text{py}$, γ -picoline, etc.)³⁷⁹ led to inner-sphere oxidation of PPh_3 to OPPh_3 forming corresponding phosphine oxide complexes. The ligand $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ formed a rhodium(I) complex, *cis*- $[\text{RhCl}(\text{CO})\text{L}]$ (39), which on reaction with CO gave a trace of *cis*- $[\text{RhCl}(\text{CO})_2\text{L}]$ ³⁸⁰ (40). The PO—Rh bond is stronger in 39 than in 40. A complex $[\text{Rh}(\text{NO}_3)(\text{NO})_2(\text{OPPh}_3)]$ ³⁸¹ was later reinvestigated and found to be $[\text{Rh}(\text{NO}_3)_2(\text{NO})(\text{Ph}_3\text{P})_2]$ ³⁸². Rhodium(III) and iridium(III) complexes of stoichiometry $[\text{RhL}_2(\text{OPBu}_3)\text{Cl}]$ and $[\text{IrL}_2(\text{OPPh}_3)\text{Cl}]$ (41) ($\text{L} = \text{C}_6\text{H}_4\text{CONR}'$, $\text{R}' = \text{pyridino}$) have been reported³⁸³. The iridium complex reacted with CO reversibly forming $[\text{IrL}_2(\text{CO})\text{Cl}]$.



iii. Nickel sub-Group. Nickel(II) forms several complexes as listed in Table 8. The complexes can be prepared by direct reactions as usual. However, complexes A can also be prepared by other routes: (a) inner-sphere oxidation of $[\text{NiX}_2\text{L}_2]$ by H_2O_2 ($\text{X} = \text{Br}$, I ; $\text{L} = \text{Ph}_3\text{P}$)³⁴⁸, air ($\text{X} = \text{halogen}$; $\text{L} = \text{Et}_3\text{P}$)⁴⁰⁸, NaClO_2 ($\text{X} = \text{Cl}$; $\text{L} = \text{Cy}_3\text{P}$, Ph_3P)³⁸⁹ and thermal heating ($\text{X} = \text{Cl}$, Br , I , NCS , $\text{L} = \text{Ph}_3\text{P}$, Ph_2EtP , PhEt_2P , Me_2PhP , etc; $\text{X} = \text{NO}_3$, $\text{L} = \text{Et}_2\text{PhP}$)^{393,409-412} and (b) reaction of NiCl_2 with molten Ph_3PO ^{351,352}. $[\text{Ni}(\text{NO}_2)\text{Cl}(\text{OPPh}_3)]$ was obtained *in situ* from $[\text{NiX}_2\text{L}_2]$ and NaNO_2 and, on bubbling CO through the solution, $[\text{Ni}(\text{NO})\text{ClL}_2]$ was formed. Here the CO has reacted with NO_2 to form CO_2 and NO. Further reaction of $[\text{Ni}(\text{NO})\text{ClL}_2]$ with O_2 gave exclusively $[\text{Ni}(\text{NO}_2)\text{XL}_2]$ ³⁹⁶. Dimeric complexes (D) were obtained on treatment of $[\text{NiX}_2(\text{PPh}_3)_2]$ with NOCl in a benzene-cyclohexane mixture³⁹⁸. For $\text{X} = \text{NCS}$, the dimer $[\text{Ni}(\text{OPPh}_3)\text{XCl}]_2$ reacted with NOCl forming $[\text{NiLCl}_2]_2$ ³⁹⁷.

Complexes A–C are suggested to have tetrahedral structures for $\text{X} = \text{halogen}$ or NCS and octahedral structures for $\text{X} = \text{NO}_3$, hfa or tta^{238,329,343,393}. For $\text{L} = \text{Me}_2\text{PhPO}$,

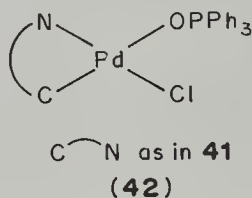
TABLE 8. Complexes of the nickel sub-Group

Complex	X	L	Ref.
A [NiX ₂ L ₂]	Cl, Br, I, NO ₃	Ph ₃ PO, Cy ₃ PO, Et ₃ PO, <i>p</i> -Tol ₃ PO	321, 322, 329, 348, 384–392
	Cl	L ^a	392
	NO ₃	L ^b	393, 394
	Cl, Br	(R ₂ NCH ₂) ₃ PO, Ph ₂ P(O)CH=CH ₂ , Me ₂ P(O)CH ₂ R (R = Cl, MeO, PhO)	66, 227, 395
	Cl, I, NCS	RPh ₂ PO ^c	337
	(NC) ₂ CC(O)NH ₂	Ph ₃ PO	341
	hfa, tta	Bu ₃ PO, topo, Ph ₃ PO	238, 343
B [NiX ₂ L(Ph ₃ P)]	Br	Ph ₃ PO	385
C [Ni(NO ₂)XL ₂]	Cl	Ph ₃ PO	396
D [NiLXCl] ₂	NCS	Ph ₃ PO	397
	Cl, Br, NO ₃	Ph ₃ PO	398
E [NiL ₄ X ₂]	Cl, I, NCS, NO ₃	(HOCH ₂) ₃ PO, Bu ₃ PO, Ph ₃ PO	228, 234
F [NiL ₂ X] ₂ [NiX ₄]	Cl, etc.	Ph ₂ P(O)CH ₂ NMe ₂	357
G [NiCl ₃ (LH)]	—	LH ^d	357
H [NiX ₂ L _n]	CF ₃ SO ₃	Bu ₃ PO, Ph ₃ PO(<i>n</i> = 4–6)	345
I (i) [NiX ₂ L ₄]	ClO ₄	Et ₃ PO, Ph ₃ PO	137, 230, 322, 360, 399
(ii) [NiL ₄]X ₂	ClO ₄	Bu ₃ PO, BzPh ₂ PO	137, 401, 402
(iii) [NiL ₄ X]X	ClO ₄	Me ₃ PO, MePh ₂ PO	231, 232, 234, 403
(iv) [NiL ₅]X ₂	BF ₄	Me ₃ PO	234
(v) [NiX ₂ L _n]	BF ₄	Ph ₃ PO(<i>n</i> = 4,5)	233
(vi) [NiL ₂ X]	SO ₄	Ph ₃ PO	276
J (i) [Ni(O ₂ CR) ₂ L] ₂ ^e	—	Ph ₃ PO	404, 405
(ii) [Ni(O ₂ CC ₆ H ₄ R) ₂ L] ₂ ^f	—	Ph ₃ PO	406
K [(C ₆ H ₅) ₂ NiL ₂]	—	Ph ₃ PO	407

^aL = Ph₂EtPO, Bz₂PhPO, BzPh₂PO, Bz₃PO.^bL = Ph₂P(O)CH=C=CH₂, Me₂P(O)CH=C=CMe₂, Me₂P(O)C≡CPh.^cR = 2-pyridylmethyl.^dLH = Ph₂P(O)CH₂CH₂N⁺HMe₂.^eR = Et, Pr, ClCH₂, Cl₂CH, Cl₃C.^fR = H, 4-CH₃, 2-Cl, 4-NO₂.

Pr₂PhPO, Bu₂PhPO, Bu₃PO and X = Cl, Br, I, the A-type complexes are assigned a *trans*-square-planar geometry⁴¹¹. Various other structures that have been suggested are square-pyramidal for cations of complexes F³⁵⁷ and for complexes I(iii) (L = Me₃PO, MePh₂PO)^{231,232,403} and I(iv)²³⁴, ligand-bridged square-pyramidal dimeric for complexes I(ii) with L = BzPh₂PO^{400,401} and tetrahedral with L = Bu₃PO^{137,402}, halogen-bridged dimeric for complexes D, *trans*-octahedral for complexes E and carboxylate-bridged dimeric for complexes J. The carboxylate complexes J involve a metal–metal exchange interaction similar to that in copper(II) acetate. An increase in Cl substitution in the chloroacetate moiety decreased the magnetic interaction between the nickel centers⁴⁰⁵. In complex G, [NiCl₃(LH)], the ligand Ph₂P(O)CH₂CH₂N⁺(H)Me₂ binds to nickel(II) via the PO group only³⁵⁷. Only one diorganonickel(II) complex, [Ni(C₆F₅)₂(OPPh₃)₂]⁴⁰⁷, is known (Table 8).

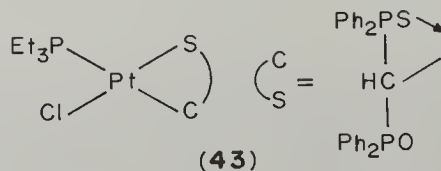
Air oxidation of diamagnetic $[\text{Pd}(\text{PPh}_3)_2\text{L}_2]$ ($\text{L} = \text{Ph}_2\text{PC}_6\text{H}_4\text{X}$; $\text{X} = \text{F}, \text{Cl}, \text{Me}, \text{MeO}, \text{CO}_2\text{H}$) gave a paramagnetic species $[\text{Pd}(\text{OPPh}_3)_2\text{L}_2]^{413}$. Similarly, inner-sphere oxidation of *trans*- $[\text{PdL}_2\text{X}_2]$ ($\text{L} = \text{Ph}_3\text{P}, \text{Ph}_2\text{EtP}$; $\text{X} = \text{Br}, \text{I}$) and *cis*- $[\text{Pd}(\text{Ph}_2\text{EtP})_2\text{Cl}_2]^{414}$ gave the corresponding phosphine oxide complexes. A series of palladium(II) nitrate complexes, $[\text{Pd}(\text{NO}_3)_2\text{L}_2]$ ($\text{L} = \text{R}_3\text{PO}$, $\text{R} = \text{Pr}, \text{Bu}, \text{Ph}, \text{isopentyl}$) were prepared by extraction from HNO_3 solutions of the metal salt⁴¹⁵. Other palladium(II) complexes, including those of organopalladium(II) are $[(\text{PdCl}_2)_4\text{L}_2]$ $\{\text{L} = (o\text{-XC}_6\text{H}_4)_2\text{PhP}(\text{O}); \text{X} = \text{PhC}\equiv\text{C}\}^{416}$, $[\text{PdL}(\text{OPPh}_3)\text{Cl}]$ (**42**, $\text{HL} = \text{C}_6\text{H}_4\text{CONR}'$; $\text{R}' = \text{pyridino}$)³⁸³, $[\text{Pd}(\text{ONO}_2)_2(\text{OPPh}_3)\text{PPh}_3]^{417}$, $[\text{Pd}(\text{C}_6\text{F}_5)_2(\text{OPPh}_3)_2]^{418}$ and $[\text{Pd}(\text{C}_6\text{F}_5)(\text{AsPh}_3)_2(\text{OPPh}_3)](\text{ClO}_4)^{419}$. The X-ray crystal structure of the nitrate complex has shown a *trans*-square-planar structure⁴¹⁷. *cis*- $[\text{PdL}_2]\text{X}_2$ complexes $\{\text{X} = \text{NO}_3, \text{PF}_6; \text{L} = \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{PPh}_2\}^{420}$ have also been reported.



The monodentate ligand Ph_3PO forms complexes with platinum(II) of the type (A) $[\text{PtRL}_2\text{L}'](\text{ClO}_4)$ ($\text{R} = \text{C}_6\text{F}_5, \text{Ph}$; $\text{L} = \text{Et}_3\text{P}, \text{Ph}_3\text{AS}$; $\text{L}' = \text{Ph}_3\text{PO}$)⁴²¹⁻⁴²⁴ and (B) $[\text{PtL}(\text{Ph}_3\text{PO})\text{Cl}]$ ($\text{HL} = \text{C}_6\text{H}_4\text{CONR}'$, $\text{R}' = \text{pyridine}$), analogous to palladium(II) above³⁸³.

Unsymmetrical phosphorus ligands, such as $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_n\text{PPh}_2$ ($n = 1, 2$) form *cis*- $[\text{PtL}_2]\text{X}_2$ complexes ($\text{X} = \text{NO}_3, \text{PF}_6, \text{BF}_4$)⁴¹⁹. Similarly, *cis*- and *trans*- $[\text{PtCl}(\text{PR}_3)_2\text{L}]\text{X}$ $\{\text{R} = \text{Et or Bu}; \text{X} = \text{ClO}_4, \text{BF}_4; \text{L} = \text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{R}'_2; \text{R}' = \text{Ph}, \text{CHMe}_2, \text{CMe}_3\}$ are known⁴²⁵. These complexes on treatment with NaH form *cis*- and *trans*- $[\text{PtCl}(\text{PR}_3)_2\{\text{Ph}_2\text{PCHP}(\text{O})\text{R}'_2\}]$. An X-ray structure of the *trans* isomer with $\text{R}' = \text{CMe}_3$ has been reported. It is notable that the $\text{Pt}-\text{O}$ bond is weaker than the $\text{Pt}-\text{S}$ bond in analogous complexes⁴²⁵.

Finally, reaction of $[\text{Pt}_2\text{Cl}_4(\text{PEt}_3)_2]$ with $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{S})\text{Ph}_2$ gave $[\text{PtCl}(\text{PEt}_3)_2\text{L}]^+^{426}$, which on treatment with 1,8-bis(dimethylamino)naphthalene gave **43**. A platinum(II) complex, $[\text{Pt}_2(\mu\text{-S})(\mu\text{-L})(\eta'\text{-L}')] \{\text{L} = \text{Ph}_2\text{PCH}_2\text{PPh}_2; \text{L}' = \text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2\}^{427}$ was found to possess no $\text{Pt}-\text{O}$ interaction.



g. Complexes of the copper Group (IB). Table 9 shows various types of complexes of copper(II). Only a few copper(I), silver(I), gold(I) and gold(III) complexes have been reported. Apart from the usual methods of preparation, some indirect methods have been used which are briefly described as follows: (a) oxidation of copper metal with Ph_3PO and CCl_4 in MeCOEt gave $[\text{CuCl}_2\text{L}_2]$ and $[\text{Cu}_4\text{OCl}_6\text{L}_4]^{290,454}$; (b) reaction of copper(II) chloride with molten Ph_3PO gave $[\text{CuCl}_2(\text{OPPh}_3)_2]^{351}$; (c) grinding of CuCl_2 and Ph_3PO to a fine powder for some time gave $[\text{CuCl}_2\text{L}_2]^{352}$; (d) reaction of copper(II) chloride with Ph_3P in acetone gave a mixture of Ph_3PO , $[\text{CuCl}_2(\text{OPPh}_3)_2]$, $\text{CuCl}_2(\text{OPPh}_3)_4 \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_4\text{OCl}_6\text{L}_4]^{455,456}$ (separated by chromatography). It may

TABLE 9. Complexes of the copper Group (IB)

Complex	X	L	Ref.
A [CuX ₂ L ₂]	Cl, Br, NO ₃	Ph ₃ PO, Cy ₃ PO, Ph ₂ BzPO, PhBz ₂ PO, Bz ₃ PO, Ph ₂ P(O)CH=CH ₂	66, 322, 428–434
B [CuCl ₂ L]	—	[Me ₂ P(O)CH ₂] ₂ O, [Me ₂ P(O)CH ₂ OCH ₂] ₂ [Me ₂ P(O)CH ₂ OC ₂ H ₄] ₂ O	435
C [CuX ₂ L ₄]·2H ₂ O	Cl, Br	Ph ₃ PO	429, 436–438
D (i) [CuX ₂ L ₄]	NO ₃	Ph ₃ PO	366
(ii) [CuX ₂ L ₄]	Cl, NO ₃	(HOCH ₂) ₃ PO	234
E [Cu ₄ OX ₆ L ₄]	Cl	Ph ₃ PO	429, 439–446
	Br	Ph ₃ PO	444
F [CuX ₂ L]	(i) hfa, tta, tfa, acac, Et ₂ NC(S), etc.	Ph ₃ PO, topo	238, 343, 447–450
	(ii) HA ^a	Bu ₃ PO	97
G [CuX ₂ L _n]	(i) hfa, dbm, tta, cupferron	Bu ₃ PO topo(<i>n</i> = 1,2)	238, 451
	(ii) CF ₃ SO ₃	Bu ₃ PO, topo(<i>n</i> = 4,6)	345
H [CuX ₂ L ₂]	2,4,6-X ₃ C ₆ H ₂ O ₂ (X = Cl, Br)	Ph ₃ PO	452
I (i) [CuL ₄]X ₂	ClO ₄	Me ₃ PO, Bu ₃ PO, Ph ₂ BzPO, PhBz ₂ PO, Bz ₃ PO	137, 343, 432
(ii) [CuL ₄ X]X	ClO ₄	Me ₂ PO, Ph ₃ PO, MePh ₂ PO	229–232, 453
(iii) [CuX ₂ L ₄]	BF ₄	Bu ₃ PO, Ph ₃ PO	233, 234
(iv) [CuL ₅]X ₂	BF ₄	Me ₃ PO	234

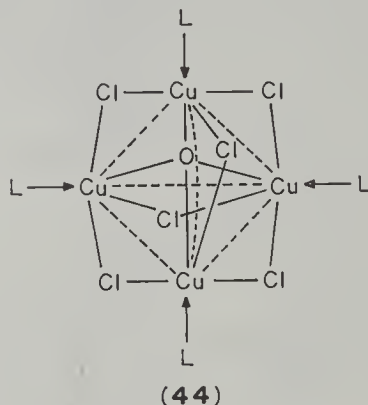
^aHA = 5-methoxy-5-methyl undecane-2,4-dione.

be added that sometimes in the direct reaction of a metal salt with a ligand, unexpected products were obtained. For example, reaction of copper(II) chloride with Ph₃PO under different conditions gave [CuCl₂L₂], 2[CuCl₂L₃] and (Cu₄OCl₆L₄)⁴⁵⁷. A complex with a quaternary cation, namely (Ph₂P(O)CH₂CH₂NEt₂(H))⁺[CuCl₂][−] is also known^{458,459}; X-ray analysis has confirmed this formulation.

X-ray study has shown a slightly elongated tetrahedron for [CuBr₂(OPPh₃)₂]⁴²⁸, with angles at oxygen, viz. Cu—O—P, being 144.0° and 154.8°. Similarly, for [CuCl₂(OPPh₃)₂], a compressed tetrahedral geometry (*C*₂ symmetry) was inferred from single-crystal ESR and polarized electronic spectra^{429,431}. [Cu(O₂NO)₂(OPPh₃)₂] has *trans*-rhombic octahedral geometry⁴³⁴. Other complexes of type A and also complexes of type B (coordination via PO only have been assigned a distorted tetrahedral geometry (Table 9).

Complexes C exhibit coordination isomerism: [CuCl₂(OH₂)₂](Ph₃PO)₄^{429,436,437} (isomer I) and [CuCl₂(OPPh₃)₄]·2H₂O (isomer II)⁴³⁸. Isomer I has a tetrahedral geometry (X-ray) about copper with no coordination by Ph₃PO. Each H₂O interacts with Ph₃PO via hydrogen bonding. In isomer II, H₂O is not coordinated and the complex has a *trans*-octahedral geometry. On heating, isomers I and II formed [CuL₂X₂]⁴⁶⁰. Complexes D presumably have *trans*-octahedral structures with monodentate NO₃ in mutually *trans* positions.

One of the most widely studied compounds is $[\text{Cu}_4\text{OCl}_6\text{L}_4]$ ($\text{L} = \text{Ph}_3\text{PO}$) (complexes E). Apart from the methods mentioned earlier, this cluster compound can be readily obtained by refluxing $[\text{CuCl}_2(\text{OPPh}_3)_2]$ in methyl isobutyl ketone⁴⁴⁶. X-ray study has shown that the copper atoms are at the vertices of an almost regular tetrahedron (44). Each copper is surrounded by a slightly distorted trigonal bipyramid^{440-442,446}; six bridging 'Cl' atoms form an octahedron about the central oxygen. There is antisymmetric super-exchange between orbitally degenerate magnetic ions⁴⁴⁵. Further, the EPR spectrum has shown separation of the $S = 2$ state from the $S = 1$ state (ground state) of $14 \pm 1 \text{ cm}^{-1}$ (zero-field splitting, $0.53 \pm 0.01 \text{ cm}^{-1}$)⁴⁴³.



The 1:1 adducts $[\text{CuX}_2\text{L}]$ (complexes F and G) either possess square-pyramidal geometry or dimeric octahedral structures involving bridging via oxygen or sulphur donor atoms of the anions. The 1:2 adducts G have *trans*-octahedral structures. However, none of these have been characterized by X-ray studies. The triflate complexes $[\text{Cu}(\text{SO}_3\text{CF}_3)_2\text{L}_n]$ ($n = 4, 6$) have only been poorly studied. The Lewis acidity of copper(II) β -diketonates, CuX_2 , towards the ligands decreased in the order $\text{Cu}(\text{hfa})_2 > \text{Cu}(\text{tta})_2 > \text{Cu}(\text{tfa})_2 > \text{Cu}(\text{acac})_2$.

In copper(II)-dithiocarbamate adducts (F)⁴⁴⁸, low-temperature ESR studies showed that the axial binding to copper by L weakens the Cu—S bonding in the square-plane. Phenoxo complexes (H) are also believed to possess *trans*-octahedral geometries⁴⁵² and on thermal degradation they form $[\text{Cu}_4\text{OCl}_6\text{L}_4]$. For the perchlorate or fluoroborate complexes, tetrahedral, square-pyramidal, or octahedral structures have been assigned for I(i), I(ii, iv) and I(iii), respectively. For $[\text{CuL}_4](\text{ClO}_4)_2$, a square-planar structure has been suggested when $\text{L} = \text{Me}_3\text{PO}$ ³⁴³, whereas when $\text{L} = \text{Bu}_3\text{PO}$ the structure is believed to be between tetrahedral and square-planar.¹³⁷

The unsymmetrical phosphorus-sulphur ligands $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{SR}$ ($\text{R} = \text{Et}, \text{Ph}$) also formed complexes of the type $[\text{CuL}_2] \cdot \text{X}_2$ ($\text{X} = \text{ClO}_4$), $[\text{CuL}_2](\text{BF}_4)_2$ ($\text{R} = \text{Et}$) and $\{[\text{CuL}'_2]\text{X} \cdot [\text{CuL}_2]\text{X}_2\}$ ($\text{L}' = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{SEt}$; $\text{L} = \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{SPh}$)⁴⁶¹. Complexes $\{[\text{CuL}'_2]\text{X} \cdot [\text{CuL}_2]\text{X}_2\}$ are double salts and the presence of $[\text{CuL}'_2]\text{X}$ induces asymmetry in the g_{\perp} line of $[\text{CuL}_2]\text{X}_2$ ($\text{X} = \text{ClO}_4, \text{BF}_4$) species which showed $g_{\parallel} = 2.220$ and $g_{\perp} = 2.089$; the double salt complexes showed three g values (2.269, 2.064 and 2.034). From solution-phase studies, species of the type $[\text{CuLCl}]^+ \{ \text{L} = \text{Me}_2\text{P}(\text{O})\text{CH}_2\text{R}; \text{R} = \text{Cl}, \text{OMe}, \text{OPh}^{227}, \text{Ph}_3\text{PO}, \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{Ac}, \text{Ph}_3\text{P}=\text{CHP}(\text{O})\text{Ph}_2^{364} \}$ and $[\text{CuL}_2\text{Cl}]^+ \{ \text{L} = \text{Me}_2\text{P}(\text{O})\text{CH}_2\text{OPh} \}^{227}$ were detected.

Addition of Me_3P to a rapidly dehydrated copper(II) Y-zeolite reduced the copper(II) to copper(I), which on treatment with O_2 was deoxidised forming $[\text{Cu}(\text{Me}_3\text{PO})_4]^{2+}$ species in the supercages of the Y-zeolite's lattice⁴⁶².

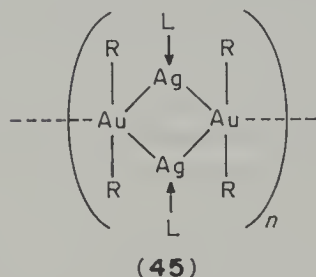
A large number of adducts of copper(II) carboxylates with Ph_3PO have been reported: $[\text{Cu}_2(\text{O}_2\text{CR})_4\text{L}_2]$ $\{\text{R} = \text{Me, Et, Pr}^{343,463,464}, \text{FCH}_2, \text{ClCH}_2, \text{Cl}_2\text{CH}, \text{Cl}_3\text{C}, \text{F}_3\text{C}, \text{etc.}^{465-467}, \text{BrCH}_2\text{CH}_2, \text{MeCHBr}, \text{MeC}(\text{Cl}_2), \text{ClCH}_2\text{CH}_2, \text{MeCH}(\text{Cl})^{464,468-470}, \text{PhC}\equiv\text{C}^{471}, \text{R}'\text{C}_6\text{H}_4, \text{R}' = \text{H, 4-Me, 2-Cl, 4-NO}_2^{406}, \text{2-F, etc.}^{464}\}$ and $[\text{Cu}(\text{O}_2\text{CCX}_3)_2(\text{Ph}_3\text{PO})_2]$ $(\text{X} = \text{F, Cl})^{472}$.

X-ray analyses of $[\text{Cu}_2(\text{O}_2\text{CCH}_2\text{CH}_2\text{Cl})_4(\text{OPPh}_3)_2]^{469}$ and $[\text{Cu}_2(\text{O}_2\text{CCHClMe})_4(\text{OPPh}_3)_2]^{470}$ have shown dimeric structures (46) similar to that of copper(II) acetate. Magnetic moment, ESR and other studies have revealed antiferromagnetic exchange interactions between the copper(II) centres of the carboxylate complexes. In one case, viz. $[\text{Cu}_2(\text{PhC}\equiv\text{CO}_2)_4\text{L}_2]^{471}$, there was inter-dimer antiferromagnetic interaction.

Recently 1:2 adduct of substituted glycine, namely $[\text{CuA}_2\text{L}_2]$ ($\text{HA} = N\text{-formyl-L-phenylalanylglycine}$; $\text{L} = \text{Ph}_3\text{PO}$) was reported to have a *trans*-octahedral structure⁴⁷³. However, an ESR study revealed the existence of monomeric and dimeric forms of the adduct.

A few tetrameric copper(I)-phosphine oxide complexes, $[\text{CuLX}]_4$ ($\text{L} = \text{Ph}_3\text{PO}$, *p*-tol₃PO; $\text{X} = \text{Cl, Br, I}$), were formed by the thermal decomposition of $[\text{Cu}(\text{PPh}_3)\text{X}]$ in O_2 ⁴⁷⁴ and oxidation of $[\text{CuX}(\text{p-tol}_3\text{P})]$ with H_2O_2 ⁴⁷⁵. Similarly, reaction of Ph_3P with CuCl_2 in Me_2CO gave $[\text{CuClL}_n]$ ($n = 1-3$; $\text{L} = \text{Ph}_3\text{PO}$)⁴⁵⁶. Reaction of CuCl with $\text{Ph}_2\text{P}(\text{O})\text{CH}(\text{R})\text{Li}^+$ {from $\text{BuLi} + \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{R}$ } led to *trans*-metallation of copper(I) forming $\text{CuCH}(\text{R})\text{P}(\text{O})\text{Ph}_2$ ($\text{R} = \text{H, Pr, etc.}$)⁴⁷⁶.

The β -tri- α -methylindolphosphine oxide $(\text{C}_6\text{H}_4\text{NHCM}=\text{C})_3\text{PO}$ and β -triindolylphosphine oxide, $(\text{C}_6\text{H}_4\text{NHCH}=\text{C})_3\text{PO}$, were reported to interact with AgNO_3 , but no details were given⁴⁷⁷. Other silver(I) complexes reported are $[\text{Ag}(\text{NO}_3)\text{L}]$, $[\text{AgXL}_5]$ ($\text{X} = \text{ClO}_4, \text{BF}_4, \text{PF}_6$), $[\text{AgL}_4]^+(\text{SbF}_6)^-$ ($\text{L} = \text{Ph}_3\text{PO}$)⁴⁷⁸ and $(\text{R}_2\text{AuAgL})_n$ ⁴⁷⁹ ($\text{R} = \text{C}_6\text{F}_5, \text{C}_6\text{F}_3\text{H}_2$; $\text{L} = \text{Ph}_3\text{PO}$; 45).



Gold(I, III) complexes of the type $[\text{Au}(\text{Ph}_3\text{PO})(\text{Ph}_3\text{P})](\text{ClO}_4)$,⁴⁸⁰ $[(\text{C}_6\text{F}_5)_2\text{Au}(\text{Ph}_3\text{P})(\text{Ph}_3\text{PO})](\text{ClO}_4)$ ⁴⁸¹ and $(\text{HL}_2)[\text{AuX}_4]$ ($\text{X} = \text{Cl, Br}$; $\text{L} = \text{Ph}_3\text{PO}$)⁴⁸²⁻⁸⁴ have been reported. Au X-ray study of $(\text{H}(\text{Ph}_3\text{PO})_2)[\text{AuCl}_4]$ ⁴⁸⁵ showed a hydrogen-bonded centrosymmetric interaction with Ph_3PO .

h. Complexes of the zinc Group (IIB). Various complexes of this group are given in Table 10. Most of the adducts have 1:1 or 1:2 metal to ligand ratios, although a few complexes with other stoichiometries have also been reported. For example, zinc(II) forms $[\text{ZnX}_2\text{L}_n]$ ($\text{X} = \text{SO}_3\text{CF}_3$; $n = 4-6$) complexes³⁴⁵. X-ray analysis of $[\text{ZnCl}_2(\text{OPPh}_3)_2]$ showed a distorted tetrahedral geometry about zinc(II)⁴⁸⁶. Other A complexes are also suggested to have similar structures.

For B complexes, $[\text{MX}_2\text{L}]$, when the anion is halogen, a dimeric structure (46) is suggested. When the anion is tta, hfa or bfa, square-pyramidal or dimeric octahedral structures (47a and b) have been suggested. The unsymmetrical phosphorus ligands $\text{Ph}_2\text{P}(\text{O})\text{CH}(\text{R})\text{PPh}_2$ chelate to a metal centre via P and O donor atoms, forming

TABLE 10. Complexes of the zinc Group (IIB)

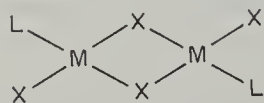
	Complex	M	X	L	Ref.
A	$[MX_2L_2]$	Zn	Cl, Br, I, NO_3 , CH_3COO	L^a	16, 66, 73, 227, 230, 322, 486–490
			$(NC)_2CC(O)NH_2$	Ph_3PO	341
		Cd	I	Ph_3PO	16, 230, 490
		Hg	Cl	$Ph_3PO, Ph_2P(O)R$ ($R = CH_2=CH$)	16, 66, 491, 492
B	$[MX_2L]$	Zn, Cd	tta, bfa, hfa	$Ph_3PO, topo$	343, 449, 493, 494
		Cd	Cl	$(HOCH_2)_3PO$	234
		Cd, Hg	Cl, Br	$R_3PO(R = HOCH_2)$ $Ph_2P(O)CH(R)PPh_2$ ($R = H, Pr^n$) ^b	143
		Hg	Cl, Br	$Me_3PO, Ph_3PO,$ $p-Tol_3PO$	491, 492, 495
C	$[MX_2L_n]$	Zn	CF_3SO_3	Bu_3PO, Ph_3PO ($n = 4-6$)	345
D	$[ML_4]X_2$	Zn	$BF_4, ClO_4,$ SbF_6	$Me_3PO, Bu_3PO,$ Cy_3PO	137, 234, 496
		Cd	SbF_6	Cy_3PO^c	497
E	$[ZnL_4X]X$	—	ClO_4	$Me_3PO, MePh_2PO,$ Ph_3PO	229, 231 232
F	$[ML_4X_2]$	Zn, Cd, Hg	$BF_4, ClO_4,$ $N(SO_3F)_2$	Me_3PO, Ph_3PO	233, 234, 498

^a $L = Me_3PO, Ph_3PO, R_2P(O)CH=CH_2$ ($R = Bu^n, Ph$), $Me_2P(O)CH_2R$ ($R = Cl, MeO, PhO$).

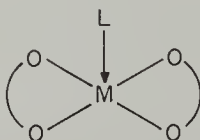
^b³¹P NMR study.

^c³¹P, ¹¹³Cd NMR study.

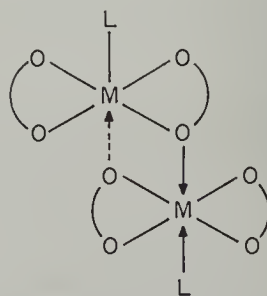
tetrahedral complexes, $[MX_2L]^{143}$. For complexes D–F, tetrahedral, square-pyramidal or octahedral structures have been suggested.



(46)



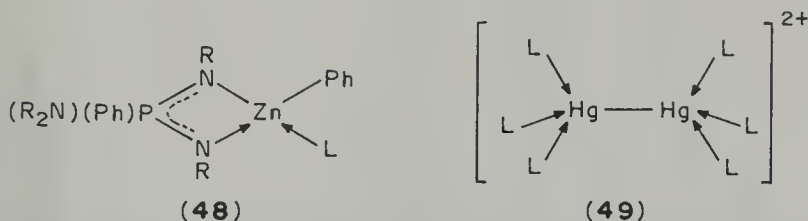
(47a)



(47b)

Using ³¹P and ¹¹³Cd NMR, the formation of $[CdL_4](SbF_6)_2$ ($L = Cy_3PO$) was detected⁴⁹⁷, and insoluble product, $[CdL_3(SbF_6)_2]$ ($L = Cy_3PO$) was isolated. From another solution-phase study, the order of metal–ligand interaction was found to be $Zn-O > Cd-O > Hg-O$ ^{499,500}. Recently, an adduct of a substituted glycine, viz. $[ZnA_2(OPPh_3)_2]$ ($HA = N$ -formyl- L -phenylalanylglycine), with a *trans*-octahedral structure was reported⁴⁷³. A few reactions of organo-zinc(II) and -mercury(II) have also

been reported⁴⁷³. For instance, reaction of *N,N,N'',N''*-tetrakis(trimethylsilyl)diamidophosphonimide, $R_2N(P=NR)_2$ ($R = Me_3Si$) with Ph_2Zn formed a 3-coordinate complex $[(R_2N)(Ph)P(NR)_2Zn]$, which further reacted with Ph_3PO forming a 1:1 adduct (48)⁵⁰¹. Similarly, $(C_6F_5)_2Hg$ and $[(O_2N)_3C]_2Hg$ formed 1:1 adducts with Ph_3PO ^{502,503}. From another study (solution phase)⁵⁰³, the Lewis acidity of R_2Hg towards Ph_3PO was indicated to decrease in the order $R = o-HC_6F_4 > C_6F_5 > p-HC_6F_4 \approx p-MeOC_6F_4$. Only a few mercury(I) complexes, $[Hg_2L_6(ClO_4)_2]$ ($L = Ph_3PO$)^{498,505}, $[Hg_2L_4(ClO_4)_2]$ ⁵⁰⁶ and $[Hg_2L_5(SiF_6)]$ ($L = Ph_3PO$)⁵⁰⁶, have been reported. An X-ray study of $[Hg_2L_6(ClO_4)_2]$ showed a dimeric structure (49), the geometry about each mercury being approximately tetrahedral.



i. Complexes of the lanthanides. Numerous complexes of the lanthanides have been reported (Table 11). Lanthanide halides generally form 6- or 7-coordinate $[MX_3L_n]$ ($n = 3, 4$) complexes. There is a tendency to extend the coordination number from 6 to 7 either by reaction with an additional ligand or absorbing moisture or solvent molecules. An iodo complex, $[SmL_4I_3]$, showed ionization forming $[SmL_4I_2]I$ ⁵¹⁵, probably for steric reasons. A thermal study of the complexes $[MCl_3L_3(H_2O)]$ ⁵¹⁸ revealed an increase in thermal stability from holmium to samarium. Cerium(IV) complexes had low thermal stability, decomposing between 45 and 80 °C; decomposition was rapid in water also⁵¹⁰.

An interesting feature noted in lanthanide chemistry was the abstraction of halogens with a Lewis acid from the $[ML_3X_3]$ complexes. Coordination of R_3PO to the metal weakens the $M-X$ bonds and thus ionic complexes such as $[MClL_5][FeCl_4]_2$ ⁵²⁰ and $[MCl_2L_4][CuCl_3]$ ^{521,522} are formed. X-ray analysis of the gadolinium complex showed a *trans*-octahedral structure for $[GdCl_2L_4]^+$ and a trigonal planar $CuCl_3^-$ anion⁵²². Similarly, X-ray analysis showed an octahedral structure for $[LaClL_5]^{2+}$ ⁵²⁰ and *trans*-octahedral structures for $[CeCl_4L_2]$ ($L = Ph_3PO$)⁵⁰⁹ and $[SmI_2L_4]I$ ($L = Ph_2MePO$)⁵¹⁵.

The nitrate complexes B in Table 11 involve chelation by the NO_3 groups and hence the coordination number varies from 7 to 10. X-ray studies of $[La(O_2NO)_3L_3] \cdot EtOH$ ⁵²³, $[Nd(O_2NO)_3L_2] \cdot EtOH$ ⁵³⁰, $[Eu(O_2NO)_3L_3](Me_2CO)_2$ ⁵³¹ and $[Eu(O_2NO)_3L_2(EtOH)]$ ⁵³¹ ($L = Ph_3PO$) have shown 9-coordination about the metal centre, whereas $[Ce(O_2NO)_4L_2]$ ($L = Ph_3PO$)⁵²⁷ has 10-coordinate cerium. Here the general tendency of the metal ion is to extend the coordination number up to 9 readily and owing to this various complexes acquire solvent molecules. Preliminary X-ray data on $[Nd(NO_3)_3(Ph_3PO)_3]$ showed that the complex exists in two phases⁵²⁹.

The metal thiocyanate complexes showed coordination numbers similar to those in the metal halides. The complexes possess $M-NCS$ bonding as expected. An X-ray study of $[Nd(NCS)_3L_4]$ ($L = Ph_3PO$) has shown that it possesses C_s symmetry. The perchlorate complexes also have coordinating ClO_4^- groups. For example, in $[Nd(O_2ClO_4)_2L_4](ClO_4)$ ⁵²², an X-ray study has confirmed the chelation by the ClO_4 groups as deduced from IR spectrometry for several complexes. The geometry of the neodymium complex involves a distorted delta dodecahedron. The complexes $[ML_6]^{3+}$ ($L = Me_3PO$)⁵⁴³ are other examples where six monodentate R_3PO ligands coordinate to the metal.

TABLE 11. Complexes of the lanthanides

Complex	M	L	Ref.
A	$[\text{MCl}_4\text{L}_2]$	Ph_3PO	507–509
	$[\text{MCl}_4\text{L}_2]\cdot\text{EtOH}$	Ph_3PO	510
	$[\text{MCl}_3(\text{OMe})\text{L}_2]$	Ph_3PO	510
	$[\text{MCl}_3\text{L}_n]\cdot m\text{BuOH}$ ($m = 1, 2$)	topo, Ph_3PO , Ph_2BzPO ($n = 1-4$)	511–514
	$[\text{ML}_4\text{I}_2]\text{I}$	Ph_2MePO	515
	$[\text{MCl}_3\text{L}_n]$	Ph_3PO ($n = 3, 4$)	512, 513
	$[\text{MX}_3\text{L}_n]\cdot\text{S}$ ($\text{S} = 0, 0.5$ or 2 $\text{C}_4\text{H}_8\text{O}_2$; $\text{X} = \text{Cl}, \text{Br}$)	Ph_3PO , Ph_2BzPO , Ph_2EtPO ($n = 3$)	516, 517
	$[\text{MCl}_3\text{L}_3]\cdot\text{H}_2\text{O}$	Ph_3PO	518
	$[\text{MCl}_3\text{L}_4]$	Ph_3PO	518
	$[\text{MCl}_3\text{L}_3]$	topo, Ph_3PO	519
	$[\text{MCl}_5][\text{FeCl}_4]_2$	Ph_3PO	520
	$[\text{MCl}_2\text{L}_4][\text{CuCl}_3]$	Ph_3PO	521, 522
	$[\text{M}(\text{O}_2\text{NO})_3\text{L}_3]\cdot\text{EtOH}$	Ph_3PO	523
	$[\text{M}(\text{O}_2\text{NO})_4\text{L}_2]$	Ph_3PO	524–527
	$[\text{M}(\text{O}_2\text{NO})_3\text{L}]\cdot\text{EtOH}$	Me_3PO , Et_3PO , Ph_3PO , Bz_3PO , Ph_2BzPO , PhBz_2PO	528
B	$[\text{M}(\text{O}_2\text{NO})_3\text{L}_3]$	Ph_3PO	512, 529
	$[\text{M}(\text{O}_2\text{NO})_3\text{L}_2]\cdot\text{EtOH}$	Ph_3PO	512, 530
	$[\text{M}(\text{NO}_3)_3\text{L}_2]\cdot\text{EtOH}$	Ph_3PO	512
	$[\text{M}(\text{O}_2\text{NO})_3\text{L}_2]\cdot\text{EtOH}$	Ph_3PO	512
	$[\text{M}(\text{O}_2\text{NO})_3\text{L}_3]\cdot 2\text{Me}_2\text{CO}$	Ph_3PO	531–533
	$[\text{M}(\text{O}_2\text{NO})_3\text{L}_2\cdot\text{EtOH}]\cdot\text{EtOH}$	Ph_3PO	531–533
	$[\text{M}(\text{NO}_3)_3\text{L}_3]$	R_3PO ($n = 3, 4$; $\text{R} = \text{isoamyl}$)	534
	$[\text{M}(\text{NO}_3)_3\text{L}_2]\cdot\text{EtOH}$	Pr_3PO	534
	$[\text{M}(\text{NO}_3)_3\text{L}_n]\cdot\text{S}_m$ [$\text{S} = \text{EtOH}$, Me_2CO ; $m = 1, 2$]	Ph_3PO	512, 535
	$[\text{M}(\text{NO}_3)_2\text{L}_4](\text{NO}_3)$	Ph_3PO ($n = 3, 4$)	535
	$[\text{M}(\text{O}_2\text{NO})_3\text{L}_3]$	Ph_3PO	535
	$[\text{M}(\text{NCS})_3\text{L}_4]$	Bu_3^aPO , topo	519, 536
	$[\text{M}(\text{NCS})_3\text{L}_n]$	Ph_3PO , topo, PhBz_2PO	537, 538
	$[\text{M}(\text{NCS})_3\text{L}_n]$	Ph_3PO ($n = 3, 4$)	512
	$[\text{M}(\text{NCS})_3\text{L}_n]$	Ph_3PO , Bu_3PO , topo,	513, 519
	$[\text{M}(\text{NCS})_3\text{L}_n]$	Pr_3PO , R_3PO ($\text{R} = \text{isoamyl}$; $n = 3, 4$)	534, 539
C	$[\text{M}(\text{ClO}_4)_3\text{L}_4]$	Ph_2EtPO	516
	$[\text{M}(\text{OCIO}_3)_2\text{L}_4](\text{ClO}_4)$	Bu_3^aPO	137

	$[M(ClO_4)_3L_4]$	Nd	$Ph_xBz_{3-x}PO, Ph_2EtPO$ ($x = 0-3$)	516, 540
	$[M(O_2ClO_2)_2L_4](ClO_4)_2S$ ($S = EtOH, Me_2CO$)	Nd	Ph_3PO	541, 542
	$[M(ClO_4)_3L_4]$	Eu, Er	$Ph_3PO, Bz_3PO, Ph_2BzPO, Ph_2EtPO$	516-517
	$[ML_6](ClO_4)_3$	La, Gd, Eu, Lu, Y	Me_3PO	543
	$[ML_4(OCIO_3)_2](ClO_4)_2$	La-Lu	Bu_3PO	544
	$[ML_4(O_2ClO_2)_2](ClO_4)_2$	Y, Gd-Er	Bu_3^nPO	544
	$[ML_4(OCIO_3)_2](ClO_4)_2$	Yb	Bu_3^oPO	544
E	$[ML_6](PF_6)_3$	La, Ce, Nd, Eu, Gd, Tm, Lu, Y	$Me_3PO, MePh_2PO$	543, 545
	$[ML_5](PF_6)_3]$	La, Eu, Gd, Tb, Dy	$CyPh_2PO$	545
F	$[MA_3L_2]^c$	Ce, Pr, Nd, Sm, Eu, Dy, Tb, Er	Ph_3PO	546
	$[M(OCCF_3)_3L]$	La-Lu, Y	Ph_3PO	547
G	$[MA_3L]$ ($HA = Hacac, Hba, Hdbm, Htta$)	Ce	$Ph_3PO, topo$	548-552
H	$[M(tta)_2(NO_3)_2L_2]$	Ce	Ph_3PO	553
	$[M(dbm)_2(NO_3)_2L]$	Ce	Ph_3PO	525
	$[MA_4L]$ ($HA = Hacac, Hba, Hdbm$)	Ce	$topo, Ph_3PO$	551
	$[MA_3L]^b$ ($HA = Hdpvm$)	Ce	Ph_3PO	554, 555
	$[MA_3L_2]$ ($HA = Htta, Hhfa$)	Nd, Eu	$Et_3PO, topo, Ph_3PO$	49, 51, 556-561
	$[MA_3L]^c$	Eu	Et_3PO, Ph_3PO	499, 562
	$[MA_2(O_2NOIL)_2]$ ($HA = Htta, Hdbm, Hba$)	Eu, etc.	Ph_3PO, Bu_3PO	570, 571
	$[MA_3L]$ ($HA = Hdbm, Hacac, Hba, Hdpvm$)	Nd, Pr, Er, Gd, Ha, Tn, Yb, Y	$topo, Ph_3PO$	52, 53, 554, 555, 563-566
	$[MA_3L_4]$ ($HA = Htta, etc.$)	La, Nd, Pr, Er, Gd, Dy, Ho, Yb, Tm	$topo, Ph_3PO$ ($n = 1, 2$)	567, 568
I	$[MA_3L_n]$ ($HA = Hacac$)	Y, La, Pr, Sm, Gd, Dy	$PhMe_2PO, MePh_2PO, EtPh_2PO$ ($n = 2$)	569
J	$[MA_3L_2] \cdot 2H_2O^d$	La	Ph_3PO ($n = 2$ for Y, 3 for others)	572
	$[M(PMBP)_4L]$	Ce	Ph_3PO	573
K	$[M(PMBP)_3L_n]$	Pr-Gd	Ph_3PO, Bu_3PO	574, 575
	$[MA_3L]^e$	Y, La, Eu, Lu	Ph_3PO ($n = 1, 3$)	576, 577
	$[MA_2(PPh_3)_2L]^e$	Y, La, Eu	Ph_3PO	576
	$[M_2A_4(O_2)_2L_3]^e$	La, Pr, Sm, Eu, Lu	Ph_3PO	577
L	$[MA_3L]^f$	Ce, etc.	Et_3PO, Ph_3PO	54, 578
	$[M(SO_3Cl)_3L_2]$	Ce, Nd, Sm, Gd, Dy, Ho, Er	Ph_3PO	579-581

^aHA = 5-chlorosalicylic acid.

^bHA = Hdpvm - dipivaloyl methane.

^cHA = 1-trifluoromethoxy-1,1-difluoro-5,5-dimethylhexane-2,4-dione. Hdpvm, etc.

^dHA = N-nitrosophenylhydroxylamine.

^eHA = HN (SiMe₃)₂.

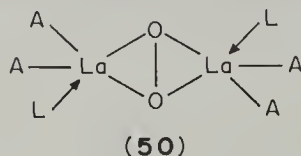
^fHA = 2,6-Me₃CC₆H₃OH, 2,6-di-*tert*-butyl-4-methylphenol, 2,6,4-(CMe₃)₂MeC₆H₂OH.

Hexafluorophosphate complexes (E) probably do not contain the coordinated anion whereas complexes G have coordinating carboxylate groups, the salicylate complexes being 8-coordinate and the trifluoroacetate complexes 9-coordinate. However, X-ray analysis is needed to confirm such possibilities. All the trifluoroacetate complexes decomposed at 300 °C forming metal trifluoride compounds. A polymeric europium(III) complex, $\text{Eu}_4\text{A}_3 \cdot 9\text{H}_2\text{OL}$ ($\text{L} = \text{Ph}_3\text{PO}$) ($\text{H}_4\text{A} = \text{benzene-1,2,4,5-tetracarboxylic acid}$), has also been reported⁵⁸².

Several adducts of metal β -diketonates have been reported (complexes H, Table 11.) The coordination number varies from 7 to 8 with coordination number 9 being shown only by $[\text{CeA}_4\text{L}]$ adducts. The adducts $[\text{Ce}(\text{tta})_4\text{L}]$ ^{550,551} were unstable and were reduced to $[\text{Ce}(\text{tta})_3\text{L}]$ ($\text{L} = \text{topo}, \text{Ph}_3\text{PO}$), whereas other adducts were stable. X-ray studies of $[\text{M}(\text{tta})_3(\text{OPPh}_3)_2]$ ($\text{M} = \text{Nd}, \text{Eu}$)^{557,561} and $[\text{Eu}(\text{dbm})_2(\text{O}_2\text{NO})(\text{OPPh}_3)_2]$ ⁵⁷¹ showed dodecahedral structures for these complexes. However, an X-ray study of $[\text{PrA}_3\text{L}]$ ($\text{HA} = \text{dipivaloylmethane}$) showed that it has a pentagonal bipyramidal structure^{554,555}. Europium(III) complexes $[\text{EuA}_3\text{L}_n]$ ($n = 1, 2$) fluoresce^{570,583}.

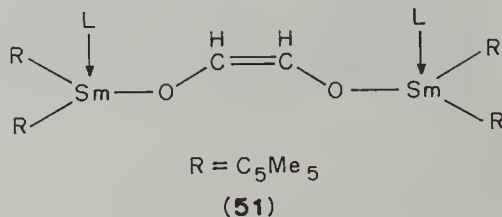
A thermal study of $[\text{MA}_3\text{L}]$ ($\text{HA} = \text{Hdbm}$)⁵⁶³ revealed that the adducts sublime in vacuum; the decomposition temperature of the adducts increases as the lanthanide increases in atomic number. A mass spectral study of $[\text{EuA}_3(\text{OPPh}_3)]$ ($\text{HA} = \text{RC}(\text{O})\text{-CH}_2\text{C}(\text{O})\text{CMe}_3$; $\text{R} = \text{CF}_3, \text{CF}_3\text{OCF}_2, \text{C}_3\text{F}_7$), the complexes with $\text{R} = \text{CF}_3\text{OCF}_2$ and CF_3 showed dimer formation in the gas phase⁵⁸⁴.

N-Nitrosophenylhydroxylamine, 4-benzoylpyrazolone and chlorosulphate complexes (I–K) formed 7- to 9-coordinate complexes. Using $(\text{Me}_3\text{Si})_2\text{N}^-$ or Ph_2P^- as the anions, novel 4-coordinate complexes, and peroxo complexes, were obtained (Table 11). The diphenylphosphido complexes were obtained from $[\text{MA}_3\text{L}]$ and Ph_2PH ($\text{HA} = \text{HN}(\text{SiMe}_3)_2$). An X-ray study of $[\text{La}_2\text{A}_4(\text{O}_2)\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$, $\text{HA} = \text{HN}(\text{SiMe}_3)_2$)⁵⁷⁷ showed that it exists as a centrosymmetric dimer (50), each Lanthanum has a distorted tetrahedral environment if the fourth side is considered to be occupied by the peroxo group, O_2^{2-} . Similarly, 4-coordinate peroxo complexes (M) have been reported^{54,578}.



Reaction of $\text{Na}[\text{M}(\text{S}_2\text{PR}_2)_4]$ ($\text{M} = \text{La-Lu}$, except Pm) with Ph_3PO gave dithiophosphinate adducts, $[\text{MA}_3\text{L}_2]$ and $[\text{MA}_2\text{L}_3]$ ($\text{A} = \text{S}_2\text{PR}_2$) complexes ($\text{R} = \text{EtO}$)^{585–586}. X-ray analysis showed 8-coordinate square-antiprism geometry about lanthanum and a pentagonal bipyramidal geometry about samarium.

A few organosamarium(II) and -(III) complexes, $[(\text{C}_5\text{Me}_5)_2\text{SmL}(\text{thf})]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁵⁷² and $[(\text{C}_5\text{Me}_5)_2\text{SmL}(\text{OCH}=\text{CHO})\text{SmL}(\text{C}_5\text{Me}_5)_2]\text{L}$ ⁵⁸⁸, have been reported. The latter was obtained from the reaction of $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$ and CO in the presence of Ph_3PO and it exhibited *cis-trans* isomerism. X-ray analysis of the *cis* isomer showed a distorted tetrahedral geometry about each samarium (51).

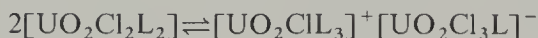


j. Complexes of the actinides. Several complexes of the actinides reported are given in Tables 12 and 13. Whereas only a few organolanthanide complexes were formed, a large number of organoactinide complexes have been reported (Table 13). As discussed earlier, some indirect methods of preparation also gave phosphine oxide complexes. For instance, oxidation of $(\text{Ph}_3\text{PH})_2[\text{UCl}_6]$ with chlorine gave $[\text{UCl}_4\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁶⁰². Similarly, $[\text{UBr}_4(\text{OPPh}_3)]$ was obtained from the reaction of UCl_4 with bromine in the presence of Ph_3PO ⁵⁹⁹ and $[\text{PuBr}_3\text{L}_2]$ from PuCl_3 and bromine in the presence of Ph_3PO ⁵⁹⁹. Air oxidation of Ph_3P in the presence of $[\text{UO}_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}$) gave $[\text{UO}_2\text{X}_2\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁶²⁴. From Table 12, it can be seen that a maximum of six phosphine oxide molecules can coordinate to an actinide. As Me_3PO is a small molecule it has low steric hindrance and hence six molecules can be accommodated about the central metal, unlike Ph_3PO , where only four molecules are accommodated about the metal.

An X-ray study of $[\text{ThCl}_4(\text{OPPh}_3)_3]$ ⁵⁹⁴ showed 7-coordinate geometry in an approximately capped octahedral environment with one oxygen in the capping position and three chlorine atoms in the capped face. Similarly, X-ray analysis of $[\text{UCl}(\text{OPMe}_3)_6]\text{Cl}_3$ ⁶⁰⁹ showed a distorted monocapped trigonal antiprismatic structure or distorted monocapped octahedral structure.

An X-ray study showed a *trans*-octahedral geometry for $[\text{UBr}_4(\text{OPPh}_3)_2]$ ⁵⁹⁰ and *cis*-octahedral for $[\text{UCl}_4(\text{OPPh}_3)_2]$ ⁶⁰³. The latter complex exists in the two different crystal phases, α and β ^{590,608a}, the β -phase being a metastable phase of the α -form. Heating $[\text{UCl}_4(\text{OPMe}_3)_2]$ at 100 °C for 6–7 h gave β - $[\text{UCl}_4\text{L}_2]$ ⁵⁹⁸. X-ray analysis of $[\text{UCl}_5(\text{OPPh}_3)]$ ⁶¹² and $[\text{UO}_2\text{Cl}_2(\text{OPPh}_3)_2]$ ⁶¹⁶ showed distorted octahedral geometries. In the latter, the ligands display a *trans*-octahedral disposition.

A thermodynamic study of the interaction of UCl_4 with Ph_3PO revealed that the UCl_4 – OPPh_3 interaction was weaker than the UCl_4 –*dms**o* interaction⁷¹⁵ ($\Delta H = -35.9$ versus $-45.3 \text{ kcal mol}^{-1}$). In the solution phase $[\text{UO}_2\text{Cl}_2(\text{topo})_2]$ undergoes restructuring:



None of the perchlorate, sulphate and halogeno sulphate complexes of thorium, uranium and neptunium (Table 12) have been studied by X-ray analysis making it difficult to confirm coordination by the perchlorate groups, although XSO_3^- groups ($\text{X} = \text{F}, \text{Cl}, \text{CF}_3$) are probably bidentate. In some thorium(IV) and neptunium(V) complexes, H_2O is coordinated: $[\text{ThL}_5(\text{OH}_2)](\text{ClO}_4)_4$ ⁶³² and $[\text{NpO}_2\text{L}_4(\text{OH}_2)]\text{ClO}_4$ ^{627,635}. Only two borohydride complexes of the actinides have been reported, $[\text{U}(\text{BH}_4)_4\text{L}_2]$ ^{638,639} and $[\text{U}(\text{BPh}_4)_2(\text{NO}_3)_2\text{L}_5]$ ⁶⁴⁰. An X-ray study of $[\text{U}(\text{BH}_4)_4\text{L}_2]\text{C}_6\text{H}_6$ ($\text{L} = \text{Ph}_3\text{PO}$) showed a *trans*-octahedral geometry⁶³⁹. C_6H_6 was lying as solvate molecules. The U – BH_4 distances (2.55 and 2.75 Å) reveal bi- and tri-dentate BH_4^- ions. In the solution phase, $[\text{U}(\text{BH}_4)_4\text{L}_2]$ exists as a mixture of *cis* and *trans* isomers.

Among the nitrate and thiocyanate complexes (Table 12), only one 1:1 adduct, $[\text{Th}(\text{NO}_3)_4(\text{OPPh}_3)]$, was obtained by electrochemical synthesis, the other complexes being obtained by routine methods. X-ray studies of $[\text{Th}(\text{O}_2\text{NO})_4\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁶⁴² and $[\text{Th}(\text{O}_2\text{NO})_4 \cdot 2.67\text{Me}_3\text{PO}]$ ⁶⁴⁰ showed chelation by the NO_3^- groups and 10-coordinate thorium. Similarly, an X-ray study of $(\text{Ph}_4\text{P}) [\text{Th}(\text{O}_2\text{NO})_5(\text{OPMe}_3)_2]$ ⁶⁴⁰ showed a 12-coordinate polyhedron.

X-ray studies of $[\text{U}(\text{NO}_3)_4\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁶⁵⁰ and $[\text{UO}_2(\text{NO}_3)_2\text{L}_2]$ ($\text{L} = \text{Bu}_3\text{PO}, (2\text{-O}_2\text{NC}_6\text{H}_4)\text{Ph}_2\text{PO}$)^{645,658} showed distorted *trans*-octahedral and 8-coordinate geometries, respectively. In the complex $[\text{U}(\text{NO}_3)_4\text{L}_2]$, the NO_3^- group is unidentate and in the uranyl nitrate complexes it is bidentate with a linear UO_2^{2+} moiety. An X-ray photoelectron study⁶⁴⁸ of the former complex also revealed distortion in the geometry and its decomposition pattern was suggested as



TABLE 12. Complexes of the actinides

Complex		X (or H _m A)	n	L	Ref.
A	(i) [ThX ₄ L _n]	Cl, Br	2, 3	Me ₃ PO, Et ₃ PO, Et ₂ PhPO, EtPh ₂ PO, Ph ₃ PO, Pr ⁱ ₃ PO, MePh ₂ PO	589–596
	(ii) [Th(OEt)Br ₃ L _n]	Cl, Br	3, 5	Me ₂ PhPO	596
	(iii) [Th(OH)Cl ₃ L ₂]·H ₂ O	—	5, 6	Me ₂ PhPO, Me ₃ PO	592, 596–598
	(i) [PaX ₄ L _n]	—	2, 3	Ph ₃ PO	593
B	(ii) [PaCl ₅ L ₅]	—	—	Ph ₃ PO	71
	(iii) [Pa(OEt) ₂ X ₃ L]	Cl, Br	2	Ph ₃ PO	590, 595
	(iv) [PaOX ₃ L ₂]	Cl	6	Me ₃ PO	598
	(i) [UCl ₃ L]	—	—	Ph ₃ PO, Ph ₂ BzPO	102, 110
C	(ii) [UX ₄ L _n]	Cl, Br	—	Ph ₃ PO	110
	(iii) [PaCl ₅ L ₅]	—	—	Ph ₃ PO	110
	(iv) [Pa(OEt) ₂ X ₃ L]	—	—	Ph ₃ PO	60
	(i) [UCl ₃ L]	—	—	Ph ₃ PO	599
	(ii) [UX ₄ L _n]	Br	1	R ₃ PO (R = Ph, Pr ⁱ , Et, Me, Bu, Bz)	507, 590–592, 596, 598,
	(iii) [PaCl ₅ L ₅]	Cl, Br	2	Et ₂ PhPO, Me ₂ PhPO, Ph ₂ MePO	600–607
	(iv) [U(OEt) ₂ X ₂ L]	Cl	3, 4	Me ₃ PO, Me ₂ PhPO, MePh ₂ PO, Bz ₃ PO	596, 598 601, 607
	(v) [UF _{5-x} Cl _x L _n] (0 ≤ x ≤ 5)	Cl, Br	6	Me ₃ PO, Me ₂ PhPO	592, 597, 598, 608b, 609
	(vi) [UF ₄ L ₂] (SbF ₆)	I	2	Ph ₃ PO	610
	(vii) [UF ₄ L ₂] (SbF ₆)	F, Cl, Br	1, 2	Ph ₃ PO	110, 611–613
	(viii) [UX ₅ L _n]	Cl, Br	—	Ph ₃ PO	614
	(ix) [UF _{5-x} Cl _x L _n] (0 ≤ x ≤ 5)	—	1, 2	Ph ₃ PO	613, 615a
	(x) [UF ₄ L ₂] (SbF ₆)	—	—	Ph ₃ PO	615b

D	(i) $[\text{NpX}_4\text{L}_n]$	Cl, Br	2	$\text{Me}_3\text{PO}, \text{Ph}_3\text{PO}$	590, 595, 598
		Cl	3–3.5	Ph_2MePO	607
		Cl	6	Me_3PO	598
	(ii) $[\text{PuX}_4\text{L}_n]$	Cl, Br	2	$\text{Ph}_3\text{PO}, \text{MePh}_2\text{PO}$	590, 595, 598, 599, 607
		Cl	3	Me_2PhPO	607
			6	Me_3PO	598
E	(i) $[\text{UO}_2\text{X}_2\text{L}_n]$	Cl, Br, I, NCS, NO_3	2	$\text{Et}_3\text{PO}, \text{Ph}_3\text{PO}, \text{Bu}_3\text{PO},$ $\text{topo}, \text{Bz}_3\text{PO}$	71, 616–625
		F	1.5–3	topo	626
		I	3, 4	Bu_3PO	623
		F	1.33	Bu_3PO	623
		—	4	topo	627
		—	2	topo	628
		Cl, Br	—	$\text{Bu}_3\text{PO}, \text{topo}$	628–630
F	(ii) $[\text{NpO}_2\text{ClL}_n]$ $[\text{NpO}_2\text{Cl}_2\text{L}_n]$	ClO_4	4, 5	$\text{Pr}_3\text{PO}, \text{Ph}_3\text{PO}$	631
	(iii) $(\text{R}_4\text{N})[\text{MO}_2\text{X}_3\text{L}]$ ($\text{R} = \text{C}_{10}\text{H}_{21}$; $\text{M} = \text{U}, \text{Np}$)	ClO_4	—	Ph_3PO	632
	(i) $[\text{ThX}_4\text{L}_n]$	ClO_4	4–6	$\text{Me}_3\text{PO}, \text{Pr}_3\text{PO}, \text{Ph}_3\text{PO}$	631
	(ii) $[\text{ThL}_5(\text{H}_2\text{O})\text{X}_4]$	ClO_4	2, 4	$\text{Bu}_3\text{PO}, \text{Me}_3\text{PO},$ $\text{Pr}_3\text{PO}, \text{Ph}_3\text{PO}$	632, 634
	(iii) $[\text{UX}_4\text{L}_n]$	ClO_4	—	topo	627, 635
	(iv) $[\text{UO}_2\text{X}_2\text{L}_n]$	—	—	Ph_3PO	579, 637
G	(v) $[\text{NpO}_2\text{L}_4(\text{H}_2\text{O})](\text{ClO}_4)$	$\text{SO}_3\text{F}, \text{SO}_3\text{Cl}$	2.5–3	Bu_3PO	633
	(i) $[\text{ThX}_4\text{L}_2]$	SO_4	1, 2	topo, Ph_3PO	579, 636
	(ii) $[\text{UO}_2\text{XL}_n]$	$\text{SO}_3\text{Cl}, \text{SO}_3\text{CF}_3$	—	topo	636
	(iii) $[\text{UO}_2\text{X}_2\text{L}_n]$	—	—	Ph_3PO	638, 639
	(iv) $[\text{UO}_2\text{L}_5](\text{SO}_3\text{CF}_3)_2$	BH_4	—	Me_3PO	640
H	(i) $[\text{UX}_4\text{L}_2]$	BPh_4	1	Ph_3PO	641
I	(ii) $[\text{UX}_2(\text{NO}_3)_2\text{L}_5]$	NO_3	2	$\text{Ph}_3\text{PO}, \text{Bu}_3\text{PO}, \text{topo},$ $(2\text{-O}_2\text{NC}_6\text{H}_4)\text{Ph}_2\text{PO}$	642–645
	(i) $[\text{Th}(\text{X})_4\text{L}_n]$		2.67	Pr_3PO	644
			2.67–5	Me_3PO	640, 644, 646
			3	topo, R_3PO ($\text{R} = 2\text{-ethylhexyl}$)	647

(continued)

TABLE 12. (continued)

Complex	X (or H _n A)	n	L	Ref.
(ii) [Th(NO ₃) ₂ L ₅ X ₂]	BPh ₄	—	Me ₃ PO	640
(iii) (Ph ₄ P)[Th(X)L ₂]	NO ₃	—	Me ₃ PO	640
(iv) [U(X) ₄ L _n]	NO ₃	2-5	Ph ₃ PO, Pr ₃ PO, Me ₃ PO	640, 644, 646, 648-651
(v) [UO ₂ (X) ₂ L ₂]	NO ₃	—	R ₃ PO ^a , RPh ₂ PO (R = 2-O ₂ NC ₆ H ₄)	617, 618, 620, 622, 626, 634, 643-645, 648, 652-660, 739b
(vi) [UO ₂ XL'L] ₂ X ₂ {L' = (BuO) ₃ PO}	NO ₃	—	Bu ⁿ PO	661, 662
(vii) [NpX ₄ L _n]	NO ₃	2-3	Bu ₃ PO, Ph ₃ PO, Pr ₃ PO, Me ₃ PO	644
(viii) [NpO ₂ (NO ₃)L ₃]	—	—	topo	627
(ix) [Pu(NO ₃) ₄ L ₂]	—	—	Ph ₃ PO	739c
(i) [ThX ₄ L _n]	NCS	4	Ph ₃ PO, Pr ⁱ ₃ PO, Bz ₃ PO	591, 663
(ii) [U(X) ₄ L _n]	NCS	6	Me ₃ PO	663
(iii) [UX ₄ L _n]	NCS	4	Me ₃ PO, Ph ₃ PO, Me ₂ PhPO, MePh ₂ PO, Pr ⁱ ₃ PO, Bz ₃ PO	591, 596, 663-665
(iv) [UO ₂ (NCS) ₂ L _n]	NCSe	4	Bu ₃ PO	666
(v) [UO ₂ (NCS) ₂ L ₂]·Me ₂ CO	—	2, 3	Ph ₃ PO, Bu ₃ PO	618, 620, 633
(vi) (R ₄ N)[UO ₂ (NCS) ₃ L _n] (R = C ₁₀ H ₂₁)	—	—	Ph ₃ PO	667
(vii) [M(NCS) ₄ L _n] (M = Np, Pu)	—	2	Bu ₃ PO	668
(i) [M(O ₂ CR) ₄ L _n] (M = Th, U; R = CH ₂ Cl, CHCl ₂ , CCl ₃ , CF ₃)	—	4	Me ₃ PO, Ph ₃ PO, Me ₂ PhPO, MePh ₂ PO	663, 669
(ii) [Th(O ₂)AL _n]	—	1-4	Ph ₃ PO, Me ₃ PO, Me ₂ PhPO,	670-672
(iii) [U(O ₂) ₂ A ₂ L]	<i>o</i> -C ₆ H ₄ (COOH) ₂ , 2,6-C ₅ H ₃ N(COOH) ₂ (CH ₂ COOH) ₂ H ₂ NNHC(S)SCH ₂ Ph ^b	1, 2	MePh ₂ PO Ph ₃ PO	79, 673, 674
		—	Ph ₃ PO	176

(iv) [$\{\text{UO}_2(\text{NO}_3)_2\}_2(\mu\text{-O}_2)\text{L}_n$]	—	CH ₃ COOH	—	Ph ₃ PO	675
(v) [$\text{UO}_2\text{A}_2\text{L}_n$]	1.5–2	—	—	Ph ₃ PO, Bu ₃ PO, topo, Bu ₃ PO, Pr ⁱ ₂ PhPO, Bz ₃ PO	622, 625, 626, 633, 654, 657, 676–679 645, 679
(vi) [$\text{UO}_2\text{A}_2\text{L}$]	—	RCOOH (R = Me, Me ₂ CH, Me ₃ C)	—	Ph ₃ PO, Pr ⁱ ₂ PhPO, RPh ₂ PO (R = 2-O ₂ N ⁺ C ₆ H ₄)	657, 677, 681 633, 682, 683 684a 49–51 684b 685
(vii) [$\text{UO}_2\text{A}_2\text{L}_2$]	—	MeCOOH	—	Ph ₃ PO	688, 689
(viii) [UO_2AL]	—	(COOH) ₂	—	R ₃ PO ^c	49, 51, 449, 493, 690–693
(ix) [UO_2ACIL_2] $\cdot\text{CH}_2\text{Cl}_2$	—	Cl ₃ CCOOH	—	Ph ₃ PO	694
(i) [ThA_4L]	—	Htta	—	topo, Ph ₃ PO	695
(ii) [MA_4L] (M = Th, U)	—	HA ^d	—	Ph ₃ PO	696
(iii) [$\text{MA}_2(\text{NCS})_2\text{L}_n$] (M = Th, U)	2	Hacac	2	Pr ⁱ ₃ PO	49–51, 343 697–699
(iv) [$\text{ThA}_m(\text{NO}_3)_{4-m}\text{L}_n$] (m = 1, 2)	2	Htta, Hdbm, Hbfa, Hba	2	Ph ₃ PO	698, 700, 701 702, 703
(v) [$\text{UA}_2\text{Cl}_2\text{L}_n$]	1, 2	Hacac	1, 2	Ph ₃ PO	688, 689
(vi) [$\text{UO}_2\text{A}_2\text{L}$]	—	Htta, Hbfa, Htfa	—	Ph ₃ PO, topo, Bu ₃ PO, Me ₃ PO, (2-EtC ₆ H ₁₁) ₃ PO	49, 51, 449, 493, 690–693
(vii) [$\text{UO}_2\text{A}_2\text{L}$] $\cdot\text{C}_6\text{H}_6$	—	MeCOCH(R)COMe (R = H, Me, Et, PhCH ₂ , Cl, NO ₂ , CN) R ¹ COCH ₂ COR ² (R ¹ , R ² = Me, CF ₃ , Bu ^t)	—	Ph ₃ PO	694
(viii) [$\text{UO}_2\text{A}_2\text{L}_n$]	—	Hacac	—	Me ₃ PO	695
(ix) [NpA_4L_n]	2, 3	Htta, Hacac	2, 3	Ph ₃ PO	696
(x) [$\text{NpO}_2\text{A}_2\text{L}$]	1–3	Hhfa, Hpvtf ^e , Htta	1–3	topo, Ph ₃ PO	49–51, 343 697–699
(xi) [MA_3L] (M = Pu, Am, Cm)	—	Hhfa, Htfa, Hpvifa, Hdppvm Htta	—	Me ₃ PO Ph ₃ PO, topo	698, 700, 701 702, 703

^aR = Me, Et, Pr, Bu, Ph, *n*-octyl, isopentyl, nonyl, decyl, hexadecyl, *sec*-octyl.

^bS-Benzylidithiocarbamate.

^cR = Me, Et, Bu, Ph, isoamyl, octyl, nonyl, decyl.

^dHA = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione.

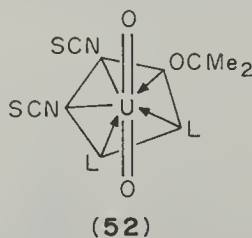
^eHpvifa = Pivaloyltrifluoroacetone.

TABLE 13. Complexs of the organoactinides

Complex	X	L	Ref.
A [(π -cp)ThX ₃ L _n] (n = 1,2)	Cl, Br	Ph ₃ PO	704
[(π -C ₉ H ₇)ThX ₃ LL'] (L' = thf)	Cl, Br	Ph ₃ PO	683
[(π -cp)MCl ₃ L ₂] (M = Np, Pu)	—	Ph ₃ PO, Me ₂ PhPO, MePh ₂ PO, Ph ₃ PO	705, 706
[(π -cp)M(NCS) _{3-n} L _n] (M = Np, Pu; n = 2,3)	—	Ph ₃ PO, Me ₂ PhPO, MePh ₂ PO, Ph ₃ PO	669
B [(π -MeC ₅ H ₄) ₃ UL]	—	Ph ₃ PO	707
C (i) [(π -cp)UX ₃ L _n]·xthf (x = 0,1)	Cl, Br	Ph ₃ PO(n = 2)	419, 708, 709
	Cl	Ph ₃ PO, Me ₂ PhPO, MePh ₂ PO(n = 2)	710
	NCS	Me ₂ PhPO(n = 3)	710
	BH ₄	Ph ₃ PO	711
(ii) [(π -C ₅ Me ₄ Et)UCl ₃ L ₂]	—	Ph ₃ PO	712
D (i) [(π -C ₉ H ₇)UX ₃ L]·thf	Cl, Br	Ph ₃ PO	683
(ii) [(π -C ₉ H ₇)UX ₃ L ₂]	Cl, Br	Ph ₃ PO	683
E (i) [(π -cp) ₂ UX ₂ L ₂]	Cl, Br	Ph ₃ PO	709
(ii) [(π -cp) ₂ UCl(acac)L ₂]	—	Ph ₃ PO	713
(iii) [(π -cp)UCl(acac) ₂ L]	—	Ph ₃ PO	689
(iv) [(π -cp)UCl ₂ (HBR ₃)L] (R = pyrazol-1-yl)	—	Ph ₃ PO	714
(v) [(π -cp)UCl ₂ (H ₂ BR ₂)L ₂]	—	Ph ₃ PO	714
(vi) [(π -cp)UCl(H ₂ BR ₂) ₂ L ₂]	—	Ph ₃ PO	714

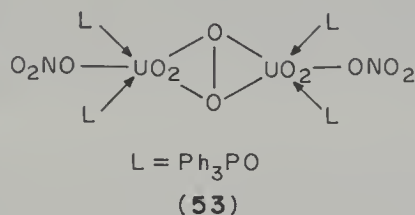
For [UO₂(NO₃)₂L₂] (L = Ph₃PO)⁶⁵⁷, only preliminary X-ray data have been reported. In [UO₂(NO₃)L'L₂(NO₃)₂] (L' = tbp; L = BuⁿPO)^{661,662}, bridging by L' with unidentate nitrate groups has been suggested.

As expected, thiocyanate or selenocyanate groups are N-bonded. The geometry about uranium in [U(NCS)₄L₄] (L = Me₃PO, Ph₃PO)^{664,665} was shown as square-antiprismatic by X-ray analysis. The structure of [UO₂(NCS)₂L₂(Me₂CO)] (L = Ph₃PO)⁶⁶⁷ is pentagonal bipyramidal (**52**) with a coordinated Me₂CO group.



The carboxylate and peroxo complexes of only thorium and uranium are known (Table 12). The peroxo complexes are very stable and inert towards oxidation. The peroxo complex [{UO₂(NO₃)L₂ }₂(μ -O₂)₂] has a dimeric structure (**53**)⁶⁷⁵. X-ray analyses have not been reported for any thorium(IV) carboxylate complexes; however, X-ray analysis of [UO₂ACIL₂]CH₂Cl₂(HA = Cl₃CCOOH; L = Ph₃PO)⁶⁸⁴ has shown a pentagonal bipyramidal geometry with apical oxygens of UO₂²⁺ moiety. An X-ray study of a 1:1 adduct has confirmed the dimeric structure of [UO₂(OAc)₂L₂] (L = Ph₃PO)⁶⁷⁷.

For the 1:2 uranyl acetate adduct $[\text{UO}_2(\text{OAc})_2\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$), only preliminary X-ray data (crystals monoclinic) are available⁶⁵⁷. The complexes are thermally stable, e.g. $[\text{UO}_2\text{A}_2\text{L}]$ ($\text{HA} = \text{Me}_3\text{CCOOH}$, Me_2CHCOOH , $\text{L} = \text{Ph}_3\text{PO}$)⁶⁸⁰ sublime in vacuum. In the thermal study of uranyl oxalate complexes, $[\text{UO}_2\text{AL}]$ ⁶⁸² ($\text{L} = \text{R}_3\text{PO}$), it was noted that heating splits off R_3PO . The oxalate decomposed either prior to the loss of R_3PO or simultaneously.

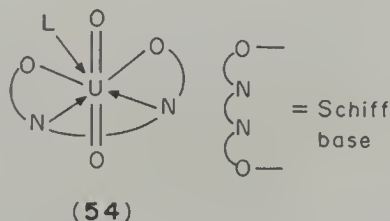


A series of adducts of actinide β -diketonates are known (Table 12). An X-ray study of $[\text{Th}(\text{O}_2\text{NO})_3(\text{dbm})(\text{OPPh}_3)_2]$ ⁶⁸⁷ has shown an irregular 10-coordinate polyhedron. X-ray analyses of $[\text{UO}_2(\text{tta})_2(\text{topo})]$ ⁶⁹¹, $[\text{UO}_2\text{A}_2(\text{OPPh}_3)]$ ($\text{HA} = \text{CH}_3\text{COCH}(\text{Cl})\text{COCH}_3$)⁶⁹⁴ and $[\text{UO}_2(\text{acac})_2(\text{OPPh}_3)]\text{C}_6\text{H}_6$ ⁶⁹⁶ have shown pentagonal bipyramidal geometry with linear UO_2^{2+} moieties. The benzene in the last complex lies as a solvate although solvation of the actinide diketonates is a rare observation.

¹H NMR study revealed *cis-trans* isomeric forms for $[\text{MO}_2\text{A}_2\text{L}]$ ($\text{M} = \text{U}, \text{Np}$; $\text{HA} = \text{Htta}, \text{Hbfa}$, etc.; $\text{L} = \text{Bu}_3\text{PO}, \text{Me}_3\text{PO}$)^{692,701}. $[\text{UCl}_2(\text{acac})_2\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁶⁸⁹ also showed fluxional behaviour, undergoing ligand exchange with the free ligand to form the $[\text{UCl}_2(\text{acac})_2\text{L}_2]$ species. Mass spectral study of $[\text{UO}_2\text{A}_2\text{L}]$ ($\text{HA} = \text{Htta}$, $\text{R}^1\text{COCH}_2\text{COR}^2$, $\text{R}^1, \text{R}^2 = \text{Me}, \text{CF}_3, \text{Bu}$)^{693,695} and $[\text{NpO}_2\text{A}_2\text{L}]$ ^{698,700} showed that the complexes were stable and formed molecular ions (dominant abundance). Also, the presence of the ligand in a metal β -diketonate facilitates the cleavage of β -diketone during fragmentation⁶⁹³.

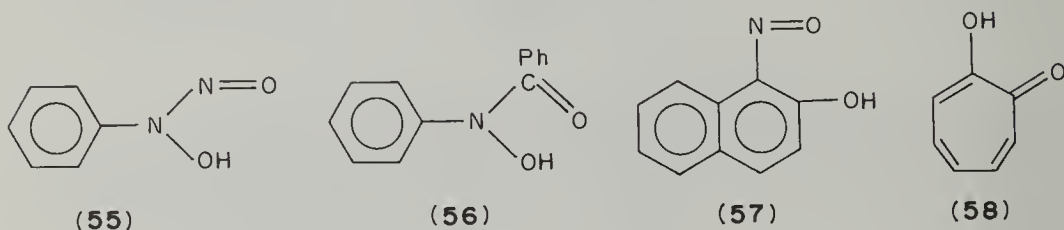
Interestingly, the bis(trimethylsilylamide)-stabilized 3-coordinate uranium complex $[\text{U}\{\text{N}(\text{SiMe}_3)_2\}_3\text{L}]$ in the presence of Ph_3PO ⁷¹⁶. A few pyrazolone complexes, $[\text{Th}(\text{pmbp})_4(\text{topo})]$ ⁷¹⁷, $[\text{UO}_2(\text{pmbp})_2(\text{topo})]$ ⁷¹⁷ and $[\text{UO}_2\text{A}_2(\text{topo})]$ ($\text{HA} = 1\text{-phenyl-3-methyl-4-acetylpyrazol-5-one}$)⁷¹⁸, have been reported as having 7-coordinate uranium and 9-coordinate thorium geometries.

N-(2-Carboxyphenyl)salicylideneimine (H_2A) forms a stable peroxy complex, $[\text{ThA}(\text{O}_2)(\text{OPPh}_3)]$ ⁷¹⁴. Tetradentate Schiff bases form 7-coordinate pentagonal bipyramidal complexes: $[\text{UO}_2\text{AL}]$ (54, $\text{L} = \text{Ph}_3\text{PO}$, $\text{H}_2\text{A} = \text{HOC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OH}$, $\text{HOC}_6\text{H}_4\text{CH}=\text{NC}_2\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OH}$ and $\text{HOC}_6\text{H}_4\text{CH}=\text{NC}_3\text{H}_6\text{N}=\text{CHC}_6\text{H}_4\text{OH}$ ⁹⁹³; $\text{HOC}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{PH}$ ⁷²⁰ and $\text{HOC}_6\text{H}_4\text{N}=\text{CHCH}=\text{NC}_6\text{H}_4\text{OH}$ ⁷²¹). A terdentate Schiff base, $\text{C}_6\text{H}_4(2\text{-OH})\text{CH}=\text{NCH}_2\text{C}_6\text{H}_4(2\text{-OH})(\text{H}_2\text{A})$ formed a 6-coordinate complex, $[\text{UO}_2\text{A}(\text{OPPh}_3)]$ ⁷²².



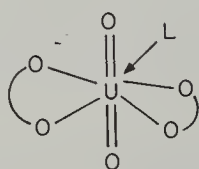
N-Nitrosophenylhydroxylamine (HA , 55) formed $[\text{ThA}_4(\text{OPPh}_3)]$ and $[\text{UO}_2\text{A}_2\text{L}] \cdot 3\text{H}_2\text{O}$ ⁵⁷². Similarly, 2-hydroxypyridine *N*-oxide, 2-hydroxypyridine-2-thione and

N-phenylbenzoylhydroxamic acid (HA, **56**) formed 7-coordinate $[\text{UO}_2\text{A}_2(\text{OPPh}_3)]$ complexes^{572,723,724}, whereas 1,2-naphthoquinone-1-oxime (HA, **57**) formed the 8-coordinate complex $[\text{UO}_2\text{A}_2(\text{OPPh}_3)(\text{OH}_2)]$ ^{739d,e} as confirmed by X-ray analysis. Oxamic acids, namely *N*-phenylbenzo-, *N*-phenylcinnamo- and *N*-phenylphenyl-aceto-hydroxamic acids also formed the adducts $[\text{UO}_2\text{A}_2(\text{OPPh}_3)]$ ⁷²⁵. 2-Hydroxycyclohepta-2,4,5-trien-1-one (tropolone, HA, **58**) formed the chelate complex $[\text{UO}_2\text{A}_2(\text{OPPh}_3)]$ ⁷²⁶⁻⁷²⁸. A few 8-coordinate complexes of hydrotris(pyrazol-1-yl)borate (HA) of the type $[\text{M}(\text{NCS})_2\text{A}_2\text{L}_n]$ ($\text{L} = \text{Me}_3\text{PO}, \text{Ph}_3\text{PO}, \text{Me}_2\text{PhPO}, \text{MePh}_2\text{PO}, \text{M} = \text{Th}, n = 2; \text{L} = \text{Me}_3\text{PO}, \text{M} = \text{U}, n = 2; \text{M} = \text{U}, \text{L} = \text{Ph}_3\text{PO}, \text{Me}_2\text{PhPO}, \text{MePh}_2\text{PO}, n = 1$)⁷²⁹ are known. Here when $n = 1$, the complexes have one bidentate and one tridentate pyrazol-1-yl ligand.

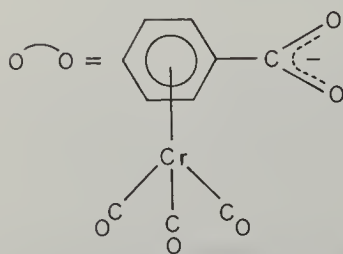


A number of adducts of uranyldithiocarbamates and phosphorodithioate and other sulphur-containing anions have been reported, viz. $[\text{UO}_2\text{A}_2\text{L}_2]$ HA = *N,N*-dialkyldithiocarbamic acid, e.g. Et_2NCSSH , $\text{L} = \text{Ph}_3\text{PO}$, Bu_3PO ^{654,730-733}, {HA = $\text{R}_2\text{PS}_2\text{H}$, $\text{R} = \text{MeO}, \text{PhO}$, etc., $\text{L} = \text{Ph}_3\text{PO}$ ⁷³⁴; HA = $\text{MeC}(\text{O})\text{SH}$, PhCS_2H , $\text{L} = \text{Ph}_3\text{PO}$ ^{654,735}; HA = $\text{Me}_2\text{CS}_2\text{H}$, $\text{L} = \text{Ph}_3\text{PO}$ ⁷³⁵}. X-ray studies of $[\text{UO}_2(\text{S}_2\text{CNEt}_2)_2(\text{OPPh}_3)]$ ^{730,731} and $[\text{UO}_2(\text{S}_2\text{CMe}_2)_2(\text{OPPh}_3)]$ ⁷³⁵ have shown irregular pentagonal bipyramidal structures with linear UO_2^{2+} moieties lying along the *z*-axis. A 1:2 adduct of the $(\text{NC})_2\text{N}^-$ anion $[\text{UO}_2(\text{N}(\text{CN})_2)_2(\text{OPPh}_3)_2]$ ⁷³⁶ has also been reported.

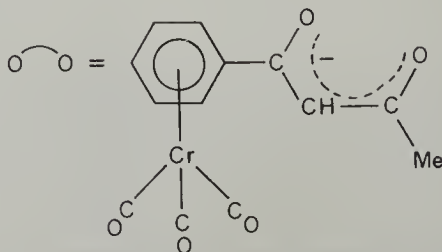
A few complexes with anions derived from ferrocene and chromium carbonyl derivatives are known: $[\text{UO}_2\text{A}_2\text{L}]$ {**59-62**; HA = $\text{Cr}(\text{CO})_3(\text{PhCOOH})$, $\text{Cr}(\text{CO})_3(\text{PhC}(\text{O})\text{CH}_2\text{C}(\text{O})\text{Me})$, $\text{L} = \text{Bu}_3\text{PO}, \text{Ph}_3\text{PO}$ ⁷³⁷; HA = $(\pi\text{-cp})(\pi\text{-C}_5\text{H}_4\text{R}')\text{Fe}$, $\text{R}' = \text{CH}_2\text{CO}_2^-$, $\text{Fe}(\text{C}_5\text{H}_4\text{-COCH}_2\text{COPh})_2$, $\text{L} = \text{Bu}_3\text{PO}, \text{Ph}_3\text{PO}$ }^{738,739a}.



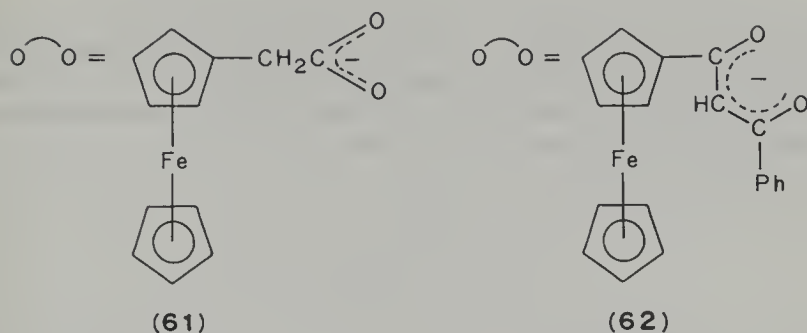
(59-62)



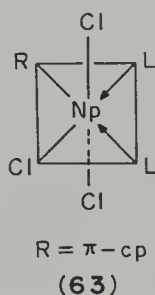
(59)



(60)



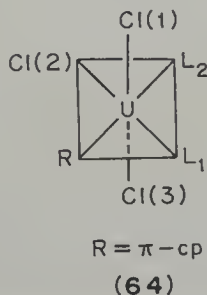
Adducts of the organoactinides (Table 13) with π -cyclopentadienyl or its substituted derivatives and π -indenyl and π -C₉H₇ as the organic moieties are known. Only a few adducts of thorium, neptunium and plutonium have been reported as compared with many for uranium. X-ray analysis of $[\pi\text{-cpNpCl}_3(\text{OPMePh}_2)]$ showed a *cis*-octahedral structure (63) about neptunium⁷⁰⁵.



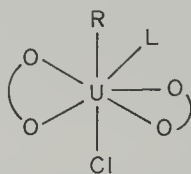
The adduct $[(\pi\text{-MeC}_5\text{H}_4)_3\text{U}(\text{OPPh}_3)]$ ⁷⁰⁷ was obtained from the reaction of $[(\text{MeC}_5\text{H}_4)_3\text{U}] \cdot \text{thf}$ and Ph_3PO and confirmed by X-ray analysis. Interestingly, similar reactions with Ph_3PS , Bu_3PSe and Bu_3PTe gave bridging chalcogenide complexes, $[\{(\text{MeC}_5\text{H}_4)_3\text{U}\}_2\text{E}]$ (E = S, Se, Te).

NMR (¹H, ³¹P) studies have revealed the existence of two isomers of $[(\pi\text{-cp})\text{UCl}_3(\text{OPPh}_3)_2]$ ⁴¹⁹. This and other complexes, namely $[(\pi\text{-cp})\text{U}(\text{BH}_4)_3\text{L}_2]$ ⁷¹¹ and $[(\pi\text{-cp})\text{UCl}(\text{acac})_2\text{L}]$ ⁶⁸⁹ (L = Ph_3PO), exhibit fluxional behaviour involving exchange phenomena between coordinated and free Ph_3PO ligands. The lability of the U—OPPh₃ bond in organouranium(IV) adducts was further demonstrated by preparing $[(\pi\text{-cp})\text{UCl}_3\text{L}_2]$ from $[(\pi\text{-cp})_3\text{UCl}]$ and $[\text{UCl}_4\text{L}_2]$ (L = Ph_3PO)¹¹⁰⁹ as well as the disproportionation of $[(\pi\text{-C}_9\text{H}_7)\text{UX}_3(\text{OPPh}_3)_2]$ in solution to give $[(\pi\text{-C}_9\text{H}_7)_3\text{UX}]$, $[\text{UX}_4\text{L}_2]$ and L.⁶⁸³

An X-ray study of $[(\pi\text{-cp})\text{UCl}_3\text{L}_2]\text{thf}$ (L = Ph_3PO)⁷⁰⁸ showed a highly distorted *mer*-octahedral structure with the L ligands in *cis* positions (64); the angles $\angle \text{Cl}(2)\text{UCl}(3)$



and $\angle \text{Cl}(1)\text{UL}(1)$ are 158.1° and 162.7° , respectively, whereas the others lie between 78° and 87° . An X-ray study of $[(\pi\text{-cp})\text{UCl}(\text{acac})_2(\text{OPPh}_3)]^{689}$ showed a pentagonal bipyramidal geometry (65). X-ray analysis of the indenyl complex $[(\pi\text{-C}_9\text{H}_7)\text{UBr}_3(\text{OPPh}_3)(\text{thf})]^{683}$ showed a structure similar to that of $[(\pi\text{-cp})\text{UCl}_3\text{L}_2]\text{thf}^{708}$, the only difference being that one ligand position is occupied by a thf molecule.



$\text{R} = \pi\text{-cp}$

(65)

2. Main Group elements

a. Complexes of the boron Group (IIIA). Boron(III) halides and boranes form a number of tetrahedral 1:1 adducts with R_3PO ligands, viz. $[\text{BX}_3\text{L}]$ [$\text{X} = \text{F}$, $\text{L} = \text{Me}_3\text{PO}$, Et_3PO , Pr_3PO , Bu_3PO , $\text{Ph}_3\text{PO}^{41,740-743}$; $\text{X} = \text{Cl}$, $\text{L} = \text{Me}_3\text{PO}$, Et_3PO , $\text{Ph}_3\text{PO}^{41,740,744,745}$; $\text{X} = \text{Br}$, $\text{L} = \text{Me}_3\text{PO}^{740}$; $\text{X} = \text{I}$, $\text{L} = \text{Ph}_3\text{PO}^{746}$]; $[\text{BF}_2\text{CIL}]$, $[\text{BFCl}_2\text{L}]$, $[\text{BF}_2\text{BrL}]$, $[\text{BFBr}_2\text{L}]$ ($\text{L} = \text{Me}_3\text{PO}$)⁷⁴⁰; $[(0.5)\text{B}_2\text{H}_6\text{L}]$ ($\text{L} = \text{R}_3\text{PO}$, $\text{R} = \text{Me}$, Ph)⁷⁴⁷, $[\text{B}_{10}\text{H}_{12}(\text{OPR}_3)_2]$ ($\text{R} = \text{Ph}$ or alkyl)⁷⁴⁸; $[\text{L}\cdot\text{H}_2\text{B}(\text{NMe}_3)](\text{PF}_6)$ ($\text{L} = \text{Me}_3\text{PO}$)⁷⁴⁹ and $[\text{Me}_3\text{P}(\text{OH})](\text{BF}_4)_2$ ⁷⁵⁰. Most of these complexes were studied using NMR spectroscopy (^1H , ^{13}C , ^{11}B , ^{19}F , ^{31}P)^{41,740,743,744}. The complex $\text{BF}_3(\text{OPMe}_3)$ was stable and distillable, but in water ligand replacement takes place⁷⁴¹. $\text{BI}_3(\text{OPPh}_3)$ is moisture sensitive.⁷⁴⁶ The X-ray structure of $\text{Ph}_3\text{PO}\cdot\text{BF}_3$ shows a tetrahedral structure with a $\text{B}-\text{O}-\text{P}$ angle of 134.5° ⁷⁵¹.

The complexes $[(0.5)\text{B}_2\text{H}_6(\text{OPR}_3)]$ ($\text{R} = \text{Me}$, Ph) are in fact $\text{BH}_3(\text{L})$ adducts⁷⁴⁷. The hydroxyphosphonium salt $[\text{Me}_3\text{P}(\text{OH})](\text{BF}_4)_2$ (prepared from BF_3 , HF and Me_3PO) is stable and sublimes without decomposition. The materials $[\text{B}_{10}\text{H}_{12}(\text{R}_3\text{PO})_2]$ ignite when brought into contact with HNO_3 , and reduce AgNO_3 to silver. This material is useful as a reducing agent, a high-energy fuel and a curing agent for natural or synthetic rubber¹²⁸¹.

Aluminium halides form adducts $[\text{AlX}_3\text{L}]$ ($\text{X} = \text{Cl}$, $\text{L} = \text{Me}_3\text{PO}$, Et_3PO , Bu^nPO , $\text{Ph}_3\text{PO}^{41,60,752,753}$; $\text{X} = \text{Br}$, $\text{L} = \text{Ph}_3\text{PO}^{41}$), $[\text{AlCl}_3(\text{OPMe}_3)(\text{OEt}_2)]^{752}$ and $[\text{AlCl}_3\text{L}_n]$ [$n = 2$ for Ph_3PO , $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CH}_2$, $n = 6$ for Me_3PO]^{66,752}. NMR data (^{13}C , ^{27}Al , ^{31}P) and X-ray data for $[\text{AlX}_3(\text{OPPh}_3)]^{41,751}$ supported tetrahedral structures about aluminium with linear $\text{Al}-\text{O}-\text{P}$ bonding (180°), of which these complexes represent the first examples.

Organoaluminium(III) forms stable adducts of the type $[\text{R}_3\text{Al}(\text{L})]$ ($\text{R} = \text{Me}$, Et , $\text{L} = \text{Me}_3\text{PO}$, Et_3PO , $\text{Ph}_3\text{PO}^{754-756}$; $\text{R} = \text{HC}\equiv\text{C}$, $\text{L} = \text{Ph}_3\text{PO}$)⁷⁵⁷; $[\text{Me}_2\text{AlOC}(\text{Me})=\text{CHCMe}_3(\text{OPPh}_3)]^{249}$. $[\text{Me}_3\text{Al}(\text{OPMe}_3)]$ was found to be distillable, but stable below 150°C , and had a low solubility in non-polar solvents^{758,759}. The adducts $[\text{Et}_3\text{AlL}]$ ($\text{L} = \text{Me}_3\text{PO}$, Et_3PO) are isosteric with hexaalkyldisiloxanes⁷⁵⁴. Similarly, the adduct $[\text{Al}(\text{OR})_3(\text{OPMe}_3)]$ ($\text{R} = \text{SiMe}_3$)²⁹⁹ is known. The enthalpy of adduct formation between Me_3Al and L was high for Me_3PO versus Ph_3PO (Me_3PO , $\Delta H = -32.0 \text{ kcal mol}^{-1}$; Ph_3PO , $\Delta H = -28.69 \text{ kcal mol}^{-1}$)⁷⁵⁵.

The adducts formed with gallium(III) are $[\text{GaX}_3\text{L}_n]$ ($\text{X} = \text{Cl}$, Br , I , $n = 1$, $\text{L} = \text{Ph}_3\text{PO}^{41,760-762}$; $\text{X} = \text{NCS}$, NCS_2 , $n = 3$, $\text{L} = \text{Pr}_3\text{PO}$, $\text{Ph}_3\text{PO}^{763,764}$); $[\text{Me}_3\text{Ga}(\text{OPMe}_3)]^{759}$ $[\text{R}_3\text{GaL}]$ (R , $\text{L} = \text{Me}$, OPMe_3 ; $\text{HC}\equiv\text{C}$, Ph_3PO)^{757,759} and $[\text{Ga}(\text{OR})_3]$

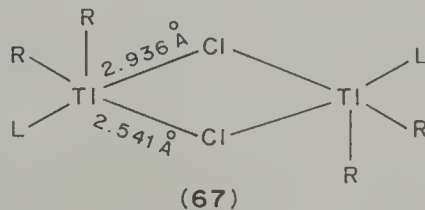
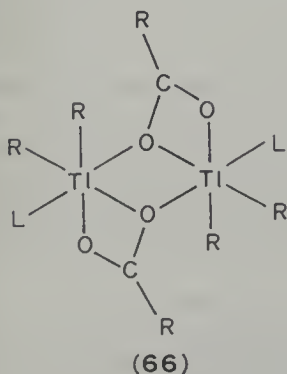
(OPMe₃) (R = SiMe₃)²⁹⁹; [Me₃Ga(OPMe₃)] was stable and distillable⁷⁵⁹. NMR (¹³C, ³¹P, ⁷¹Ga) and X-ray studies of [GaCl₃(OPPh₃)] showed a tetrahedral structure, again with a linear Ga—O—P moiety (180°) similar to that of [AlCl₃(OPPh₃)]⁴¹.

Indium(I) perchlorate gave an 1:4 adduct, [InL₄](ClO₄) (L = Ph₃PO)⁷⁶⁵. Indium(III) halides and pseudohalides formed 1:2 and 1:3 adducts of the type [InX₃L₂] (X = Cl, Br, I, NCO, SO₃F, L = Ph₃PO⁷⁶⁶⁻⁷⁶⁸; X = Cl, Br, L = Me₃PO, Ph₂MePO, Ph₃PO⁷⁶⁹), [InCl₃L₂(MeOH)] (L = Me₃PO)⁷⁶⁹, [InCl₃L₂(OH₂)]H₂O (L = Me₃PO)⁷⁶⁹, [InX₃L₃] (X, L = Cl, Me₃PO, Me₂PhPO, MePh₂PO, NCS, NCSe, NCO, Pr₃PO, Ph₃PO^{764,767,771,772}) and [(C₆F₅)₃InL] (L = Ph₃PO)⁷⁷³.

The complexes [InX₃L₂] (X = Cl, Br) exist as ionic complexes, [InX₂L₄][InX₄] (L = Ph₃PO, Ph₂MePO; X = Cl, Br)⁷⁶⁹. The cations presumably have *trans*-halogen groups. X-ray studies of [InCl₃L₂(MeOH)], [InCl₃L₂(OH₂)]H₂O (L = Me₃PO)⁷⁶⁹ and [InCl₃L₃] (L = PhMe₂PO) have shown *fac*-octahedral structures, whereas [InCl₃L₃] (L = Me₃PO) has a *mer*-octahedral structure⁷⁶⁹. A mixed heterometallic In—Co complex, [L₃In][Co(CO)₄]₃ (L = Ph₃PO) (⁵⁹Co NMR), has been reported⁷⁷⁰.

Thallium(III) halides and mixed halides form adducts of the type [TlX₃L₂] (X = Cl, Br, I, L = Ph₃PO)⁷⁷⁴⁻⁷⁷⁷ [TlBr₂XL₂] (X = Cl, I), [TlCl₂IL₂] (L = Ph₃PO)⁷⁷⁸⁻⁷⁷⁹, [TlClBrIL₂] (L = Ph₃PO)⁷⁸⁰ and [HL₂]⁺[TlCl₄]⁻ (L = Buⁿ₃PO)⁷⁸¹. An initial attempt to isolate [TlI₃L₂] failed and instead [TlI₃L₃] (L = Ph₃PO) was isolated⁷⁷⁴. [TlX₃L₂] adducts were formulated (X = Br, I) as [TlBr₂L₄][TlBr₄] and [TlI₂L₄][TlI₄L₂]⁷⁷⁴. However, X-ray analysis of [TlBr₃L₂] and [TlClBrIL₂] (L = Ph₃PO)^{775,778,780} confirmed the non-ionic nature of the complexes. The geometry about thallium is slightly distorted trigonal bipyramidal with *trans*-Ph₃PO groups.

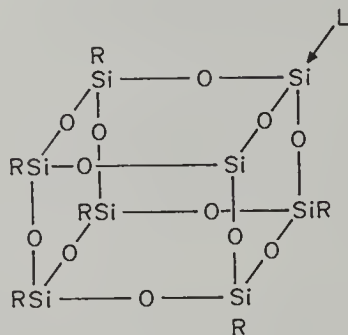
Mono-, di- and tri-organothallium(III) form complexes such as [RTlX₂L] (R = Ph, *p*-tol; X = Cl, Br, O₂CCCl₃; L = Ph₃PO)^{782,783}, [R₂TlX₂L₄] (X = Cl, Br, O₂CCF₃, O₂CCF₅, acac, hfa, tfa, dbm, R = C₆F₅, *p*-HC₆H₄, *n* = 1; X = NO₃, *n* = 2, L = Ph₃PO)⁷⁸⁴⁻⁷⁸⁸, [R₂Tl(O₂SR')L] (R = C₆F₅; R' = Ph, *p*-MeC₆H₄; L = Ph₃PO)⁷⁸⁹ and [R₃TlL] (R = C₆F₅, 3, 5-H₂C₆F₃, L = Ph₃PO)⁷⁹⁰. X-ray analyses of [(C₆F₅)₂·Tl(O₂CCF₅)L]⁷⁸⁷ and [(*p*-HC₆F₄)₂TlClIL] (L = Ph₃PO)⁷⁸⁸ revealed dimeric structures with unsymmetrical C₆F₅CO₂ and chloro bridging. The thallium has a distorted octahedral structure with unsymmetrically bonded C₆F₅CO₂ groups. In **66** each thallium has a distorted octahedral structure with unsymmetrically bonded C₆F₅CO₂ groups, and in **67** each thallium has approximately trigonal bipyramidal geometry with two R and more tightly held Cl groups in the equatorial plane.



b. Complexes of the silicon Group (Si, Ge, Sn, Pb) (IVA). Silicon(IV) complexes have been reported of the type [SiX₄L_n] (*n* = 2, 4; X = F, Cl, Br; L = Ph₃PO, Me₃PO)⁷⁹¹⁻⁷⁹³, [SiBr₂L₄(ClO₄)₂]⁷⁹¹, [SiL₄(ClO₄)₄]⁷⁹¹ and [Me₃SiCIL] (L = Ph₃PO)⁷⁹⁴. The 1:4 (M:L) complexes were shown to possess cations of the type [SiX₂L₄]²⁺ or [SiL₄]⁴⁺⁷⁹¹. Further,

the formation constant for $[\text{SiCl}_4(\text{OPPh}_3)_2]$ was higher (180 l mol^{-1}) than for $[\text{Me}_3\text{SiClL}]$ ($60 \pm 5 \text{ l mol}^{-1}$)⁷⁹⁴.

Reaction of Me_3Al or $(\text{Me}_2\text{CHO})_3\text{Al}$ with $\text{R}_7(\text{Si}_7\text{O}_9)(\text{OH})_3$ ($\text{R} = \text{cyclohexyl}$) gave quantitatively $[\text{R}_7(\text{Si}_7\text{O}_{12}\text{Al})_2]$, which on further reaction with Ph_3PO gave **68**, characterized by X-ray analysis⁷⁹⁵. Compound **68** represents the first well characterized example of aluminium-containing polyhedral silsesquioxanes proposed as models for the secondary building units of aluminosilicate minerals and zeolites.

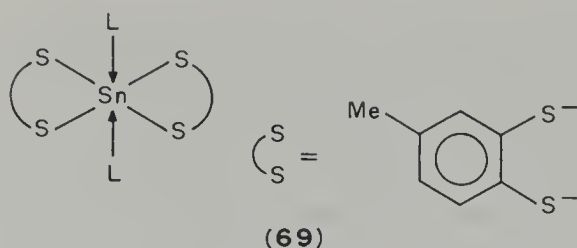


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The only known germanium(IV) complex is $[\text{GeCl}_4(\text{OPMe}_3)_2]$ ⁷³. In comparison with tin(IV), there are a few complexes with tin(II). Tin(II) forms complexes of the type $[\text{SnX}_2\text{L}_n]$ ($\text{X} = \text{Cl}, \text{Br}, \text{NCS}, \text{ClO}_4$, $n = 1$, $\text{L} = \text{Ph}_3\text{PO}$ ^{796,797}; $\text{X} = \text{Cl}, \text{Br}$, $\text{L} = \text{Ph}_3\text{PO}$, $n = 2$ ⁷⁹⁷). A ^{31}P NMR study revealed the formation of $[\text{SnL}_m]$ (SbF_6)₂ ($m = 2, 3$; $\text{L} = \text{Ph}_3\text{PO}$)⁷⁹⁸. $[\text{SnCl}_2(\text{OPPh}_3)]$ behaves as a ligand in the complexes $[\text{Mn}(\text{SnCl}_2\text{L})_5\text{Cl}]\text{Cl}$ ($\text{M} = \text{Ru}, \text{Os}$), $[\text{Rh}(\text{SnCl}_2\text{L})_4(\text{SnCl}_3\text{Cl})\text{Cl}]\text{Cl}$ and $[\text{Ir}(\text{SnCl}_2\text{L})_5\text{Cl}]\text{Cl}$ ³⁰⁶. Recently, $[\text{SnLi}_2]$ ($\text{L} = \text{dimethyl(phthalimidomethyl)phosphine oxide}$) was also used as a ligand, forming $[\text{PtCl}_2(\text{SnLi}_2)_2]$ ⁷⁹⁹.

Tin(IV) halides form 1:2 adducts with R_3PO ligands of the type $[\text{SnX}_4\text{L}_2]$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$; $\text{L} = \text{R}_3\text{PO}$, $\text{R} = \text{Me}, \text{Et}, \text{Bu}, \text{Cy}, \text{Ph}$ ^{63,64,73,800-816}, $\text{L} = \text{R}_2\text{R}'\text{PO}$, $\text{R} = \text{Et}, \text{R}' = \text{Et}, \text{Pr}, \text{Cy}$ ^{811,817,818}; $\text{R} = \text{Ph}, \text{R}' = \text{CH}=\text{CH}_2$ ⁶⁶; $\text{R} = \text{Me}, \text{R}' = \text{Me}$, etc., $\text{R} = \text{Ph}, \text{R}' = \text{Me}$ ⁸²⁰; $\text{L} = \text{RR}'\text{R}''\text{PO}$, $\text{R}, \text{R}', \text{R}'' = \text{Ph}, \text{Me}, i\text{-Pr}$ ⁸²¹), $[\text{SnCl}_3(\text{O}_2\text{CCH}_3)\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁸²² and $[\text{SnCl}_3(\text{OCH}_2\text{CF}_3)\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁸²³. The geometry about tin is variable for $[\text{SnX}_4\text{L}_2]$ complexes. Mössbauer data suggest *cis*-octahedral structures^{812,815,816}. However, X-ray studies showed a *trans*-octahedral structure in $[\text{SnBr}_4\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁸⁰⁶, but a *cis*-octahedral structure for $[\text{SnI}_4(\text{OPPh}_3)_2]$ ⁸⁰⁷, and $[\text{SnCl}_4(\text{OPPh}_3)_2]$ ⁸²⁴. An NMR study of $[\text{SnCl}_4\text{L}]$ ($\text{L} = \text{R}_2\text{R}'\text{PO}$, $\text{R} = \text{Me}, \text{R}' = \text{Me}$, etc.)⁸¹⁹ revealed *cis-trans* isomerism. Similarly, NMR data (^{31}P , ^{119}Sn) for $[\text{SnX}_4\text{L}_2]$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{Bu}_3\text{PO}$) complexes revealed that $[\text{SnCl}_4\text{L}_2]$ predominantly exist in the *trans*-octahedral form with the *cis* isomer in low abundance⁸²⁵. The formulation of $[\text{SnCl}_x\text{Br}_{4-x}\text{L}]$ and $[\text{SnCl}_x\text{Br}_{5-x}\text{L}]^-$ ($\text{L} = \text{Bu}_3\text{PO}$) has been established by NMR spectrometry⁸²⁵. X-ray analysis of the acetatotrichlorotin(IV) adduct $[\text{SnCl}_3(\text{O}_2\text{CCH}_3)(\text{OPPh}_3)]$ ⁸²² showed an octahedral structure with CH_3CO_2 acting as a chelating agent.

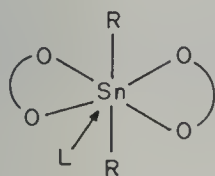
A sulphur-containing spirocyclic tin(IV) complex $[\text{SnX}_2(\text{OPPh}_3)_2]$ ($\text{H}_2\text{X} = \text{toluene-3,4-dithiol}$) (**69**) has been reported⁸²⁶. Monoorganotin(IV) forms 1:1 and 1:2 complexes of the type $[\text{RSnX}_3\text{L}_2]$ ($\text{R}, \text{X}, \text{L} = \text{Me}, \text{Et}, \text{Bu}^n, \text{Ph}, \text{Cl}, \text{Br}, \text{I}, \text{Ph}_3\text{PO}$ ^{807,812,816,824,827-830}, $\text{Bu}^n, \text{Cl}, \text{Cy}_3\text{PO}$ ^{827,830}; $\text{R}'\text{CO}_2\text{CH}_2\text{CH}_2, \text{Cl}, \text{topo}, \text{Ph}_3\text{PO}$ ($\text{R}' = \text{Me}, \text{Bu}$)⁸³¹, $\text{Me}, \text{Ph}, \text{Cl}, \text{Br}, \text{Bu}_3\text{PO}$ ^{832,1}; $[\text{PhSnCl}_2\text{BrL}]$, $[\text{PhSnClBr}_2\text{L}]$ ($\text{L} = \text{Bu}_3\text{PO}$)⁸³², $(\text{Et}_4\text{N})[\text{RSnCl}_4\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁸³³ and $[\text{RSnCl}_3\text{L}]$ ($\text{L} = \text{Et}_3\text{PO}, \text{Ph}_3\text{PO}$)⁸³⁴. For $[\text{EtSnX}_3\text{L}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} = \text{Ph}_3\text{PO}$), X-ray analysis established *trans*-octahedral structures. Mössbauer data favoured a *cis*-octahedral structure for $\text{PhSnCl}_3\text{L}_2$ ($\text{L} = \text{Ph}_3\text{PO}$)^{816,827}. Similarly, a



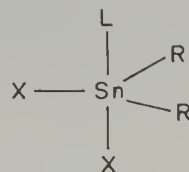
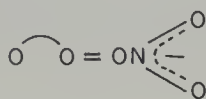
trans-octahedral was suggested for $[\text{BuSnCl}_3\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$, Cy_3PO)^{827,830}, a *cis*-octahedral structure (wrt, R, L) for $(\text{Et}_4\text{N}) [\text{RSnCl}_4\text{L}]$ and a trigonal bipyramidal structure was suggested for $[\text{PhSnCl}_2\text{BrL}]$ and $[\text{PhSnClBr}_2\text{L}]$ (^{31}P , ^{119}Sn NMR)⁸³².

Diorganotin(IV) forms 1:1 and 1:2 complexes of the type (A) $[\text{R}_2\text{SnX}_2\text{L}]$ [R , X , $\text{L} = \text{Et}$, Bu , Ph , $p\text{-MeOC}_6\text{H}_4$, Cl , Br , NCS , Ph_3PO , Bu_3PO]^{827,830,835-840}; Et , Bu , Cl , Cy_3PO ⁸³⁰], (B) $[\text{Et}_2\text{SnX}_2\text{L}]$ ($\text{L} = \text{Et}_2\text{RPO}$; $\text{R} = \text{Bu}$; $\text{X} = \text{Cl}$, etc.)⁸⁴¹, (C) $[\text{R}_2\text{SnX}_2\text{L}_2]$ ($\text{R} = \text{Me}$, Et , $\text{H}_2\text{C}=\text{CH}$, Bu , Ph , $p\text{-MeC}_6\text{H}_4$, PhCH_2 , Cl , Br , I , NCS , OCOCF_3 , Ph_3PO ^{812,816,827,837,839,842-851}, $\text{R}'\text{CO}_2\text{CH}_2\text{CH}_2$, Cl , Br , Et_3PO , Bu_3PO , *topo*, Ph_3PO ^{344,831,834,836,840}), (D) $[\text{PhMeSnCl}_2(\text{OPPh}_3)]$ ⁸⁵² and (E) $[\text{Me}_2\text{SnL}_4]$ (Ph_4B)₂, $[\text{Me}_2\text{SnL}_2(\text{OAsPh}_3)_2]$ (BPh_4)₂ ($\text{L} = \text{Ph}_3\text{PO}$)^{728,853,854}.

Complexes A were formed by the direct reaction of diorganotin(IV) compounds with a ligand whereas complexes B were formed on thermal heating of $[\text{Et}_2\text{SnX}_2[\text{Et}_2\text{P(OR)}]]$, wherein $\text{Et}_2\text{P(OR)}$ isomerized to Et_2RPO . An X-ray study of the nitrate complex $[\text{Ph}_2\text{Sn}(\text{O}_2\text{NO})_2(\text{OPPh}_3)]$ revealed a pentagonal bipyramidal structure (70)⁸⁵⁵. On the basis of Mössbauer data, trigonal bipyramidal geometry with R groups in the equatorial plane are suggested for complexes A (71)^{836,837,839}. An NMR study (^{31}P , ^{119}Sn) of the exchange of free and coordinated Bu_3PO in $[\text{Ph}_3\text{SnX}_2\text{L}]$ ($\text{X} = \text{Cl}$, Br) revealed that the exchange was rapid at room temperature but slow at 60°C. When $[\text{Ph}_2\text{SnX}_2]$ and L were mixed, the formation of $[\text{Ph}_2\text{SnClBrL}]$ complexes was detected^{836,838}.

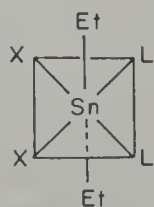


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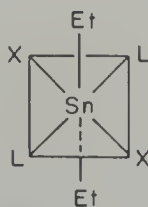


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Mössbauer and IR data supported a *trans* disposition of the R groups in complexes C–E. X-ray studies of $[\text{Et}_2\text{SnX}_2\text{L}_2]$ ($\text{X} = \text{Cl}$, I ; $\text{L} = \text{Ph}_3\text{PO}$)^{847,848} revealed the existence of *cis* and *trans* isomers (72, 73). NMR studies (^{31}P , ^{119}Sn)^{836,840} also revealed the formation of 1:2 complexes $[\text{Ph}_2\text{SnX}_2\text{L}_2]$ ($\text{X} = \text{Cl}$, Br ; $\text{L} = \text{Bu}_3\text{PO}$, Ph_3PO), while another study revealed partial dissociation of the complexes $[\text{R}_2\text{SnCl}_2\text{L}_2]$ ($\text{L} = \text{Et}_3\text{PO}$, Ph_3PO)^{344,834}.

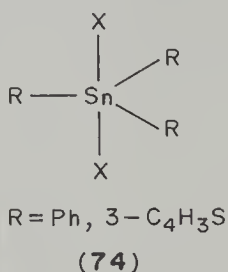


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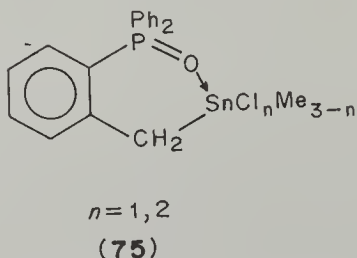


(73)

Triorganotin(IV) forms complexes of the type (A) $[R_3SnXL]$ ($R, X, L = \text{Me, Bu, Ph, } p\text{-MeC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, 3\text{-furyl, 3-thienyl, Cl, Br, NCS, NCO, NO}_3, \text{N}_3, \text{OCOCF}_3, \text{O}_2\text{COCCl}_3, \text{Ph}_3\text{PO}^{794,839,846,851,856-871}; \text{Et, Ph, etc., Cl, Br, I, Et}_3\text{PO, MePh}_2\text{PO, Et}_2\text{BuPO, Ph}_3\text{PO}^{834,841,872-875}$), (B) $[R_2R'SnXL]$ ($R_2R', X, L = \text{Bu}_2\text{Ph, Ph}_2\text{Bu, Cl, Br, Ph}_3\text{PO}^{876}$ and (C) $[R_3SnL_2]X_2$ ($R_3, L, X = \text{Me}_3, \text{Bu}_3, \text{Bu}_2\text{Ph, Ph}_2\text{Bu, Ph}_3\text{PO, BF}_4, \text{BPh}_4^{853,876,877}$). The formation of $[Et_3SnXL]$ ($L = Et_2RPO$) takes place via $[Et_3SnXL']$ ($L' = Et_2(OR)P$) involving isomerization of L' to $L^{841,875}$. Other complexes were formed by usual methods. Mössbauer and NMR data for numerous complexes have favoured *trans*-trigonal bipyramidal geometries for A–C complexes with R_3 groups in the equatorial plane. X-ray analyses of $[Ph_3Sn(ONO_2)(OPPh_3)]^{864,865}$ and $[Sn(C_4H_9S)_3Br(OPPh_3)]^{869,870}$ have confirmed the proposed structures (74) for A, B and cations of C. The carboxylate groups O_2COCR_3 ($R = \text{F, Cl}$) were also unidentate^{867,868}.



Triphenyltin phosphinylacetate, $[Ph_3SnO_2CCH_2P(O)Ph_2]$, forms a 1:1 adduct with $[Ph_3SnCl]^{878}$. A few organotin(IV) complexes involve intramolecular coordination (75)⁸⁷⁹. A few lead(II) complexes $[PbL_m]$ (SbF_6)₂ have been reported ($m = 2, 3$; $L = Ph_3PO$); their existence was established by a ³¹P NMR study⁷⁹⁸. Lead(IV) chloride formed 1:2 whereas lead(IV) acetate and dihydrogenphosphate formed 1:1 adducts with $Ph_3PO^{880,881}$. $[Pb(H_2PO_4)_4(OPPh_3)]$ is a superior oxidizing agent to $Pb(OAc)_4(OPPh_3)$ for organic compounds owing to the higher thermal and moisture stability of the former. However, hot water hydrolyses the $[Pb(H_2PO_4)_4(OPPh_3)]$ adduct⁸⁸¹.



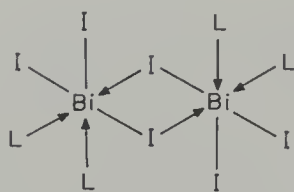
Diorganolead(IV) adducts have been reported: (A) $[Ph_2PbX_2L_n]$ ($X, L = \text{Cl, Br, I, Ph}_3\text{PO}$ for $n = 1, \text{Br, I, Ph}_3\text{PO}$ for $n = 2^{840,882}, \text{NCS, Ph}_3\text{PO}$ for $n = 2^{883}$) and (B) $[Me_2PbX_2L]$ ($L = R_3PO, R = \text{Me, Et, Bu}^n, \text{Ph; } X = \text{quinolin-8-olate, YC}_6\text{H}_4\text{CO}_2, Y = \text{H, } o\text{-Me, } m\text{-Me, } p\text{-Me, } p\text{-MeO}^{884}$. The complexes A were labile, particularly for $X = \text{Br, I}$ and solvents such as $\text{MeOH, Me}_2\text{CO}$ replaced Ph_3PO^{882} . Trigonal bipyramidal structures were suggested for $n = 1$ and octahedral for $n = 2$. Complexes B studied by NMR (Job's method) are 7-coordinate and the stability constants decreased in the order $R = \text{Me} > \text{Et} > \text{Bu}^n > \text{Ph}^{884}$. A few triorganolead(IV) adducts, $[R_3PbXL]$ ($R = \text{Me, Ph; } X = \text{Cl, NCO; } L = \text{Ph}_3\text{PO}$) with trigonal bipyramidal geometry are also known^{851,885}.

c. Complexes of the phosphorus Group (P, As, Sb, Bi) (VA). The phosphorus(V) complexes $[\text{PF}_5\text{L}]$ ($\text{L} = \text{Bu}_3\text{PO}$, Ph_3PO) and *trans*- $[\text{PF}_4(\text{OPBu}_3)_2]^+\text{F}^-$ have been studied using ^{19}F and ^{31}P NMR⁸⁸⁶. ^{31}P NMR revealed the basicity order of the ligands to be $\text{Bu}_3\text{PO} > \text{Ph}_3\text{PO} > \text{Bu}_3\text{P}$. Similarly, arsenic complexes of the type (A) $[\text{AsCl}_3(\text{OPMe}_3)]$, (B) $[\text{AsCl}_5(\text{OPMe}_3)]^{491,492}$, (C) $[\text{AsCl}_5(\text{OPPh}_3)_2]^{887}$ and (D) $[\text{Me}_3\text{POH}][\text{AsF}_6]^{750}$ have been reported. Complex C was prepared at 0°C and evolved Cl_2 at room temperature. Fresh samples were weakly paramagnetic, possibly owing to a low concentration of an arsenic(IV) species as an intermediate in the solid-state reduction of arsenic(V) to arsenic(III)⁸⁸⁷. Complex D, obtained from Me_3PO , HF and AsF_5 , decomposed on heating, forming $[(\text{Me}_3\text{PO})\text{AsF}_5]^{750}$.

Antimony(III) and antimony(V) form complexes of the type (A) $[\text{SbX}_3\text{L}_n]$ ($\text{X} = \text{Cl}$, Br , I ; $\text{L} = \text{R}_3\text{PO}$, $\text{R} = \text{Me}$, Ph , $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CH}_2$; $n = 1$ or $2^{66,491,492,888-890,907}$), (B) $[\text{SbCl}_5\text{L}]$ ($\text{L} = \text{R}_3\text{PO}$, $\text{R} = \text{Me}$, Ph , Bu^n)^{59,64,491,492,891-895}, (C) $[\text{SbCl}_3\text{Br}_2\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁸⁹⁶, (D) $[\text{SbF}_n\text{Cl}_{5-n}\text{L}]$ ($\text{L} = \text{R}_3\text{PO}$; $\text{R} = \text{Bu}$, Ph ; $n = 1-5$)⁸⁹⁷, (E) $[\text{Sb}(\text{OR})\text{Cl}_4\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$; $\text{R} = \text{Me}$, Et , ClC_2H_4 , $\text{Cl}_3\text{C}_2\text{H}_2$, $\text{F}_3\text{C}_2\text{H}_2$)^{823,898-900}, (F) $[\text{SbCl}_4(\text{NR}_2)\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$; $\text{R} = \text{SO}_2\text{F}$)⁹⁰¹, (G) $[\text{Sb}(\text{SO}_3\text{CF}_3)_3\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁹⁰² and (H) $[\text{L}_2\text{H}]^+[\text{SbCl}_6]^-$ and $(\text{L}_3\cdot\text{H}_3\text{O})^+[\text{SbCl}_6]^-$ ($\text{L} = \text{Ph}_3\text{PO}$)⁹⁰³. Similarly, a number of organo-antimony(V) complexes are known: (I) $[\text{R}_3\text{SbL}_2](\text{ClO}_4)_2$ ($\text{L} = \text{Ph}_3\text{PO}$; $\text{R} = \text{Me}$, Ph)⁹⁰⁴, (J) $[\text{R}_2\text{SbCl}_3\text{L}]$ ($\text{R} = \text{Me}$, Et , Ph ; $\text{L} = \text{Ph}_3\text{PO}$)⁹⁰⁵ and (K) $[\text{R}_n\text{SbX}_{5-x}\text{L}]$ ($\text{X} = \text{F}$, Br ; $\text{L} = \text{Ph}_3\text{PO}$, $\text{R} = \text{Ph}$, *p*- MeC_6H_4 , *p*- ClC_6H_4 ; $n = 1-3$)⁹⁰⁶.

A single-crystal X-ray study of $[\text{SbCl}_5(\text{OPMe}_3)]$ showed a distorted octahedral structure⁸⁹². The angle $\text{Sb}-\text{O}-\text{P}$ of 139° reveals considerable deviation from the tetrahedral angle at oxygen. For other complexes of type B, and also for complexes C-F, J and K, octahedral and in the case of $[\text{R}_3\text{SbL}_2](\text{ClO}_4)_2$ ⁹⁰⁴ trigonal bipyramidal structures are suggested. As expected, the Lewis acidity of the metal halides decreased as the halide increased in atomic number, i.e. $\text{F} > \text{Cl} > \text{Br} > \text{I}$ ^{897,906}.

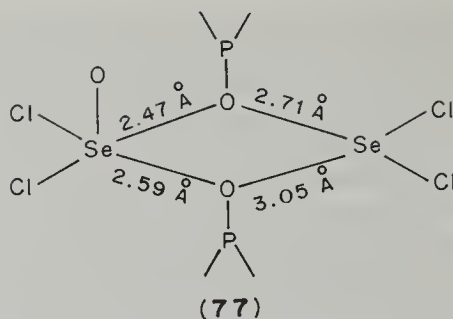
Bismuth(III) and bismuth(V) form complexes of the type (A) $[\text{BiCl}_3\text{L}_n]$ ($n = 1-3$; $\text{L} = \text{Ph}_3\text{PO}$)^{890,907,908}, (B) $[\text{BiI}_3\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁹⁰⁹, (C) $[\text{Ph}_3\text{BiL}_2]\text{X}_2$ ($\text{X} = \text{ClO}_4$, PF_6 ; $\text{L} = \text{Ph}_3\text{PO}$)⁹¹⁰, (D) $[\text{Ph}_3\text{BiL}_2]_2\text{O}(\text{ClO}_4)_2$ ($\text{L} = \text{Ph}_3\text{PO}$)⁹¹⁰ and (E) $[\text{Bi}(\text{SO}_3\text{CF}_3)_3\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$)⁹⁰². For complex B an iodo-bridged dimeric structure (76) and for complex D an oxygen-bridged dimeric structure have been suggested. However, X-ray analyses should be extended to further compounds.



(76)

d. Complexes of the selenium Group (Se, Te) (VIA). There are only two complexes of selenium(V) with R_3PO ligands, $[\text{SeOCl}_2(\text{OPMe}_3)]^{491}$ and $[\text{SeOCl}_2(\text{OPPh}_3)_2]^{911}$. An X-ray study of the latter revealed a distorted square-pyramidal geometry about the selenium atom. Ph_3PO acts as a bridge, but the $\text{Se} \cdots \text{O}-\text{P}$ bonds differ significantly (77). The former complex presumably has a similar structure.

Tellurium(IV) chloride forms hygroscopic $[\text{TeCl}_4\text{L}_n]$ adducts ($\text{L} = \text{Ph}_3\text{PO}$, Me_2PhPO ; $n = 1, 2$)⁸⁹⁷. Similarly, a series of hygroscopic organotellurium(III) and (IV) adducts have been reported: (A) $[(p\text{-RC}_6\text{H}_4)\text{TeCl}]\text{L}$ ($\text{R} = \text{MeO}$, PhO ; $\text{L} = \text{Ph}_3\text{PO}$)⁹¹², (B) $[\text{RTeCl}_3\text{L}_n]$ ($n = 1, 2$, L , $\text{R} = \text{topo}$, Ph , *p*- PhOC_6H_4)⁹¹³, $n = 1$, L , $\text{R} = \text{Ph}_3\text{PO}$, Me_2PhPO , Ph , *4*- MeOC_6H_4 , *4*- BrC_6H_4 , *p*- HOC_6H_4)^{897,914} and (C) $[\text{Ph}_2\text{Te}(\text{ONO}_2)_2(\text{OPPh}_3)]^{915}$. For



complexes B and C (except for $n = 2$), 5-coordinate monomeric distorted octahedral structures have been suggested (one site occupied by a lone pair).

3. Alkali and alkaline earth elements

a. *Complexes of the alkali metal Group (IA).* Alkali metals also form complexes, although the number of investigations is small. From solution-phase studies, formation of species of the type $[ML]X$ $\{M = \text{Li}, X = \text{Cl}, \text{Br}, \text{ClO}_4, L = \text{Ph}_3\text{PO}$ or $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{Ac}; M = \text{Na}, L = \text{Ph}_3\text{PO}, X = \text{I}\}$ ^{365,916-918} was established. Other complexes studied in the solid state include (A) $[\text{LiL}_n]X$ ($L = \text{Ph}_3\text{PO}, n = 4, X = \text{Br}, \text{ClO}_3, \text{PF}_6, \text{ReO}_4, \text{IO}_4, \text{SbF}_6, \text{AuCl}_3, \text{SnCl}_3, \text{GaCl}_4; L = \text{Ph}_3\text{PO}, n = 5, X = \text{I}, \text{NO}_3, \text{BF}_4, \text{BrO}_3$)⁴⁷⁸; (B) $[\text{NaL}_5X]$ ($L = \text{Ph}_3\text{PO}; X = \text{I}, \text{ClO}_4, \text{IO}_4, \text{BPh}_4$)⁴⁷⁸, (C) $[\text{Me}_3\text{SiOML}]_4$ ($M = \text{Li}, \text{Na}, \text{K}; L = \text{Me}_3\text{PO}$)⁹¹⁹ and (D) $[(15\text{-crown-5})\text{Na}(\text{Me}_3\text{PO})]^+[(\text{CO})_3\text{Fe}(\mu\text{-Bu}'_2\text{P})\text{Rh}(\text{CO})(\text{PMe}_3)]^-$ ⁹²⁰. For complexes A and B with $n = 5$, 5-coordinate square-pyramidal geometry, and for complexes A with $n = 4$, tetrahedral geometry have been suggested. In complex C, each alkali metal is tetrahedrally surrounded.

Alkali metal complexes in the zero-valent state, such as $[ML]$ and $[M_2L]$ ($L = \text{Ar}_3\text{PO}$), have also been reported⁹²¹.

b. *Complexes of the alkaline earth metal Group (Be, Mg, Ca) (IIA).* Only two beryllium(II) complexes, $[\text{BeL}_2(\text{NO}_3)_2]$ and $[\text{BeL}_4](\text{BF}_4)_2$ ($L = \text{Ph}_3\text{PO}$) are known⁹²². In contrast, more complexes have been reported for magnesium(II) and calcium(II), namely $[\text{ML}_n\text{X}_2]$ $\{M = \text{Mg}, \text{Ca}, L = \text{Me}_3\text{PO}, \text{Ph}_3\text{PO}, \text{Bu}^n_3\text{PO}, n = 4, X = \text{ClO}_4, \text{BF}_4$ ^{137,232,233,923}; $M = \text{Mg}, \text{Ca}, L = \text{Me}_3\text{PO}, \text{Ph}_3\text{PO}, n = 5, X = \text{ClO}_4$ ⁹²³; $M = \text{Ca}, L = (\text{HOCH}_2)_3\text{PO}, n = 6, X = \text{BF}_4$ ²³⁴\}, $[\text{MgL}_5(\text{OH}_2)](\text{ClO}_4)_2$ ($L = \text{Me}_3\text{PO}, \text{Ph}_3\text{PO}$)⁹²³ and $[\text{MgL}_2\text{Cl}_2]_n$ $\{L = (\text{HOCH}_2)_3\text{PO}\}$ ²³⁴. An X-ray study of $[\text{MgL}_5](\text{ClO}_4)_2$ ($L = \text{Me}_3\text{PO}$)⁹²⁴ showed a square-pyramidal geometry with a shorter axial $\text{Mg}-\text{O}$ bond (1.94 Å); compared with the basal $\text{Mg}-\text{O}$ bonds (2.03 Å); this is attributed to $\text{O} \rightarrow \text{Mg}$ π -bonding along the axial bond. The aquated analogue $[\text{MgL}_5(\text{OH}_2)](\text{ClO}_4)_2$ ⁹²⁵ has an octahedral structure. Each cation is hydrogen-bonded to two ClO_4^- anions via the coordinated H_2O molecules. For the 1:4 complexes, 5-coordinate species of the type $[\text{ML}_4(\text{OCIO}_3)](\text{ClO}_4)$ with presumably a square-pyramidal geometry have been suggested from spectral and other studies^{232,923}. For $[\text{MgL}_2\text{Cl}_2]_n$, a polymeric structure was suggested²³⁴.

A ³¹P NMR study on the exchange of the Ph_3PO with the coordinated ligand in $[\text{Mg}(\text{OPPh}_3)_5]^{2+}$ revealed that magnesium has harder Lewis acid character relative to zinc in $[\text{Zn}(\text{OPPh}_3)_4]^{2+}$ ⁹²⁶. The interaction of CaCl_2 with $\text{Me}_2\text{P}(\text{O})\text{CH}_2\text{R}$ ($\text{R} = \text{Cl}, \text{OMe}, \text{OPh}$) in MeCN has also been reported²²⁷. Reaction of Ph_3PO with Mg^{2+} in chlorophyll a and b involves replacement of the keto groups of the chlorophyll^{927a}.

B. Di-, Tri- and Tetra-tertiary Phosphine Oxides

Most of the complexes reported are with di-tertiary phosphine oxides, a small number of complexes with tri-tertiary phosphine oxides and a few complexes with tetra-tertiary phosphine oxides.

1. Transition elements

a. Complexes of scandium and titanium Groups (IIIB and IVB). Scandium(III) on reaction with the bidentate ligand dpeO_2 gave an octahedral complex, $[\text{Sc}(\text{dpeO}_2)_3] \cdot (\text{ClO}_4)_3$ ⁵⁵. Similarly, the tri-tertiary phosphine oxide $\{\text{Ph}_2\text{P}(\text{O})\}_3\text{CH}$ formed complexes with scandium(III) and yttrium(III) of stoichiometry $[\text{ML}_3]$ (where L is the anion $\{\text{Ph}_2\text{PO}\}_3\text{C}^-$)^{927b}. One PO end of the anion is uncoordinated and thus it acts as a bidentate ligand in these complexes. ³¹P NMR study revealed the lack of lability of $\text{Sc}-\text{OP}$ or $\text{Y}-\text{OP}$ bonds so that there was no exchange of the coordinated and uncoordinated PO groups or with the added lithium salt, $\{\text{Ph}_2\text{P}(\text{O})\}_3\text{C}^- \text{Li}^+$. The value of the $^{89}\text{Y}-^{31}\text{P}$ coupling was 6.5 Hz (for Y, $I = \frac{1}{2}$), the first reported value for such coupling.

Reaction of zirconium(IV) chloride with dpeO_2 gave a *cis*-octahedral complex, $[\text{ZrCl}_4(\text{dpeO}_2)]$ ⁷⁵. The tridentate ligand $[\text{Ph}_2\text{P}(\text{O})\text{CH}_2]_2\text{P}(\text{O})\text{Ph}(\text{L})$ formed complexes with zirconium(IV) and hafnium(IV), $[\text{ZrCl}_4\text{L}]$, $[\text{M}(\text{OH})_2\text{Cl}_2\text{L}] \cdot 8\text{H}_2\text{O}$ and $[\text{Zr}(\text{OH})_2\text{L}](\text{ClO}_4)_2$ ⁹²⁸.

b. Complexes of the vanadium, chromium and manganese Groups (VB–VIIB). The reaction of vanadyl halides, $\text{VOX}_2 \cdot n\text{H}_2\text{O}$, with dpe gave $[(\text{VOX}_2)_2(\text{dpeO}_2)] \cdot n\text{H}_2\text{O}$ ($n = 1, 4$; $\text{X} = \text{Cl}, \text{Br}$)⁹²⁹ in which dpe was oxidized to dpeO_2 , probably by the metal salt. When anhydrous vanadyl chloride, VOCl_2 (from V_2O_5 and HCl in EtOH), was reacted with dpeO_2 a 1:1 adduct, $[\text{VOCl}_2(\text{dpeO}_2)]$, was formed⁸⁶.

Hexacarbonyls of Group VIB metals, $[\text{M}(\text{CO})_6]$, undergo substitution reactions with dpmO_2 forming monomeric *cis*-octahedral $[\text{M}(\text{CO})_4(\text{dpmO}_2)]$ and dimeric *fac*- $[\text{M}_2(\text{CO})_6(\text{dpmO}_2)_3]$ ⁹³⁰. Similarly, with $\{\text{Ph}_2\text{P}(\text{O})\text{CH}_2\}_2\text{P}(\text{O})\text{Ph}$, *cis*- $[\text{M}(\text{CO})_4\text{L}]$ and *fac*- $[\text{M}(\text{CO})_3\text{L}]$ were formed⁹³⁰. Oxidation of bisphosphine complexes $[\text{M}(\text{CO})_4(\text{dpe})]$ with halogens (Cl_2 and Br_2) in $\text{CHCl}_3/\text{CCl}_4$ ⁹³¹ gave $[\text{MoOX}_3\text{L}]$ and $[\text{Mo}_2\text{X}_2\text{L}]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{dpeO}_2$). Whereas molybdenum(V) complexes are precipitated from the reaction mixture, the M^{VI} complexes must be obtained from the filtrate. Molybdenum(V) complexes show normal magnetic behaviour ($\mu = 1.65\text{--}1.73 \text{ BM}$, $T = 100\text{--}300 \text{ K}$). Halogen oxidation of $[\text{M}_2(\text{CO})_6(\text{dpmO}_2)]$ and $[\text{M}(\text{CO})_3\text{L}]$ $\{\text{L} = (\text{Ph}_2\text{POCH}_2)_2\text{P}(\text{O})\text{Ph}\}$ also gave 7-coordinate complexes, $[\text{M}(\text{CO})_3(\text{dpmO}_2)\text{X}_2]$ and $[\text{M}(\text{CO})_3\text{LX}_2]$ ($\text{X} = \text{Br}, \text{I}$)⁹³².

Treatment of the molybdenum(V) complex $\text{MoOX}_3(\text{dpeO}_2)$ ($\text{X} = \text{Cl}, \text{Br}$) with hydrogen peroxide in ethanol gave diamagnetic peroxo complexes $[\text{MoO}(\text{O}_2)_2(\text{dpeO}_2)]$ ¹⁷⁴. Two nitrosyl complexes, $[\text{Mo}(\text{NO})(\text{dpeO}_2\text{X}_2)]$ ($\text{X} = \text{Cl}, \text{Br}$), are also known⁹³³.

The reaction of manganese(II) halides with dpm, dpe and *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ gave phosphine oxide complexes, $[\text{MnX}_2\text{L}]$ $\{\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} = \text{dpmO}_2, \text{dpeO}_2, \text{cis-Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2\}$ and an ionic complex, $[\text{Mn}(\text{dpmO}_2)_2]\text{Br}_2$ ^{222,934}. Similarly, reactions of manganese(III) chloride with dpm, dpe, dpp and *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ also gave similar phosphine oxide complexes, $[\text{MnCl}_2\text{L}]$ ($\text{L} = \text{dpmO}_2, \text{dpeO}_2$, etc.); MnCl_3 chlorinated R_3P to form R_3PCl_2 , which on hydrolysis gave R_3PO ⁹³⁵.

Reactions of $[\text{Re}(\text{CO})_5\text{X}]$ and $\text{K}_2[\text{ReOX}_5]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with dpeO_2 gave the octahedral complexes $[\text{Re}(\text{CO})_3\text{LX}]$ and $[\text{ReOX}_3\text{L}]$, respectively^{259a,268}. Heating the complexes $[\text{ReOX}_3\text{L}]$ ($\text{L} = \text{dpe}, \text{cis-Ph}_2\text{PCH}=\text{CHPPh}_2$) gave the corresponding phosphine oxide complexes. Similarly, on heating $\text{H}_2\text{L}[\text{ReCl}_6]$ in Me_2CO containing HCl the $[\text{ReCl}_4\text{L}']$ complex was formed $\{\text{H}_2\text{L}^{2+} = (\text{H})\text{Ph}_2\overset{+}{\text{P}}\text{CH}_2\text{CH}_2\overset{+}{\text{P}}(\text{H})\text{Ph}_2$; $\text{L}' = \text{dpeO}_2\}$ ^{262b}. In $[\text{Re}(\text{CO})_3\text{LX}]$ the ligand L is unidentate, whereas in the other complexes it is bidentate.

c. Complexes of the iron, cobalt and nickel Groups (VIII)

i. Iron sub-Group. Reactions of iron(II) salts with di-tertiary phosphine oxides formed complexes (A) $[\text{FeX}_2\text{L}(\text{H}_2\text{O})_2] \cdot m\text{H}_2\text{O}$ $\{m = 0, 1$; $\text{X} = \text{Cl}, \text{Br}, \text{NCS}$; $\text{L} = \text{Ph}_2\text{P}(\text{O})$.

$(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$; $n = 1, 2, 4, 6$ }, (B) $[\text{FeL}_3]\text{I}_2 \cdot m\text{H}_2\text{O}$ ($n = 1, 4$ for L; $m = 1, 2$), (C) $[\text{FeL}_2\text{I}_2] \cdot m\text{H}_2\text{O}$ ($n = 2$ for L, $m = 0, 1$) and (D) $[\text{Fe}(\text{CO})_2\text{LI}] \cdot m\text{H}_2\text{O}$ ($n = 1, 2, 4, 6$ for L; $m = 1, 2$)^{936, 937}. The complexes had a tendency to absorb moisture; complexes D were light sensitive and showed low μ value (3.85–3.95 BM)⁹³⁷. The carbonyl groups in D lie in *cis* positions in a trigonal bipyramidal geometry. For complexes A–C octahedral geometry is suggested.

Iron(III) halides generally formed mixed octahedral–tetrahedral complexes of the type $[\text{FeL}_2\text{X}_2][\text{FeX}_4]$ {X = Cl, Br; L = $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$; $n = 1, 2, 4, 6$ }^{938–940}, although a complex of the type $[\text{FeL}_3][\text{FeCl}_4]_3$ is also known⁹⁴¹. Similarly, with iron(III) isothiocyanate, nitrate and perchlorate, complexes with various stoichiometries, e.g. $[\text{Fe}(\text{NCS})_3\text{L}]$ ($n = 2, 4, 6$ for L) $[\text{Fe}(\text{NCS})_2\text{L}_2](\text{NCS})$ ($n = 1$ for L), $\text{Fe}(\text{NO}_3)_3\text{L}$ ($n = 4, 6$ for L), $[\text{Fe}(\text{NO}_3)_2\text{L}_2](\text{NO}_3)$ ($n = 2$ for L), $[\text{FeL}_3](\text{ClO}_4)_3$ ($n = 1$ for L), etc., are known^{940, 942}.

The thiocyanate complexes showed low μ values (5.34–5.58 BM) compared with the typical values shown by other complexes. For the complexes $[\text{FeL}_2\text{X}_2][\text{FeX}_4]$, *trans*-octahedral cations (with respect to X) showed g_{\perp} values of about 6; however, their g_{\parallel} values (ca 2) merged with the strong ESR band due to the $[\text{FeX}_4]^-$ species at $g \approx 2$ ⁹⁴³. Interestingly, $[\text{FeL}_2\text{Cl}_2][\text{FeCl}_4]$ (L = dpeO_2) which showed only one g value of ca 2 was shown by X-ray analysis to possess *cis*-octahedral geometry for the cation^{291b, 944}.

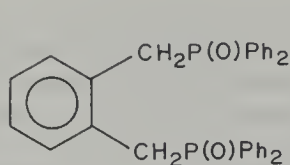
Thermal heating of the complexes FeX_3L (X = Cl, Br, L = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ and *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$) formed phosphine oxide complexes $[\text{FeL}_2\text{X}_2][\text{FeX}_4]$ ^{945a}. A tetradentate ligand, $\text{C}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_4$ (L), formed complexes $[(\text{FeCl}_3)_2\text{L}]$ and $[(\text{FeCl}_3)_4\text{L}]$ ^{945b}. Two complexes of osmium(II) of stoichiometry *cis*- $[\text{OsL}(\text{bpy})_2]^{2+}$ {L = dpmO_2 , *cis*- $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$ } were reported recently³¹³.

ii. Cobalt sub-Group. Several cobalt(II) high-spin complexes of the type (A) $[\text{CoLX}_2]$ {L = $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$; $n = 2–4$; X = Cl, Br, I, NCS, ONO_2 }^{946–948}, (B) $[\text{Co}(\text{NO})\text{IL}]$ (L = dpeO_2)⁹⁴⁹, (C) $[\text{CoL}_2\{\text{Ph}_2\text{P}(\text{O})\}_2\text{N}^-]$ ⁹⁵⁰, (D) $[\{\text{Co}(\text{S}_2\text{N}_2\text{H})_2\}_2 \cdot (\text{dpeO}_2)]$ ⁹⁵¹, (E) $[\text{Co}(\text{dpeO}_2)(\text{O}_2\text{NO})_2]$ ^{948, 952}, (F) $[\text{CoL}_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ ($n = 2, 4$ for L)^{948, 952}, (G) $[\text{Co}(\text{dpmO}_2)_3](\text{ClO}_4)_2$ ^{953, 954}, (H) $[\text{CoL}'_2](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ {L' = $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ }⁹⁵⁵, (I) $[\text{CoL}'_3](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ ⁹⁵⁵ and (J) $[\text{CoL}_3][\text{CoX}_4]$ {X = Cl, Br, I, L = dpmO_2 ^{946, 954}; X = Cl, L = $\text{Bu}^n_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Bu}^n_2$ ⁹⁴¹} have been reported. X-ray analysis of complexes B and D showed distorted tetrahedral and square-pyramidal structures, respectively; for complexes A–C distorted tetrahedral structures and for complexes E–I octahedral structures are suggested. The ligand $\{\text{Ph}_2\text{P}(\text{O})\text{CH}_2\}_2\text{P}(\text{O})\text{Ph}$ is tridentate in complex H and bidentate in complex I.

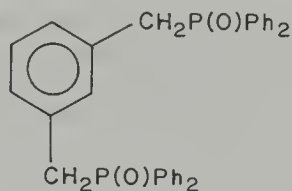
An interesting feature in cobalt(II) phosphine oxide chemistry is the tendency of dmpO_2 and $\text{Bu}^n_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Bu}^n_2$ ligands to form octahedral complexes with six-membered chelate rings (complexes G and J). When the anions are halogens, the formation of mixed octahedral–tetrahedral complexes takes place, e.g. complexes J. The higher steric requirements of seven- to nine-membered chelate rings formed by ligands with $n = 2–4$ generally favour coordination by two ligand molecules per metal ion.

A mixed valence complex, $[\text{Co}^{\text{I}}(\text{CO})\text{L}_2]_2[\text{Co}^{\text{II}}(\mu\text{-L}')\text{Cl}_6]$ (L = dpe ; L' = dpeO_2) was obtained from the reaction of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with dpe , CO and zinc powder in air⁹⁵⁶. An x-ray study showed tetrahedral geometry for each cobalt atom of the anion with dpeO_2 acting as a bridge; the cation has trigonal bipyramidal geometry. Using the ligands **78**, **79**, **80** and **81**, a series of complexes, $[\text{CoLCl}_2]$ (L = **78**, **81**), $[\text{CoL}_3](\text{ClO}_4)_2$ (L = **79**), $[(\text{CoCl}_2)_3\text{L}_2]$ (L = **80**) and $[\text{CoL}_2](\text{ClO}_4)_2$ (L = **80**), were reported^{957, 958}. $[\text{CoL}_3](\text{ClO}_4)_2$ have octahedral while the other complexes have tetrahedral structures. On heating $[\text{CoLX}_2]$ complexes (X = Cl, Br, I, NCS; L = dpe , *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$) the corresponding phosphine oxide complexes were formed^{959, 960}.

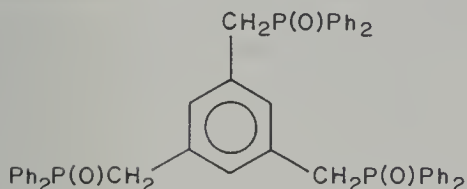
A series of square-planar rhodium(I) complexes $[\text{Rh}(\text{cod})\text{L}](\text{ClO}_4)$, *cis*- $[\text{Rh}(\text{CO})_2\text{L}](\text{ClO}_4)$, $[\text{Rh}(\text{CO})\text{L}(\text{Ph}_3\text{P})](\text{ClO}_4)$ and $[\text{Rh}(\text{CO})\text{L}(\text{Ph}_3\text{P})_2](\text{ClO}_4)$ {L = $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$; $n = 1, 2$ } (IR, ³¹P NMR) have been reported⁹⁶¹.



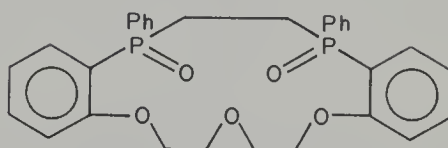
(78)



(79)



(80)



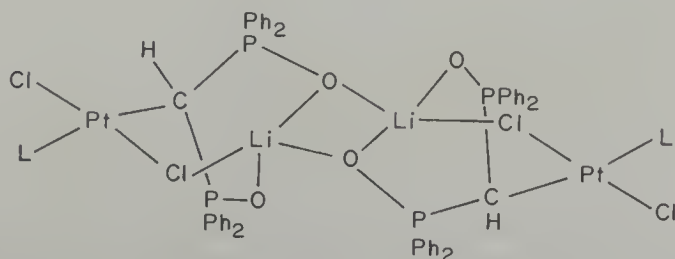
(81)

iii. Nickel sub-Group. A number of high-spin nickel(II) complexes have been reported: (A) $[\text{NiX}_2\text{L}]$ $\{\text{X} = \text{Cl}, \text{O}_2\text{NO}; \text{L} = \text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2; n = 2, 3\}$ ^{389,946,948,962}, (B) $[\text{NiL}_3]\text{X}_2 \cdot m\text{H}_2\text{O}$ ($n = 1$ for L; $\text{X} = \text{Cl}, \text{Br}, \text{I}$)⁹⁶³, (C) $[\text{NiL}_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ ($n = 2, 4$ for L)^{948,962}, (D) $[\text{NiL}'_2](\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ ⁹⁵⁵, (E) $[\text{NiL}'_3](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ $\{\text{L}' = (\text{Ph}_2\text{P}(\text{O})\text{CH}_2)_2\text{P}(\text{O})\text{Ph}\}$ ⁹⁵⁵, (F) $[\text{NiL}_3][\text{MX}_4]$ $\{\text{M} = \text{Ni}, \text{X} = \text{Cl}, \text{Br}, \text{I}, n = 1, 2 \text{ for L}; \text{X} = \text{Cl}, \text{L} = \text{Bu}^n_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Bu}^n_2; \text{M} = \text{Zn}, \text{X} = \text{Cl}, n = 1 \text{ for L}\}$ ^{941,946,954,962,963}. The complexes A–E have been assigned octahedral structures with halogen-bridging and bi-coordination by NO_3^- groups. L' acts as a tridentate in complex D, but bidentate in E. The F-type complexes have mixed octahedral–tetrahedral structures similar to those of their cobalt(II) analogues.

On heating the phosphine complexes $[\text{MLX}_2]$ ($\text{L} = \text{dpe}$, *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$; $\text{M} = \text{Ni}, \text{Pd}$; $\text{X} = \text{Cl}, \text{Br}, \text{NCS}$)^{412,959,960,964–966}, the corresponding phosphine oxide complexes were formed. Significantly, palladium(II)–phosphine complexes required higher temperatures for their oxidation than cobalt(II) or nickel(II) complexes. $[\text{PdL}(\text{NCS})(\text{SCN})]$ ($\text{L} = \text{dpe}$) did not undergo oxidation of dpe to dpeO_2 ⁹⁶⁶.

Whereas NiCl_2 with *cis*- $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$ formed $[\text{NiCl}_2\text{L}]$, there was no reaction of NiCl_2 with the *trans* analogue of the ligand⁹⁶⁷. The *trans* ligand reacted with NiCl_2 only in the molten state, although in the solution some interaction of NiCl_2 with *trans* ligand was detected.

The anionic phosphine oxide ligand $\{\text{Ph}_2\text{P}(\text{O})\}_2\text{CH}^-$ (L) formed a series of palladium(II) and platinum(II) complexes: $[\text{MCl}_2(\text{R}_3\text{P})\text{LM}']$ ($\text{M} = \text{Pd}$, $\text{R} = \text{Et}$, $\text{M}' = \text{Li}$; $\text{M} = \text{Pt}$, $\text{R} = \text{Et}$, Bu^n , $\text{M}' = \text{Li}$, Na)⁹⁶⁸. The reaction of $[(\text{Et}_3\text{P})\text{PtCl}_2\text{L}(\text{Li})]$ with $[\text{PdCl}_2(\text{Et}_3\text{P})_4](\text{BF}_4)_2$ formed an unstable complex, $[(\text{Et}_3\text{P})\text{Cl}_2\text{Pt}(\mu\text{-L})_2\text{Pd}(\text{Et}_3\text{P})_2](\text{BF}_4)$ {in which Li^+ was replaced by $\text{Pd}(\text{Et}_3\text{P})_2^{2+}$ }. The X-ray crystal structure of $[\text{Pt}(\text{Et}_3\text{P})\cdot$



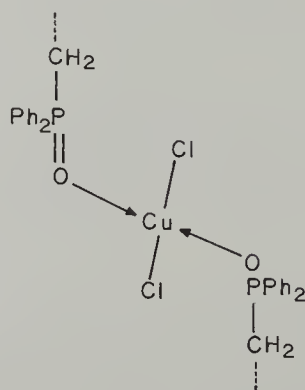
(82)

$\text{Cl}_2\text{L}(\text{Li})$] showed that the anionic ligand L was bound to platinum via the methine carbon with a square-planar geometry about platinum (82). Two PO groups, one chloride and one oxygen from an adjacent molecule complete tetrahedral geometry about lithium. From $^1J \text{ } ^{195}\text{Pt}-^{31}\text{P}$ values (^{31}P NMR) in the range 2750–2827 Hz, it was inferred that methine carbon exerts a low *trans* effect in comparison with the normal carbon bonded ligands^{968–970}. It is interesting that Li^+ ions remain intimately associated with the complex in solution.

d. *Complexes of the copper Group (IB).* Copper(II) forms complexes of the type (A) $[\text{CuX}_2\text{L}]$, (B) $[\text{CuL}_2](\text{ClO}_4)_2$ ($\text{L} = \text{dpeO}_2$; $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$)^{948,952}, (C) $[\text{CuL}_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, (D) $[\text{CuL}_3](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($\text{L} = \{\text{Ph}_2\text{P}(\text{O})\text{CH}_2\}_2\text{P}(\text{O})\text{Ph}$)⁹⁵⁵, (E) $[\text{CuL}_2][\text{CuCl}_4] \cdot \{\text{L} = \text{dpmO}_2, \text{RPhP}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{PhR}, \text{R} = o\text{-MeOC}_6\text{H}_4, \text{L} = \mathbf{79}, \mathbf{81}\}$ ^{957,958,971} and (F) $[\text{CuX}_2\text{L}]$, (G) $[(\text{CuX}_2)_2\text{L}]$ $\{\text{L} = \text{R}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{R}_2, \text{R} = \text{Ph}, n\text{-Oct}, \text{X} = \text{F}_3\text{acac}, \text{F}_6\text{acac}, \text{i.e. tri- and hexa-fluoroacetylacetonates}\}$ ⁹⁷². For $\text{R} = n\text{-Oct}$, complexes of stoichiometry $[\text{CuX}_2\text{L}_2]$ were also formed.

Other complexes of copper(II) studied in the solid and solution phases have formulae of the type $[\text{CuCl}_2\text{L}]$ $\{\text{L} = \text{R}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{R}_2, n = 1 \text{ for } \text{R} = \text{Ph}, n = 1, 2, 6 \text{ for } \text{R} = \text{Bu}\}$ ^{973–975}, $[\text{CuCl}_2\text{L}_2\text{Me}_2\text{CO}]$ ($\text{L} = \text{dpmO}_2$)⁹⁷⁵, $[\text{CuCl}_2\text{L}]$, $(\text{CuCl}_2)_2\text{L}$, $[\text{CuCl}_2\text{L}_2]$ $\{\text{L} = \text{Ph}_2\text{P}(\text{O})\text{CH}(\text{R})\text{P}(\text{O})\text{Ph}_2, \text{R} = \text{H}, \text{CH}_2\text{CH}_2\text{CO}_2\text{H}, \text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2, \text{etc.}\}$ ⁹⁷⁶, $[\text{CuClL}]\text{Cl}$ $\{\text{L} = \text{Ph}_2\text{P}(\text{O})\text{C}(\text{R})(\text{R}')\text{P}(\text{O})\text{Ph}_2, \text{R} = \text{H}, \text{R}' = \text{Cl}, \text{Br}, \text{I}, \text{Ph}, \text{CH}_2\text{Ph}, \text{etc.}\}$ ⁹⁷⁶, $\text{L} = (\text{XC}_6\text{H}_4)_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})(\text{C}_6\text{H}_4\text{X})_2, \text{X} = \text{H}, m\text{-CF}_3, \text{etc.}\}$ ⁹⁷⁷.

An X-ray analysis of $[\text{CuCl}_2\text{L}]$ ($\text{L} = \text{dpeO}_2$) showed that the geometry about copper(II) is highly distorted tetrahedral (the ClCuO angle being 140.2° , ClCuCl 100.3° and OCuO $90.6^\circ, 97.1^\circ$), with L acting as a bridging bidentate ligand (83)^{978,979}. The single crystal ESR and polarized electronic absorption spectra also suggest a compressed tetrahedral geometry about the copper(II)^{980–983}. The one-electron orbital sequence derived was $d_{xy} > d_{xz} > d_{yz} > d_{x^2-y^2} \approx d_{z^2}$. Interestingly, $[\text{CuCl}_2\text{L}]$ ($\text{L} = \text{dpmO}_2$) has a different structure⁹⁸⁴. An X-ray study showed that it exists as $[\text{CuL}_3][\text{Cu}_2\text{Cl}_6]$, where the cation is octahedral and the anion has a halogen-bridged dimeric structure with each copper having distorted tetrahedral geometry. The short axial distances (2.001–2.002 Å) versus the longer equatorial ones (2.063–2.256 Å) for the cation reveal slight compression of the octahedron. Thus complexes A, B, C and E are assigned distorted tetrahedral geometry, whereas D, F and other complexes with similar stoichiometries probably have distorted octahedral geometries. The only complex of gold(I) is $[\text{LAu}(\text{PPh}_3)](\text{ClO}_4)$ ($\text{L} = \text{dpeO}_2$)⁴⁸¹.



(83)

e. *Complexes of the zinc Group (IIB).* The interaction of Group IIB metals with bis(phosphine oxide) ligands has been studied mainly using ^{31}P NMR spectrometry.

The formation of octahedral $[\text{ZnL}_n]^{2+}$ ($\text{L} = \text{dpmO}_2$, $n = 3$; $\text{L} = (\text{Ph}_2\text{P}(\text{O})\text{CH}_2)_2\text{P}(\text{O})\text{Ph}$, $n = 2$) and tetrahedral $[\text{ZnL}_2]^{2+}$ ($\text{L} = \text{dpmO}_2$) was established by varying the L: Zn ratio⁹⁹⁸. No species formed by the interaction of zinc(II) with $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ could be detected, owing to the high lability of the system under the experimental conditions.

Similarly, cadmium(II) and mercury(II) formed $[\text{ML}_m]^{2+}$ ($\text{M} = \text{Cd}, \text{Hg}$; $\text{L} = \text{dpmO}_2$, dpeO_2 ; $m = 2, 3$) and $[\text{CdL}_2]^{2+}$ ($\text{L} = (\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2)_2\text{P}(\text{O})\text{Ph}$) (^{31}P , ^{113}Cd NMR)^{999,1000}. For L: M ≥ 3 octahedral species were detected and for L: M = 2 tetrahedral species were formed. It is significant that the $\text{Cd}^{\text{II}} - \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ system was not labile, unlike the zinc(II) system (see above), probably owing to large bite of the seven-membered chelate ring giving a worse fit for zinc(II) than cadmium(II) because of their size difference.

f. Complexes of the f-block elements. This group of elements has been poorly studied and no X-ray analyses have been reported for any complex. Lanthanum(III) chlorides form complexes of the type $[\text{M}_2\text{Cl}_6\text{L}_3] \cdot \text{H}_2\text{O}$ ($\text{M} = \text{La}, \text{Nd}, \text{Sm}$; $\text{L} = \text{dpeO}_2$; $x = 0-2$)⁹⁸⁵, $[\text{NdCl}_3\text{L}] \cdot \text{H}_2\text{O}$ ($\text{L} = \text{dpmO}_2, \text{dpeO}_2$)^{985,986} and $[\text{NdCl}_3\text{L}_3]$ ($\text{L} = \text{dpmO}_2$)⁹⁸⁶. Similarly, lanthanum(III) nitrates form complexes of the type $[\text{M}_2(\text{NO}_3)_6\text{L}_3] \cdot x\text{H}_2\text{O}$ ($\text{M} = \text{La}, \text{Nd}, \text{Sm}$; $\text{L} = \text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$; $n = 2, 4$)⁹⁸⁷. The NO_3^- groups are coordinated, but their dentancy has not been established. Other complexes of lanthanides include $[\text{M}(\text{NO}_3)_3\text{L}]$ ($\text{M} = \text{La}, \text{Nd}, \text{Gd}, \text{Ho}, \text{Lu}$; $\text{L} = \text{O}(\text{CH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{OCH}_2\text{P}(\text{O})\text{Ph}_2)_2$ and 1,2- $(\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{O})_2$ -4- $\text{Me}_3\text{CC}_6\text{H}_3$)⁹⁸⁸ as well as $[(\text{ML}_n)_2(\text{B}_{12}\text{H}_{12})_2]$ ($n = 4, \text{M} = \text{La}$; $n = 3, 5, \text{M} = \text{Pr}, \text{Nd}, \text{Sm}$; $n = 3, \text{M} = \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$)⁹⁸⁹.

Thorium(IV) forms complexes of the type $[\text{Th}(\text{NO}_3)_4\text{L}]$ ($\text{L} = \text{Cy}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Cy}_2$), $[\text{Th}(\text{NO}_3)_4\text{L}_2]$ ($\text{L} = \text{dpeO}_2$), $[\text{Th}_2(\text{NO}_3)_8\text{L}_3]$ ($\text{L} = \text{dpmO}_2, \text{dpeO}_2, \text{R}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{R}_2$; $\text{R} = 2\text{-ethylbutyl}$)^{644,647,990}. Similarly, a number of uranium(IV) and uranium(VI) complexes have been reported: $[\text{UCl}_4\text{L}]$, $[\text{UO}_2\text{X}_2\text{L}]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ or NO_3 , $\text{R}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{R}_2$; $\text{R} = \text{Ph}, \text{Hex}^n$, $n = 1-4$; $\text{R} = \text{Bu}^n$, 2-ethylbutyl, $n = 1$)^{655,991-996} and $[(\text{UO}_2)_2(\text{NO}_3)_4\text{L}_3]$ ($\text{L} = \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2$)⁶⁴⁴. Apart from the usual methods, some complexes were formed indirectly. For example, reaction of $[\text{Th}(\text{NO}_3)_4]$ with dpe^{990} and of $[\text{UO}_2\text{Cl}_2]$ with dpm and dpe^{996} gave the corresponding phosphine oxide complexes. The UCl_4 complexes are paramagnetic ($\mu = 1.50-2.02$ BM). X-ray studies are recommended.

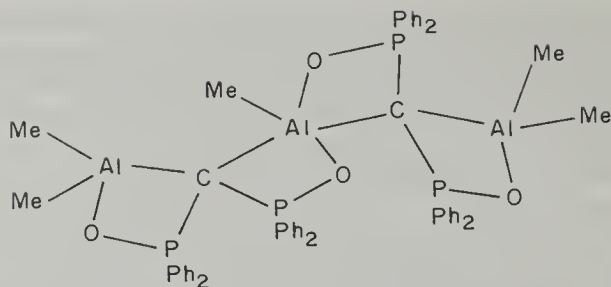
Formation of 1:1, 2:1, 3:1, 4:1 and 6:1 (L:M) complexes of $[\text{UO}_2(\text{NO}_3)_2]$ with $\text{R}_2\text{P}(\text{O})\text{EP}(\text{O})\text{R}_2$ ($\text{R} = \text{Ph}, \text{Bu}, \text{Et}, \text{PhMe}$; $\text{E} = \text{CH}_2, \text{CH}_2\text{CH}_2$, *cis*- and *trans*- $\text{CH}=\text{CH}$) has also been reported⁹⁹⁷. Here all the ligands except *trans*- $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$ were chelating whereas the latter ligand was unidentate.

The organouranium(IV) and neptunium(IV) complexes $[(\text{cp})\text{MX}_3\text{L}]$ ($\text{M} = \text{U}, \text{Np}$; $\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$) are also known^{709,994}.

2. Main Group elements

a. Complexes of the boron Group (IIIA). Reaction of $\text{Me}_3\text{Al}_2\text{Cl}_3$ with $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2(\text{L})$ gave $[(\text{AlCl}_3)_2(\text{L})]$ with a tetrahedral structure about each aluminium centre¹⁰⁰¹. An unusual product, $[\text{Al}(\text{CH}_3)]\{\text{Ph}_2\text{P}(\text{O})\text{CP}(\text{O})\text{Ph}_2\}_2[\text{Al}(\text{CH}_3)_2]_2$, was obtained from the reaction of AlMe_3 with $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ in PhCl^{1002} . Here the Al-R and C-H bonds of the CH_2 group were cleaved. X-ray analysis showed that the central aluminium atom is 5-coordinate, whereas the other two are 4-coordinate (84).

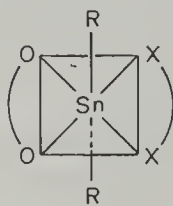
Indium(III) and thallium(III) formed complexes of the type $[\text{InCl}_3\text{L}]$ ($\text{L} = \text{dpeO}_2$), $[\text{InL}_3](\text{ClO}_4)_3$ ($\text{L} = \text{dpmO}_2, \text{dpeO}_2$)^{1003,1004}, $[\text{TlX}_3\text{L}]$, $[\text{TlClBr}_2\text{L}]$, $[\text{TlClI}_2\text{L}]$ and $[\text{TlBrI}_2\text{L}]$ ($\text{L} = \text{dpeO}_2$)¹⁰⁰⁵. Thallium(III) complexes were obtained from the reaction of thallium(I) halides with the ligand followed by oxidation with Br_2 or I_2 in CH_3CN .



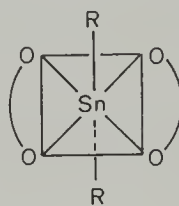
(84)

b. Complexes of the tin and lead Group (IVA). Interaction of tin(II) and lead(II) hexafluoroantimonates with dpeO_2 and $(\text{Ph}_2\text{P}(\text{O})\text{CH}_2)_2\text{P}(\text{O})\text{Ph}$ in liquid SO_2 (studied by ^{31}P NMR) revealed the formation of $[\text{ML}]^{2+}$ species⁹⁷⁸. The lead(II) complexes showed low coordination shifts and were more labile than the tin(II) complexes. Tin(IV) halides form 1:1 adducts $[\text{SnX}_4\text{L}]$ $\{\text{L} = \text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2; \text{X} = \text{Cl}, \text{Br}, \text{I}; n = 2, 4\}$ ^{1006–1008}. Mössbauer data favoured *cis*-octahedral structures. SnCl_4 forms a 2:1 adduct with the tetradentate ligand $\text{C}(\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_4$ $[\text{SnCl}_4]_2\text{L}$ ^{945a}.

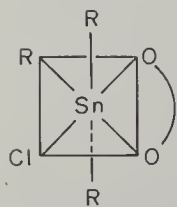
One of the most thoroughly studied group of complexes is that of organotin(IV). Several complexes have been reported: (A) $[\text{R}_2\text{SnX}_2\text{L}]$ $\{\text{X} = \text{Cl}, \text{Br}, \text{NCS}, \text{R} = \text{Me}, \text{Et}, \text{Oct}, \text{Ph}, \text{etc.}, \text{L} = \text{dpmO}_2, \text{dpeO}_2, \text{dpbO}_2; \text{X} = \text{Cl}, \text{R} = \text{Et}, \text{Pr}, \text{Bu}, \text{L} = \text{cis-Ph}_2\text{P}(\text{O})\cdot\text{CH}=\text{CHP}(\text{O})\text{Ph}_2\}$ ^{835, 1009–1017}, (B) $[(\text{Bz}_2\text{SnCl}_2)_2\text{L}]$ $(\text{L} = \text{dpeO}_2, \text{dpbO}_2)$ ¹⁰¹⁸, (C) $[\text{R}_2\text{SnL}_2](\text{BPh}_4)_2$ $(\text{R} = \text{Me}, \text{Ph}; \text{L} = \text{dpmO}_2, \text{dpeO}_2)$ ^{1009, 1017, 1019}, (D) $[\text{R}_3\text{SnXL}]$ $(\text{X} = \text{Cl}; \text{R} = \text{Me}, \text{Ph}; \text{L} = \text{dpmO}_2)$ ^{1009, 1017, 1019}, (E) $[(\text{Ph}_3\text{SnCl})_2\text{L}]$ $(\text{L} = \text{dpmO}_2, \text{dpeO}_2)$ ^{1017, 1020a} and (F) $[\text{R}_3\text{SnL}](\text{BPh}_4)$ $(\text{R} = \text{Me}, \text{Bu}, \text{Ph}; \text{L} = \text{dpmO}_2, \text{dpeO}_2)$ ^{1011, 1019, 1020b, c, 1021}. Based on Mössbauer data, complexes A and C were assigned *trans*-octahedral structures (85, 86)^{1009–1013, 1022–1024}. In contrast, the $[\text{Ph}_2\text{SnX}_2\text{L}]$ $(\text{L} = \text{phen}, \text{bipy})$ complexes have *cis* dispositions of the phenyl groups¹⁰²⁵. The *cis* or *trans* disposition of R groups is influenced by the electronic and steric factors of all the groups attached to tin¹⁰²⁶. For complexes D and F, *mer* configurations (87, 88) have been assigned. Finally, for the complexes B and E, ligand-bridged structures with R groups in the equatorial plane of a trigonal bipyramid have been suggested (89).



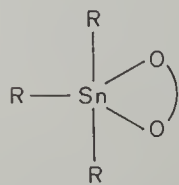
(85)



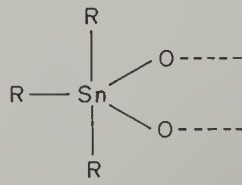
(86)



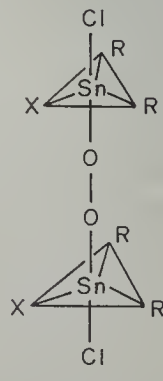
(87)



(88a)

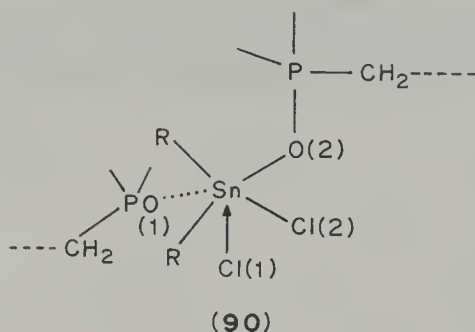


(88b)



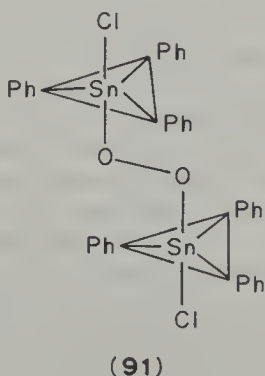
(89)

X-ray studies have been reported for a number of tin(IV) complexes. The geometry about tin in $[\text{Bu}_2\text{SnCl}_2\text{L}]$ ($\text{L} = \text{dpmO}_2$) is highly distorted *trans*-octahedral (**85**)¹⁰¹⁵. For $\text{L} = \text{dpeO}_2$ the mode of binding changes from chelation (as in the dpmO_2 complex) to bridging forming a polymeric structure^{1020a}. The geometry may be viewed as a highly distorted tetragonal pyramid with $\text{Cl}_{(2)}$ at the apex or irregular octahedron if $\text{O}_{(1)}$ is considered as part of the environment (**90**). The $\text{C}—\text{Sn}—\text{C}$ angle is 154.3° , instead of 180° as suggested by the Mössbauer data. The $\text{Sn}—\text{O}$ distances are very different (2.386 and 2.640 Å). ^{119}Sn NMR data also supported the formation of a 5-coordinate species^{874,1016}.



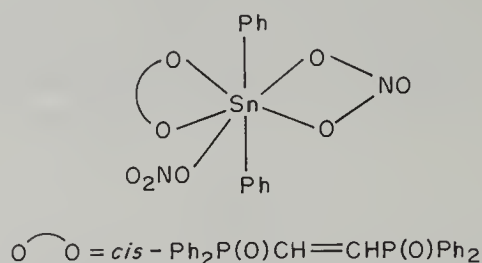
In $[\text{Et}_2\text{SnCl}_2\text{L}]$ ($\text{L} = \text{dpeO}_2$, *cis*- $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$), the ligands are chelating with the ethyl groups in the *trans* positions of the octahedron¹⁰¹⁴. Similar behaviour was observed in $[\text{Bu}_2\text{SnCl}_2\text{L}]$ for $\text{L} = \text{cis-Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$ ¹⁰¹³, but the octahedral structure is highly distorted. For $[\text{Pr}_2\text{SnCl}_2\text{L}]$, the stereochemistry is basically 5-coordinate in the form of a distorted tetragonal pyramid. Here one oxygen of *cis*- $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$ is at a distance of 2.24 Å and the other at a distance of 2.58 Å¹⁰¹³.

The complex $[(\text{Ph}_3\text{SnCl})_2\text{L}]$ ($\text{L} = \text{dpeO}_2$) has a bridging L ligand with phenyl groups in the equatorial plane (**91**). The in-plane (114 – 127°) and axial angles (174.4°) reveal distortion in the geometry^{1027,1028}. *cis*- $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$ was unidentate^{1029,1030}. The unusual unidentate behaviour of this *cis* ligand is probably due to the tendency of Ph_3Sn unit to retain an equatorial disposition of the R groups. However, in $[\text{Ph}_2\text{SnCl}_2\text{L}]$ ($\text{L} = \text{cis-Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$), the ligand is chelating¹⁰²⁹.

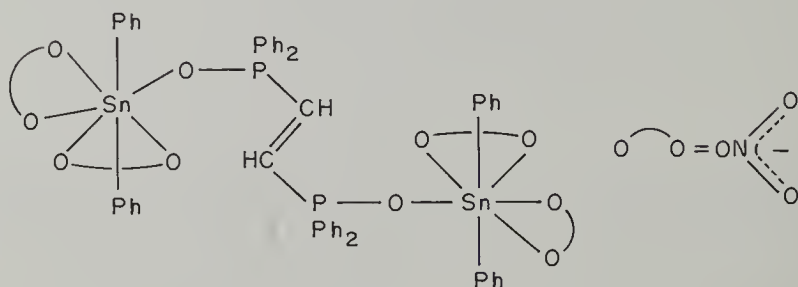


The structure of $[\{\text{Ph}_3\text{Sn}(\text{ONO}_2)\}_2\text{L}]$ ($\text{L} = \text{dpcO}_2$) is similar to that of $[(\text{Ph}_3\text{SnCl})_2\text{L}]$ ¹⁰³¹. The complexes $[\text{Ph}_2\text{Sn}(\text{NO}_3)_2\text{L}]$ ($\text{L} = \text{cis- and trans-Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$) have distorted pentagonal bipyramidal structures (**92**, **93**)¹⁰³². A structure similar to **85** was shown by $[\text{Ph}_2\text{Sn}(\text{NO}_3)_2\text{L}]$ ($\text{L} = \text{dpmO}_2$)¹⁰³³. The complex $[\{\text{Ph}_3\text{Sn}·$

$(\text{ONO}_2)_2$ (*trans*- $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$)] has a dimeric structure with the *trans* ligand acting as a bridge between two Ph_3Sn moieties. Each tin has a distorted trigonal bipyramidal geometry¹⁰³³.



(92)



(93)

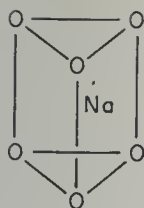
e. Complexes of phosphorus (VA). A few complexes of PF_5 with $\text{Ph}_2\text{P}(\text{O})\text{CH}(\text{X})\cdot\text{P}(\text{O})\text{Ph}_2$ ($\text{X} = \text{H}, \text{Cl}, \text{Bu}^n$) have been reported (^{19}F NMR)¹⁰³⁴. Species of the type $[\text{PF}_5\text{L}]$ (L acting as a monodentate) and $[\text{PF}_4\text{L}]^+$ (L = bidentate) were detected in all cases. An antimony(V) complex, $[(\text{SbCl}_5)_4\text{L}]$ ($\text{L} = \text{C}\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_4$), has been reported^{945a}.

3. Alkali and alkaline earth elements

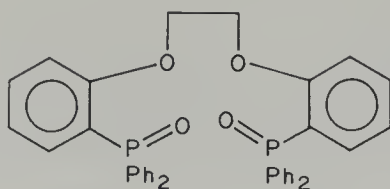
Alkali metal salts form complexes of the type (A) $[\text{MXL}]$, (B) $[\text{MLX}]$, (C) $[\text{ML}_2\text{I}]$ $\{\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Cs}; \text{X} = \text{Cl}, \text{Br}, \text{I}; \text{L} = \text{dpeO}_2, \text{R}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{R}'_2; \text{R} = \text{R}' = \text{Ph}, \text{Bu}^n, p\text{-MeOC}_6\text{H}_4; \text{R} = p\text{-MeOC}_6\text{H}_4, p\text{-CF}_3\text{C}_6\text{H}_4\}$ ¹⁰³⁵⁻¹⁰⁴², (D) $[\text{NaL}_3]\text{Br}\cdot 2\text{H}_2\text{O}$ and (E) $[\text{NaL}_3]\text{I}\cdot 2\text{H}_2\text{O}\cdot \text{C}_6\text{H}_6$ ($\text{L} = \text{dpmO}_2$)^{1043,1044}. An alkali metal salt insoluble in MeCN or CHCl_3 became soluble in the presence of a phosphine oxide, indicating the formation of a complex species. An X-ray study of complexes D and E revealed a trigonal prismatic structure with the oxygen atoms of dpmO_2 occupying corners of the prism (94). The $\text{Na}-\text{O}$ distances (2.434 Å) lay within the range typically observed for $\text{Na}-\text{O}$ bonds (2.29–2.82 Å). Water and C_6H_6 were present in the crystal lattices.

Lithium and sodium salts of 2,4-dinitrophenolate formed stable complexes with podant ligands (95, 96)¹⁰⁴⁵. The complexing abilities of 95 and 96 exceed that of 18-crown-6 and dibenzo-18-crown-6; 95 exhibited higher Li/Na selectivity than 96. Similarly, the alkali metal salts of 2,4-dinitrophenolates form complexes with several podant ligands such as $\text{Me}_2\text{P}(\text{O})(\text{CH}_2\text{OCH}_2)_n\text{P}(\text{O})\text{Me}_2$ ($n = 1, 3$), $\{o\text{-Ph}_2\text{P}(\text{O})\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2\}_2\text{O}$ and 1,2- $\{\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}\}_2\text{C}_6\text{H}_4$ ^{1046,1047}.

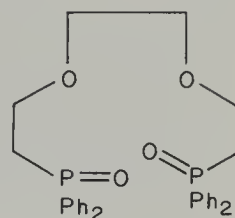
Studies on complexes of the alkaline earth metals are very limited¹⁰⁴⁸⁻¹⁰⁵⁰. Species of the type $[\text{MgL}]^{2+}$, $[\text{CaL}_2]^{2+}$, $[\text{MgLI}]^+$ and $[\text{CaClL}]^+$ ($\text{L} = \text{dpmO}_2$) were detected in solution by a conductivity method. Calcium chloride formed 1:1 and 1:2 complexes



(94)

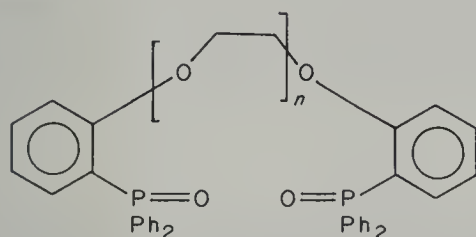


(95)

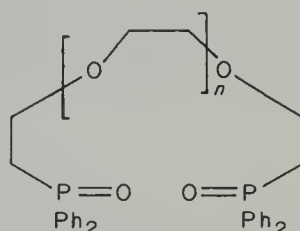


(96)

with podant ligands **97** and **98**¹⁰⁵⁰. The stability constant of the 1:2 complex is larger than that of the 1:1 complex owing to a higher enthalpy contribution to the formation of the 1:1 adduct and a higher entropy contribution to the formation of the 1:2 complex.

 $n = 1 - 5$

(97)

 $n = 4, 5$

(98)

III. TERTIARY PHOSPHINE SULPHIDES AND SELENIDES

Most of the coordination chemistry of the tertiary phosphine sulphides and selenides pertains to the d-block elements. Whereas there have been significant studies on Main Group elements, no complexes have been reported so far with s- or f-block elements. A recent attempt involving the reaction of $[(\text{Me}_5\text{C}_5)_2\text{Yb}]$ with Ph_3PE gave $[\{(\text{Me}_5\text{C}_5)_2\text{Yb}\}_2(\mu\text{-E})]$ ($\text{E} = \text{S}, \text{Se}$) instead of the expected adduct^{1051a}.

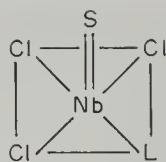
A. Transition Elements

1. Complexes of the titanium and vanadium Groups (IVB and VB)

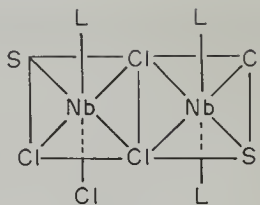
Titanium(IV) and vanadium(IV) and (V) form moisture-sensitive complexes of the type $[\text{TiCl}_4\text{L}_2]$, $[(\text{TiCl}_4)_2\text{L}]$, $[\text{TiBr}_4\text{L}]$ ($\text{L} = \text{Ph}_3\text{PS}$), $[\text{TiX}_4\text{L}']$ ($\text{X} = \text{Cl}, \text{Br}$) and $[\text{VOCl}_2\text{L}']$ $\{\text{L}' = \text{Me}_2\text{P}(\text{S})\text{NHP}(\text{S})\text{Me}_2\}$ ^{1051b, 1052-1056}. In the complexes $[(\text{TiCl}_4)_2\text{L}]$ and $[\text{TiBr}_4\text{L}]$ ($\text{L} = \text{Ph}_3\text{PS}$) halogen bridging and in the complexes $[\text{TiX}_4\text{L}']$ and $[\text{VOCl}_2\text{L}']$ chelation by L' are suggested. Niobium(V) and titanium(V) complexes $[\text{NbSCl}_3(\text{SPPH}_3)]$, $[\text{MX}_5\text{L}]$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$; $\text{L} = \text{Ph}_3\text{PS}, \text{Ph}_3\text{PSe}$) and $[\text{M}_3\text{Br}_{15}\text{L}]$ ($\text{L} = \text{dpeS}_2$)¹⁰⁵⁶⁻¹⁰⁶² have been reported; they are also moisture sensitive.

An X-ray study has shown that $[\text{NbSCl}_3(\text{SPPH}_3)]$ exists as a mixture of a square-pyramidal monomer and a chloride-bridged dimer in the same unit cell (**99** and **100**)^{1059, 1060, 1062}. The long Nb—Nb distance (4.240 Å) ruled out any possibility of metal—metal bonding in the dimer. Further Nb(V)—S interaction was weaker than that of Mo(V)—S¹⁰⁶³.

A solution-phase ¹⁹F NMR study revealed the formation of species such as *cis*- and *trans*- $[\text{TaF}_4\text{ClL}]$, *trans*- $[\text{TaF}_3\text{Cl}_2\text{L}]$, *fac*- $[\text{TaF}_2\text{Cl}_3\text{L}]$, *trans-mer*- $[\text{TaF}_2\text{Cl}_3\text{L}]$ $\{\text{L} = (p\text{-MeC}_6\text{H}_4)_3\text{PS}\}$ ¹⁰⁶⁴ and $[\text{TaF}_5\text{L}]$ $\{\text{L} = (\text{XC}_6\text{H}_4)_3\text{PS}\}$ ¹⁰⁶¹. The donor ability of the ligands decreased in the order $\text{X} = p\text{-MeO} > o\text{-Me} > p\text{-Me} > m\text{-Me} > p\text{-Cl}$ ¹⁰⁶¹.



(99)



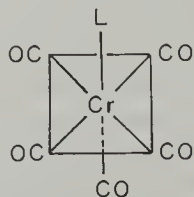
(100)

Organo-niobium(V) and -tantalum(V) complexes of stoichiometries $[\text{MeMCl}_4\text{L}]$, $[(\text{MeMCl}_4)_2\text{L}']$, $[(\text{Me}_2\text{TaCl}_3)_2\text{L}']$ and $[\text{Me}_2\text{TaCl}_3\text{L}]$ ($\text{L} = \text{Ph}_3\text{PS}$, $\text{L}' = \text{dpeS}_2$) have been reported¹¹⁷. The first two complexes have *cis* configurations whereas the latter two have *trans*-Me groups. Interestingly, $[\text{Me}_2\text{NbCl}_3]$ abstracted oxygen from Ph_3PO forming $[\text{Me}_2\text{NbOCl}_3(\text{Ph}_3\text{P})]$, and there was no analogous reaction with Ph_3PS , demonstrating the relatively large Nb—O affinity as compared with the Nb—S bond¹⁰⁶⁵. A substituted cyclopentadienyltantalum(V) complex, $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_3(\text{CH}_2\text{P}(\text{S})\text{Ph}_2)]$ with Ta—CH₂ bonding showed no Ta—S interaction¹⁰⁶⁶.

2. Complexes of the chromium Group(VIB)

Table 14 contains several complexes of Group VIB elements, which constitutes one of the most thoroughly studied Groups. The di-tertiary ligands dpmS_2 , dpmPSe and $\text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{CH}_2\text{AsPh}_2$ behaved as unidentate ligands in the complexes $[\text{M}(\text{CO})_5\text{L}]$, coordinating via S, P and As donor groups, respectively. Chromium and tungsten complexes were stable in air in the solution phase unlike molybdenum complexes, which dissociated rapidly, demonstrating the high lability of the Mo—S bond. On bubbling CO through a benzene solution of $[\text{M}(\text{CO})_5\text{L}]$ ($\text{M} = \text{Cr}, \text{W}$; $\text{L} = \text{Me}_2\text{PhPE}$), the original compound $[\text{M}(\text{CO})_6]$ was obtained. This reveals a reversible binding tendency of the phosphine chalcogenides to Group VIB metals. The addition of MeI to $[\text{M}(\text{CO})_5\cdot(\text{Me}_2\text{PhPS})]$ gave *S*-methylated ionic complexes, $\{\text{Me}_2\text{PhPS}(\text{Me})\}[\text{M}(\text{CO})_5\text{I}]$ ^{1068,1091}.

X-ray analysis of $[\text{Cr}(\text{CO})_5(\text{Me}_3\text{PS})]$ showed a nearly octahedral geometry (101) about the chromium atom¹⁰⁶⁹, which lies slightly above the square-plane towards Me_3PS . The Cr—C bond *trans* to Me_3PS was short (1.815 Å) compared with the *cis*-Cr—C bonds (1.889–1.916 Å). The normal Cr—S bond and short Cr—C distance (*trans* to Me_3PS) reveal the lack of any π -accepting ability of Me_3PS ; a similar conclusion was reached from the appearance of high-energy $\nu(\text{CO})$ peaks for the CO groups *trans* to the Me_3PS ligand.



(101)

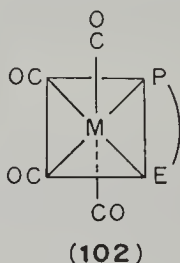
The reaction of $[\text{M}(\text{CO})_6]$ with $\text{Ph}_2\text{P}(\text{E})\text{CH}_2\text{PR}_1\text{R}_2$ gave the disubstituted *cis*-octahedral complexes $[\text{M}(\text{CO})_4\text{L}]\text{-}\{\text{complexes B(i)}\}$ ^{1072–1078}, where the ligands chelate via the P and E donor atoms (102). Since the formation of the tungsten complexes required higher temperatures at which sulphur transfer from one phosphorus to another phosphorus becomes competitive with CO substitution, the tungsten derivatives were obtained indirectly by displacing norbornadiene from $[\text{W}(\text{CO})_4(\text{C}_7\text{H}_8)]$ by $\text{Ph}_2\text{PCH}_2\text{-P}(\text{S})\text{R}_2$. The ligands dpmPSe and $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{CH}_2\text{AsPh}_2$ did not react with

TABLE 14. Known complexes of the chromium and manganese groups

Complex	L	Ref.
A $[M(CO)_5L]$ (M = Cr, Mo, W)	(i) R_3PE^a , $dpmS_2$	1067-1071
B (i) $[M(CO)_4L]$ (M = Cr, Mo, W)	(ii) $dpmPSe$, $Ph_2P(Se)CH_2CH_2AsPh_2$	1072
(ii) $[M(CO)_4L(pip)]^c$ (M = Mo, W)	$Ph_2P(E)CH_2PR_1R_2^b$	1072-1078
(iii) $cis-[M(CO)_4L_2]$ (M = Mo, W)	$Ph_2P(Se)CH_2CH_2AsPh_2$	1072
C $[M(CO)_3(NO)L]$ (M = Mo, W)	$Ph_2P(Se)CH_2CH_2AsPh_2$	1072
D (i) $[M(CO)_3LX_2]$ (M = Mo, W; X = Cl, Br)	$dpmPSe$	1079
(ii) $[M(CO)_nL_2Cl_2]$ (n = 2, 3; M = Mo, W)	$dpmPSe$, $Ph_2P(Se)CH_2CH_2AsPh_2$	1072
E $[M(CO)_3L_2I_2]$ (M = Mo, W)	Ph_3PS	203
F (i) $[W(CO)_2(NO)LI]$	Ph_3PS	204
(ii) $[W(CO)(NO)LL'I]$	$dpmPSe$, $Ph_2P(Se)CH_2CH_2AsPh_2$	1080
G $[(\eta^5-cp)(CO)LM-M(CO)_3(\eta^5-cp)]$ (M = Mo, W)	See text	1080
H $[MoOCl_3L]$	Ph_3PS	1081
I (i) $WX_4(PPh_3)L$	Ph_3PS	164b, 1082-1085
(ii) $[Br_4W(\mu-L)_2WBr_4]$	Ph_3PS , Ph_3PSe	171, 1086
(iii) $[Cl_4W(\mu-L)_2WCl_4]Cl_2$	Ph_3PS , Ph_3PSe	171, 1086
J $[WOCIL_2](PF_6)$	Ph_3PS , Ph_3PSe	171, 1086
K (i) $[M(CO)_3LX]$ (M = Mn, Re, X = Cl, Br)	$Me_2P(S)CH_2PMe_2$	1087
(ii) $[M(CO)_3LX]_2$ (X = Cl, Br, M = Mn)	$dpmPE$, $Ph_2P(E)CH_2CH_2AsPh_2$	1088
(iii) $[M(CO)_3L_2X]$ (M = Mn, Re)	$Ph_2P(E)CH_2CH_2AsPh_2$	1088
L $[MnL_2]$	$Ph_2P(E)CH_2CH_2AsPh_2$	1088
	$[Ph_2P(S)]_2N^-$	1089, 1090

^a R_3 , E = Me_3 , Me_2Ph , $MePh_2$, Ph_3 , Cy_3S ; Me_2Ph , Ph_3 , Cy_3 , Se.^b R_1R_2 , E = Ph_2 ; Ph, Pr^i ; Ph, Me: Pr^i ; Me_2 , Bu^i , S; Ph_2 , Se.^cpip = piperidine.

$[\text{M}(\text{CO})_6]$ and hence its arsenic-bonded monosubstituted complexes $[\text{M}(\text{CO})_5\text{L}]$ {A(ii) complexes} were obtained from the reaction of the anionic species $[\text{M}(\text{CO})_5\text{X}]^-$ ($\text{X} = \text{Cl}, \text{Br}; \text{M} = \text{Mo}, \text{W}$) with the ligand in the presence of AgNO_3 ¹⁰⁷². Complexes B(ii) and B(iii) also contained arsenic-bonded monodentate ligands¹⁰⁷².



The group VIB metal–chalcogen interaction decreases in the sequence $\text{W} > \text{Cr} > \text{Mo}$ and for metal– PR_2 interaction in the sequence $\text{W} > \text{Mo} > \text{Cr}$, which is same as the decreasing trend of metal to ligand π -bonding from W to Cr. Further, the metal– PR_2 interaction is stronger than metal– EPR_2 interaction. It was also observed that phenyl groups on phosphorus enhanced ^{31}P – ^{183}W coupling owing to π -interactions along the W–P bond^{1078,1093}.

Complexes $[\text{M}(\text{CO})_3(\text{NO})\text{L}]$, $[\text{M}(\text{CO})_3\text{LX}_2]$ and $[\text{W}(\text{CO})_2(\text{NO})\text{LI}]$ {C, D(i), F(i) complexes} contain chelating ligands (Table 14). $[\text{W}(\text{CO})(\text{NO})\text{LL'I}]$ { $\text{L} = \text{dpmPSe}$, $\text{L}' = \text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{CH}_2\text{AsPh}_2$ } has chelating L and unidentate arsenic-bonded L' ¹⁰⁸⁰. Complexes $[\text{M}(\text{CO})_3\text{LX}_2]$ have been shown to exist as a mixture of isomers¹⁰⁷² and their further reaction with dpmPSe gave incomplete formation of $[\text{M}(\text{CO})_2\text{L}_2\text{X}_2]$ (one L is chelated whereas the second is P-bonded). A similar reaction of complex D(i) with $\text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{CH}_2\text{AsPh}_2$ gave quantitative formation of $[\text{M}(\text{CO})_2\text{L}_2\text{X}_2]$ (one L chelating and the second L binding via arsenic only). Bubbling of carbon monoxide through a solution of the latter complex gave $[\text{M}(\text{CO})_3\text{L}_2\text{X}_2]$ (L monodentate, binding via arsenic only). Complex E is the first example of a 7-coordinate complex in metal phosphine chalcogenide chemistry²⁰⁴.

Reaction of $[(\eta^5\text{-cp})(\text{CO})_2\text{M}=\text{M}(\text{CO})_2(\eta^5\text{-cp})]$ with Ph_3PS gave complex G (Table 14), which represents an unprecedented case of 1,1-addition of Ph_3PS to a metal–metal triple bond¹⁰⁸¹. The binding of Ph_3PS to molybdenum(V) in $[\text{MoOCl}_3\text{L}]$ is similar to that of Me_3PS and X-ray analysis showed a geometry intermediate between that of a square pyramid and trigonal bipyramid¹⁰⁸⁴, analogous to that of $[\text{NbSCl}_3(\text{SPPH}_3)]$ ¹⁰⁶⁰. The behaviour of Ph_3PSe towards molybdenum(V) is similar; IR spectrometry showed a greater amount of electron density transfer to molybdenum(V) than in the case of Ph_3PS . The addition of Ph_3PS to $[\text{MoOCl}_3\text{L}]$ to form $[\text{MoOCl}_3\text{L}_2]$ showed that the 1:1 adduct predominates at equilibrium (ESR study)²⁰³.

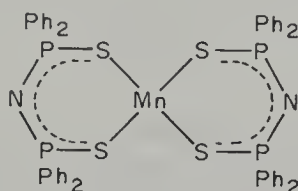
The μ values and IR data have supported ligand bridging in complexes I(ii and iii), where there is antiferromagnetic interaction ($\mu = 0.897\text{--}1.118 \text{ BM}$) between the metal centres¹⁰⁸⁶. An X-ray analysis of $[\text{WOCIL}_2](\text{PF}_6)$ has shown that the ligand $\text{Me}_2\text{P}(\text{S})\text{CH}_2\text{PMe}_2$ chelates to tungsten via P and S atoms¹⁰⁸⁷. The chelate rings are so arranged as to give *cis*- S_2 and *cis*- P_2 coordination. A thermal study of $[\text{M}(\text{CO})_n\text{L}_2\text{Cl}_2]$ ²⁰³ ($\text{L} = \text{Ph}_3\text{PS}$) has shown that for $n = 3$, the complexes lose first two CO, then one CO and finally a Ph_3PS ligand is lost in a multi-step process. For $n = 2$, loss of one CO then two CO takes place followed by loss of the Ph_3PS ligands. Tungsten complexes were more thermally stable than molybdenum complexes.

3. Complexes of the manganese Group (VIIB)

Only a few complexes with Group VIIB elements are known (Table 14). The complexes $[\text{M}(\text{CO})_3\text{LX}]$ {K(i)}¹⁰⁸⁸ resulted from a 1:1 reaction of $[\text{M}(\text{CO})_5\text{X}]$ with L chelating

via P, E or As, E donors. Complexes K(ii) have halogen bridging where $\text{Ph}_2\text{As}(\text{CH}_2)_2\text{P}(\text{E})\text{Ph}_2$ bind to manganese via As only¹⁰⁸⁸. $[\text{M}(\text{CO})_3\text{L}_2\text{X}]$ {K(iii)}, obtained from a 1:2 reaction, also have $\text{M}-\text{As}$ bonding.

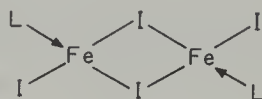
Complexes $[\text{M}(\text{CO})_3\text{LX}]$ underwent electrochemical oxidation to form 17-electron cationic species, $[\text{M}(\text{CO})_3\text{LX}]^+$, with unexpectedly large redox stability compared with species from analogous phosphine complexes, $[\text{M}(\text{CO})_3\text{L}'\text{X}]$ ($\text{L}' = \text{dpm}, \text{dpe}$)¹⁰⁸⁸. The isolation of the cationic species was difficult owing to attack by solvents such as CH_3CN . $\text{Ph}_2\text{P}(\text{S})\text{NHP}(\text{S})\text{Ph}_2$ formed $[\text{MnL}_2]$ $\{\text{L} = (\text{Ph}_2\text{P}(\text{S}))_2\text{N}^-\}$ with approximately tetrahedral geometry (103)^{1089,1090}.



(103)

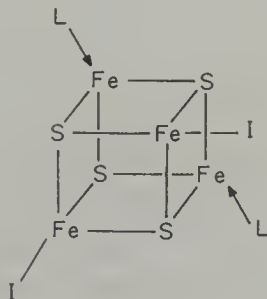
4. Complexes of the iron, cobalt and nickel Group (III)

a. Iron sub-Group. A mixed-ligand iron(0) carbonyl complex, $[\text{Fe}(\text{CO})_2(\text{Ph}_3\text{P})_2(\text{Ph}_3\text{PS})]$, was obtained from $[\text{Fe}(\text{CO})_2(\text{Ph}_3\text{P})_2\text{Br}_2]$ by its reductive elimination and substitution reaction with Ph_3PS . A *cis*-trigonal bipyramidal geometry was suggested¹⁰⁹⁴⁻¹⁰⁹⁷. Iron(II) forms tetrahedral complexes, $[\text{FeX}_2\text{L}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} = p\text{-Tol}_3\text{PS}$)³⁹¹ and $[\text{Fe}(\text{NO})_2\text{XL}]$ ($\text{X} = \text{Br}, \text{CN}$; $\text{L} = \text{Ph}_3\text{PE}$)¹⁰⁹⁸. A few poorly studied complexes include $[(\text{FeCl}_2)_n\text{L}]$, $[(\text{FeCl}_3)_n\text{L}]$ ($n = 1, 1.5$; $\text{L} = \text{Ph}_3\text{PS}$)¹⁰⁵⁶ and $[\text{FeCl}_3(\text{Bu}_3\text{PS})]$ ¹⁰⁹⁹. The iodide-bridged dimeric complexes $[\text{L}_2\text{Fe}(\mu\text{-I})_2\text{FeL}_2]\text{I}_2$ ($\text{L} = \text{Ph}_3\text{PSe}$)¹¹⁰² and $[\text{Fe}_2\text{I}_4\text{L}_2]\text{PhMe}$ ($\text{L} = \text{Ph}_3\text{PS}$) have been reported¹¹⁰³. X-ray study of the latter complex showed a distorted tetrahedral geometry about each iron centre with a long $\text{Fe}-\text{Fe}$ distance (3.397 Å) (104).



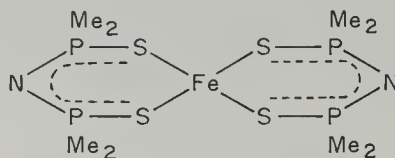
(104)

The cubane-type complex $[\text{Fe}_4\text{S}_4\text{I}_2\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PS}$) was obtained from the reaction of $[\text{Fe}(\text{thf})_6][\text{Fe}_4\text{S}_4\text{I}_4]$, Ph_3PS and sulphur¹¹⁰⁴. It has a lower stability than $[\text{Fe}_4\text{S}_4\text{I}_2]^{2-}$ and thus decomposes readily in acetonitrile-thf. The core $\text{Fe}_4\text{S}_4^{2+}$ of the complex exhibits a slight tetragonal distortion. The $\text{Fe}-\text{SPPH}_3$ distances (2.316 and 2.321 Å) are longer than the terminal $\text{Fe}-\text{S}$ bonds in RS^- -coordinated $\text{Fe}_4\text{S}_4^{2+}$ clusters with cubane structure (105).



(105)

The anionic ligands $\{\text{Ph}_2\text{P(E)}\}_2\text{CH}^-(\text{L})$ and the isoelectronic $\{\text{R}_2\text{P(S)}\}_2\text{N}^-$ ($\text{R} = \text{Me}, \text{Ph}$) form highly air-sensitive complexes, $[\text{FeL}_2]^{950,1105}$. The selenide complex decomposed rapidly in the air. An X-ray study of $[\text{FeL}_2]$ ($\text{L} = \{\text{Me}_2\text{P(S)}\}_2\text{N}^-$) showed a distorted tetrahedral structure (106)¹¹⁰⁶.



(106)

The cyclopentadienyl complexes $(\eta^5\text{-cp})\text{Fe}(\text{CO})_2\text{L}[\text{PF}_6]$ ($\text{L} = \text{R}_3\text{PE}$, $\text{R} = \text{Me}, \text{Me}_2\text{CH}, \text{Me}_3\text{C}, \text{Ph}$) were obtained from the reaction of $[(\eta^5\text{-cp})\text{Fe}(\text{CO})_2(\text{thf})](\text{PF}_6)$ with $\text{R}_3\text{PE}^{1107,1108}$. In contrast, $[(\eta^5\text{-cp})\text{Fe}(\text{CO})_2\text{L}]\text{BF}_4$ $\{\text{L} = \text{Ph}_2\text{P(E)}(\text{CH}_2)_n\text{P(E)Ph}_2; n = 1-3\}$ were formed by the oxidative cleavage of the Fe-Fe bond in the dimer $[(\eta^5\text{-cp})\text{Fe}(\text{CO})_2]_2$ in the presence of L using $[\text{cp}_2\text{Fe}]\text{BF}_4^{1109}$. Photolysis of a mixture of $[(\eta^5\text{-cp})\text{Fe}(\text{CO})_2\text{L}]\text{BF}_4$ with $[\text{Ni}(\text{NO})_4]$ gave a bimetallic complex, $[(\eta^5\text{-cp})\text{Fe}(\text{CO})_2 \cdot (\mu\text{-L})\text{Ni}(\text{CO})_3]\text{BF}_4$. The formation of similar complexes with corresponding phosphines and phosphine oxides has also been reported. The electrochemical behaviour of $[(\eta^5\text{-cp})\text{Fe}(\text{CO})_2\text{L}](\text{PF}_6)$ ($\text{L} = \text{Me}_3\text{PS}, \text{Ph}_3\text{PS}$) suggested that the products of the one-electron reduction are labile and lose the ligand L^{1108} . Oxidation of the dimer $[(\eta^5\text{-cp})\text{Fe}(\text{CO})_2]_2$ in the presence of ligands indicates the possibility of the electrochemical synthesis of the complexes $[(\eta^5\text{-cp})\text{Fe}(\text{CO})_2\text{L}](\text{PF}_6)$.

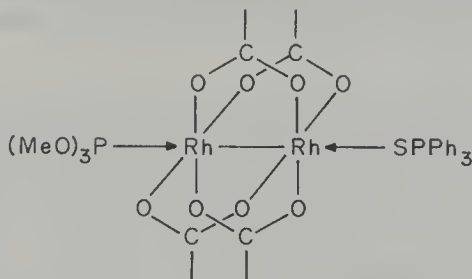
Only a few ruthenium(II) complexes of the type $[\text{Ru}(\text{CO})_2\text{L}_2\text{I}_2]$ ($\text{L} = \text{Ph}_3\text{PSe}^{1110-1111}$, $[\text{RuCl}_2\text{LL}']_2$ ($\text{L} = \text{Ph}_3\text{PS}; \text{L}' = \text{CO}, \text{Ph}_3\text{P}^{1112,1113}$ and $[\text{Ru}(\text{CO})_2\text{L}_2\text{S}]^{1112,1113}$ have been reported. *cis*-Octahedral geometry was inferred for the Ph_3PSe complex; the latter complexes involve chloride and sulphide bridging ligands, respectively.

b. Cobalt sub-Group. Cobalt(III) forms a number of complexes: (A) $[\text{CoL}_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}; \text{L} = \text{Me}_3\text{PE}^{1114,1115}$, (B) $[\text{CoLX}_2]$. *n*thf ($n = 0, \frac{1}{2}, \frac{3}{4}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}; \text{L} = \text{dpmS}_2, \text{dpmSe}_2^{1116}$, (C) $[\text{CoL}_4](\text{ClO}_4)_2$ ($\text{L} = \text{Me}_3\text{PE}^{1114,1115}$, (D) $\text{Co}(\text{NO})_2\text{LX}$ ($\text{X} = \text{Br}, \text{CN}, \text{L} = \text{Ph}_3\text{PE}^{1098}$, (E) $[\text{Co}_2\text{I}_4\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PS}^{1117}$, (F) $[\text{CoLX}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{L} = \{\text{Ph}_2\text{P(S)}\}_2\text{NH}^{1118}$, (G) $[\text{CoL}_2](\text{ClO}_4)_2$ [$\text{L} = \{\text{Ph}_2\text{P(S)}\}_2\text{CH}_2, \{\text{Ph}_2\text{P(S)}\}_2\text{-NH}^{1116,1118}$ and (H) (CoL_2) ($\text{L} = \{\text{Ph}_2\text{P(E)}\}_2\text{CH}^-, \{\text{R}_2\text{P(S)}\}_2\text{N}^-; \text{R} = \text{Me}, \text{Ph}^{950,1105,1116,1118,1119}$. A cobalt(I) complex, $[\text{CoLL}'_{1/2}]$ $\{\text{L} = \text{Ph}_2\text{P(S)CH}_2\text{P(S)Ph}_2; \text{HL}' = \text{HS}_2\text{CNHNHPh}\}$, is also known¹¹²⁰.

No X-ray studies have been reported for any of the complexes listed above. However, spectral and magnetic moment data support tetrahedral structures for complexes C and pseudo-tetrahedral for complexes A, B, D, F, G and H. The air-sensitive complexes H are similar to those of their nickel(II) analogues¹¹²¹. The Co-S and Co-Se bonds have higher covalency than the Co-O bonds in Co(II)-OPR_3 complexes (based on β values)^{1122,1123}. Further, the anionic bidentate ligands showed higher ligand field strengths¹¹²⁴. A homobimetallic complex, $[\text{Co}_2\text{I}_2(\text{Ph}_3\text{PS})_2]$, is reported to possess ligand bridging with a weak $\text{Co} \cdots \text{Co}$ interaction¹¹¹⁷, but Ph_3PS is labile and can be readily displaced by Ph_3P or Ph_3PO .

Rhodium(I) forms complexes of stoichiometry (A) $[\text{RhCl}(\text{CO})(\text{Ph}_3\text{PS})_2]^{1112,1125}$, (B) $[\text{Rh}(\text{CO})\text{Cl}(\text{Ph}_3\text{P})_2(\text{Ph}_3\text{PS})]^{1112,1125}$, (C) $[\text{RhClL}_2]_2$ ($\text{L} = \text{Ph}_3\text{PS}^{372,1112,1125}$, (D) $[\text{Rh}(\text{Ph}_3\text{PS})_3\text{Cl}]^{372}$, (E) $[\text{Rh}(\text{CO})_2(\text{Ph}_3\text{PS})\text{Cl}]^{372}$ and (F) $[\text{RhL}(\eta^2\text{-S}_2\text{PCy}_2)]$ $\{\text{L} = \text{Ph}_2\text{P(S)}(\text{CH}_2)_3\text{P}(\text{CMe}_3)(\text{CH}_2)_3\text{PPh}_2^{1126}$. Monomeric square-planar, trigonal-bipyramidal and chloro-bridged dimeric square-planar structures have been suggested for

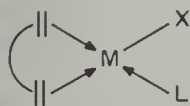
complexes A, D and E, B and C, respectively. A dimeric adduct, $[\text{Rh}_2(\text{O}_2\text{CMe})_4(\text{Ph}_3\text{PS})(\text{MeO})_3\text{P}]$, was detected in solution by ^{31}P NMR spectroscopy (107)¹¹²⁷.



(107)

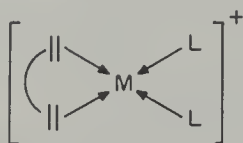
Several novel and air-stable organometallic complexes of rhodium(I) and iridium(I) with phosphine chalcogenides have been reported: (A) $[(\text{cod})(\text{RhClL})]$ ($\text{L} = \text{Me}_3\text{PS}$, Me_2PhPS , Me_2PhPSe), (B) $[(\text{cod})\text{RhL}_n]\text{X}$ ($\text{X} = \text{ClO}_4$, Ph_4B ; $n = 1$ for dmpS_2 and dpmSe_2 and 2 for Me_3PS , Me_2PhPS), (C) $[(\text{cod})\text{IrClL}]$ ($\text{L} = \text{Me}_3\text{PS}$, Me_2PhPS , MePh_2PS), (D) $[(\text{cod})\text{IrL}](\text{ClO}_4)$ ($\text{L} = \text{dpmS}_2$, dpmSe_2), (E) $[(\text{cod})\text{Ir}(\text{X})\text{Y}_2\text{L}]$ ($\text{X} = \text{H}$, Cl ; $\text{Y}_2 = \text{Cl}_2$, I_2 ; $\text{L} = \text{Me}_3\text{PS}$, MePh_2PS , Me_2PhPS)¹¹²⁸, (F) $[\text{M}(\text{dialkene})\text{L}_2](\text{ClO}_4)$ [$\text{M} = \text{Rh}$, $\text{L} = \text{R}_3\text{PS}$, $\text{R} = \text{Ph}$, Me , Et , $\text{dialkene} = \text{cod}$, nbd ; $\text{M} = \text{Ir}$, $\text{L} = \text{Ph}_3\text{PS}$, Me_3PS , $\text{dialkene} = \text{cod}$)¹¹²⁹, (G) $[\text{M}(\text{dialkene})(\text{Ph}_3\text{P})\text{L}](\text{ClO}_4)$ ($\text{L} = \text{Ph}_3\text{PS}$, Me_3PS ; $\text{dialkene} = \text{cod}$, nbd for Rh and cod for Ir)¹¹²⁹, (H) $[\text{Rh}(\text{dialkene})(\text{SePPh}_3)_2](\text{ClO}_4)$ [$\text{dialkene} = \text{cod}$, nbd , cyclooctatriene]¹¹³⁰ and (I) $[\text{M}(\text{cod})\text{L}_2]_n^{n+}$ and $[\text{M}(\text{CO})_2\text{L}_2]_n^{n+}$ $n = 1, 2$; $\text{L} = \text{Me}_3\text{PS}$, Et_3PS , Ph_3PS)¹¹³¹.

Iridium(I) complexes C underwent oxidative addition reactions with HCl or I_2 forming complexes E. In contrast, the corresponding rhodium(I) complexes showed no such activity, probably owing to the lower stability of rhodium(III) than iridium(III). The complexes $[\text{M}(\text{dialkene})(\text{Ph}_3\text{PS})_2](\text{ClO}_4)$ ($\text{M} = \text{Rh}$, Ir ; $\text{dialkene} = \text{cod}$, nbd)¹¹²⁹ were used as catalysts for the hydrogenation of hept-1-ene according to a pattern similar to the analogous complexes with alkyl sulphides used for hydrogenation of alkenes¹¹³². In the present case, the iridium(I) complexes showed greater activity than the rhodium(I) complexes. All the complexes, except E, have square-planar geometry (108–110). The



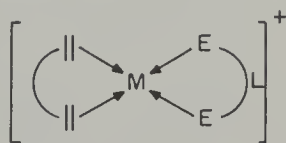
$\text{X} = \text{Cl}$, Ph_3P ; $\text{L} = \text{R}_3\text{PS}$

(108)



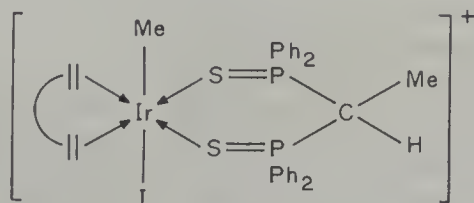
$\text{L} = \text{R}_3\text{PE}$

(109)



$\text{E}-\text{E} = \text{dpmS}_2$ or dpmSe_2

(110)

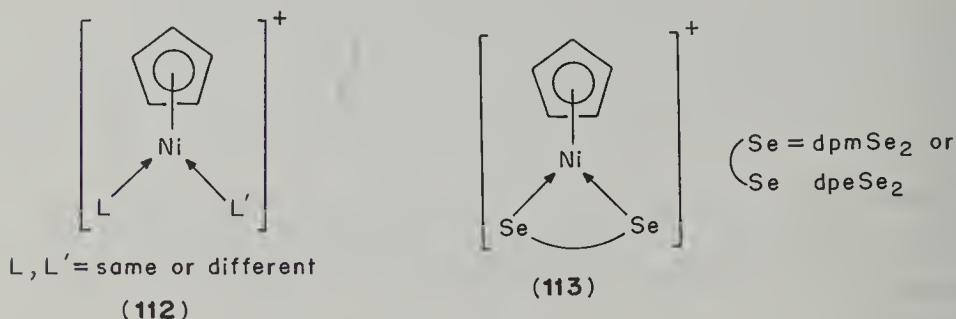


(111)

anionic ligand $\{\text{Ph}_2\text{P(S)}\}_2\text{CH}^-$ formed $[\text{Ir(L)}(\text{cod})]^{1133}$, which on further reaction with MeI gave first $[\text{Ir}(\text{Ph}_2\text{P(S)}\text{CH(Me)P(S)Ph}_2)(\text{cod})]\text{I}$ and subsequently $[\text{Ir(Me)I}(\text{Ph}_2\text{P(S)-CH(Me)P(S)Ph}_2)(\text{cod})]\text{I}$ (111). Rhodium showed the reverse sequence Iridium formed the pentacoordinate complex $[\text{Ir}(\text{tfb})_2(\text{Ph}_3\text{PS})](\text{ClO}_4)$ with pentacoordination stabilized by tfb^{1134} .

c. *Nickel sub-Group*. Nickel(II) forms complexes with various ligands of the type (A) $[\text{Ni}(\text{NO})\text{L}_2\text{X}]$ ($\text{X} = \text{Br}, \text{CN}$; $\text{L} = \text{Ph}_3\text{PE}$)¹⁰⁹⁸, (B) $[\text{NiLX}_2]^{1/2}\text{S}$ ($\text{X} = \text{Br}, \text{I}$; $\text{L} = \text{dpmS}_2$; $\text{S} = \text{thf}, \text{CH}_2\text{Cl}_2$)¹¹¹⁶, (C) $[\text{NiL}_n](\text{ClO}_4)_2$ ($n=4$ for $\text{Me}_3\text{PE}^{1111,1115}$, 2 for $\text{dpmS}_2^{1116,1135,1136}$, (D) $[\text{NiL}_2]$ ($\text{L} = \{\text{Ph}_2\text{P(E)}\}_2\text{CH}^-$, $\{\text{R}_2\text{P(S)}\}_2\text{N}^-$; $\text{R} = \text{Me}, \text{Ph}^{950,1105,1137,1138}$, (E) $[(\eta^1\text{-C}_6\text{F}_5)\text{Ni}(\text{Ph}_3\text{P})\text{L}]$ ($\text{L} = \text{Ph}_3\text{PS}$)¹¹³⁹, (F) $[(\eta^5\text{-cp})\text{NiL}_2](\text{BF}_4)$ ($\text{L} = \text{Me}_3\text{PE}, \text{Ph}_3\text{PSe}, \frac{1}{2}\text{dpmSe}_2, \frac{1}{2}\text{dpeSe}_2$)^{1140,1141} and (G) $[(\eta^5\text{-cp})\text{Ni}(\text{R}_3\text{P})\text{L}]\text{BF}_4$ ($\text{R} = \text{Pr}^i, \text{Hex}$; $\text{L} = \text{Me}_3\text{PS}$)¹¹⁴². A few nickel(I) complexes, $[\text{NiLL}'^{1/2}]$ ($\text{L} = \text{dpmS}_2$; $\text{HL}' = \text{HS}_2\text{CNRR}'$; $\text{NRR}' = \text{Et}_2\text{N}, \text{PhNH}$, etc.) have also been reported¹¹²⁰.

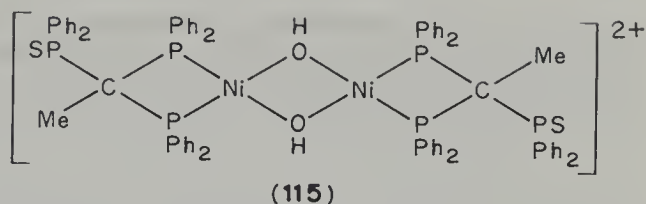
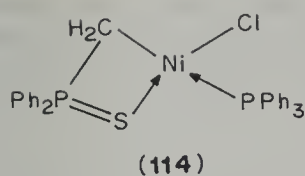
The spectral and magnetic moment data suggest distorted tetrahedral structures for the complexes A, B and C for $n=2$), tetrahedral for the complexes C ($n=4$) and D ($\text{L} = \{\text{R}_2\text{P(S)}\}_2\text{N}^-$) and square-planar for complexes D ($\text{L} = \{\text{Ph}_2\text{P(E)}\}_2\text{CH}^-$). Among the organonickel(II) complexes, E has square-planar geometry while the cations of the other complexes F and G may be represented as shown in 112 and 113.



X-ray study of the complex $[\text{NiL}_2]$ ($\text{L} = \{\text{Me}_2\text{P(S)}\}_2\text{N}^-$)¹¹³⁷ has confirmed the tetrahedral geometry about nickel. The S—Ni—S planes make a dihedral angle of 84.4° . There is no steric factor between the anionic ligands and hence a square-planar geometry should have been preferred. The reason for this apparent difference in adopting a tetrahedral rather than a square-planar structure is not clear. This complex with an NiS_4 core was the first example since all the other complexes with this core are diamagnetic with square-planar geometry^{1143–1144}.

Further comments on the complexes discussed above are that Ni—S and Ni—Se bonds have similar covalencies to those of cobalt(II)^{1145–1148} and 10 Dq values for the phosphine chalcogenide complexes are similar. When $\text{L} = \{\text{Ph}_2\text{P(E)}\}_2\text{CH}^-$, $[\text{NiL}_2]$ complexes are air-sensitive and diamagnetic. The selenide complex decomposes rapidly in solution and in the solid state, whereas the sulphide complexes decompose rapidly in solution but slowly in the solid state. In contrast, $[\text{NiL}_2]$ ($\text{L} = \{\text{R}_2\text{P(S)}\}_2\text{N}^-$) are air-stable and paramagnetic ($\mu = 3.4 \text{ BM}$)^{950,1137,1138,1149}. For $\text{R} = \text{Me}$, spin-state cross-over, tetrahedral \rightleftharpoons square planar, was observed.

A C,S-bonded nickel(II) complex (114) similar to $[(\text{Et}_3\text{P})\text{ClPtCH}(\text{Ph}_2\text{PS})_2]$ has been reported^{462,1150}. Recently, a hydroxo-bridged dimeric cation, $[(\text{Ni}(\text{L})(\mu\text{-OH}))_2](\text{ClO}_4)_2 \cdot \text{Me}_2\text{CO}$ (115) was obtained¹¹⁵¹ from the reaction of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ with $(\text{Ph}_3\text{P})_3\text{CMe}$ and polysulphide, S_n^{2-} . The reaction of $(\text{Ph}_3\text{P})_3\text{CMe}$ with S_n^{2-} oxidizes one arm of the ligand. X-ray measurements showed a square-planar geometry about each nickel atom. Interestingly, the $\text{Ph}_2\text{P(=S)CH}_2$ arm of the ligand is uncoordinated.



Numerous air-stable complexes of palladium(II) and platinum(II) and some of palladium(IV) and platinum(IV) have been reported (Table 15). The complexes generally possess poor solubility, which may be responsible for the lack of NMR and other solution-phase studies.

X-ray analyses of the complexes $[\text{PdCl}_2\text{L}_2]$ $\{\text{L} = \text{PhEt}_2\text{P}(\text{S}), \text{Bu}_3^i\text{PS}\}$ have been shown them to have *trans*-square-planar structures^{1154–1155}. The short Pd—S distance for $\text{L} = \text{Bu}_3^i\text{PS}$ shows that it has a better σ -donor ability than PhEt_2PS (2.334 versus 2.350 Å). It may be cautioned here that, on the basis of IR studies, *cis*-square-planar structures were suggested earlier¹¹⁵⁵. For other complexes (Table 15), square-planar, bromo- or sulphur-bridged square-planar dimeric and square-planar polymeric structures have been assigned for the complexes A, B, E(i) and (iv), G and H, C and F and D, E(ii) and (iii), respectively. The anionic ligand $\{\text{Ph}_2\text{P}(\text{S})\}_2\text{CH}^-$ in $[\text{PtCl}(\text{Et}_3\text{P})\text{L}]$ binds to platinum(II) via the methine carbon and one sulphur atom, forming a four-membered chelate ring (116)⁴⁶². Owing to the lability of the Pt^{II} —S bond, three isomers (A, B and C) were identified (³¹P NMR) (116–118). An X-ray study of isomer 116 showed nearly square-planar geometry about platinum(II)⁴⁶². The Pt—S (bonded) distance (2.390 Å) is one of the longest reported for platinum(II) complexes, but is similar to that found in Pt—SO₂ complexes^{1166–1169}; The Pt—S (non-bonded) distance is 3.70 Å. A slight rotation

TABLE 15. Known complexes of palladium(II) and platinum(II)

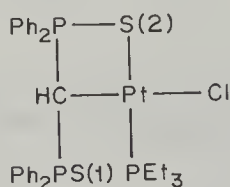
Complex	L	Ref.
A MX_2L_2 (M = Pd, Pt, X = Cl, Br)	R_3PE^a	18, 391, 1152–1156
B MX_2L (X = Cl, Br)	$[\text{Ph}_2\text{P}(\text{E})]_2\text{CH}_2$, $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{S})\text{Me}_2$, $[\text{Ph}_2\text{P}(\text{E})]_2(\text{CH}_2)_n$ ($n = 1-4, 6$)	1116, 1152, 1157–1161
C $\text{Pd}_2\text{Br}_4\text{L}$	Ph_3PE	1132
D (i) $\text{Pd}_3\text{X}_6\text{L}_m$ (X = Cl, Br, $m = 2, 4$)	$[\text{Ph}_2\text{P}(\text{Se})]_2(\text{CH}_2)_n$ ($n = 2-4, 6$)	1159, 1160
(ii) $\text{Pd}_4\text{X}_8\text{L}_3$ (X = Cl, Br)	$[\text{Ph}_2\text{P}(\text{Se})]_2(\text{CH}_2)_n$ ($n = 4, 6$)	1159
E (i) $[\text{Pt}(\text{CNS})_2\text{L}]_2^b$	Ph_3PE	1162
(ii) $\text{M}_3(\text{CNS})_6\text{L}_2^b$		
(iii) $\text{Pt}_2(\text{CNS})_4\text{L}^b$		
(iv) $\text{ML}(\text{SCN})_2^c$	$[\text{Ph}_2\text{P}(\text{E})]_2\text{CH}_2$	1163
F (i) $[\text{PdL}_2\text{S}]_2$	Ph_3PS	1164
(ii) $[\text{PdL}(\text{Ph}_3\text{P})\text{S}]_2$	Ph_3PS	1164
G (i) $[\text{PtCl}(\text{Et}_3\text{P})\text{L}]$	$[\text{Ph}_2\text{P}(\text{S})]_2\text{CH}^-$	462
(ii) ML_2	$[\text{Ph}_2\text{P}(\text{S})]_2\text{N}^-$	1118
(iii) PdBr_2L	$[\text{Ph}_2\text{P}(\text{S})]_2\text{NH}$	1118
H $[\text{PhPt}(\text{PEt}_3)_2\text{L}]^+$	Ph_3PS	1165
(ii) $[(\text{C}_6\text{F}_5)\text{Pt}(\text{Ph}_3\text{As})_2\text{L}]\text{ClO}_4$	Ph_3PS	423

^a $\text{R}_3 = \text{Ph}_3$, *o*-, *m*- or *p*-Tol₃, Cy₃, Bu_3^i , PhEt_2 .

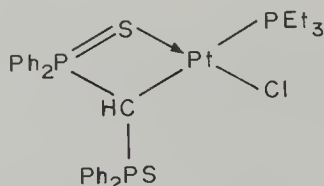
^bSCN-bridged polymer.

^cM—SCN bonding.

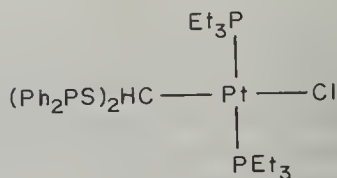
about the Pt—C bond would replace bonded S by non-bonded S. Isomer **118** is formed when excess of Et_3P is added to isomer **116**. ^{31}P NMR showed interchange of the P(S) groups in isomer **116**, probably owing to the higher *trans* effect of Et_3P . Isomer **117** was static as here Cl is *trans* to S.



(116)

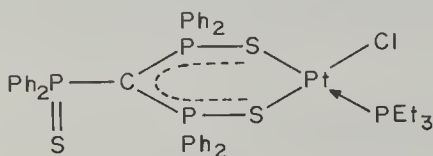


(117)

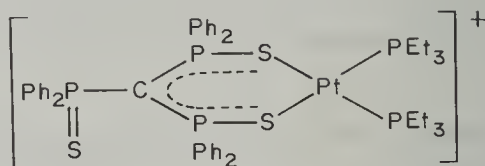


(118)

Reaction of the tripod ligand $\{\text{Ph}_2\text{P}(\text{S})\}_3\text{CH}(\text{HL})$ with $[\text{Pt}_2\text{Cl}_4(\text{Et}_3\text{P})_2]$ $[\text{Pt}_2\text{Cl}_2(\text{Et}_3\text{P})_4]$ $(\text{BF}_4)_2$ gave $[\text{PtCl}(\text{Et}_3\text{P})\text{L}]$ (**119**) or $[\text{Pt}(\text{Et}_3\text{P})_2\text{L}]$ $(\text{BF}_4)_2$ (**120**), studied by NMR (^{13}C , ^{31}P and ^{195}Pt) and X-ray methods¹¹⁷⁰. ^{13}C NMR showed deprotonation of methine proton. The ^{31}P and ^{195}Pt NMR data showed a dynamic intramolecular exchange process involving the two PS groups in isomer **119** and all three PS groups in isomers **119** and **120**. The X-ray crystal structure of **119** has confirmed the binding of two PS groups to platinum(II) with a planar CP_3 chromophore (P—C—P angles 116.2 – 124.2°). The Pt—S bond *trans* to Et_3P was longer than that *trans* to the Pt—Cl bond¹¹⁷¹.

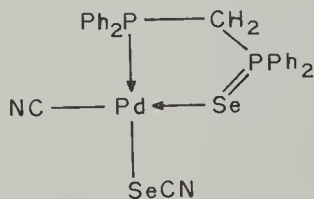


(119)

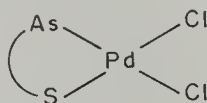


(120)

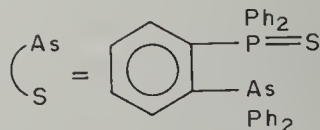
The reaction of $[\text{Pd}(\text{SeCN})_4]^{2-}$ with dpm gave $[\text{PdL}(\text{CN})(\text{SeCN})]$ ($\text{L} = \text{dpmPSe}$) (**121**) instead of the expected product. $[\text{Pd}(\text{SeCN})_2\text{L}]$ ¹¹⁷². Heating of $[\text{Pd}(\text{SeCN})_2\text{L}]$ also gave **121** with the cyanide group *trans* to Se as shown by X-ray analysis. An S,As-bonded complex, $[\text{PdX}_2\text{L}]$ (**122**) ($\text{X} = \text{Cl}, \text{Br}$), has also been reported¹¹⁷³.



(121)



(122)

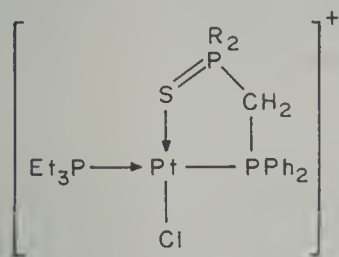


A platinum(II) complex, $[\text{PtL}_2](\text{O}_3\text{SCF}_3)_2$ underwent extrusion of selenium forming initially $[\text{PtLL}'](\text{O}_3\text{SCF}_3)_2$ and finally $[\text{PtL}'_2](\text{O}_3\text{SCF}_3)_2$ $\{\text{L} = \text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{PPh}_2$; $\text{L}' = \text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{P}(\text{Se})\text{Ph}_2\}$ ¹¹⁷⁴. Rearrangement of $[\text{PtLL}'](\text{O}_3\text{SCF}_3)_2$ also gave the same product, $[\text{PtL}'_2](\text{O}_3\text{SCF}_3)_2$ $\{\text{L}'$ is same as above, $\text{L}'' = \text{Ph}_2\text{PCH}_2\text{PPh}_2\}$ ¹¹⁷⁴.

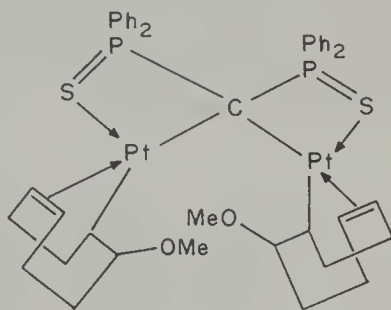
Reactions of $\text{Ph}_2\text{PCH}_2\text{P}(\text{E})\text{R}_2$ ($\text{E} = \text{S}, \text{Se}$; $\text{R} = \text{Ph}, \text{CHMe}_2, \text{CMe}_3$) with chlorobridged complex $[\text{M}_2\text{Cl}_4(\text{PR}_3)_2]$ ($\text{M} = \text{Pd}, \text{Pt}$, $\text{R} = \text{Et}$ or Bu^n) in the presence of NaClO_4 or NaBF_4 gave *cis*- and *trans*- $[\text{PtCl}(\text{PR}_3)_2\{\text{Ph}_2\text{PCH}_2\text{P}(\text{E})\text{R}_2\}]\text{X}$ ($\text{X} = \text{ClO}_4, \text{BF}_4$)⁴²⁵. Here

cis- and *trans*- refer to M—P bonds. Deprotonation of these complexes using NaH or using $\text{Li}^+[\text{Ph}_2\text{PCHP(E)R}_2]^-$ instead of the neutral ligand gave the corresponding *cis*- and *trans*- $\text{PtCl(PR}_3)_2\{\text{Ph}_2\text{PCH-P(E)R}_2\}$. The products were studied using ^{13}C , ^{31}P , ^{77}Se , ^{195}Pt NMR and X-ray data (one complex). The X-ray study of $[\text{PtCl(PEt}_3)_2\{\text{Ph}_2\text{PCH}_2\text{P(S)-(CMe}_3)_2\}](\text{ClO}_4)$ showed *trans*-square planar structure (123).

An interesting platinum(II) complex, $[\text{PtL(MeOcod)}]$ with the anionic ligand $\{\text{Ph}_2\text{P(S)}\}_2\text{CH}^-(\text{L})$, (123) has been reported¹¹³³. This showed both ligand and metal site reactivity in transforming to a novel dimer, $[\text{Pt}_2(\text{Ph}_2\text{P(S)CP(S)Ph}_2)(\text{MeOcod})_2]$ (124) containing a quaternary carbon bridge between platinum atoms (X-ray analysis).

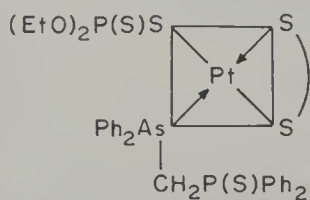


R = Me_3C
(123)

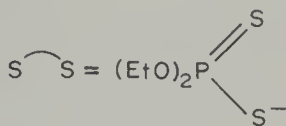


(124)

Interaction of $\text{Pt}[\text{S}_2\text{P(OEt)}_2]_2$ with $\text{Ph}_2\text{PCH}_2\text{P(E)Ph}_2(\text{L})$ gave (A) $[\text{LPtR}]_2\text{R}$ $\{\text{R} = \text{S}_2\text{P(OEt)}_2\}$, (B) $[\text{LPt}(\text{S}_2\text{P(O)OEt})]$ and (C) *cis*- and *trans*- $[\text{PtL}_2]\text{R}_2$ (*cis*, *trans* refer to M—P bonds linking L to M)¹¹⁷⁵. Compounds B are formed from A on slow reaction of the free anion R with A. The analogous ligand $\text{Ph}_2\text{P(E)CH}_2\text{CH}_2\text{AsPh}_2(\text{L}')$ also gave $[\text{Pt}(\eta^1\text{-L}')(\eta^1\text{-S}_2\text{P(OEt)}_2)(\eta^2\text{-S}_2\text{P(OEt)}_2)]$. X-ray analysis for E = S showed a square-planar structure (125) with $\text{Ph}_2\text{P(S)}$ as a free dangling ligand end. Similarly, reactions of $\text{Ph}_2\text{P(E)CH}_2\text{PPh}_2(\text{L})$ with $[\text{Pt}(\text{S}_2\text{CNEt}_2)_2]$ gave a number of interesting products¹¹⁷⁶, namely $[(\eta^1\text{-L})\text{Pt}(\eta^1\text{-S}_2\text{CNEt}_2)(\eta^2\text{-S}_2\text{CNEt}_2)]$ and $[(\eta^2\text{-L})\text{Pt}(\eta^2\text{-S}_2\text{CNEt}_2)]^+$. Owing to the higher Pt—Se lability, a number of side-products such as dpm and dpmSe₂ were also detected in the case of the selenium analogue (^{31}P , ^{77}Se and ^{195}Pt NMR).



(125)

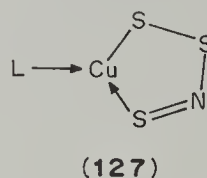
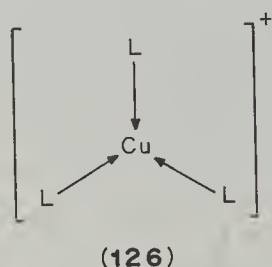


A small number of palladium(IV) and platinum(IV) complexes have been reported; (A) $(\text{Bu}_4\text{N})[\text{Pd}(\text{Ph}_3\text{PS})\text{Cl}_5]$ ¹¹⁷⁷, (B) $[\text{PtCl}_4\text{L}_2]$ (L = *o*, *m*- and *p*- ToI_3PS)¹¹⁵⁶, (C) $[\text{PtCl}_4\text{L}]$ $\{\text{L} = \text{Ph}_2\text{P(S)}(\text{CH}_2)_n\text{P(S)Ph}_2; n = 2-4\}$, (D) $[\text{PtBr}_4\text{L}]$ $\{\text{L} = \text{Ph}_2\text{P(Se)}(\text{CH}_2)_6\text{P(Se)Ph}_2\}$ and (E) $[\text{PtBr}_4\text{L}_2]$ $\{\text{L} = \text{Ph}_2\text{P(E)}(\text{CH}_2)_3\text{P(E)Ph}_2\}$ ¹¹⁶⁰. In complex E, L is unidentate, whereas in C and D, L are bidentate. The Pt^{IV} —Se bond is not stable as the ligand decomposes, as seen for Ph_3PSe and Ph_3AsS ¹¹⁵³. Hence these complexes mentioned above were prepared at low temperature (20–25 °C) by slowly evaporating the reaction mixture.

5. Complexes of the copper Group (IB)

Table 16 contains a number of copper(I) and some copper(II) complexes with mono- and di-tertiary phosphine chalcogenides. Owing to the tendency of copper(II) to undergo reduction to copper(I) in the presence of phosphine chalcogenides, only a small number of copper(II)–phosphine sulphide complexes have been isolated using Me_2CO as the solvent. Normally, copper(I) complexes were obtained after reducing copper(II) to copper(I) using ascorbic acid or hypophosphorous acid prior to its reaction with ligand.

An X-ray study of $[\text{Cu}(\text{Me}_3\text{PS})_3](\text{ClO}_4)$ showed nearly trigonal planar geometry (126)¹¹⁸⁰. The complexes, $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{X}$ and $[\text{Cu}(\text{Ph}_3\text{PS})_3]\text{X}$ ($\text{X} = \text{ClO}_4, \text{BF}_4$) are isomorphous¹¹⁸⁴. The Cu—L bond strength was found to decrease in the order $\text{Ph}_3\text{PS} > \text{PhMe}_2\text{PS} > \text{Me}_3\text{PS}$ (IR)¹¹⁸⁴. A copper(I) complex, $[\text{Cu}(\text{Ph}_3\text{PS})(\text{NS}_3)]$ (127), obtained from $[\text{CuCl}(\text{Ph}_3\text{P})_3]$ and S_7NH , also possesses trigonal planar geometry about copper(I) (X-ray analysis)¹¹⁹⁶.



Whereas the ionic complexes A were soluble in various organic solvents, the non-ionic complexes of the type $[\text{CuLX}]_n$ {B(i), (ii)} have poor solubility in common organic

TABLE 16. Known complexes of copper(I) and copper(II)

Complex		L	Ref.
A	(i) CuL_3X^a ($\text{X} = \text{ClO}_4, \text{BF}_4, \text{NO}_3$)	R_3PE^b	1178–1185
	(ii) $[\text{CuL}_2]\text{X}^c$ ($\text{X} = \text{ClO}_4, \text{BF}_4$)	$\text{dpmS}_2, \text{dpmSe}_2, \text{dpseS}_2,$ $o\text{-(PSPH}_2\text{)}(\text{Ph}_2\text{As})\text{C}_6\text{H}_4$	1157, 1158 1173
B	(i) $[\text{CuLX}]_n^d$ ($\text{X} = \text{Cl, Br, I, SCN}$)	R_3PS^e	1158, 1182, 1184, 1186–1188
	(ii) $[\text{CuXL}]_m^d$ ($\text{X} = \text{Cl, Br}$)	$\text{dpmS}_2, \text{dpeS}_2$	1157, 1158, 1173, 1189–1191
	(iii) $[\text{CuClL}] \cdot \text{Me}_2\text{CO}^a$	dpmS_2	1157, 1158, 1178
	(iv) $[(\text{CuClL})_2 \cdot 2(\text{CuClL})]^f$	dpmS_2	1178
	(v) $[\text{CuBrL}]$	$\text{Ph}_2\text{P(S)NHP(S)Ph}_2$	1118
C	(i) $[\text{CuCl}_2\text{L}_2]^g$	$\text{Me}_2\text{PhPS, MePh}_2\text{PS}$	1157, 1158
	(ii) $[\text{CuCl}_2\text{L}]^g$	$\text{dpmS}_2, \text{dpeS}_2, \text{dppS}_2$	1157, 1158, 1189, 1192–1194
D	$[\text{CuLL}'](\text{ClO}_4)^h$	Ph_3PS	1195

^aTrigonal planar.

^b $\text{R}_3 = \text{Me}_3, \text{Et}_3, \text{Pr}_3^i, \text{Ph}_3, \text{Me}_2\text{Ph}$.

^cTetrahedral.

^dPolymeric.

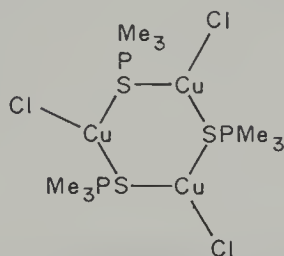
^e $\text{R}_3 = \text{Me}_3, \text{Ph}_3, \text{Me}_2\text{Ph}$.

^fTrigonal planar monomer and tetrahedral dimer.

^gDistorted tetrahedral.

^h $\text{L}' = 2,2'\text{-bithiazole}$, trigonal planar.

solvents, suggesting polymeric structures. IR and X-ray measurements established the trimeric structure of $[\text{Cu}(\text{Me}_3\text{PS})\text{Cl}]_3$ with a distorted trigonal planar geometry about each copper atom^{1188,1197}. The angles about copper vary in the range 109.8 – 125.2° . Three Cu and three Cl atoms form a six-membered ring(128) which is very rarely observed in copper(I) chemistry.

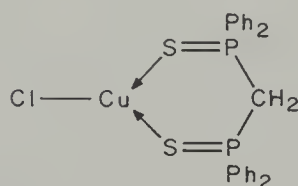


(128)

Polymeric $[\text{Cu}(\text{Me}_3\text{PS})\text{X}]_n$ ($\text{X} = \text{Br}, \text{I}$) are isomorphic but different from $[\text{Cu}(\text{Me}_3\text{PS})\text{Cl}]_3$. Similarly, in $[\text{Cu}(\text{Ph}_3\text{PS})_3\text{X}]_n$, IR data rule out any ligand bridging¹¹⁸⁷. The difference may be attributed to the different electronic environments of Me_3PS (the better Lewis base) and Ph_3PS . $[\text{Cu}(\text{Me}_3\text{PS})(\text{SCN})]_n$ is a long-chain polymer involving SCN^- bridging with terminal Me_3PS ligands^{1184,1198}. The chains interact via SCN^- leading to pseudo-tetracoordination for some copper atoms.

The complex $[\text{CuClL}]\text{Me}_2\text{CO}$ {B(iii)} was obtained by reduction of a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and dpmS_2 in Me_2CO using hypophosphorous acid, whereas the same reaction in EtOH gave $[(\text{CuClL})_2 \cdot 2(\text{CuClL})]$ {B(iv)}^{1157,1158,1178}. Heating the monomer $[\text{CuClL}]\text{Me}_2\text{CO}$ leads to loss of Me_2CO and formation of a dimer, $[\text{CuClL}]_2$, at temperatures $> 140^\circ\text{C}$.

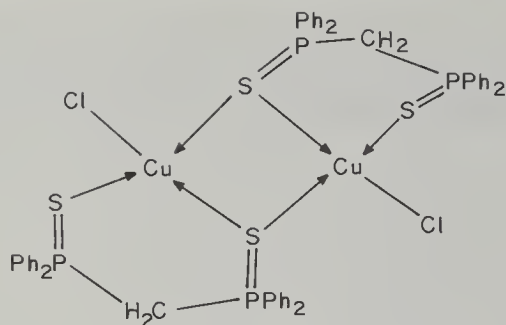
An X-ray study of $[\text{CuClL}]\text{Me}_2\text{CO}$ (129) has shown that the geometry about copper is distorted trigonal-planar ($\text{S}-\text{Cu}-\text{S}$ angles 113 – 123°)^{1157,1158}, the distortion being larger than that normally observed in mononuclear copper(I) complexes. The Me_2CO is unbonded.



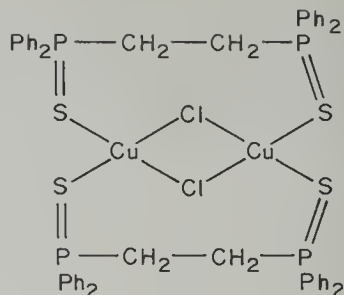
(129)

The X-ray structure of $[(\text{CuClL})_2 \cdot 2(\text{CuClL})]$ { $\text{L} = \text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{S})\text{Ph}_2$ } shows that the monomer, CuClL , and dimer, $(\text{CuClL})_2$, exist in the same unit cell¹¹⁷⁸. The monomer has the same geometry as above (129), whereas the dimer has each sulphur of the ligand acting as a bridge (130). The geometry about each copper is distorted tetrahedral. There was no evidence for $\text{Cu} \cdots \text{Cu}$ interaction. The reaction of $[\text{CuClL}]\text{Me}_2\text{CO}$ with Me_3PS gave $[\text{Cu}(\text{Me}_3\text{PS})\text{Cl}]_3$, and this indicates the lability of the $\text{Cu}-\text{S}$ bonds in the acetone complex. Treatment of the acetone complex with Cl_2 gave an orange solution due to $[\text{CuCl}_4]^{2-}$ ¹¹⁹⁹.

The complex $[\text{CuClL}]$ ($\text{L} = \text{dpeS}_2$) also exists as a dimer (131)¹¹⁹⁰. The geometry about each copper is distorted tetrahedral. The $\text{Cu}-\text{S}-\text{P}$ angles (109.9° , 106.6°) are larger than those found in the acetone complex (91.52° , 95.68°), from which it is concluded that when the ring strain is less, sulphur binds tetrahedrally¹¹⁸⁸.



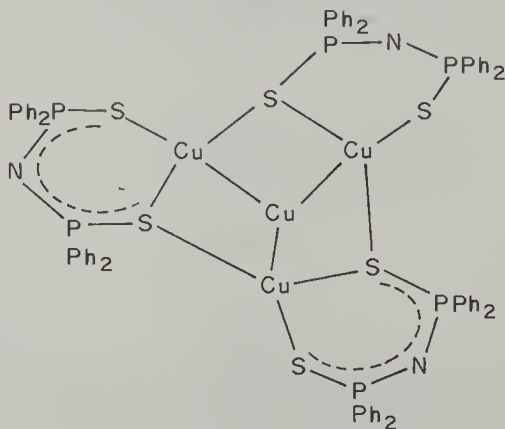
(130)



(131)

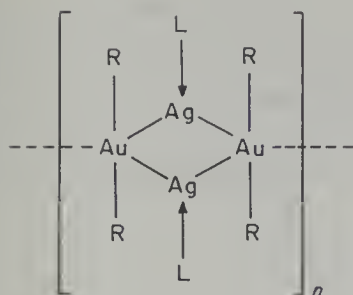
Reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with the sodium salt of $\text{Ph}_2\text{P(S)NHP(S)Ph}_2$ in aqueous solution gave the dark purple compound, $[\text{Cu}_3\text{L}_4]$ (A). Purification of A in toluene- CCl_4 gave $[\text{Cu}_3\text{L}_3]$ or $[\text{Cu}_3\text{L}_3] \cdot 2.5\text{CCl}_4$ (B). Similarly, when A was worked up in CH_2Cl_2 - CCl_4 , a pink compound, $[\text{Cu}_4\text{L}_3][\text{CuCl}_2](\text{CCl}_4)$ (C) was obtained. When $[\text{Cu}(\text{ClO}_4)_2]$ solution in dmf was added to solution of A in toluene, the white compound $[\text{Cu}_4\text{L}_3](\text{ClO}_4)_2$ (D) was obtained. The compound $[\text{CuL}_2]$ ($\text{L} = \{\text{Ph}_2\text{P(S)}\}_2\text{N}^-$) (E) was obtained by the reaction of $\{\text{Ph}_2\text{P(S)}\}_2\text{N}^-\text{K}^+$ with CuCl_2 in methanol at -78°C ^{1090,1119,1200-1202}.

An X-ray study of C showed that the copper(I) atoms in $[\text{Cu}_4\text{L}_3]^+$ are tetrahedral (132)¹²⁰². A has a μ value of 1.90 BM, suggesting the presence of one copper(II) site and two copper(I) sites. Other cluster compounds are diamagnetic. The blue copper(II) complex E has a pseudo-tetrahedral structure (ESR)¹²⁰³⁻¹²⁰⁷. A diamagnetic tetramer, $[\text{CuL}_4]$ ($\text{L} = \{\text{Ph}_2\text{P(S)}\}_2\text{CH}^-$), was obtained from organocopper(I), $[\text{ArCu}]$, and $\text{Ph}_2\text{P(S)CH}_2\text{P(S)Ph}_2$ ¹²⁰⁸.

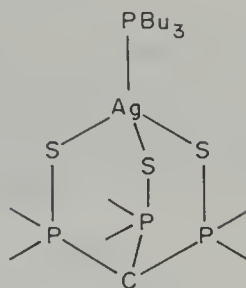


(132)

Only a few silver(I) complexes are known: (A) $[\text{AgL}_2](\text{ClO}_4)$ ($\text{L} = \text{Ph}_3\text{PSe}$, dpmS_2 , dpmSe_2 , dpeSe_2)^{1157,1158}, (B) $[\text{Ag}(\text{Cy}_3\text{PS})_2(\text{NO}_3)]$ ¹²⁰⁹ and (C) $[\text{AgL}(\text{NO}_3)] \cdot 2\text{H}_2\text{O}$ ($\text{L} = \text{dpmS}_2$)^{1157,1158}. The NO_3^- ions are in the coordination sphere, but their uni- or bi-dentate nature has not been established. The heterobimetallic complexes $[\text{AuAgR}_2(\text{Ph}_3\text{PS})]_n$ ($\text{R} = \text{C}_6\text{F}_5$, $\text{C}_6\text{H}_2\text{F}_3$ -2,4,6) (133)¹²¹⁰ and a cage complex $[\text{Ag}(\text{Bu}_3\text{P})\text{L}]$ (134) ($\text{L} = \{\text{Ph}_2\text{P(S)}\}_3\text{C}^-$)¹²¹¹ have been reported. In 134, silver has a tetrahedral geometry.



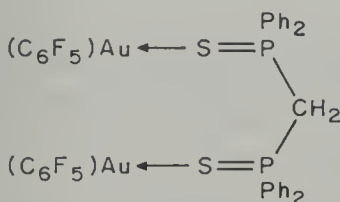
(133)



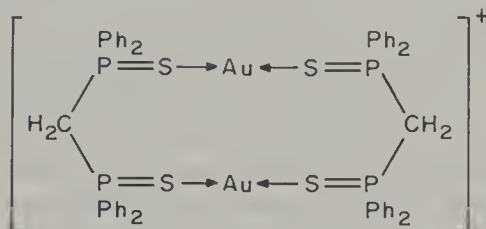
(134)

Gold forms a number of complexes (A) $[\text{AuClL}]$ $\{\text{L} = \text{Ph}_3\text{PE}, o\text{-(Ph}_2\text{PS)}(\text{Ph}_2\text{As})\text{C}_6\text{H}_4\}$, (B) $[\text{Au}(\text{Ph}_3\text{PS})_2](\text{PF}_6)$ and (C) $[\text{AuCl}_3(\text{Ph}_3\text{PS})]$ ^{1153,1173,1181,1212-1217}. No adduct of gold(III) with Ph_3PSe or the related ligands Ph_3AsS and Ph_3SbS could be isolated on account of ligand decomposition on reaction with a gold(III) salt^{1153,1215}. An X-ray study of $[\text{AuClL}]$ ($\text{L} = \text{Ph}_3\text{PE}$) has shown a nearly linear geometry about gold(I)^{1212,1218}. B has a similar geometry. In $[\text{AuClL}]$ $\{\text{L} = o\text{-(PSPH}_2)(\text{Ph}_2\text{As})\text{C}_6\text{H}_4\}$, the $\text{P}=\text{S}$ group is uncoordinated and only Ph_2As binds to gold(I)¹¹⁷³.

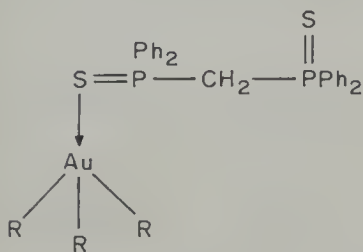
Reactions of $\text{dpmS}_2(\text{L})$ with $[(\text{C}_6\text{F}_5)\text{Au}(\text{tht})]$, $[\text{Au}(\text{tht})_2](\text{ClO}_4)$, $[(\text{C}_6\text{F}_5)_3\text{Au}(\text{OEt}_2)]$ and $[(\text{C}_6\text{F}_5)_2\text{Au}(\text{tht})_2](\text{ClO}_4)$ gave the air- and moisture-stable products $[(\text{C}_6\text{F}_5)_2\text{Au}_2\text{L}]$ (135), $[\text{Au}_2\text{L}_2](\text{ClO}_4)_2$ (136), $[(\text{C}_6\text{F}_5)_3\text{AuL}]$ (137) and $[(\text{C}_6\text{F}_5)_2\text{AuL}](\text{ClO}_4)$ (138), respectively. They were studied by ^1H , ^{19}F and ^{31}P NMR spectroscopy¹²¹⁹. Reaction of 138 with NaH gave $[(\text{C}_6\text{F}_5)_2\text{AuL}]$ ($\text{L} = \{\text{Ph}_2\text{P}(\text{S})\}_2\text{CH}^-$) (139), involving C,S-bonding similar to a platinum(II) complex⁴⁶². Reaction of 139 with $[\text{RAu}(\text{tht})]$, $[\text{Au}(\text{tht})_2](\text{ClO}_4)$ or AgClO_4 gave bi- or tri-nuclear complexes (140 and 141). A binuclear complex, $[\text{Au}_2\text{L}_2]$ ($\text{L} = \{\text{Ph}_2\text{P}(\text{S})\}_2\text{N}^-$) (142) was obtained from the reaction of $\text{Ph}_2\text{P}(\text{S})\text{-NHP}(\text{S})\text{Ph}_2(\text{LH})$ with either $[\text{Au}(\text{tht})\text{Cl}]$ or $[(\text{C}_6\text{F}_5)_2\text{Au}(\text{tht})]$ ¹²¹⁹. Similarly, $[\text{R}_2\text{AuL}]$ (143) was obtained from LH and $[\text{R}_2\text{AuCl}]_2$.



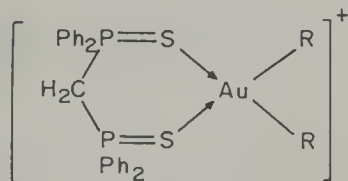
(135)



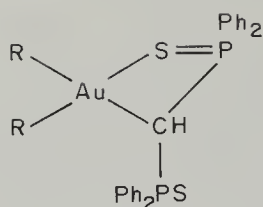
(136)



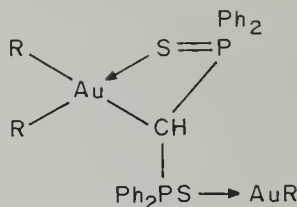
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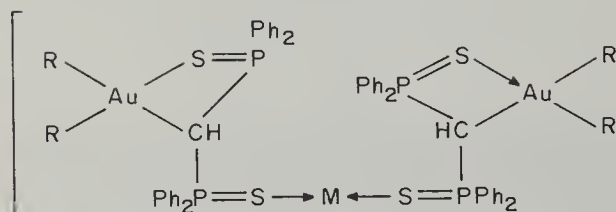
(138)



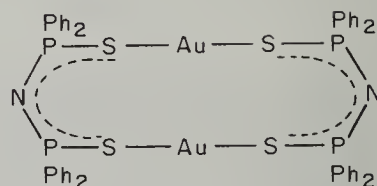
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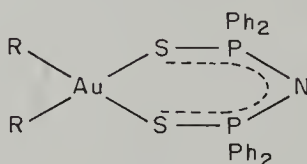
(140)



(141, M = Ag, Au)



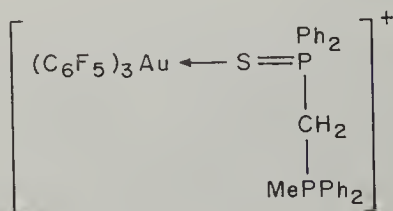
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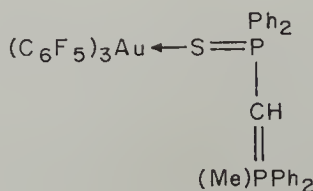
(143)

The unsymmetrical bis(phosphine) ligand dpmPS, on reaction with $[(C_6F_5)_2Au(tht)]^+$, forms $[(C_6F_5)_2AuL]^+$, which on treatment with NaH loses a CH_2 proton forming $[(C_6F_5)_2Au(Ph_2PCHP(S)Ph_2)]^{1220}$. The anionic ligand chelates via P and S. Expectedly, the P—C bond length was shorter than that in a complex in which dpm acts as a chelating agent.

$[Au(C_6F_5)_3(Ph_2P(S)CH_2PPh_2Me)](ClO_4)$ (**144**) was obtained from the reaction of $[Au(C_6F_5)_3(OEt_2)]$ with $(Ph_2P(S)CH_2PPh_2Me)(ClO_4)^{1221}$. Compound (**144**) is air and moisture stable. Reaction of **144** with NaH gave the neutral methanide complex $[Au(C_6F_5)_3(Ph_2P(S)CHPPh_2Me)]$ (**145**). Reaction of **145** with $[Au(C_6F_5)(tht)]$ (1:2) gave $[Au(C_6F_5)\{Ph_2P(S)CH[Au(C_6F_5)]PPh_2Me\}]$ (**146**). Reaction of **145** with $[AuCl(tht)]$ gave the mixed-valence binuclear complex $[Au(C_6F_5)_3\{Ph_2P(S)CH(AuCl)PPh_2Me\}]$ (**147**). Compound **147** reacted with $\{N(PPh_3)_2\}Cl$ and $\{NBu_4\}Br$ to form $[AuX(Ph_2P(S)CHPPh_2Me)]_2$ ($X = Cl, Br$) (**148** and **149**). Compound **148** reacted with $AgClO_4$ to give the cationic complex $[Au(Ph_2P(S)CHPPh_2Me)_2](ClO_4)_2$ (**150**), and **150** reacted with Cl_2 to give the gold(II) complex $[AuCl(Ph_2P(S)CHPPh_2Me)]_2(ClO_4)_2$ (**151**).

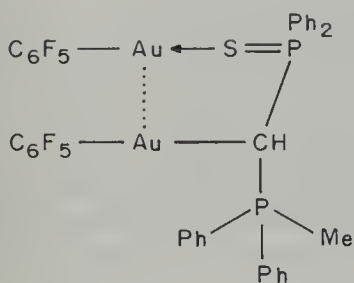


(144)

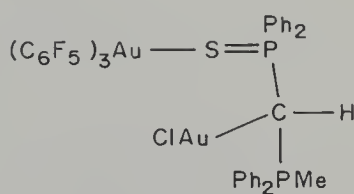


(145)

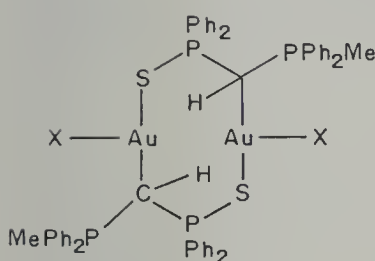
Compound **145** reacted with $[\text{Ag}(\text{OClO}_3)(\text{PPh}_3)]$ (1:1) to afford a mixture of $[\text{Ag}(\text{Ph}_2\text{P}(\text{S})\text{CHPPh}_2\text{Me})_2](\text{ClO}_4)_2$ (**152**). $[\text{Ag}(\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{PPh}_2\text{Me})](\text{ClO}_4)_2$ was obtained from AgClO_4 and $[\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{PPh}_2\text{Me}](\text{ClO}_4)$. An X-ray study of **146** showed that the structure involved an $\text{Au} \cdots \text{Au}$ interaction (3.224 Å). Further compounds of gold(III) have also been reported¹²²²: $[\text{Au}(\text{C}_6\text{F}_5)\text{Cl}\{\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{PPh}_2(\text{CH}_2\text{R})\}](\text{ClO}_4)$ ($\text{R} = \text{H}, \text{Ph}$), $[(\text{C}_6\text{F}_5)_2\text{ClAu}\{\text{Ph}_2\text{P}(\text{S})\text{CHPPh}_2(\text{CH}_2\text{R})\}]$ and $[(\text{C}_6\text{F}_5)_2\text{ClAu}\{\text{Ph}_2\text{P}(\text{S})\text{CH}(\text{AuX})\text{PPh}_2\text{Me}\}]$ ($\text{X} = \text{C}_6\text{F}_5, \text{Cl}$).



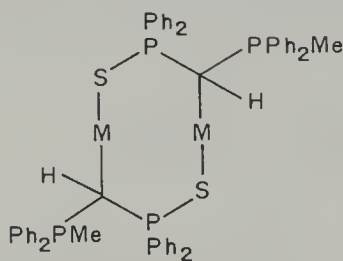
(146)



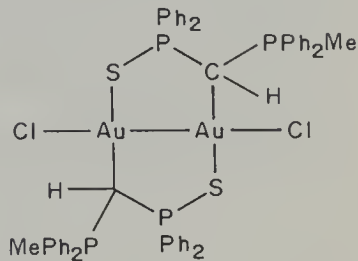
(147)



(148 and 149)

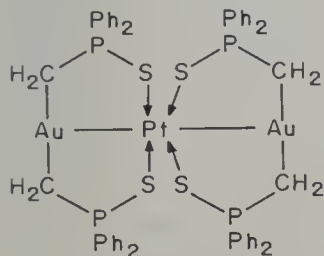


$\text{M} = \text{Ag}, \text{Au}$
(150 and 152)

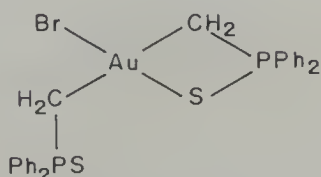


(151)

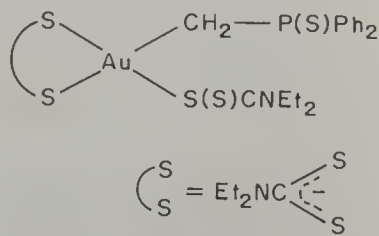
Reaction of the lithium salt $\text{LiCH}_2\text{P}(\text{S})\text{Ph}_2$ with $[\text{Au}(\text{C}_4\text{H}_8\text{S})\text{Cl}]$ in a 2:1 ratio gave $\text{Li}[\text{Au}\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}_2]$, characterized as $\{(\text{Ph}_3\text{P})_2\text{N}\}[\text{Au}\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}_2]$ (A)^{1223,1224}. Reaction of A with *cis*- $[\text{PtCl}_2(\text{SET}_2)_2]$ in a 2:1 ratio gave the neutral, linear trinuclear complex $[\text{Au}_2\text{Pt}\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}_4]$ (B). Treatment of A with $\text{K}_2[\text{PtCl}_4]$ gave $[\text{Au}_2\text{Pt}\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}_4\text{Cl}_2]$ (C). Oxidation of B with Cl_2 in CCl_4 or reaction of B with PhICl_2 also gave C. A, B and C have been characterized by X-ray measurements. A contains a $\text{C}-\text{Au}-\text{C}$ linkage; B contains an $\text{Au}-\text{Pt}-\text{Au}$ unit with $-\text{CH}_2\text{P}(\text{S})\text{Ph}_2$ acting as the bridge (**153**). In C, Cl is bound to the terminal gold atoms, the remainder of bonding being the same. Similarly, SO_2 adds to the gold atoms forming $[\text{Au}_2\text{Pt}\{\mu\text{-C}, \text{S}-\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}_4(\text{SO}_2)]$ ¹²²⁴. The oxidation of A with Br_2 in CH_2Cl_2 gave



(153)



(154)



(155)

$[\text{Au}\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}_2\text{Br}]$ (**154**)¹²²⁵, exhibiting a dynamic rearrangement involving CH_2 resonances (NMR). Reaction of $[\text{Au}\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}_2\text{Cl}]$ with $[\text{Au}(\text{tht})\text{Cl}]$ gave a mixed valence complex, $[\text{Au}^{\text{I}}\text{Au}^{\text{III}}\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}_2\text{Cl}_2]$ and a dimer, $[\text{Au}^{\text{II}}\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}\text{Cl}]_2$. Similarly, reaction of tetraethylthiuram disulphide with $[\text{Au}\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}]_2$ cleaves the dimer, forming $[\text{Au}\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}(\text{S}_2\text{CNEt}_2)_2]$ (**155**).

6. Complexes of the zinc Group (IIB)

Several complexes of Group IIB elements are given in Table 17. Except for the mercury(I) complexes J, all the other mercury(II) complexes are stable to air and moisture. Owing to the low solubility of the complexes, X-ray data have only been obtained for a few of the compounds listed. However, as discussed below, a large number of solution-phase investigations using NMR spectroscopy have been reported.

An X-ray study of $[\text{HgCl}_2(\text{Ph}_3\text{PSe})]$ showed that it has a dimeric structure (**156**)¹²³². It may be mentioned that $[\text{HgCl}_2(\text{Ph}_3\text{AsO})]$, an analogous complex, has an oxygen-bridged dimeric structure¹²⁴². For $[\text{HgCl}_2(\text{Ph}_3\text{PS})]$, a structure similar to that of

TABLE 17. Known complexes of zinc(II), cadmium(II) and mercury(II)

Complex	L	Ref.
A $[\text{MX}_2\text{L}_2]^a$ (M = Zn, Cd, Hg; X = Cl, Br, I, NO_3)	R_3PE^b	1115, 1154, 1227–1230
B $[\text{MX}_2\text{L}]$ (Zn, Cd, Hg; X = Cl, Br, I, NO_3 , SCN)	(i) $\text{R}_3\text{PE}^{c,d}$	1056, 1153, 1154, 1156, 1187, 1209, 1227, 1229, 1231, 1232
	(ii) $[\text{Ph}_2\text{P}(\text{S})_2]\text{CH}_2^a$, $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{S})\text{Me}_2^a$, $[\text{Ph}_2\text{P}(\text{E})]_2(\text{CH}_2)_n^a$ ($n = 2-4,6$) $\text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{PPh}_2^a$	1075, 1157, 1158, 1161, 1227, 1233–1236
	(iii) $[\text{Ph}_2\text{P}(\text{S})]_2\text{NH}^a$	1118, 1193, 1237–1239
C $[\text{M}_2\text{X}_4\text{L}]^c$ (M = Cd, Hg; X = Cl, Br, I)	$[\text{Ph}_2\text{P}(\text{E})]_2(\text{CH}_2)_n$ ($n = 4,6$)	1234, 1235
D $[\text{CdBr}_2\text{L}_3]^e$	$p\text{-Tol}_3\text{PSe}$	1227
E (i) $[\text{Hg}_3(\text{NO}_3)_6\text{L}_4]^f$	Ph_3PSe	1227
(ii) $[\text{Hg}_3\text{X}_6\text{L}_2]$ (X = Cl, I)	$[\text{Ph}_2\text{P}(\text{E})]_2(\text{CH}_2)_3$	1233, 1234
F $[\text{Hg}_4\text{X}_8\text{L}_3]$ (X = Cl, Br, I)	$[\text{Ph}_2\text{P}(\text{E})]_2(\text{CH}_2)_n$ ($n = 2,4$)	1234
G $[\text{ZnL}_4](\text{ClO}_4)_2^a$	Me_3PE	1115, 1179, 1226, 1240
H $[\text{ML}_2]\text{X}_2^a$ (M = Zn, Cd, Hg; X = NO_3 , ClO_4)	$[\text{Ph}_2\text{P}(\text{S})]_2\text{CH}_2$	1157, 1158, 1193
I (i) $[\text{ML}_2]^a$ (M = Cd, Hg)	$[\text{Ph}_2\text{P}(\text{S})]_2\text{N}^-$	1118, 1138
(ii) $[\text{HgClL}]$	$[\text{Ph}_2\text{P}(\text{S})]_2\text{NH}$	1118
J $[\text{Hg}_2(\text{AsF}_6)_2\text{L}]$	Ph_3PE , $p\text{-Tol}_3\text{PS}$	1241

^aTetrahedral.

^bR = Ph, Me, Buⁿ, (CNCH₂CH₂).

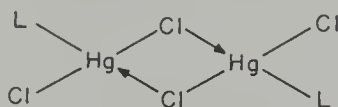
^cHalogen-bridged dimer.

^dR = Ph, Cy, *o*-, *m*-, *p*-Tol, (CNCH₂CH₂).

^eOctahedral dimer.

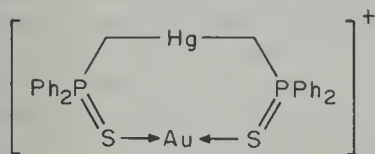
^fPolymeric tetrahedral.

$[\text{HgCl}_2(\text{Ph}_3\text{PSe})]$ is suggested¹²³². In a study by Lobana and Sandhu¹²⁴³, the formation of $[\text{HgBr}_2(1.5)\text{Ph}_3\text{PS}]$, which is probably a mixture of the 1:1 and 1:2 (M:L) adducts, and $[\text{HgBr}_2(\text{Ph}_3\text{PSe})_2]$ were reported. It was also reported that the previous reports on the formation of $[\text{HgCl}_2(\text{Ph}_3\text{PS})_2]$ ¹²²⁸ and $[(\text{HgX}_2)_2\text{Ph}_3\text{PSe}]$ ($\text{X} = \text{Cl}, \text{Br}$)¹²⁴⁴ were incorrect.

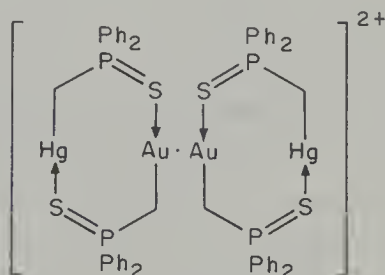


(156)

A number of investigations of cadmium(II) and mercury(II) have been reported recently using unsymmetrical phosphine chalcogenides, anionic ligands, tridentate ligands and some related ligands. A 2,2-dimethyl-2-silabut-3-enyldiphenylphosphine chalcogenide, $\text{Ph}_2\text{P}(\text{E})\text{CH}_2\text{SiMe}_2(\text{CH}=\text{CH}_2)$, reacted with HgCl_2 to form pseudo-tetrahedral dimeric complexes $[\text{HgCl}_2\text{L}]_2$ ¹²⁴⁵. Reaction of $\text{Li}\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}$ with HgCl_2 in thf gave a ylide complex, $[\text{Hg}\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}_2]$ ¹²⁴⁶, which on further reaction with $[\text{Au}(\text{tht})\text{Cl}]$ in CH_2Cl_2 in the presence of TlPF_6 formed $[\text{HgAu}\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}_2](\text{PF}_6)$ (**157**). Similarly, reaction of $[\text{Au}\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}_2]$ with HgCl_2 in the presence of TlPF_6 formed **158**. Compounds **157** and **158** have been studied by X-ray methods. These compounds do not interconvert on heating in thf.

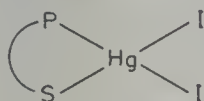


(157)

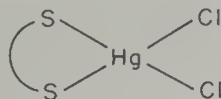
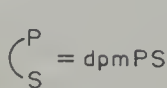


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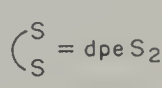
Reaction of HgX_2 with unsymmetrical phosphine chalcogenides formed a series of complexes of the type (A) $[\text{HgX}_2\text{L}]$ $\{\text{X}, \text{L} = \text{Cl}, \text{Br}, \text{I}, \text{Ph}_2\text{P}(\text{E})\text{CH}_2\text{PPh}_2; \text{Cl}, \text{Ph}_2\text{P}(\text{S})(\text{CH}_2)_2\text{PPh}_2; \text{Cl}, \text{Br}, \text{I}, \text{Ph}_2\text{P}(\text{Se})(\text{CH}_2)_2\text{PPh}_2; \text{Cl}, \text{Br}, \text{I}, \text{Ph}_2\text{P}(\text{S})(\text{CH}_2)_n\text{P}(\text{Se})\text{Ph}_2, n = 1, 2\}$ and (B) $[\text{Hg}_3\text{X}_6\text{L}_2]$ $\{\text{X} = \text{Br}, \text{I}; \text{L} = \text{Ph}_2\text{P}(\text{S})(\text{CH}_2)_2\text{PPh}_2\}$ ^{1100,1101}. Tetrahedral structures were suggested. An X-ray study of $[\text{HgI}_2\text{L}]$ ($\text{L} = \text{dpmPS}$) has confirmed a tetrahedral geometry about mercury^{1247a} (**159**). The $\text{Hg}-\text{S}$ distance was 2.760 Å, which was longer than that (2.559 Å) in another phosphine sulphide complex, $[\text{HgCl}_2\text{L}]$ ($\text{L} = \text{dpeS}_2$)^{1247a} (**160**). The ligand dpeS_2 forms a seven-membered chelate ring which represents the first example in tertiary phosphine chalcogenide chemistry. Recently, X-ray analysis of $[\text{HgCl}_2(\text{dpmS}_2)]$ has confirmed six-membered ring formation about mercury with tetrahedral geometry^{1247b}.



(159)

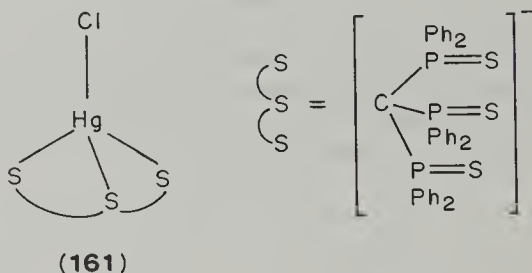


(160)

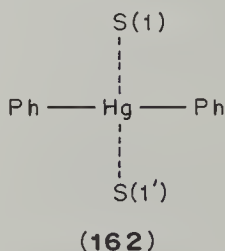


The complexes $[\text{HgL}_2]$ ($\text{L} = \text{dpmPS}, \text{dpmPSe}$) (A)¹²⁴⁸ were obtained from the reaction of $\text{Li}(\text{Ph}_2\text{P}(\text{E})\text{CHPPH}_2)$ with HgCl_2 and these represent rare examples of deprotonated

dpmPE (E = S, Se). The product A contains P,E-bonded chelates (^{31}P , ^{199}Hg NMR study). Tripod ligands, $\{\text{Ph}_2\text{P}(\text{S})\}_3\text{CH}(\text{LH})$ and $(\text{Ph}_2\text{PS})(\text{Me}_2\text{PS})_2\text{CH}(\text{LH})$ reacted with HgX_2 (X = Cl, Br, I) to form the complexes $[\text{HgXL}]$ ($\text{L} = \{\text{Ph}_2\text{PS}\}_3\text{C}^-$ and $(\text{Ph}_2\text{PS})(\text{Me}_2\text{PSC}^-)$). $[\text{CdXL}]$ complexes were obtained in a similar manner^{20,1249,1250}. In the case of the cadmium(II) complexes, the presence of Et_3N as the base was essential. All these were studied using ^1H , ^{13}C , ^{31}P and ^{199}Hg NMR and X-ray diffraction methods. ^1H and ^{13}C NMR data confirmed the deprotonation of CH proton. The X-ray study of $[\text{HgCIL}]$ $\{\text{L} = \text{Ph}_2\text{P}(\text{S})(\text{Me}_2\text{PS})_2\text{C}^-\}$ has shown tetrahedral geometry about mercury (161). The Hg—SPPh₂ bond was longer than the Hg—SPMe₂ bond (2.710 Å versus 2.536 Å). The non-bonding Hg—C distance was 3.437 Å.



Recently a series of organomercury complexes have been reported: (A) $[\text{PhHgXL}]$ [X, $\text{L} = \text{CH}_3\text{COO}^-$, $\text{Ph}_3\text{PS}^{1251}$, Cl_3CCOO^- , $\text{Ph}_3\text{PSe}^{1251}$, $\text{Ph}_3\text{PS}^{1252}$], (B) $[\text{Ph}_2\text{HgL}]$ $\{\text{L} = \text{Ph}_2\text{P}(\text{S})(\text{CH}_2)_2\text{P}(\text{S})\text{Ph}_2\}^{1253}$, (C) $[\text{RHgCIL}]$ $\{\text{R} = m\text{-NO}_2\text{C}_6\text{H}_4$ or $p\text{-ClC}_6\text{H}_4$; $\text{L} = (\text{Ph}_2\text{PSe})_2(\text{CH}_2)_n$, $n = 1, 2$; $\text{R} = m\text{-NO}_2\text{C}_6\text{H}_4$, $\text{L} = (\text{Ph}_2\text{PS})_2\text{CH}_2\}^{1254}$ and (D) $[(\text{RHgCl})_2\text{L}]$ $\{\text{L} = (\text{Ph}_2\text{PS})_2\text{CH}_2, (\text{Ph}_2\text{PSe})_2(\text{CH}_2)_3\}^{1254}$. They were studied by IR, ^{31}P , ^{77}Se and ^{199}Hg NMR and X-ray methods (for complex B). The interaction of PhHg^{II} with S or Se was weak and could only be established from ^{77}Se and ^{199}Hg NMR measurements¹²⁵¹. X-ray analysis of $[\text{Ph}_2\text{HgL}]$ ($\text{L} = \text{dpeS}_2$)¹²⁵³ showed an $\text{Hg}\cdots\text{S}$ distance of 3.913 Å. Hence this complex may be labelled as a weak molecular adduct (162). Only sulphur atoms from the two L molecules passing above and below the plane containing Ph_2Hg moiety are shown. Complexes C and D were shown by IR study to have stronger $\text{RHg}\cdots\text{E}$ interaction, although this interaction was weaker than that found in HgX_2 -phosphine chalcogenide complexes.



In the following text, solution-phase interactions of zinc(II), cadmium(II) and mercury(II) with tertiary phosphine chalcogenides studied by ^{31}P , ^{113}Cd , ^{77}Se and ^{199}Hg NMR spectroscopy are discussed. The anions in the case of zinc(II) and cadmium(II) were generally the bulky AsF_6^- or SbF_6^- ions, which have little interaction with the metal centres, whereas for mercury(II) halides or SCN were used. Table 18 contains various complexes that have been detected which have coordination numbers ranging from 2 to 4. The metal to ligand ratios are varied in order to obtain the desired predominant species. At room temperature, there was generally exchange between the free and the coordinated ligands. It may be mentioned that cadmium(II) formed $[\text{Cd}(\text{Ph}_3\text{PO})_4]^{2+}$ and

TABLE 18. Complexes of Group IIB (studied by NMR)

Complex	L	Ref.
A $[\text{ZnL}_n]^{2+}$ ($n = 3, 4$)	R_3PE^a	998
B $[\text{ZnL}_2]^{2+}$	(i) R_3PE^b (ii) dpmS_2	998 998
C $[\text{ML}_n\text{L}'_{4-n}]^{2+}$ ($\text{M} = \text{Zn}, \text{Cd}; n = 1-3$)	$\text{L} = \text{Cy}_3\text{PSe}; \text{L}' = \text{Cy}_3\text{PS}$	998, 1000
D $[\text{ML}]^{2+}$ ($\text{M} = \text{Zn}, \text{Cd}$)	$[\text{Ph}_2\text{P(E)CH}_2\text{CH}_2]_2\text{P(E)Ph}^c$	998
E $[\text{ML}_2]^{2+}$ ($\text{M} = \text{Zn}, \text{Cd}$)	$[\text{Ph}_2\text{P(E)CH}_2]_3\text{CMe}^d$	998
F $[\text{CdL}_n]^{2+}$ ($n = 3, 4$)	R_3PE^e	999, 1000, 1255
G $[\text{CdL}_2]^{2+}$	(i) $\text{dpmSe}_2, \text{dpeSe}_2, \text{dppSe}_2$ (ii) $o\text{-Tol}_3\text{PE}$	999, 1255 1000
H $[\text{CdL}_n\text{L}'_{4-n}]^{2+}$ ($n = 1-3$)	$\text{L} = \text{Cy}_3\text{PS}; \text{L}' = \text{Cy}_3\text{PSe}$	1000
(i) $[\text{HgX}_2\text{L}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$)	$\text{Bu}_3^a\text{PE}, \text{Bu}_2^a\text{PhPSe},$ $\text{Bu}^a\text{Ph}_2\text{PSe}$	1256-1259
(ii) $[\text{Hg}_2\text{X}_4\text{L}_2]$ ($\text{X} = \text{Cl}, \text{Br}$)	Bu_3^aPSe	1258
(iii) $[\text{HgX}_2(\text{Bu}_3\text{P})\text{L}]$	Bu_3^aPSe	1259

^a $\text{R}_3 = \text{Ph}_3, o\text{-Tol}_3, \text{Cy}_3$.^b $\text{R}_3 = o\text{-Tol}_3, \text{Cy}_3$.^cTridentate.^dBidentate.^e $\text{R}_3 = \text{Ph}_3, \text{Ph}_2(o\text{-Tol}), \text{Ph}(o\text{-Tol})_2, p\text{-Tol}_3, \text{Cy}_3, \text{Bu}_3^t$.

$[\text{Cd}(\text{Ph}_3\text{PO})_6]^{2+}$ species against only four-coordinate cadmium(II)-phosphine chalcogenide species. Moreover, whereas $\text{Cd}-\text{E}$ ($\text{E} = \text{S}, \text{Se}$) bonds are labile, $\text{Cd}^{\text{II}}-\text{O}$ bonds are comparatively inert. Hence it may be concluded that phosphine chalcogenides cannot compete with phosphine oxides for coordination to cadmium(II).

From ^{113}Cd NMR, it was observed that for $[\text{Cd}(\text{R}_3\text{PE})_4]^{2+}$, the shielding of cadmium(II) decreased in the order $\text{E} = \text{O} \gg \text{Se} > \text{S}$. Owing to the higher affinity of cadmium(II) for oxygen, any attempt to prepare mixed-ligand species of the type $[\text{Cd}(\text{Cy}_3\text{PO})_x(\text{Cy}_3\text{PS})_{4-x}]^{2+}$ instead gave $[\text{Cd}(\text{Cy}_3\text{PO})_4]^{2+}$ and $[\text{Cd}(\text{Cy}_3\text{PS})_4]^{2+}$ ^{1000,1260}. It was further noted that interaction of MX_2 ($\text{M} = \text{Cd}, \text{Hg}$) with the ligands decreased in the sequence $\text{Cl} > \text{Br} > \text{I}$ ^{1256,1257}.

The unsymmetrical phosphine chalcogenides $\text{Ph}_2\text{P(E)CH}_2\text{PPh}_2(\text{L})$ reacted with Cd^{2+} to form $[\text{CdL}_2](\text{ClO}_4)_2$, $[\text{CdL}_2(\text{dmsO})_x](\text{CF}_3\text{SO}_3)_2$ ($x = 1, 2$) and $[\text{Cd}(\eta^2\text{-L})(\eta^1\text{-L})(\text{dmsO})_x]^{2+}$ ($x = 1-3$)¹²⁶¹. Similarly, $[\text{CdL}'_2]\text{X}_2$ $\{\text{L}' = \text{Ph}_2\text{P(E)CH}_2\text{P(E)Ph}_2; \text{X} = \text{ClO}_4, \text{CF}_3\text{SO}_3\}$ were formed (^{31}P , ^{77}Se and ^{113}Cd NMR)¹²⁶¹. It was observed that the $\text{Cd}-\text{P}$ bond was weaker than either $\text{Cd}-\text{S}$ or $\text{Cd}-\text{Se}$ bonds when the interaction of Ph_3P was compared with that of Ph_3PSe . From cyclic voltametric studies, it was found that both $[\text{CdL}_2]^{2+}$ and $[\text{CdL}'_2]^{2+}$ complexes undergo two-electron reversible processes at a mercury electrode. Similarly, the ligands mentioned above formed $[\text{HgL}_2]^{2+}$ and $[\text{HgL}'_2]^{2+}$, as shown by ^{31}P , ^{77}Se and ^{199}Hg NMR studies¹²⁶². Competitive exchange studies revealed that mercury(II) prefers to bind $\text{Ph}_2\text{P(E)CH}_2\text{PPh}_2(\text{L})$ more than $\text{Ph}_2\text{P(E)CH}_2\text{P(E)Ph}_2(\text{L}')$. The electrochemical reduction of both $[\text{HgL}_2]^{2+}$ and $[\text{HgL}'_2]^{2+}$ at a mercury electrode occurs via a mercury(I) intermediate:



$\{\text{L} = \text{Ph}_2\text{P(E)CH}_2\text{PPh}_2; \text{L}' = \text{Ph}_2\text{P(E)CH}_2\text{P(E)Ph}_2; \text{E} = \text{S}, \text{Se}\}$. Whereas the complexes with L showed both chemical electrochemical reversibility, the complexes with L' showed chemical reversibility, but electrochemical irreversibility.

B. Main Group Elements

1. Complexes of boron, aluminium, indium and thallium(IIIA)

Boron(III) halides form moisture-sensitive adducts, $[BX_3L]$ ($X = Cl, Br, I$; $L = R_3PE$, $R = Me, Cy, Ph$; $E = S, Se$)¹²⁶³⁻¹²⁶⁵. The B(III)—E bond strengths decreased as shown by IR and 1H NMR data in the order $BI_3 > BBr_3 > BCl_3 > BF_3$ ^{740,1263}. Ligand exchange was slow in the BI_3L complexes but fast with other adducts. An adduct with diborane, $\frac{1}{2}B_2H_6 \cdot R_3PS$ ($R = Me, Ph$) has been reported⁷⁴⁷.

A few aluminium(III) adducts of composition $[(AlCl_3)_n(Ph_3PS)]$ ($n = 1-3$) and $[AlBr_3(Ph_3PS)]$ have been reported^{1056,1266}. Reaction of $dpmS_2$ with diisobutylaluminium hydride gave $[(AlCH_2CHMe_2)_2\{Ph_2P(S)CPh_2(S)\}_2\{Al(CH_2CHMe_2)_2\}_2]$ ¹²⁶⁷. X-ray study of this complex has shown an unusual S_4Al_4 core.

Indium(III) forms $[InX_3(Me_3PS)_2]$ complexes ($X = Cl$ or Br)¹²⁶⁸. An X-ray analysis for $X = Cl$ showed a distorted trigonal bipyramidal geometry with the thio ligands in the apical positions. Thallium(III) also forms complexes of the type $[TlCl_3L]$ ($L = Ph_3PE$) and $[PhTl(O_2CCF_3)_2(Ph_3PS)]$ ¹²⁶⁹⁻¹²⁷¹.

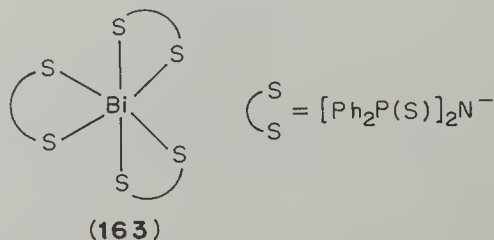
2. Complexes of Tin(II, IV) and lead(II) (IVA)

The interaction of $[Sn(SbF_6)_2]$ and $[Pb(SbF_6)_2]$ with tertiary phosphine chalcogenides has been studied using ^{31}P , ^{119}Sn and ^{207}Pb NMR spectroscopy¹²⁷². The formation of $[ML_3]^{2+}$ ($L = Cy_3PE$; $M = Sn, Pb$), $[M(Cy_3PS)(Cy_3PSe)_2]^{2+}$ and $[M(Cy_3PS)_2(Cy_3PSe)]^{2+}$ was established. In contrast, Cy_3PO formed both $[M(Cy_3PO)_2]^{2+}$ and $[M(Cy_3PO)_3]^{2+}$. From ^{207}Pb NMR studies it was concluded that $\delta(Pb)$ values decrease in the sequence $Se > S > O$ ¹²⁷³⁻¹²⁷⁷. For the complexes $[ML_3]^{2+}$, trigonal pyramidal geometry with a stereochemically active lone pair has been suggested.

Tin(IV) forms a number of complexes: (A) $[SnCl_4L_2]$ ($L = Ph_3PS$)¹⁰⁵⁶, (B) $[SnX_4L_2]$ ($X = Cl, Br, I$; $L = Ph_3PE$)^{18,1278}, (C) $[SnCl_4L_2]$ $\{L = (p-RC_6H_4)_3PS, R = Me_2N, H, MeO, Me, Cl\}$ ¹²⁷⁹, (D) $[SnX_4L_2]$ ($X = Cl, Br$; $L = R_3PS$; $R_3 = Me_3, Et_3, Pr_3^n, Bu_3^n, Me_2P$)¹²⁸⁰, (E) $[SnCl_4L_m]$ ($m = 1, 2$; $L = Bu_3^nPE$)¹²⁸¹, (F) $[SnCl_4L]$ [$L = dpeS_2$]^{1193,1278} and (G) $[Ph_3SnXL]$ ($X = NCS, NCO, N_3$; $L = Ph_3PS$)^{866,1282,1283}. X-ray data are not available for any of these complexes.

3. Complexes of antimony(V) and bismuth(III) (VA)

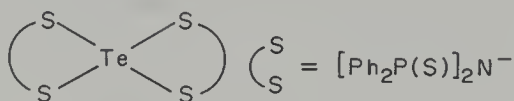
A few antimony(V) and bismuth(III) complexes are known: $[SbCl_5L]$, $[SbCl_3Br_2L]$ ($L = Ph_3PS$)^{1056,1284}, $[(SbCl_5)_2L]$ ($L = Bu_3PS, Bu_3PSe$)⁸⁹⁴ and $[BiL_3]$ ($L = \{Ph_2P(S)\}_2N^-\}$ ¹²⁸⁵. The 2:1 antimony complexes dissociate in CH_2Cl_2 to form $[SbCl_4L][SbCl_6]$ ion pairs. The geometry about bismuth in $[BiL_3]$ is distorted octahedral (163). This is the first example of a complex of a Main Group element with $\{Ph_2P(S)\}_2N^-$ whose X-ray structure has been reported.



4. Complexes of tellurium (II, IV) (VIA)

Tellurium(II) forms a complex $[TeL_2]$ ($L = \{Ph_2P(S)\}_2N^-$), for which X-ray studies showed a square-planar geometry (164)¹²⁸⁶. A series of tellurium(IV) and organo-

tellurium(IV) complexes have been reported: (A) $[\text{TeCl}_4\text{L}_n]$, (B) $[\text{RTeCl}_3\text{L}_n]$ ($n = 1, 2$; $\text{L} = \text{Ph}_3\text{PE}$, $\text{R} = \text{Ph}$, $4\text{-MeOC}_6\text{H}_4$, $4\text{-BrC}_6\text{H}_4$)¹²⁸⁷, (C) $[\text{R}_2\text{TeCl}_2\text{L}]$ ($\text{R} = \text{Ph}$, $p\text{-MeOC}_6\text{H}_4$; $\text{L} = \text{R}'_3\text{PSe}$; $\text{R}' = \text{Ph}$, $p\text{-MeC}_6\text{H}_4$, Bu^n , dpeSe_2)^{1287,1288}. For C a distorted octahedral geometry with one site occupied by a lone pair has been suggested (dpeSe_2 coordinates via one selenium only).



(164)

IV. TERTIARY PHOSPHINE TELLURIDES

In comparison with tertiary phosphine oxides, sulphides and selenides, very little work has been reported on the coordination chemistry of tertiary phosphine tellurides. The difference is attributed to the lower stability of $\text{P}=\text{Te}$ bond versus $\text{P}=\text{O}$, $\text{P}=\text{S}$ or $\text{P}=\text{Se}$ bonds. Before discussing the coordination chemistry of phosphine tellurides, it may be appropriate to give a brief account of the synthesis, stability and reactivity of the phosphine tellurides, which will be useful in understanding the poor reports on their coordination chemistry.

Tributylphosphine telluride (Bu_3PSe) was prepared by the reaction of Bu_3P with tellurium in a large excess of toluene by refluxing for 21 h under a methane atmosphere (m.p. 35.0°C)¹²⁸⁹. The ligand decomposes on storage. Other papers have dealt with the synthesis of ligands of the R_3PTe type ($\text{R} = \text{alkyl or alkylaryl}$)^{32,1290,1291}.

Tellurium in tertiary phosphine tellurides is labile, as evidenced by various studies. R_3P makes nucleophilically attacks on tellurium in R_3PTe . It has been suggested that linear intermediates of the type R_3PTePR_3 are formed ($\text{R} = \text{Me}_3\text{C}$, Me_2N)¹²⁹². Rapid transfer of tellurium between $(\text{Me}_3\text{C})_3\text{P}$ and $(\text{Me}_3\text{C})_3\text{PTe}$ was observed by NMR spectroscopy¹²⁹¹. The $\text{P}-\text{Te}$ bond length is 2.368 \AA , indicating a bond order of 1.5 ¹²⁹³.

An X-ray study of $\text{Ph}_3\text{PTePPh}_3$ (obtained by the reaction of $\text{Ph}_4\text{As}^+\text{TeCN}^-$ with excess of Ph_3P in MeCN containing LiClO_4) has shown a linear $\text{P}-\text{Te}-\text{P}$ moiety¹²⁹⁴. There is a normal bond between one P and Te , while the interaction between Te and the other P is weak. The IR spectra of Oct_3PTe in CCl_4 showed a hydrogen-bond interaction with MeOH and MeCN ¹²⁹⁵. ^{31}P and ^{125}Te NMR showed that the two nuclei couple in $\text{RR}'\text{R}''\text{PTe}$ (R groups chosen from Bu , Me , Me_2N , Et , EtO , NEt_2)¹²⁹⁶.

Tellurophosphoranes (R_3PTe) react with MeI to form $\text{R}_3\text{P}^+\text{TeMeI}^-$ ($\text{R} = \text{Me}$, Me_2CH , Bu^n , Me_3C , Me_2N)¹²⁹⁷. A thin film of CdTe was deposited cathodically on titanium in a photoelectrochemical cell using Bu_3PTe and a propylene carbonate solution of cadmium(II)¹²⁹⁸. Cyclic voltametry revealed the formation of a cadmium(II) complex with Bu_3PTe so that electron transfer can be effective. R_3PTe ($\text{R} = \text{Me}$, Et) reacted with HgR_2 ($\text{R} = \text{Et}$, Ph) at 115°C to form mercury telluride (HgTe) as the sole solid-state product¹²⁹⁹. In the case of Ph_2Hg , it was observed that Ph_2Te and Ph_2Te_2 are the major organic products.

The reaction of Et_3PTe with $[\text{Mn}_2(\text{CO})_{10}]$ under mild conditions gave $[(\text{Et}_3\text{P})_2(\text{CO})_3\text{MnTe}]_2$ (A)¹³⁰⁰. A has a structure similar to that of RTeTeR with the $(\text{Et}_3\text{P})_2(\text{CO})_3\text{Mn}$ moiety replacing the R groups. Pyrolysis of A at 300°C gave crystalline MnTe . A similar reaction of Et_3PTe with $[\text{cp}_2\text{Fe}_2(\text{CO})_4]$ in the presence of Et_3P gave $[\text{cp}(\text{Et}_3\text{P})(\text{CO})\text{Fe}]_2\text{Te}$ and $[\text{cp}(\text{Et}_3\text{P})(\text{CO})\text{FeTe}]_2$ ¹³⁰¹.

Dications of the type $[\text{R}_3\text{PTeTePR}_3]^{2+}$ were obtained when R_3PTe ($\text{R} = \text{Me}_3\text{C}$, Me_2CH) was oxidized by ferricinium salts¹³⁰². The compounds $[(\text{Me}_3\text{P})_3\text{CoTe}_2\text{Co}(\text{PMe}_3)_3]$ (B) (similar to A) were obtained when $[\text{CoX}(\text{PMe}_3)_3]$ ($\text{X} = \text{Cl}$, PMe_3 , etc.), $[\text{Li}[\text{CoL}(\text{PMe}_3)_3]]$ ($\text{L} = \text{ethene}$), $[\text{CoCl}_2(\text{PMe}_3)_3]$ and $[\text{Co}(\text{CO})_2(\text{PMe}_3)_2]_2$ were oxidized by tellurium¹³⁰³. The reaction of B with CO gave $[\{(\text{Me}_3\text{P})_2(\text{CO})_2\text{Co}\}_2\text{Te}_2]$.

Extrusion of tellurium from Bu_3PTe takes place when it reacts with (i) $[(\text{MeC}_5\text{H}_4)_3\text{U}]\cdot\text{thf}$ and (ii) $[(\text{Me}_5\text{C}_5)_2\text{Yb}]$. Tellurium-bridged complexes, $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2\text{-Te}^{1304}$ and $[(\text{Me}_5\text{C}_5)_2\text{Yb}]_2\text{Te}^{1051a}$ are formed. Whereas extrusion of sulphur and selenium from Ph_3PS and Bu_3PSe respectively, was observed, no extrusion of oxygen from Ph_3PO took place. Instead $[(\text{MeC}_5\text{H}_4)_3\text{UPh}_3\text{PO}]$ was formed¹³⁰⁴.

The first stable tellurophosphorane complexes $[\text{M}(\text{CO})_5(\text{R}_3\text{PTe})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{R} = \text{Me}_3\text{C}$) (A) were reported by Kuhn *et al.*¹⁹ in 1985. The photolysis of $[\text{M}(\text{CO})_6]$ in thf in the presence of R_3PTe for 12 h gave monosubstituted products (A) in quantitative yield. An X-ray analysis of $[\text{W}(\text{CO})_5(\text{Bu}^t\text{PTe})]$ showed octahedral geometry with $\text{W}-\text{Te}$ bonding.

Reaction of $[(\eta\text{-cp})\text{Fe}(\text{CO})_2(\text{thf})]^+$ with R_3PTe gave $[(\pi\text{-cp})\text{Fe}(\text{CO})_2(\text{R}_3\text{PTe})]^+$ ($\text{R} = \text{Me}, \text{Me}_2\text{CH}, \text{Me}_3\text{C}, \text{Me}_2\text{N}, \text{morpholino}$)¹³⁰⁵. NMR data reveal $\text{Fe}-\text{Te}$ π -bonding. Reaction of $\text{Li}(\text{Ph}_2\text{P}(\text{Te})\text{CHPPH}_2)$ {prepared from Te and $(\text{Ph}_2\text{P})_2\text{CHLi}$ } with HgCl_2 gave $[\text{Hg}(\text{Ph}_2\text{P}(\text{Te})\text{CHPPH}_2)_2]$ containing P and Te bonds with Hg (^{31}P and ^{199}Hg NMR)¹²⁴⁸.

V. APPLICATIONS

The applications covered in this section are analytical and catalytic applications. Among the analytical applications, liquid-liquid extraction of metal ions constitutes one of the most extensively studied areas, other areas including reversed-phase chromatography and ion-selective electrodes.

A. Analytical Applications

In this section, the separation and determination of metals using various types of phosphine oxides and chalcogenides are described. Broadly, the following areas are covered: (1) liquid-liquid extraction; (2) reversed-phase chromatography (liquid-solid extraction system); (3) ion-selective electrodes; (4) miscellaneous applications; (4.1) extractive and direct determination of metals; and (4.2) Fluorimetric determination and related applications.

Section 1 contains a number of systems which relate to the quantitative separation and determination of metals, whereas Section 4 describes only such systems not covered in Sections 1-3.

1. Liquid-liquid extraction

The ligands used for extraction studies can be divided into three types: (a) mono-tertiary phosphine oxide; (b) di-tertiary phosphine oxides; (c) Poly-tertiary phosphine oxides; and (d) Mono- and di-tertiary phosphine sulphides or selenides.

a. Extraction with mono-tertiary phosphine oxides. There have been numerous investigations on the use of mono-tertiary phosphine oxides (R_3PO), either alone or together with β -diketones, pyrazolones, etc., for the extraction of metals. The d- and f-block elements have been studied to much greater extent than the s- and p-block elements. When these ligands are used together with other reagents, they generally act synergistically. Thus, the most interesting work on liquid-liquid extraction chemistry deals with the use of these ligands as synergists. The phenomenon of synergism may be attributed to the formation of a mixed-ligand complex or an adduct complex which has a higher solubility in the organic phase than that of the simple chelate¹³⁰⁶. In the adduct complex, coordinated water is replaced by an organophosphorus reagent. The synergistic extraction of the metal ions has various advantages: enhanced extractability, widening of the optimum pH range, stabilization of an extracted species by forming an adduct

and a favourable kinetic effect¹³⁰⁷. In the kinetic effect, equilibrium is reached in a shorter time on the addition of the adduct molecules such as the organosphosphorus reagents. The addition of alcohols, esters, ketones, etc., also leads to enhanced extraction¹³⁰⁸.

Among mono-tertiary phosphine oxides, tri-*n*-octylphosphine oxide (topo) is the most extensively used ligand, probably owing to its high donor property, low toxicity and vapour pressure and poor miscibility with water. Two other ligands used extensively are tri-*n*-butylphosphine oxide (Bu₃PO) and triphenylphosphine oxide (Ph₃PO). Some other phosphine oxides have been used and are described. In the synergistic systems, β -diketones, pyrazolones, di(2-ethylhexyl)phosphoric acid and a few others are the reagents used for extraction, with phosphine oxides acting as the synergists. There are a few other cases with different synergistic combinations.

i. Elements of Groups IA and IIA. Topo (in benzene) extracts alkali metal iodides (MI, M = Li, Na, K, Cs) from the aqueous phase¹³⁰⁹. Alkali metal chlorides or bromides are not extracted. The difference is attributed to the lower solvation energy and higher metal-iodide covalency, which promote extraction of the alkali metal iodides. The extraction ability of topo is higher than that of tbp or diisooamyl methylphosphonate; the latter possess more electronegative RO groups bonded to phosphorus, which lowers their basicity. Also, tbp and related analogues have higher miscibilities with water, which lowers the effective reagent concentration.

The extraction of alkali metals (Li, Na, K, Cs) from basic media (pH > 9) with the synergistic pairs HA-R₃PO (HA = Htta, Hdbm; R = *n*-octyl, Ph, BuⁿO) in benzene followed the trend Li > Na > K > Cs^{1310,1311}. The separation factors, for example for Li/Na, varied as ~2000 (Hdbm-topo), 1000 (Hdbm-tbp), 100 (Hdbm-Ph₃PO) and ~10 (Hdbm). The extracted species had the composition [MAL₂] and the order of extraction was topo > tbp > Ph₃PO (e.g. for Li, log β = 7.55, 4.42 and 3.95, respectively). The larger size of Ph₃PO relative to the smaller Li⁺ appears to be responsible for this sequence, but the incomplete data on Ph₃PO prohibit comments on the other metals.

The fluorinated β -diketones RC(O)CH₂C(O)R' (R = CF₃, C₂F₅, C₃F₇; R' = CMe₃) and topo in benzene also showed selective extraction of lithium over the other alkali metals from neutral solutions; the selectivity of Li over Mg, Ca and Sr was poor¹³¹². For the C₃F₇C(O)CH₂C(O)CMe₃-topo pair, the separation factors were as follows:

Li/M:	1300	3800	3700	2500	0.019	0.067	1
M:	Na	K	Rb	Cs	Mg	Ca	Sr

These Li/M values vary directly with the variation in the ionic radii. The extracted species was [Li(A)(topo)_n] [*n* = 1, 2; A = anion of a β -diketone). A change of solvent affected the extraction sequence in the order: dodecane > xylene > CCl₄ > benzene (*K*_{ex} = 315, 125, 93 and 55, respectively). Interestingly, a 94% recovery of the lithium present in a brine sample (Li 0.080, Na 145, K 29 g l⁻¹) was readily obtained. Another β -diketone, nonyltrifluoroacetone, and topo (or Ph₃PO) in benzene extracted Li, Na, K and Cs synergistically¹³¹³.

The combinations α -acetyl-*m*-dodecylacetophenone (LIX 54)-topo and α -perfluoro-alkanoyl-*m*-dodecylacetophenone (LIX 51)-topo extracted Li⁺ synergistically¹³¹⁴. The extracted species were [Li(A)(topo)_{1.3}] (HA = LIX 51 or LIX 54). The extraction performance of LIX 51-topo is 4.65×10^4 times higher than that of LIX 51 alone or LIX 54-topo. Only LIX 51-topo extracted Na⁺ {[NaA(topo)_{1.3}]} and the extractability of Na⁺ was much less than that of Li⁺.

The 4-acyl-5-pyrazolones with bulky substituents and topo are able to extract lithium quantitatively¹³¹⁵. As the general trend shows, Ph₃PO caused much less enhancement in the extraction. Similarly, the extraction of Na⁺ is enhanced by a mixture of the reagents, although the overall extraction is less than that of lithium. Topo caused an

increase in the extraction of Li^+ (or K^+) by dibenzo-18-crown ether or 18-crown-6 ethers¹³¹⁶.

Only a few studies have been reported for the alkaline earth metals. Topo (in kerosene) showed poor extraction of Ca^{2+} from nitrate media¹³¹⁷ {as $[\text{Ca}(\text{NO}_3)_2\text{topo}]$, $K_{\text{ex}} = 0.61$ } and also extraction from an HCl medium using Htta and topo {as $[\text{Ca}(\text{tta})_2(\text{topo})_2]$ } was even less ($K_{\text{ex}} = 1.1 \times 10^{-2}$)^{1318,1319}. The same appears to be true for Ph_3PO ¹³²⁰. Significantly, *N*-phenylthioacetohydroxamic acid (HA) (in cyclohexane) showed no extraction of Ca^{2+} , but in the presence of topo the extraction was quantitative¹³²¹. The stability constant for the extracted species {as $[\text{CaA}_2(\text{topo})_2]$ } is 5.8×10^{11} , which explains the reason for the quantitative extraction of calcium. The pair 1-phenyl-3-methyl-4-stearoyl pyrazol-5-one and topo (in benzene) extracted Ca^{2+} and Sr^{2+} from a citrate medium (pH 9)¹³²². This method was applied to the extraction and determination of strontium in solar salt samples.

Topo and a series of crown ethers, e.g. 12-crown-4, 15-crown-5 and benzo-15-crown-5, synergistically extracted calcium, rubidium and caesium as their picrates, $[\text{M}^n(\text{ether}) \cdot (\text{topo})] (\text{picrate})_n$ ($n = 1, 2$)¹³²³. The extractability of the rubidium complex was higher than that of the caesium complex.

ii. Elements of Group IIIA. No extraction of aluminium has been reported. However, gallium(III) was extracted from chloride or HCl solution using topo, Ph_3PO and $\text{Bz}(p\text{-MeC}_6\text{H}_4)_2\text{PO}$ in an organic solvent and the extracted species was $[\text{GaCl}_3\text{L}]$ ¹³²⁴⁻¹³²⁷. Indium(III) was extracted from HCl solutions with topo, Bu_3PO or *tbp* (in benzene and other solvents) and extraction followed the sequence $\text{topo} > \text{Bu}_3\text{PO} > \text{tbp}$ ¹³²⁸. It is surprising that Ph_3PO showed no extraction of indium¹³²⁸. Formation of $[\text{InCl}_3\text{L}_2]$ as the species was observed from $\leq 6 \text{ M HCl}$, whereas $\text{H}[\text{InCl}_4\text{L}_2]$ was formed from concentrated HCl solutions.

From the chloride medium, the extraction of indium(III) with different ligands varied in the order $\text{R}_3\text{PO} > \text{R}_2(\text{R}'\text{O})\text{PO} > \text{R}(\text{R}'\text{O})_2\text{PO} > (\text{R}'\text{O})_3\text{PO}$ (R and $\text{R}' = \text{alkyl}$)^{1329,1330}. The species extracted, $[\text{InCl}_3\text{L}_2(\text{H}_2\text{O})]$, was the same as that observed from HCl solution. The synergistic extraction of indium(III) was noted from ClO_4^- medium with a bipyrazolone, viz. 4,4'-sebacylbis(2,5-diphenyl-2*H*-pyrazol-3-one) and topo (in toluene)¹³³¹. However, no synergism was observed when 1-phenyl-3-methyl-4-acylpyrazol-5-one (acyl = benzoyl, thenoyl, lauroyl) and topo in toluene were used¹³³². This observation can be regarded as an exception. Among the pyrazolones alone, benzoylpyrazolone was described as the best extractant. Another synergistic system for the extraction of indium(III) from sulphate medium is the combination of versatic 10 acid and topo (in benzene)¹³³³.

The only investigation of thallium(III) is its extraction with Bu_3PO from $\text{HCl-H}_2\text{SO}_4$ solutions, where the extracted species was $\text{H}[\text{TlCl}_4\text{L}_3(\text{H}_2\text{O})]$ ¹³³⁴.

iii. Elements of Groups IVA-VIA. Topo (in CCl_4) extracted tin(II) as $[\text{SnCl}_2(\text{topo})_2]$ from HCl solution¹³³⁵ and it was observed that on varying the organic solvents, the extraction decreases on decreasing the polarity of the solvent:

Solvent:	PhNO_2	PhMe	$o\text{-C}_6\text{H}_4\text{Me}_2$	C_6H_6	CCl_4
<i>D</i>	10.12	5.98	5.65	5.52	2.22

The solvents *m*-cresol and CHCl_3 showed very poor extraction ($D = 0.08$ and 0.12 respectively). The extraction of tin(IV) from chloride media with Bu_3PO (in cyclohexane) involved the species $[\text{SnCl}_4\text{L}_m]$ ($m = 1, 2$)¹³³⁶. In contrast, *tbp*-type ligands showed poor extraction. Bis(2,4,4-trimethylpentyl)-*n*-octylphosphine oxide and tris-(2,4,4-trimethylpentyl)phosphine oxide¹³³⁷ were found to be more selective than topo for the separation of Sn^{4+} from Zn^{2+} , Cu^{2+} , Pb^{2+} , Fe^{2+} and Fe^{3+} .

Lead(II) was extracted with topo from NO_3^- media¹³³⁸. Topo also acted as a synergist in the extraction of lead(II) using Hpmtpf in cyclohexane (from NO_3^- medium)¹³³⁹; 1,1,1-trifluoro-5-methyl hexane-2,4-dione in xylene (from NaClO_4 medium)¹³⁴⁰ and htta in *n*-hexane (from NaSCN – NaClO_4 medium)¹³⁴¹. The topo–Hpmtpf combination¹³³⁹ gave >98% extraction; Ca, Sr and Ba ions caused no interference in the extraction. In the topo–Htta system¹³⁴¹, several species, $[\text{Pb}(\text{ClO}_4)_2\text{L}_4]$, $[\text{Pb}(\text{ClO}_4)(\text{SCN})\text{L}_n]$ ($n = 3, 4$) and $[\text{Pb}(\text{SCN})_2\text{L}_3]$ ($\text{L} = \text{topo}$), were detected in the organic phase. The extraction of NaSCN alone was poor, but $[\text{Pb}(\text{ClO}_4)_2]$ has a high extractability and thus the mixed species $[\text{Pb}(\text{ClO}_4)(\text{SCN})]$ were readily formed. Significantly, $[\text{Pb}(\text{ClO}_4)(\text{SCN})\text{L}_3]$ and $[\text{Pb}(\text{SCN})_2\text{L}_3]$ showed similar extraction ($K_{\text{ex}} = 6.96$ and 7.48 , respectively). This indicates the instability of $[\text{Pb}(\text{SCN})_2]$, making it prone to acquire a high solvation number ($n = 3$). It is well known that stable MX_2 species form $[\text{MX}_2\text{L}_2]$ -type compounds¹³⁴².

Antimony(III) was extracted from 1–10 M HCl using Bu_3PO , topo or Ph_3PO (in benzene)¹³²⁸. The species extracted were $[\text{SbCl}_3\text{L}]$ from ≥ 6 M HCl and $\text{H}[\text{SbCl}_4\text{L}_m]$ ($m = 1, 2$) from 4–8 M HCl. There are reports of the extraction of bismuth(III) (from NO_3^- medium) with topo (neat)¹³³⁸ and selenium(IV) and tellurium(IV) (from Cl^- medium) with Ph_3PO ¹³²⁰.

iv. Elements of Group IIIB. Topo–Hacac (in benzene or CCl_4) extracted scandium(III) present in trace amounts from aqueous NaClO_4 solution; it transferred to the organic layer as $[\text{Sc}(\text{acac})(\text{ClO}_4)_2(\text{topo})]$ ¹³⁴³. A series of organophosphorus reagents extracted scandium(III) and yttrium(III) from NaNO_3 solution as $[\text{M}(\text{NO}_3)_3\text{L}_2]$ ($\text{L} = \text{R}_3\text{PO}$, etc.; $\text{R} = \text{alkyl}$)¹³⁴⁴. The replacement of R by $\text{R}'\text{O}$ successively reduced the extraction, as noted earlier. Topo and Ph_3PO both extracted scandium(III) as $[\text{Sc}(\text{tta})_3\text{L}_2]$ ⁴⁹.

The ligands Bu_3PO , topo or R_3PO (R is a group containing C_7 – C_9 carbon atoms) and Ph_3PO extracted yttrium(III) from HNO_3 solutions as $[\text{Y}(\text{NO}_3)_3\text{L}_m]$ $m = 1$ or 3 ^{1345–1347}. Synergistic combinations Bu_3PO –Htta and topo–Hpmbp (in benzene) extracted yttrium(III) as $[\text{Y}(\text{tta})_3(\text{Bu}_3\text{PO})_2]$ (from NO_3^- medium)¹³⁴⁸ or $[\text{Y}(\text{pmbp})_3(\text{topo})]$ ¹³⁴⁹. The species extracted was $[\text{Y}(\text{pmtfp})_3\text{L}_m]$ ($m = 1, 2$) when topo–Hpmfp in benzene (from HClO_4 medium) was used¹³⁵⁰. Calorimetric and temperature-dependent studies of extraction methods showed that the synergistic effect was attributed to the replacement of coordinated H_2O by the topo molecule¹³⁵¹. A mixture of *tbp* and triisobutylphosphine oxide or diisooctyl methylphosphonate and triisobutylphosphine oxide also extracted yttrium(III) from Cl^- – SCN^- medium¹³⁵². Bis(2-ethylhexyl)ethylphosphine oxide¹³⁵³ or a mixture of R_3PO ($\text{R} = n\text{-Hex}$) and topo (60:40)¹³⁵⁴ in kerosene is able to separate yttrium(III) quantitatively from aqueous nitrate solutions of rare earths. Here yttrium(III) is left in the aqueous phase.

v. Elements of Group IVB. Bu_3PO (in cyclohexane) is reported to extract titanium(IV) from Cl^- medium (as $[\text{TiCl}_4\text{L}_m]$; $m = 1, 2$)¹³³⁶, but extraction from HCl or H_2SO_4 solutions with topo was greatly enhanced by the addition of NH_4SCN and the method could be used to determine titanium spectrophotometrically^{1355,1356}. The intense yellow species $[\text{Ti}(\text{SCN})_4\text{L}]$ ($\text{L} = \text{topo}$) absorbed at $\lambda_{\text{max}} = 432$ nm. A number of metal ions tested {iron(III), uranium(VI), cerium(III), platinum(IV), etc.} did not interfere. The presence of NO_3^- ions was detrimental to the system as it decomposed the thiocyanate complex. Topo (in kerosene) can extract titanium from ore leach¹³⁵⁷. The extraction is carried out after treatment of the acid leach of Ti–Fe ore with a chloride of Na, K, Mg or NH_4 .

Topo (in cyclohexane) ensured the quantitative separation of zirconium(IV) from uranium(VI) and iron(II) and iron(III)¹³⁵⁸ (from SCN^- medium). Titanium, as expected, interfered. Uranium(VI), which is normally extracted from 7 M HCl, was suppressed in

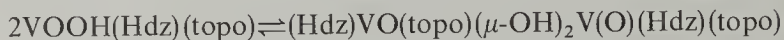
the presence of SCN^- ions. For separating zirconium from hafnium by this method, the addition of H_2SO_4 to the aqueous phase enhanced the separation^{1359,1360}. Zirconium forms stronger complexes with SO_4^{2-} ions than hafnium does, whereas for hafnium the order is the reverse with SCN^- or OH^- ions. Further, the addition of HCl inhibited the separation, as the chloro complexes of both were extracted equally by the organic layer.

Topo (in cyclohexane) could be used to determine zirconium(IV) in Cl^- medium by an extractive spectrophotometric method involving addition of pyrocatechol (ethanol) direct to the organic extract¹³⁵⁸ ($\lambda_{\text{max}} = 655 \text{ nm}$; sensitivity = $1 \times 10^{-6} \text{ g ml}^{-1}$ zirconium). The method is useful even in the presence of large amounts of Al, U, V, Fe, Cr and Th (moderate). However, Ti, Hf and Mo interfered. PO_4^{3-} and SO_4^{2-} in low concentrations do not interfere; in the presence of NO_3^- , U, Th and Hf interfere.

Using topo in cyclohexane, the D value for zirconium was 1000 (from 7 M HCl), 478 (from 7 M HNO_3) and 10 (from 1 M HCl or HNO_3 solutions)¹³⁶¹⁻¹³⁶². An enhancement in extraction occurred on addition of Cl^- or NO_3^- salts of uni-, bi- or tri-valent metals. The extracted species were $[\text{ZrCl}_4\text{L}_2]$ and $[\text{Zr}(\text{NO}_3)_4\text{L}_2]$ with $>99\%$ extraction. It was possible to separate zirconium from hafnium and niobium¹³⁶³. The extraction from HClO_4 solutions was less and was also low from H_2SO_4 or HF solutions. Whereas interference from tartrate was small, EDTA in sufficient amount prevented extraction^{1362,1364}. The behaviour of Bu_3PO was similar¹³⁶⁵. At $>8 \text{ M}$ HNO_3 concentration, the species $[\text{Zr}(\text{NO}_3)_4(\text{L}_2)_x\text{HNO}_3 \cdot y\text{H}_2\text{O}]$ was formed. The topo-Htta pair probably formed $[\text{Zr}(\text{tta})_4(\text{topo})]$ species in the extraction of zirconium(IV) from HNO_3 medium¹³⁶¹. On variation of the substituents in $\text{R}_2\text{R}'\text{PO}$ in the system $\text{R}_2\text{R}'\text{PO}-\text{HNO}_3$ ($\text{R}, \text{R}' = \text{Me}$ to C_8H_{17} and Ph)¹³⁶⁶, the distribution coefficient increases with decreasing B (where $B = \Sigma\text{H}/\Sigma\text{C}$, ΣH and ΣC being the sums of the number of H and C atoms, respectively, in the extractant) until R and R' are C_8H_{17} . Branching of the chain decreases D , although the reverse effect would be expected on the basis of electrophilicity and solubility considerations.

In the extraction of hafnium(IV) from a mixture of acids ($\geq 3 \text{ M}$ $\text{HClO}_4 + \text{HNO}_3$ or 5 M $\text{HClO}_4 + \text{HCl}$) using Htta, Hpmbp or *N*-benzoyl-*N*-phenylhydroxylamine in benzene, CHCl_3 or *n*-octane, Ph_3PO , topo and tbp acted as synergists^{1367,1368}. The order of synergistic effect was $\text{topo} > \text{Ph}_3\text{PO} > \text{tbp}$. Bu_3PO , however caused no synergism. Hafnium forms mixed complexes and HClO_4 has a considerable salting-out effect. No synergism occurred when a mixture of HClO_4 and H_2SO_4 was used.

vi. Elements of Group VB. The pairs $\text{R}_3\text{PO}-\text{Htta}$ (in cyclohexane) and $\text{R}_3\text{PO}-\text{dithizone}$ (H_2dz) (in benzene) ($\text{R} = n\text{-butyl}$ and $n\text{-octyl}$) extracted vanadium(IV,V) from aqueous solutions ($\text{pH} \approx 4.1$)¹³⁶⁹⁻¹³⁷². Various species were identified $[\text{VO}_2(\text{tta})\text{L}]$, $[\text{VO}(\text{tta})_2\text{L}]$, $[\text{VO}_2(\text{Hdz})(\text{tbpo})]$ (A) and $[\text{VOOH}(\text{Hdz})(\text{topo})]$ (B). A was stable for 1 h whereas the colour of B faded during the standing time, probably owing to the dimerization



H_2dz alone showed poor extraction. In the $\text{R}_3\text{PO}-\text{H}_2\text{dz}$ system, topo gave a higher extraction than Bu_3PO ($K_{\text{ex}} = 10^{2.5}$ for topo, 3×10^2 for Bu_3PO). Topo-Hpmtfp (in cyclohexane) showed incomplete extraction of VO_2^+ from aqueous solution (pH 1.5–2.8)¹³³⁹. A mixture of trialkylphosphine oxides (R_3PO) in kerosene extracted vanadium(IV) or vanadium(V) from low pH (1.0–2.5) solutions¹³⁷³. On increasing the concentration of vanadium in the solution, the extraction maximum shifted to the low pH range and metavanadic acid, $[\text{HVO}_3(\text{R}_3\text{PO})_2]$, transferred to the organic layer.

Topo (in cyclohexane) separated tantalum(V) from aqueous HCl solution and this separation was more complete than that of zirconium from hafnium¹³⁶³. Similarly, niobium(V) was separated from $\text{Ti}(\text{SO}_4)_2$ solution¹³⁷⁴. For high niobium extraction, the

addition of HCl or HF was necessary. Topo and $R_2R'PO$ ($R, R' = \text{Me to } C_8H_{17} \text{ and Ph}$) have been used to extract Nb and Ta from different media: HNO_3 ¹³⁶⁶, $HF-H_2SO_4$ ¹³⁷⁵ and HCl, HF, $HClO_4$ ¹³⁶⁴.

vii. Elements of Group VIB. The extraction of these metals has been possible only when present in their hexavalent state, although a recent report reveals that the extraction of chromium(III) can be achieved by a cooperative action of light (photoreduction) and topo on chromium(VI) species¹³⁷⁶. The back-extraction of chromium(III) was also promoted by photoirradiation. Except for this, all other studies require oxidation of the metal to its hexavalent state prior to extraction. For example, while extracting chromium(III) from concentrated NaCl or KCl solutions using topo (in benzene)¹³⁷⁷, it was oxidized to the chromium(VI) state with silver oxide solution in H_2SO_4 (or bromine water when HCl is present). By this procedure, the extraction is feasible at the microgram level (diphenylcarbazide in ethanol was added to the organic layer for the determination of chromium).

Chromium(VI) has been extracted from different solutions (1M MX; $M = H, Na$; $X = Cl, ClO_4, NO_3$)¹³⁷⁸ by forming hydrogen-bonded species $H_2[CrO_4L_2]$, $H_2[CrO_4(HX)L_m]$ and $H_2[CrO_4(HX)_2L_m]$ ($n = 2$ for ClO_4^- , NO_3^- and 3 for Cl^- ions; $L = \text{topo}$). The greatest extraction was obtained from the ClO_4^- medium: $ClO_4^- > Cl^- \approx NO_3^- > SO_4^{2-}$. It was demonstrated that Ph_3PO could separate chromium(VI) from solutions of iron(III), yttrium(III), gold(III) and molybdenum(VI) in mineral acids¹³⁴⁵.

A series of organophosphorus reagents, R_3PO ($R = \text{octyl, isopentyl and Ph}$), extracted molybdenum(VI) from mineral acid solutions^{1345,1379,1380}. The species, for instance, from aqueous HCl was $[MoO_2Cl_2L_2]$. High separation factors from Cr, Au and Fe were observed with Ph_3PO ¹³⁴⁵. Topo showed significant synergism when molybdenum(VI) was extracted from various mineral acids using H_2dehp ¹³⁸¹. The greatest extraction ($D > 1000$) was observed from 3.5 M HCl solutions ($HCl > H_2SO_4 > HNO_3$). Bu_3PO-H_2dchp selectively extracted molybdenum when present as an impurity in tungsten produced from impure scheelite and related ores¹³⁸².

Using topo (in kerosene) tungsten(VI) was extracted from mineral acids in the sequence $HCl > H_2SO_4 > NO_3$ ($D > 250$, ≈ 50 , low, respectively)¹³⁸³. Topo-Adogen-381 and tricaprilmethylammonium chloride in xylene quantitatively separated $[WO_4]^{2-}$ from $[ReO_4]^-$ when present in mineral acids¹³⁸⁴.

viii. Elements of Group VIIB. Topo-Hpmtfp (in cyclohexane) extracted manganese(II) quantitatively ($> 98\%$) from aqueous solutions (pH 1.5–2.8)¹³³⁹. The extraction of manganese(II) with a series of reagents, Topo- β -diketones (Hacac, Htfa, Hhfa, Hba and Hbfa) in CCl_4 from ClO_4^- solutions was poor for various practical purposes except with Hba¹³⁸⁵. Topo-Htta extracted manganese(II) as $[Mn(tta)_2topo]$ ¹³⁸⁶. A less common non-aqueous system involves the extraction of manganese(II) from ethylene glycol with topo (in cyclohexane or toluene) in the presence of 10^{-3} – 10^{-2} M HCl¹³⁸⁷. The addition of LiCl had a salting-out effect.

Technetium(VII) was extracted from $(NH_4)[TcO_4]-HCl$ solution with a series of phosphine oxides (in benzene or cyclohexane) in the sequence $R_3PO > tbp > Ph_3PO$ ($R = n\text{-butyl, } n\text{-octyl, } n\text{-hexyl, } n\text{-ddecyl, } 2\text{-ethylhexyl}$)^{1326,1388,1389}. The highest percentage extraction was 85% with R_3PO . The hydrogen-bonded $(L)HTcO_4$ appears to be the extracted species and Ph_3PO shows the weakest hydrogen bonding.

Rhenium(IV) was quantitatively extracted from aqueous 3–4 M HCl (HBr) using Bu_3PO (in CCl_4) and the formation of $(Bu_3PO)_3(H_3O)_2[ReX_6]$ was established¹³⁹⁰. A similar species, $(R_3PO)_2(H_3O)[RcO_4]$ was suggested when rhenium(VII) was extracted from aqueous HCl using topo (in C_6H_6 , CCl_4 , etc.)^{1391–1393}. As expected, the extraction with phosphine sulphides and selenides was poor ($R_3PO > R_3PS > R_3PSe$; $R = n\text{-octyl}$).

A method for the quantitative separation of $[\text{ReO}_4]^-$ from $[\text{WO}_4]^{2-}$ was mentioned in the previous section¹³⁸⁴. Pure $(\text{NH}_4)_2[\text{ReO}_4]$ was obtained from H_2SO_4 solution containing molybdate ions using topo and by varying the basicity of the amines¹³⁹⁴. $[\text{ReO}_4]^{2-}$ and $[\text{MoO}_4]^{2-}$ were stripped stepwise by adjustment of the pH of NH_4^+ -containing solutions.

ix. Elements of Group VIII. *Iron sub-group*. Topo extracted iron(III) from 4 M HCl (or 1 M HCl + 3 M NaCl)¹³⁹⁵ and SCN^- - HNO_3 ²⁹⁴ quantitatively. The nature of the species was probably $[\text{FeX}_3\text{L}_n]$ ($n = 1, 3$; $\text{X} = \text{Cl}, \text{NCS}$). Other investigations have involved the extraction of trace Fe¹³⁹⁶, the removal of iron from organic leaches¹³⁹⁹ and the separation of iron from aluminium and zinc¹³⁹⁸ (Table 19). Synergistic combinations of topo-Hdbm (in benzene)¹⁴⁰⁵ or topo-Hpmtfp (in cyclohexane)¹³³⁹ quantitatively extracted iron(II) from aqueous solutions of pH 6–7 and 1.5–2.8, respectively. The topo-Hdbm system was used for the determination of iron(II) in spring water (sensitivity $0.0047 \mu\text{g cm}^{-3}$ of iron). The complex extracted, $[\text{Fe}(\text{dbm})_2(\text{topo})_2]$, absorbed at λ_{max} 408 nm. Zinc(II), lead(II), chromium(III), tin(II), PO_4^{3-} , CN^- and citrate all interfered; $\text{S}_2\text{O}_3^{2-}$, F^- and tartrate were used to mask the interference of copper(II), aluminium(III) and manganese(II), respectively.

Similarly, Hacac-topo (in cyclohexane)(I)¹⁴⁰⁶, topo-Htta (in benzene)(II)^{1407–1409} topo-H₂dehp (in kerosene)(III)¹⁴¹⁰ and Ph_3PO -Hacac (in CHCl_3)(IV)¹⁴¹¹ extracted iron(III) from perchlorate, chloride, sulphate and thiocyanate solutions, respectively. In system I, the presence of ClO_4^- was necessary to produce synergism and the presence of NO_3^- or SO_4^{2-} showed poor extraction. The extracted species was $[\text{Fe}(\text{acac})_2(\text{topo})_2] \cdot (\text{ClO}_4)$. In system II, maximum extraction occurred at pH 2.63 and at higher pH the extraction decreased. Also, it was observed that with Htta in benzene alone, the extraction

TABLE 19. Extraction of iron(III) using tertiary phosphine oxides

System	Comments and extracted species	Ref.
1 topo-NaSCN	Extraction of trace Fe, but extraction non-quantitative	1396
2 topo-C ₆ H ₆ -(HCl + H ₂ SO ₄)	Simultaneous removal of Fe (2.43%), Cu(0.4%), Cd(7.65%) and Zn(74.2%) from a leached powdered residue from zinc smelting	1399, 1400
3 topo-CCl ₄ (or C ₆ H ₁₂)-NaClO ₄ (or NaClO ₄ + NaX, X = Cl, Br)	Extraction is increased with added X ⁻ ions and was pH dependent $[\text{Fe}(\text{topo})_4(\text{ClO}_4)_3]$	1402, 1403
4 topo-amines-(octan-2-ol)-SO ₄ ²⁻ (pH 1–2)	Separation was possible even in the presence of Al and Zn	1397
5 topo (or R ₂ R'PO, R = n-hexyl, R' = n-octyl)-Acid	Iron ($\geq 1 \text{ g l}^{-1}$) was removed from organic leaches obtained from phosphate minerals containing uranium(VI)	1396
6 Ph ₃ PO-C ₆ H ₆ -mineral acids	Iron separation from chromium(VI), molybdenum(VI), yttrium(III) and gold(III)	1320, 1345
	H-bonded species, $(\text{Ph}_3\text{PO} \cdot \text{H})[\text{FeCl}_4]$ suggested	1404
7 R ₃ PO-xylene-NaCl (R = Ph, alkyl)	Phenyl substituent on P showed lower extraction than alkyl substituent. Species $\text{FeCl}_3(\text{R}_3\text{PO})_2 \cdot \text{H}_2\text{O}$ was formed	1329, 1330

rate was very slow^{1408,1409} and the addition of topo enhanced both the rate and the extent of extraction. In system III, the extraction was quantitative (>98%). In system IV¹⁴¹¹, the extraction was quantitative and selective in the presence of the ions tested, chromium(III), manganese(II), cobalt(II), nickel(II), zinc(II), CH_3COO^- , Cl^- , SO_4^{2-} and NO_3^- ; however, copper(II) interfered. Multiple extractions were needed for chromium, nickel and zinc when Cl^- was the anion, whereas in all other cases a single extraction was sufficient to remove iron quantitatively from the aqueous SCN^- medium (pH 2.7–2.8). The synergistic species identified was $[\text{Fe}(\text{NCS})(\text{acac})_2(\text{Ph}_3\text{PO})]$. Extraction with Ph_3PO alone was poor. The method was suitable for the extractive determination of iron in steel samples^{1411b}.

Ruthenium(III) was extracted with topo or Oct_3PO in *n*-hexane from an acidic solution of the nitroso complex, $\text{Na}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})]$ ¹⁴¹², but the extraction was lower than that of the chlororuthenium complexes¹⁴¹³. In extracting ruthenium(III) from 2 M HCl with topo or Bu_3PO in CHCl_3 , the addition of *n*-octanol or cyclohexanol lowered the extraction on account of their hydrogen-bonded interaction with R_3PO , thus lowering the effective concentration of the reagents¹⁴¹⁴.

Osmium(III) was extracted from HCl or HBr media using topo, *tbp*, etc., as their halide complexes¹⁴¹⁵, and higher extraction was achieved from HBr over HCl and with topo in place of other reagents.

Cobalt sub-group. The alkyl ligand Bu_3PO extracted cobalt(II) from a mixture of aqueous HCl, LiCl and CaCl_2 solutions and the extraction follows a hydration–solvation mechanism, forming $[(\text{M}^{x+} \cdot m\text{H}_2\text{O})_{2/x} \cdot n'\text{Bu}_3\text{PO}][\text{CoCl}_4]$ (where $x = 1$ for HCl and LiCl and 2 for CaCl_2 , and m and n' are hydration and solvation numbers, respectively¹⁴¹⁶. Similarly, topo extracted cobalt(II) from LiCl, KSCN, HCl and HNCS solutions. It showed higher extraction than Alamine 336-S from acid-deficient systems, but lower extraction from acid-rich solutions^{1326,1417}. Extraction of cobalt(II) with tris(2,6-dimethylphenyl)phosphine oxide perchlorate ($\text{R}_3\text{POH}^+\text{ClO}_4^-$) in CHCl_3 was poor¹⁴¹⁸.

Topo–Hpmbp (in benzene)¹⁴¹⁹ and topo–Hpmtfp (in hexane)¹³³⁹ extracted cobalt(II) quantitatively (>98%) from acidic media (pH 4.9–6.0 and 1.5–2.8, respectively). A series of other β -diketone– R_3PO systems which extract cobalt(II) under different conditions are topo–Htta (in different organic solvents; pH 5.1)¹⁴²⁰ and R_3PO –Htta (or Hhfa, Hpvt, Hbfa, Hacac, Hba and Htfa) ($\text{R} = n$ -butyl, *n*-octyl or phenyl) (in benzene^{1421,1422}, CCl_4 ¹⁴²³, cyclohexane^{1424a} or ClO_4^- medium). The extracted species was generally $[\text{CoA}_2\text{L}]$ ^{1420–1423} ($\text{A} = \text{anion of chelating ligand}$; $\text{L} = \text{organophosphorus reagent}$), although the formation of $[\text{CoA}_2\text{L}_2]$ ($\text{HA} = \text{Htfa, Hbfa, Hhfa}$) in CCl_4 ¹⁴²⁴ has also been reported. Some other conclusions drawn are: (a) the stabilities of the cobalt(II) adducts decrease in the sequence $\text{topo} > \text{Bu}_3\text{PO} > \text{tbp} > n$ -hexanol, which corresponds to the order of basicity of the Lewis bases¹⁴²¹; (b) the sequence of the extraction constants and adduct formation constants is $\text{Htta} > \text{Hhfa} > \text{Hpvt}$ ¹⁴²²; and (c) Topo–Hbfa (in cyclohexane)^{1424a} could be used for the extractive–spectrophotometric microdetermination of cobalt(II) (≤ 20 ppm) ($\lambda_{\text{max}} = 380$ nm for $[\text{Co}(\text{bfa})_2\text{topo}]$). Copper(II), nickel(II), iron(III), manganese(II), EDTA, citric acid and larger amounts of lead(II), strontium(II), chromium(III) and bismuth(III) interfere in the determination, however.

Recently, Hpmbp and topo (or dpmO_2 , dpeO_2) extracted synergistically cobalt(II), nickel(II), zinc(II) and cadmium(II), forming $[\text{M}(\text{pmbp})_2(\text{topo})_n]$ ($n = 2$ for Co, Ni and 1 for Zn) and $[\text{M}(\text{pmbp})_2\text{L}]$ ($\text{L} = \text{dpmO}_2$ or dpeO_2)^{1424b}. Other synergistic systems studied are R_3PO –quinolin-8-ol¹⁴²⁵ ($\text{R} = n$ -butyl or octyl), topo-4-methyl-*N*-8-quinolinylbenzenesulphonamide¹⁴²⁶, topo–resacetophenone oxime¹⁴²⁷ and R_3PO –phosphinic acid ($\text{R} = \text{alkyl}$)¹⁴²⁸. The species identified is $[\text{CoA}_2\text{L}]$; the order of extraction in the quinolin-8-ol system is $\text{topo} > \text{Bu}_3\text{PO} > \text{tbp}$ ¹⁴²⁵. In the phosphinic acid system, the addition of R_3PO enhanced the separation of cobalt and nickel¹⁴²⁸.

A mixture of quinolin-8-ol (HQ) and triphenylphosphine oxide (Ph_3PO) showed

synergism of 10–12% in the extraction of cobalt(II) compared with the use of HQ alone¹⁴²⁹. At the synergic point, cobalt(II) was separated from its binary mixtures with chromium(III), silver(I), mercury(II), magnesium(II) or aluminium(III) with a recovery of over 97%. Mercury(II) and silver(I) were transferred to the organic layer together with cobalt(II) and zinc(II) and this was sorted out by stripping the organic layer with concentrated HCl, which released cobalt(II) to the aqueous layer. Further stripping of the organic layer with concentrated HNO_3 facilitated the release of mercury(II) or silver(I) to the aqueous layer. The extraction was at a maximum in the pH range 4.0–10.0 and poor at pH 2.0. In cobalt(II) extraction with *S*-tert-dodecylthioglycolic acid (HA), topo or tbp inhibited the extraction; this represents the only example where no synergism was observed¹⁴³⁰. Hydrogen-bonded interaction of HA with R_3PO , which would lower the concentration of HA, might be responsible for the observed difference.

Investigations with rhodium and iridium are few: topo–trichloroacetic acid (or pentadecafluorooctanoic acid) in benzene quantitatively and rapidly extracted rhodium(III) as $[\text{Rh}(\text{A})_3(\text{topo})_4]$ (A = anion of the acid)^{1431–1432}. H_2dehp showed a similar extraction, but topo caused no enhancement¹⁴³¹. $\text{R}_3\text{PO}-\text{C}_6\text{H}_6$ (R = alkyl) was employed for the extraction of rhodium and iridium from 4 M HCl solution prior to the determination of the micro amounts of rhodium present in large amounts of iridium in an anodic stripping voltammetric method¹⁴³³.

Nickel sub-group. Topo–hexane extracted nickel(II) from aqueous $\text{SCN}^- - \text{ClO}_4^-$ medium¹⁴³⁴, although the extraction was less than that of cobalt(II) from solutions with high concentrations of SCN^- ions. From ClO_4^- alone, the extraction of both metals was similar. The formation of various species in the organic phase, namely $[\text{Ni}(\text{ClO}_4)_2\text{L}_4]$, $[\text{Ni}(\text{NCS})(\text{ClO}_4)\text{L}_4]$ and $[\text{Ni}(\text{NCS})_2\text{L}_4]$ for nickel(II) and $[\text{Co}(\text{ClO}_4)_2\text{L}_3]$, $[\text{Co}(\text{NCS})(\text{ClO}_4)\text{L}_3]$, $[\text{Co}(\text{NCS})_2\text{L}_2]$ and $\text{Na}[\text{Co}(\text{NCS})_3(\text{topo})_3]$ for cobalt(II), was established¹⁴³⁵. Other extraction studies have been made with topo¹³³⁸ and Ph_3PO ¹³²⁰ from aqueous chloride media.

The quantitative extraction of nickel(II) was achieved with topo–Hpmtfp in cyclohexane from aqueous solution (pH 1.5–2.8)¹³³⁹. Other synergistic systems used for the extraction of nickel(II) include topo–[4-(2-pyridylazo)resorcinol]¹⁴³⁶, topo–(Kelex 100 and 8-sulphonamidoquinolines) in chlorobenzene¹⁴³⁷ and topo– β -diketones (Htta, Hacac, Hba, Htfa, Hbfa or Hhfa) in CCl_4 from perchlorate medium^{1435,1438–1443}. Table 20 gives a summary of the extraction data for nickel(II), cobalt(II) and copper(II). The extraction of cobalt(II) and nickel(II) with Hacac or Hacac–topo was poor; likewise, extraction with Htfa and Hhfa was poor, but the addition of topo enhanced the extraction to a measurable extent. From Table 20, a number of conclusions may be drawn: (a) the stability constants of nickel(II) chelates in the aqueous phase are generally higher than those of cobalt(II) chelates but lower than those of copper(II) chelates; (b) the partition constants of nickel(II) chelates are one tenth to one thirtieth of those of cobalt(II) chelates and much lower than those of copper(II) chelates; and (c) the adduct formation constants are similar. The higher hydration of nickel(II) and cobalt(II) is responsible for their low partition coefficients.

Topo–cyclohexane (in CHCl_3 , mibk or 2,2'-dichlorodiethyl ether) mixtures are useful in the mutual separation of palladium, platinum and gold from aqueous HX (X = Cl, Br)¹⁴⁴⁴. Other reagents used for extraction studies are topo– R_3PO (in toluene or decanol)^{1445,1446} for palladium and platinum from HCl (I), topo–molten diphenyl for palladium and platinum from HCl (or HNO_3)¹⁴⁴⁷ (II), topo– R_3PO for palladium from HNO_3 (III)¹⁴⁴⁸ and topo–toluene for platinum from HCl(IV)^{1449a}. For system I, maximum extraction (as $[\text{MCl}_2\text{L}_2]$) was observed at 5 M HCl, and an increase in the length of the hydrocarbon chain of the alkyl substituent increased the extraction¹⁴⁴⁵. Significantly, topo showed lower extraction than the corresponding phosphine sulphides. When > 20% of topo with decanol was used, the extraction was same as that when topo

TABLE 20. Summary of data for extraction of cobalt(II), nickel(II) and β -diketone-topo system^a

Reagent	M	Log β_1 (aq.)	Log β_2 (aq.)	Log D	Log β_1 (org.)	Log β_2 (org.)
Hacac	Co	—	—	−0.94	1.46	NC ^b
	Ni	—	—	−2.25	2	NC
	Cu	7.81	14.22	0.83	1.28	NC
Hba	Co	4.55	8.14	1.37	3.44	NC
	Ni	4.41	9.86	−0.14	3.50	NC
Htfa	Co	3.50	5.60	−2.14	5.36	7.76
	Ni	3.74	6.68	−3.25	5	8
	Cu	4.80	9.14	1.40	2.96	NC
Hbfa	Co	3.40	5.24	2.06	6.15	9.34
	Ni	3.60	6.68	0.76	5.19	8.98
Hhfa	Co	1.56	2.32	−1.02	5.19	10.58
	Ni	1.90	3.10	−2.1	5.80	10.50
	Cu	2.25	3.20	1.39	5.63	9.36

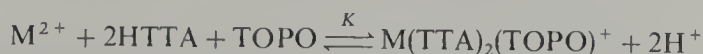
^aData from refs. 1438–1441.^bNo complex.

alone was used¹⁴⁴⁶. Hence for the lower topo concentration, decanol had a synergistic effect. In system II, the D value was nearly same for palladium and platinum from HCl (Pd 126, Pt 123), but from HNO₃, D was higher for platinum(II) (107) than palladium(II) (6.7)¹⁴⁴⁷. There was no extraction from H₂SO₄ medium. System III showed a higher extraction for palladium with phosphine oxides over phosphonates or phosphates¹⁴⁴⁸. Various species identified were [Pd(NO₃)₂L₂] \cdot n H₂O ($n = 0, 2, 4$). System IV showed a high extraction of platinum(IV), probably because the extraction steps involve a solvating mechanism ($K_{\text{ex}} = 2.6 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$); in contrast, rhodium(III) showed poor extraction.

x. Elements of Group IB. Extraction studies for copper(II) with phosphine oxides alone are scarce. Thus, although topo showed extraction of copper(II) from Cl[−] medium¹³³⁸, there was no extraction from HCl, H₂SO₄ or HNO₃¹⁴⁴⁷. As a result, phosphine oxides are mainly used as synergists in the extraction of copper(II) with different reagents. Various synergistic systems used for the extraction of copper(II) include topo- β -diketones (Htta, Htfa, Hhfa, Hacac or Htfma) in benzene^{1449b, 1450–1453}, n -hexane⁴⁴⁹ or xylene(I)¹³⁴⁰, topo-Hpmap in benzene and other solvents (II)¹⁴⁵⁴ and topo (or Ph₃PO)-benzeneazo-2-naphthol(HA) from NaOAc-HOAc (pH, 5.5)¹⁴⁵⁵ (III) (no synergism). From system I, the order of extraction efficiency of the β -diketones was inferred from D values to be Htta > Hhfa > Htfa > Hacac^{449, 1449b}. The lower D value for Hhfa than for Htta is attributed to the solubility of [Cu(HFA)₂] \cdot 2H₂O in water¹⁴⁵⁰. Topo-Hacac showed no synergism, probably owing to the low stability of the adduct¹⁴⁵¹. Interestingly, the formation constants for



in benzene¹⁴⁵² supported the above sequence [HA, K (l mol^{−1}): Htta, 1700; Htfa, 940; Hacac, 45]. For the Htta-topo system¹⁴⁵⁰, it was observed that copper(II) showed a higher value for the equilibrium constant for the reaction



than zinc(II) (K : Cu, 1800; Zn, 0.1).

Another observation for system I(topo-Htta-C₆H₆)¹⁴⁵³ is that higher topo concentrations destroyed the synergism owing to (Htta.topo) adduct formation and to increased TOPO...H₂O interaction, which increases the amount of H₂O in the organic layer, which in turn would compete with TOPO for adduct formation with [Cu(tta)₂]. For system II, it was observed that the extraction constant increases monotonously with a decrease in temperature (37–7 °C)¹⁴⁵⁴. For system III, the decrease in the formation constants of [CuA₂] with increasing solubility of H₂O in the solvent indicates the lack of any H₂O in the coordination sphere of the extracted complex¹⁴⁵⁵. This explains the lack of synergism when topo or Ph₃PO was added to benzeneazo-2-naphthol solution for extraction. The species extracted were generally of the type [CuA₂L] (A = anion of the chelating ligand; L = organophosphorus reagent).

Recently, silver(I) was extracted using Ph₃PO in CHCl₃ from the aqueous phase (pH 6, HoAc–NaOH buffer)¹⁴⁵⁶. A number of ions tested (Mn, Co, Ni, Cu, Zn, Cd, Sn, Pb, Mg, Al, Cr, Fe, NO₃[–], CH₃COO[–], SO₄^{2–}) did not interfere, but mercury(II) did interfere. The extracted species was established as [Ag(Ph₃PO)_n(NO₃)] (*n* = 1, 3 depending on Ph₃PO concentration). Silver(I) was synergistically extracted with dibenzo-18-crown-6–topo¹⁴⁵⁷ and the species was [Ag(E)(topo)]⁺ (picrate)[–] (E = crown ether).

Unlike copper(II), there have been several investigations of gold(III) extraction with tertiary phosphine oxides, namely topo in C₆H₆ (or CHCl₃, CCl₄, PhMe, C₆H₁₂ or isooctane) from HCl solutions^{1391,1392,1445}, topo in CCl₄ from hydrohalic acids (gold present in traces)¹⁴⁶⁰, topo in molten diphenyl¹⁴⁴⁷ from HCl, H₂SO₄ or HNO₃ and Ph₃PO in C₆H₆^{1345,1458,1459}. From these studies, it was concluded that (a) gold was generally extracted as a hydrogen-bonded ion-pair species, (R₃PO)_nHAuCl₄ (*n* = 1, 2)^{1391,1392,1445}, or H₃O⁺·3R₃PO·yH₂O...[AuX₄][–] (0 ≤ *y* ≤ 3) (R = Ph, *n*-octyl; X = Cl, Br)^{1459,1460}; (b) the separation factors for Au, Mo, Cr and Fe are fairly good for mutual separations¹³⁴⁵; (c) the maximum *D* was at 4 M acid concentration and its value increased from 3.53 to 10.32 on changing trihexylphosphine oxide to topo; *D* was also at a maximum when the number of carbons atoms in the extractant was between 23 and 24; the introduction of an electron-withdrawing group lowered the value of *D*¹⁴⁴⁵; in contrast, the tertiary phosphine sulphides were found to be better extractants than the phosphine oxides; and (d) the extraction of gold(III) from HCl or H₂SO₄ with topo in the diphenyl system¹⁴⁴⁷ was higher than that from HNO₃ (*D* > 10³ versus 86.4). The tendency of HNO₃ to be extracted with R₃PO appears to be responsible for this apparent difference. Significantly, the topo–diphenyl pair showed no extraction of silver(I)¹⁴⁴⁷.

Bis(2-ethylhexyl)dithiophosphate and topo in toluene extracted silver and gold simultaneously from copper- or bismuth-containing materials prior to their determination by atomic absorption spectrometry¹⁴⁶¹.

xi. Elements of Group IIB. Topo in C₆H₁₂ extracted zinc(II) from NaX–NaClO₄ (X = Cl, Br, I) solutions¹³⁴². A variety of extracted species such as [Zn(ClO₄)₂(topo)₄], ZnX (ClO₄)(topo)₃] and [ZnX₂(topo)₂] were identified, and the extraction decreased in the sequence I[–] > Br[–] > Cl[–] (*K*_{ex} = 6.12, 4.51 and 3.64, respectively). The higher covalent bonding character of iodide and its hydrophobic nature increased the extraction of ZnI₂ complexes over other zinc(II) halide complexes. From SCN[–] media, zinc(II) showed enhanced extraction as [Zn(NCS)₂(topo)₂]¹⁴⁶². The difference is attributed to the greater stability of Zn(NCS)₂ species over ZnX₂ in the aqueous phase.

The extraction of zinc(II) from molten KSCN at 195 °C with R₃PO in phenanthroline decreased in the order topo > Ph₃PO > (Me₂N)₃PO > bipy (*K*_{ex} = 3.80, 3.20, 2.0 and 1.60, respectively), the extracted species being [ZnL_n(NCS)₂]{*n* = 2 for topo, (Me₂N)₃PO, 3 for Ph₃PO and 1 for bipy}¹⁴⁶³.

Using tertiary phosphine oxides, other extraction systems for zinc(II) are topo in PhMe from HCl or Cl[–] medium^{1326,1338,1464,1465}, topo in C₆H₆ from 3 M HCl + 1 M

H_2SO_4 ¹⁴⁶⁶ or 4 M H_2SO_4 (I)¹⁴⁶⁷, R_3PO -xylene from Cl^- media (II)^{1329,1330} and topo in toluene or decalin from glycol or $\text{MeOH-H}_2\text{O}$ phases containing Cl^- and ClO_4^- ions (III)^{1468,1469}. System I showed a higher recovery of zinc(II) over cadmium(II) (79.5% versus 2.6%). Here water was used as the stripping agent instead of the acids or bases commonly employed. Similarly, system II showed excellent selectivity for zinc(II) over iron(II), copper(II) and lead(II) and moderately good selectivity over iron(III); as usual the extraction decreased in the sequence $\text{R}_3\text{PO} > \text{R}_2(\text{R}'\text{O})\text{PO} > \text{R}(\text{R}'\text{O})_2\text{PO} > (\text{R}'\text{O})_3\text{PO}$. System III showed an extraction order for the glycols of propylene glycol > ethylene glycol > ethylene glycol-water.

Topo-Htta (or Hhfa) extracted zinc(II) from HClO_4 solution as $[\text{ZnA}_2(\text{topo})_n]$ (⁶⁵Zn tracer study) ($n=1$ for Htta and 1,2 for Hhfa)^{1449,1450}. The extraction constants (K_{ex}) followed the sequence $[\text{Zn}(\text{Hfa})_2(\text{topo})] > [\text{Zn}(\text{tta})_2(\text{topo})] > [\text{Zn}(\text{tta})_2(\text{topo})] > [\text{Zn}(\text{tta})_2]$ ($K_{\text{ex}} = 1000, 12, 0.1$ and 8.5×10^{-10} , respectively). The excess of topo destroyed the synergism in the case of Hhfa system, which was avoided when the aqueous phase was buffered with acetate (pH 5). The fluorinated β -diketones showed a higher extraction of zinc(II) owing to the increased stability of topo adducts with zinc(II) chelates¹⁴⁷⁰. As expected, a CF_3 group in β -diketones increases the Lewis acidity of the zinc(II) chelates.

Distribution studies on $[\text{Zn}(\text{tta})_2(\text{topo})]$ ¹⁴⁷¹ revealed that the order of extraction in a series of organic solvents(S) decreased in the order hexane > cyclohexane > CCl_4 > C_6H_6 > CHCl_3 ($D = 0.175, 0.135, 0.051, 0.028$ and 0.0003 , respectively). The addition of water to the Zn^{II} -Htta-topo system lowers the extraction as topo is replaced from $[\text{Zn}(\text{tta})_2(\text{topo})]$ by H_2O forming $[\text{Zn}(\text{tta})_2(2\text{H}_2\text{O})]$. Addition of topo increases the extraction again. Other β -diketone- R_3PO systems for zinc(II) extraction are topo (or Ph_3PO)-Hbfa (or Hpvt) in C_6H_6 from ClO_4^- medium^{1472,1473} (I), topo (or Bu_3PO)-Hbfa (or thiobenzoyltrifluoroacetone) in C_6H_6 from ClO_4^- medium(II)^{1421,1474} and topo-Hbfa-Hba in CCl_4 (III)¹⁴⁷⁵. System I revealed that topo gave better extractions than Ph_3PO or even dpmO_2 or dpeO_2 ¹⁴⁷³. In system II, Htbfa gave a higher extraction than Hbfa in the absence of topo, whereas in the presence of topo it gave a lower extraction ($\log K_{\text{ex}} = 5.04$ for Htbfa-topo and 5.72 for Hbfa-topo). Additionally, Htbfa alone showed gave a extraction than topo or Bu_3PO . Species of the type $[\text{ZnA}_2\text{L}]$ were formed in systems I and II, whereas in the ternary system III species of the type $[\text{Zn}(\text{bfa})(\text{ba})(\text{topo})]$, $[\text{Zn}(\text{bfa})_2(\text{topo})]$ and $[\text{Zn}(\text{ba})_2(\text{topo})]$ were detected¹⁴⁷⁵.

Pyrazolone- R_3PO and other combinations that have been used for the extraction of zinc(II) are topo-Hpmsp in C_6H_6 (I)¹⁴⁷⁶, topo-Hpmbp in different organic solvents¹⁴⁷⁷, topo-Hpmtip in C_6H_{12} (II)¹³³⁹, topo- H_2dehp (III)^{1478,1479}, topo-NaD (NaD = sodium dinonylnaphthalenesulphonate, a liquid cation exchanger) in C_6H_6 from HClO_4 (IV)¹⁴⁸⁰ and topo-(4-methyl-N-8-quinolinylnbenzenesulphonamide) in toluene(V)¹⁴⁸¹. System I was most effective for the separation¹⁴⁷⁶ of zinc(II) from cadmium(II) at pH 4.5. An amount as low as 20 μg of zinc in 20 mg of cadmium (1:1000 ratio) could be separated. In system II, quantitative extraction (>98%)¹³³⁹ of zinc(II) was achieved from aqueous solutions of pH 1.5–2.8. System III showed a lower extraction than those shown by topo- β -diketones^{1478,1479}, probably owing to the steric hindrance in the former. Addition of more topo reduced the extraction (antisynergism) owing to H_2dehp -topo hydrogen-bonded adduct formation, which lowered the effective concentration of H_2dehp . Similarly, system IV showed¹⁴⁸⁰ lower synergism than topo-Htta. However, the extraction was quantitative ($K_{\text{ex}} = 6.1 \times 10^4$). Significantly, NaD alone showed a greater extraction than Htta by a factor of 10^3 . The use of HD-topo in place of NaD-topo lowered the extraction due to HD-topo adduct formation. The extracted species was suggested to be $[\text{ZnD}_2(\text{topo})_n]$ ($n = 1, 2$). System V also extracted zinc(II) quantitatively from 0.1 M HNO_3 solution. Quinolinc-8-ol and Ph_3PO synergistically extracted zinc(II) in a manner similar to that of cobalt(II) as described earlier¹⁴²⁹.

TOPO has been used to extract cadmium(II) from NO_3^- or $\text{Na}(\text{X}, \text{ClO}_4)$ ($\text{X} = \text{Cl}, \text{Br}$,

I) media^{1326,1338,1482}, but efficient extractions occur when topo is combined with other chelating agents. For instance, extraction of cadmium(II) with topo-Hbfa in C_6H_6 ^{1483,1484} was efficient, whereas topo or Hbfa alone showed negligible extraction. The extracted species was established to be $[Cd(bfa)_2(topo)_2]$. Other effective combinations topo- $F_3CC(O)CH_2C(O)C_2H_5$ in xylene from perchlorate medium¹³⁴⁰ and topo-Hpmt in C_6H_{12} showed quantitative extraction¹³³⁹. Extraction with topo- H_2dehp in tetradecane has also been reported¹⁴⁸⁵.

Topo in molten diphenyl¹⁴⁴⁷ showed a higher extraction of mercury(II) from HCl ($D = 61.3$) and lower from HNO_3 or H_2SO_4 ($D = 0.1-0.6$), suggesting a higher extractability of $[HgCl_2(TOPO)_n]$ ($n = 1, 2$) type of species over corresponding nitrate or sulphate species. In comparison, the extractions of gold, palladium and platinum were high. Triisopentylphosphine oxide in various solvents extracted mercury(II) as $[HgCl_2L]$ and $[HgCl_2L_2]$ ¹⁴⁸⁶.

xii. f-Block elements. This group of elements has attracted considerable interest in extraction science on account of both the separation difficulties posed by these elements and their importance in the generation of nuclear energy and in radiochemistry.

Lanthanides. For convenience, the extraction studies are divided into different sections based on the nature of the reagent used.

Extraction of lanthanides with R_3PO alone. Table 21 contains various metals extracted with tertiary phosphine oxides (R_3PO). It can be seen that the most commonly extracted species is $[MX_3L_3]$ ($X = \text{anion}$) and the coordination number varies depending on the coordinating ability of the anion; NO_3^- generally acts as a chelate and thus 8- or 9-coordinate species are formed. Some important comments on the systems may be made as follows. In system I, the addition of $Na_2H_2edta \cdot 2H_2O$ promoted extraction, but the mechanism involved is not known¹⁴⁸⁷. In system II, the extraction increased in the order $topo > Bu_3^nPO \gg tbp$ ⁵³⁷. For a given reagent, $\log K_{ex}$ was found generally to increase with decrease in the metal ion radius (e.g. for topo, the $\log K_{ex}$ values are 8.35 for La and 9.39 for Cu).

In system III, topo showed a lower extraction¹⁴⁸⁸ than tbp , which is probably the only case of reversal of the general trend, followed by R_3PO , namely, $topo > Bu_3^nPO > Ph_3PO > tbp$. In system IV, maximum extraction of cerium(III) was noted at 2 M topo¹⁴⁸⁹. Similarly, system V showed a maximum value of D at 0.3–0.5 M HNO_3 ¹³⁴⁶. System VI showed¹⁴⁹¹ that K_{ex} is not necessarily higher for smaller ionic radii ($K_{ex}:M = Nd, 5.8 \times 10^7$; Er, 1.5×10^6 ; Gd, 5.3×10^4) and can follow a complicated trend depending on the system. System VII showed a case of the salting-out effect¹⁴⁹², where the presence of NH_4NO_3 was necessary for extraction.

From systems IX and X, it was observed that the replacement of an R group by an alkoxy group (RO) lowered the extraction^{1344,1352}, obviously owing to decreased Lewis basicity of $(RO)_3PO$ and also to enhanced $H_2O \cdots (RO)_3PO$ interaction. A decreasing trend in extraction of the type $R_3PO > R_2(RO)PO > R(RO)_2PO > (RO)_3PO$ is followed. Interestingly, system XI (at ≥ 0.25 M topo) is the most selective¹⁴⁹⁴ for lanthanide separations to date. It also represents the first report of the extraction of lanthanides as their hydroxides. System XII involves the extraction of the rare earths¹⁴⁹⁵ from several geosamples. Here Sc, Fe, Cr, U and Th are also removed. The use of mixed R_3PO ligands did not show any improvement in extraction over the use of individual ligands (XIII)¹⁴⁹⁶.

Europium(III) showed a higher extraction from LiCl than HCl media (XIV)¹⁴⁹⁷ and it may be attributed to the lowered effective concentration of topo due to topo \cdots HCl interaction. System XV is very useful for separating europium from americium and curium¹⁴⁹⁸⁻¹⁴⁹⁹. System XVI shows the effect of temperature (20–60 °C) on the extraction of europium(III)¹⁵⁰⁰. It was found that $-\Delta H$ values were higher for R_3PO than for tbp , although the trend was the reverse for $-\Delta S$ values. Hence the extraction was enthalpy driven.

TABLE 21. Extraction of lanthanides with tertiary phosphine oxides

System	Metal extracted	Reagent and medium	Species extracted	Ref.
I	La	topo; ClO_4^-	$[\text{La}(\text{ClO}_4)_3\text{L}_n]$	1487
II	La, Eu, Lu	R_3PO -xylene ($\text{R} = n$ -octyl, Bu^n); SCN^-	$[\text{M}(\text{NCS})_3\text{L}_n](n = 3, 4)$	537
III	Ce	topo-PhMe; HNO_3 or LiNO_3	$[\text{Ce}(\text{NO}_3)_3\text{L}_3]$	1488
IV	Ce	topo; NH_4SCN	$[\text{Ce}(\text{NCS})_3\text{L}_3]$	1489
V	La, Sm, Pr, Gd, Dy, Ho	R_3PO -kerosene ($\text{R} = \text{C}_n\text{H}_{2n+1}$, $n = 7-9$); NO_3^-	$[\text{M}(\text{NO}_3)_3\text{L}]$	1346, 1490
VI	Nd, Gd, Er	topo-polyphenyl; LiNO_3 - KNO_3 (molten)	$[\text{M}(\text{NO}_3)_3\text{L}_n](n = 2, 3)$	1491
VII	Nd	topo-kerosene; NH_4NO_3	$[\text{Nd}(\text{NO}_3)_3\text{L}_n]$	1492
VIII	Ln	R_3PO ($\text{R} = \text{Ph}$; n -octyl); HNO_3	$[\text{M}(\text{NO}_3)_3\text{L}_3]$	1493
IX	Ln (except Pm)	R_3PO ; NO_3^-	$[\text{M}(\text{NO}_3)_3\text{L}_2]$	1344
X	Ln	R_3PO ($\text{R} = \text{isoalkyl}$, etc.); Cl^- , SCN^-	$[\text{M}(\text{NCS})_3\text{L}_n](?)$	1352
XI	La, Pr, Eu, Tb, Ho, Yb	topo- CHCl_3 ; Cl^-	$[\text{M}(\text{OH})_3\text{L}_n]$	1494
XII	Ln	topo- C_6H_{12} ; acidic solutions	—	1495
XIII	Ln	topo- Bu_3PO -PhMe; NO_3^-	—	1496
XIV	Eu	topo- p -xylene; HCl (or LiCl)	$[\text{M}(\text{NO}_3)_3\text{L}_3]$ ($\text{L} = \text{topo}$, Bu_3PO) and $\text{M}(\text{NO}_3)_3(\text{topo})(\text{Bu}_3\text{PO})$	1497
XV	Eu	topo- p -xylene; NH_4NO_3	$[\text{EuCl}_3\text{L}]$	1498-1499
XVI	Eu	R_3PO ($\text{R} = \text{mixed alkyl groups}$); HNO_3 (or NH_4NO_3)	$[\text{Eu}(\text{NO}_3)_3\text{L}_3]$	500

TABLE 22. Extraction of lanthanides with tertiary phosphine oxides- β -diketones

System	Metals extracted	Reagent and medium	Species extracted	Ref.
I	Ce	(a) topo-Htta; lactic acid (b) R_3PO-HA ($HA = \text{naphthoyltrifluoroacetone}$; $R = Ph, n\text{-octyl}$); acidic	$[Ce(tta)_3L_2]$ $[CeA_3L_2]$	1501 1502, 1503
II	La, Nd, Eu, Tb, Lu	topo-Hbfa; acidic	$[M(bfa)_3L_n](n = 1, 2)$	533a
III	Nd, Ho, Er	(a) topo-Htta- C_6H_6 ; acidic (b) topo-Htta- $PhMe$; CH_3COO^-	$[M(tta)_3L_n](n = 1, 2)$	1504, 1505
IV	Nd, Ho, Er	topo-Htta; X^- ($X = ClO_4, NCS, NO_3, Cl$)	$[M(tta)_3L_2]$	1506
V	Sm, Pm, Tm	$R_3PO-Htta-C_6H_6$ ($R = Ph, n\text{-octyl}$); HCl	$[M(tta)_3L_n](n = 1, 2)$	1318-1319, 1507
VI	Ho, Er	topo-Htta; ClO_4^-	$[M(tta)_2L_5](ClO_4)$	1509
VII	Tb	$Ph_3PO-Htta\text{-}bipy$; $LiNO_3-NH_4NO_3$ (molten)	—	1508
VIII	Ln (except La, Ce, Pm)	$Bu_3^aPO-Htta$	$[M(tta)_3L_n](n = 2-4)$	1348
IX	Ln (except Pm, Lu)	$Ph_3PO-Htta-C_6H_6$; ClO_4^-	$[M(tta)_3L_2]$	1510
X	Ln	topo-high mol. wt β -diketones (LIX 51, LIX 54) or Hdbm (HA)-kerosene; acidic	$[MA_3L_n](n = 1, 2)$	1511
XI	Nd	topo (or Ph_3PO)-Htta; acidic	$[Nd(tta)_3L_2]$	49
XII	Eu	(a) $R_3PO-Hbfa-C_6H_6$ (or $CHCl_3, CCl_4$) ($R = Ph, n\text{-octyl}$); ClO_4^- (b) $Bu_3^aPO-Htta-C_6H_{12}$; NO_3^- (c) topo-Htta- C_6H_{12} ; Cl^- (d) topo (or Bu_3^aPO)- $ASCN\text{-}xylene\text{-}NH_4SCN$ (e) topo-Htta-different solvents (see text); acidic (f) $Ph_3PO-Htta-CHCl_3$; ClO_4^-	$[Eu(bfa)_3L_n](n = 1, 2)$ $[Eu(tta)_2(NO_3)_3L_2]$ and $[Eu(tta)_3]$ $[Eu(tta)_3L_2]$ See text $[Eu(tta)_3L_n](n = 2, 3)$ $[Eu(tta)_3L_2]$ See text	1473, 1512, 1513 1514 1515 1516 1517 1518 ^a 1519
XIII	Lu	(a) topo-(Hba + Hdbm)- C_6H_6 ; acidic (b) topo-(Hba + Hbfa)- C_6H_6 ; acidic	—	—
XIV	Lu	topo- β -diketones- C_6H_6 ; acidic	$[LuA_3L]$	1520

^a Ph_3AsO , an analogous ligand, showed a higher extraction than that with Ph_3PO .

Synergic extractions of lanthanides with R_3PO - β -diketones. Table 22 lists various metals studied using β -diketones with R_3PO as the synergists. Europium(III) is the most studied element and is therefore discussed in detail. The extracted species are generally of the $[MA_3L_2]$ type, having 8-coordination. Species with different numbers of A^- and L ligands attached to M have also been detected. Topo again is a superior synergist to Bu_3^nPO , Ph_3PO and tbp , in that sequence.

Some comments may be made on the systems shown in Table 22. System Ib shows more efficient extraction of cerium(III) than system Ia, although both showed better extraction than with either β -diketone or R_3PO alone¹⁵⁰¹⁻¹⁵⁰³. A separation factor of 4.0 for Ce/Am was achieved in system Ia; the separation factors for other elements are (Ce/Eu, 4.3, Ce/Pm, 6.7). From system II, based on stability constant data^{533a}, it was concluded that the stability of an adduct increases with increase in the ionic radius: $Lu > Tb > Eu > Nb > La$. However, system VIII shows that the stability constants¹³⁴⁸ increase with increasing atomic number of the lanthanides and this difference may be attributed to the different set of reagents used.

From system IV, the extraction was found to vary with the anions in the sequence, for example, for Ho¹⁵⁰⁶ $ClO_4 > NCS > NO_3 > Cl$. Also, the nature of species varied from $[M(tta)_3L_2]$ at low metal concentration to $[M(tta)_2XL_5]$ at high metal concentrations.

The variation in the nature of the solvents^{1318,1319,1507,1509} affected the D values in the sequences (V, VI): (a) cyclohexane $> n$ -hexane $> CCl_4 > C_6H_6 > CHCl_3$ ^{1318,1319} and (b) 1,2- $C_2H_4Cl_2 > CH_2Cl_2 > C_6H_5Cl > Cl_2C=CHCl > C_6H_6$ ¹⁵⁰⁹. These orders represent the decreasing sequence of their dielectric constants. From system V, it was further observed that samarium(III) extraction¹⁵⁰⁷ was quantitative with topo or Ph_3PO (topo, $\beta = 3.9 \times 10^{13}$; Ph_3PO , $\beta = 8.2 \times 10^{10}$), which provides an efficient method for samarium(III) extraction, but the effect of interferents is not known.

The use of high-molecular-weight β -diketones (system X)¹⁵¹¹ did not show any improvement in the separation factors between neighbouring metals (separation factors are 2.33 for Hdbm and 1.97 for LIX 51 and 1.72 for LIX 54). From system XIIa, it was concluded that the stability of an adduct increased in the order topo $> Ph_3PO > tbp > quinoline$ ^{1473,1512,1513} and also that higher $\log \beta_2$ values were observed in CCl_4 than in $CHCl_3$ ¹⁵¹². A significant observation from system XIIc is that the stability constants were higher for topo than for bis(n -hexylphosphinyl)alkanes¹⁵¹⁵ discussed later.

In the Eu^{III} -Htta-topo system^{1513,1521}, it was established that the synergistic reactions in the organic phase are predominantly enthalpy stabilized, whereas complex formation reactions with the trivalent lanthanides in the aqueous phase are invariably entropy stabilized¹⁵²¹. The increased electrostatic interactions between the metal chelate and the donor molecules in the organic phase of low polarity increase the enthalpy values. Further, the energy required to remove H_2O from the hydrated metal chelate in the organic phase is small because only a small number of H_2O molecules are attached in the organic phase, which lowers the entropy.

In the extraction of europium(III) with topo (or Bu_3^nPO) and ASCN (XIIId)¹⁵¹⁶ (where ASCN is the thiocyanate form of Aliquat 336-S, a quaternary ammonium chloride liquid anion exchanger), the extracted species were: $[Eu(NCS)_4 \cdot A \cdot (topo)_n]$ ($n = 2, 3$) and $[Eu(NCS)_4 \cdot A \cdot (Bu_3^nPO)_4]$. The species with R_3PO alone were $[Eu(NCS)_3(topo)_n]$ ($n = 3, 4$) and $[Eu(NCS)_3(Bu_3^nPO)_4]$. The mechanism of synergistic extraction appears to be the replacement of R_3PO by ASCN molecules and the preferential extraction of the bulky ammonium-like species $[M(NCS)_4(topo)_3]^-$ by the cation of the quaternary amine. Equilibrium constants for the synergistic extraction vary in the sequence topo $< Bu_3^nPO \ll tbp$. The strongly basic topo is replaced with more difficulty than the weakly basic tbp . Thus, topo showed antisnergism with ASCN, Bu_3^nPO caused no change and tbp showed

synergism. The synergism appears to be solvent dependent and thus no synergism was observed in *n*-hexane.

The extraction data for system XIIIe¹⁵¹⁷ as a function of effect of solvents is shown in Table 23. The adduct formation constants $K_{S,m}$ are strongly dependent on the diluent, e.g. $K_{S,2} = 15.08$ in pentane and 7.68 in CHCl_3 . The solubility parameter, δ_{org} , of the diluent and $\log K_{S,m}$ are correlated by a linear equation:

$$\log K_{S,m} = 2B\delta_{\text{org}} + \text{constant}$$

where B is a negative constant obtained as the slope of the plot of $\log K_{S,m}$ vs δ_{org} . The extraction constant, $K_{\text{ex},S}$, varies in proportion to $K_{S,m}$ in each diluent and a similar relationship,

$$\log K_{\text{ex},S} = 2B\delta_{\text{org}} + \text{constant}$$

can be written. Generally, $K_{S,m}$ and $K_{\text{ex},S}$ decrease with increasing solubility of the adduct in a solvent, with a few exceptions. The values increase in the order aliphatic diluents $> \text{CCl}_4 >$ benzene and its derivatives $>$ some halogenated diluents. From similar studies on the uranyl system, which forms $[\text{UO}_2(\text{tta})_2(\text{topo})]^{1522}$, $\log K_{\text{ex},S}$ decreases to a lesser extent with increasing δ_{org} and thus separation from europium(III) is difficult in aliphatic diluents, but it is very easy in diluents with large solubility parameters. Hence the choice of solvent is very important not only for synergism but also for separation from other components.

The shift reagent $[\text{Eu}(\text{tta})_3]$ has been used to study the synergistic extraction of rare earths¹⁵²³ by analysing the NMR shifts in the phenylortho-protons of Ph_3PO by its interaction with $[\text{Eu}(\text{tta})_3]$. The concentration dependence of the induced shifts gives the stoichiometry and the stability constant of the adduct, $[\text{Eu}(\text{tta})_3\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$).

TABLE 23. Adduct formation and synergistic extraction constants for the Eu-Htta-topo system (25 °C)^{a,b}

Diluent	S_{org}	$\log K_{S,2}$	$\log K_{\text{ex},S}$
Pentane	7.05	15.08	7.02
Hexane	7.3	14.96	6.85
Heptane	7.4	14.76	6.71
Cyclohexane	8.2	14.46	6.54
Isopropylbenzene	8.5	13.04	4.92
Carbon tetrachloride	8.6	12.88	4.43
Toluene	8.9	12.02	4.01
Benzene	9.15	11.78	4.10
Chloroform	9.3	7.68	-0.74
Chlorobenzene	9.5	11.34	3.00
Dichloromethane	9.7	10.14	1.87
<i>o</i> -Dichlorobenzene	10.0	11.66	3.39
Bromoform	10.5	9.04	0.53

^aFrom ref. 1577.

^bEquations:

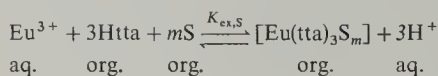
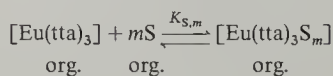


TABLE 24. Extraction data for the lutetium(III)– β -diketone–topo systems^a

$R^1C(O)CH_2C(O)R^2$			
R^1	R^2	Log K	Log β_1
Me	Me	—	4.35
Et	Et	–16.57	4.35
Pr ⁱ	Pr ⁱ	–16.57	4.80
Me	Bu ⁱ	–16.90	4.80
Bu ⁱ	Bu ⁱ	–18.37	4.80
Me	Ph	–15.21	5.25
Me	Naphthalene	–15.06	5.45
Ph	Ph	–15.16	6.15
Me	CF ₃	—	6.25
Ph	CF ₃	–7.69	7.50
2-C ₄ H ₃ S ^b	CF ₃	–6.50	7.25
2-C ₄ H ₃ O ^c	CF ₃	–6.78	7.15
CF ₃	CF ₃	—	6.25

^aAll data from ref. 1520.^b2-Thiophenyl.^c2-Furyl.

Ph₃PO interacts with [Eu(tta)₃] in CDCl₃ in two steps, 1:1 and 1:2 (log β_1 = 7.93, log β_2 = 9.67).

The ternary system XIII revealed that the stability of an adduct of the mixed chelate varies in the order¹⁵¹⁹ [Lu(ba)(bfa)₂] > [Lu(ba)₂(bfa)] > [Lu(ba)(dbm)₂] ≈ [Lu(ba)₂(dbm)]. A detailed study of the extraction of lutetium(III) with a series of β -diketones reveals a number of interesting observations (system XIV, Tables 22 and 24)¹⁵²⁰: (a) β -diketones with a CF₃ group can extract lutetium(III) from a lower pH region owing to the enhanced acidity of the OH groups; (b) β -diketones with bulky groups such as benzoyl, thenoyl and pivaloyl showed high extractability, attributed to the hydrophobic structure of the chelating molecule; and (c) the stability of the topo adducts (log β) increase with increase in log K , indicating that there is no steric hindrance by the terminal groups.

Extraction of lanthanides with R₃PO–pyrazolones and other reagents. Like β -diketones, pyrazolones also constitute an important class of reagents, although they have attracted less attention. Table 25 gives the synergistic systems used for the extraction of lanthanides together with the various types of species extracted. From systems I–VI, it was concluded that (a) the extraction constants showed a maximum at europium or holmium and the change was monotonic with increasing atomic number^{1524,1525}; (b) Hpmop is more selective than Hpmbp (the separation factors with Hpmop were, Pr/Eu 1.33 and Eu/Tb 2.02)¹⁵²⁶; (c) the synergism is attributable to expansion of the coordination sphere and not to replacement of H₂O by topo^{1349,1351}; (d) Hpmbup–topo showed a higher synergic effect than Hpmbp–Bu₃PO (system V)¹⁵³²; (e) the ternary systems also show synergism, e.g. for terbium(III) (system IV)¹⁵²⁸ N-503 enhanced the extraction significantly (log β = 4.01 versus 1.45 when no N-503 was used); and (f) the pyrazolonethione ligand alone gave no detectable extraction in the ranges studied, but the addition of topo resulted in synergistic extraction (system VI)¹⁵²⁹.

When R₃PO-substituted phosphoric acid combinations were used (systems VII–X), the following conclusions were made: (a) in the case of cerium(III) extraction, a large Ce/Am separation factor of 150 was achieved in system VII(a)¹⁵⁰¹; (b) an antagonistic effect was observed in the extraction of dysprosium(III) (VIIb) when excess of topo was

TABLE 25. Extraction of lanthanides with tertiary phosphine oxides-pyrazolones and other synergistic systems

System	Metals extracted	Reagent and medium	Species extracted ^a	Ref.
I	La, Pr, Eu, Ho, Yb	topo (or cmpo) ^b -Hpmtp-CHCl ₃ ; ClO ₄ ⁻	[MA ₃ L ₂]	1524, 1525
II	Pr, Eu, Yb	topo-Hpmop-CHCl ₃ ; acidic	[MA ₃ L]	1526
III	Nd	(a) topo-Hpmbp; acidic (b) Bu ₃ PO-Hpmbp-PhMe; HClO ₄	[NdA ₃ L] —	1349, 1351 1527
IV	Tb	topo-Hpmbp-N 503 ^c -PhMe	[TbA(N 503) ₂ L ₃]	1528
V	Yb	Bu ₃ PO-Hpmbp-PhMe	[YbA ₃ L _n] (n = 1, 2)	1532
VI	Eu	topo-HA ^d -C ₆ H ₆ ; HClO ₄	[EuA ₂ (HA)L ₂ (ClO ₄)]	1529
VII	Ce	topo-H2dehp; lactic acid	[CeA ₃ L ₂]	1501
	Dy	topo-H2dehp-kerosene; HCl	—	1530
VIII	Ln	R ₃ PO-H2dehp; NO ₃ ⁻ (R = 1-methylheptyl)	[MA ₃], [M(NO ₃) ₃ L ₃]	1531
IX	Tm	topo-HA-PhMe; HCl (HA = mono-2-ethylhexyl-phosphoric acid)	—	1533
X	Ln	topo-HA ^e ; Cl ⁻	[MA ₃ (HA)(topo)]	1534
XI	La, Pr, Eu, Yb	topo-HA-CCl ₄ ^f	[M(OH)A ₂ L ₂]	1535
XII	La, Pr, Eu, Yb	topo-HA-CCl ₄ ^g ; Cl ⁻	[MCIA ₂ L ₃]	1536
XIII	Eu	(a) topo-HA-CHCl ₃ ^h (b) topo-HA-CHCl ₃ ⁱ	[EuA ₃ L ₂] [EuA ₂ (HA)L _n]	1537 1538
XIV	Ln	R ₃ PO-nta-deta ^j (R = isoamyl)	—	1539
XV	Pm	topo-HA-CHCl ₃ ⁱ	[PmA _{1.5} (HA) _{1.5} L _n]	1538
XVI	Eu	Ph ₃ PO-H ₂ Sal-C ₆ H ₆ (or <i>n</i> -hexane) ^k	[Eu(HSal) ₃ L ₂]	1540

^a HA represents pyrazolones or other similar reagents.^b cmpo = octylphenyl (*N,N*-diisobutylcarbamoylmethyl)phosphine oxide.^c N 503 = *N,N*-dimethylheptylacetamide.^d HA = 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-thione.^e HA = bis(2,4,4-trimethylpentyl)phosphoric acid.^f HA = 2-(3,5-dibromo-2-pyridylazo)-5-diethylaminophenol.^g HA = 2-(2-pyridylazo)-4-nonylphenol.^h HA = 1-nitroso-2-naphthol.ⁱ HA = *N*-benzol-*N*-phenylhydroxylamine.^j NTA = nitroacetic acid; deta = diethylenetriaminepentaacetic acid.^k H₂Sal = salicylic acid.

used¹⁵³⁰; (c) system VIII showed a lack of mixed chelates, an observation against the normal trend¹⁵³¹; and (d) system IX promises¹⁵³³ interesting mutual and group separations of f-block elements as the trend in their extraction shows: Tm > Y >> Eu > Am. Extraction with substituted phenols suggests that the separation factors for the heavier lanthanide elements become large; they are the highest to date (system XII)¹⁵³⁶. Additionally, the species are different to those normally observed. System XIIIb revealed that extraction decreases in the order topo < tbp > bipy, a behaviour against the common trend¹⁵³⁸. Similarly, system XIV shows that an amine reagent can be suitable for the separation of the cerium sub-group¹⁵³⁹. The extraction of europium(III) from nitrate solutions with trioctylammonium nitrate, {Oct₃NH}(NO₃)¹⁵⁴¹, forms the species

$\{R_3NH\}[Eu(NO_3)_4]$, which reacts with R_3PO ($R = Ph, n\text{-octyl}$) in benzene to form $[Eu(NO_3)_4L]^-$. However, the exact nature of the species requires further investigations.

Actinides. Most of the extraction studies reported for the actinides deal with Th, U, Pu and TPE elements. Only a few investigations on the other actinide elements have been reported. Uranium is the single most studied element among f-block elements, with europium and americium occupying second and third positions respectively.

Actinium. Actinium(III) was extracted from 8M LiCl with topo as $Li_2[AcCl_5L_2]$ and the recovery was more than 95%¹⁵⁴².

Thorium. Topo (in cyclohexane) extracted thorium(IV) from HCl, HNO_3 ¹⁵⁴³ or Cl^- solutions¹³³⁷. A single extraction quantitatively removed thorium(IV) from 1M HNO_3 or 7M HCl; extractions from acids at other concentrations were low. Extraction from H_2SO_4 or H_3PO_4 solutions was poor and in the case of $HClO_4$ solution two immiscible phases formed, complicating the recovery of thorium. This method (topo- C_6H_{12}) was useful in the quantitative recovery of thorium from monazite and other raw materials after their leaching with H_2SO_4 or H_3PO_4 . Rare earths do not interfere, but zirconium(IV) is co-extracted with thorium(IV). The nature of the extracted species depended on the anion, being $[ThX_4L_3]$ for $X = Cl, NO_3$ ^{1543,1544} and $[ThX_4L]$ for $X = Br$ ¹⁵⁴⁵, but was independent of the organic solvent (PhMe, Me_2CO , etc.) Interestingly, from bromide solutions, the separation of thorium from uranium was facile. Other studies of the extraction of thorium include topo in dodecane from aqueous $LiNO_3$ solution¹⁵⁴⁶ and R_3PO ($R = isopentyl$, etc.) in C_6H_6 , CCl_4 , $CHCl_3$ or heptane^{1547,1548}. The species extracted were of the type $[Th(NO_3)_4L_n]$ ($n = 1-4$).

Topo-Htta in different organic solvents (e.g. hexane)^{49,1318,1319,1505,1549} synergistically extracted thorium from HCl as $[Th(tta)_4L]$. Whereas topo enhanced extraction, the addition of other oxygen donors such as ethanol and isobutanol lowered synergism due to the replacement of coordinated topo by these alcohols. The Htta- Bu_3^oPO (or Ph_3PO) also synergistically extracted thorium forming the species: $[Th(tta)_4(Ph_3PO)]$, $[Th(tta)(NO_3)_3]$ ^{49,1550}. With Bu_3^oPO , the synergism was attributed to the tendency of thorium to acquire 8-coordination and not to the replacement of H_2O by Bu_3^oPO . Whereas topo-Hdbm in C_6H_6 showed no synergism¹³¹⁰, topo-LIX 54 (a β -diketone, HA) in C_6H_6 showed quantitative extraction of thorium (as ThA_4L) from acidic solutions (pH 2.8)¹⁵⁵¹.

Thermodynamic studies on the extraction of thorium^{1349,1351} by topo-Hpmbp suggested that synergism was associated with the replacement of solvate water by an adduct molecule with no change in the coordination number. Other extraction systems are topo-benzoic acid in CCl_4 ¹⁵⁵² and topo-quinolin-8-ol¹⁵⁵³. The topo-benzoic acid system offers an easy method for the separation of Th from La, Gd, Y or Tb.

Protactinium. Ph_3PO in $CHCl_3$ separated protactinium(V) from thorium(IV) in HNO_3 solution¹⁵⁵⁴. An analogous arsenic ligand, Ph_3AsO , could also be used. Another study described the extraction of protactinium(V) from a variety of acids such as HF, $HClO_4$, oxalic or tartaric acid; extraction was highest from $HClO_4$ ¹³⁶⁴.

Uranium. Uranium extraction occurs essentially in the hexavalent state and only a few studies have dealt with the tetravalent state. The work reported is split into various parts. A separate section describes the recovery of uranium from wet-process phosphoric acid solutions and ores.

Extraction of uranium with R_3PO alone. In a number of investigations the use of R_3PO alone for the extraction of uranium(VI) from various media was studied. Topo has been most commonly used for the extraction of uranium(VI). It was observed that the nature of the extracted species remained more or less the same when the aqueous phase contained different anions (Cl^- , NO_3^- , etc.). The most common species was $[UO_2X_2(R_3PO)_2]$ ($X = Cl, NO_3, ClO_4, \frac{1}{2}SO_4$; $R = n\text{-octyl}, n\text{-butyl}$, etc.) and the organic solvents commonly used were cyclohexane, toluene, benzene, $CHCl_3$ or CCl_4 ^{1326,1338,1356,1548,1555-1561}.

The formation of species of the type $[\text{UO}_2(\text{NO}_3)(\text{ClO}_4)(\text{Bu}_3^{\text{n}}\text{PO})]^{1560}$, $[\text{UO}_2(\text{NO}_3)_2(\text{topo})]^{1564}$, $[\text{UO}_2(\text{SO}_4)_2\text{L}_2]\cdot\text{H}_2\text{SO}_4$ ($\text{L} = \text{topo}$, $\text{Bu}_3^{\text{n}}\text{PO}$)¹⁵⁵⁷ has also been observed.

Some other conclusions on and applications of the use of R_3PO for the extraction of uranium(VI) are as follows: (a) topo in cyclohexane¹⁵⁶² or topo in molten naphthalene (at 80 °C)¹⁵⁶³ quantitatively separated uranium from several elements present in HNO_3 solutions¹⁵⁶³; (b) topo in toluene separated uranium, present in urine, with 90.5% recovery; Na, K, Ca, Mg and Fe did not interfere¹⁵⁶⁴; (c) recovery of uranium from aquatic sediments¹⁵⁶⁵ and that of uranium and thorium (in traces from rare earths¹⁵⁶⁶) using topo in cyclohexane; (d) recovery of uranium from uranium liquors with R_3PO ($\text{R} = n\text{-butyl}$, $n\text{-octyl}$) or Ph_3PO ¹⁵⁶⁷; (e) separation of uranium(VI) from bismuth (1:10 000 ratio) with tris(2-ethylhexyl)phosphine oxide in cyclohexane from NaNO_3 solution (pH 2.5–3.0)¹⁵⁶⁸; (f) separation of uranium(VI) from rare earths dissolved in a fused NaSCN-KSCN eutectic with topo–tetralene¹⁵⁶⁹; (g) topo in toluene extracted $\text{U}^{234,238}$ from a sample of Ra^{226} in HClO_4 solution¹⁵⁷⁰; (h) extraction was high from HNO_3 or HCl and poor from H_2SO_4 or H_3PO_4 ¹⁵⁵⁶; (i) the extractability of uranium(VI) from $\text{HNO}_3\text{--H}_2\text{SO}_4$ with R_2MePO ($\text{R} = \text{HOCH}_2\text{—}$) in benzene was much higher than that with tbp ¹⁵⁷¹; however, thorium is co-extracted; and (j) UO_2^{2+} was synergistically extracted when Oct_3N was added to topo for extraction from aqueous $(\text{NH}_4)_2\text{SO}_4$ ¹⁵⁷²; the extracted species was identified as $(\text{R}_3\text{NH})_2[\text{UO}_2(\text{SO}_4)_2(\text{topo})]$.

The only investigation into the extraction of uranium(IV) with phosphine oxides is its extraction from HCl with topo in cyclohexane¹⁵⁷³. It was observed that an increase in temperature (10–45 °C) led to a higher transfer of UCl_4 from the aqueous to the organic layer. The activation energy was 45.2 kJ mol^{−1} for topo and 38.5 kJ mol^{−1} for tbp .

Extraction of uranium with R_3PO – β -diketones. Only R_3PO – Htta ($\text{R} = \text{Bu}^{\text{n}}$, $n\text{-octyl}$, Ph) combinations have been used for the synergistic extraction of uranium. The extraction of uranium with R_3PO – Htta in benzene, CHCl_3 , etc., from HCl or HNO_3 formed $[\text{UO}_2(\text{tta})_2\text{L}_n]$ ($\text{L} = \text{topo}$, $\text{Bu}_3^{\text{n}}\text{PO}$ or Ph_3PO ; $n = 1\text{--}3$)^{49,449,1318,1319,1504,1574–1576} in the organic layer. The extraction with Htta alone was poor and addition of R_3PO enhanced the extraction^{1575,1576} by a factor of 10^4 . The K_{ex} values for the extraction of uranium(VI) from HCl with R_3PO – Htta varied in the order $\text{topo} \gg \text{Bu}_3^{\text{n}}\text{PO} > \text{tbp}$ ($K_{\text{ex}} = 4.1 \times 10^8$, 3.5×10^3 and 3.0×10^2 , respectively)^{1318,1319}. Further, the highest extraction was observed when the organic solvent was cyclohexane. Studies on the effect of temperature¹⁵⁷⁸ on extraction from HCl with Htta –topo revealed that a 10 °C rise in temperature lowered the extraction by 20–30% whereas it remained unaffected with Htta alone. The extraction of uranium(IV) with Htta – Ph_3PO has been reported and the species $[\text{U}(\text{tta})_4\text{L}]$ was formed¹⁵⁷⁷. The formation constants of 1.24×10^4 and 2.67×10^5 for $[\text{U}(\text{tta})_4\text{L}]$ and $[\text{UO}_2(\text{tta})_2\text{L}]$, respectively, revealed a higher extraction of uranium(VI) than uranium(IV).

Extraction of uranium with R_3PO –pyrazolones. A series of combinations of pyrazolones and topo in the usual solvents were used for the extraction of uranium(VI). The extracted species was $[\text{UO}_2\text{A}_2\text{L}]$ ($\text{HA} = \text{Hpmbp}$ ^{1349,1351,1574,1579}; $\text{Hpmbcp} = 1\text{-phenyl-3-methyl-4-(2'-chlorobenzoyl)pyrazol-5-one}$ ¹⁵⁸⁰; HPMTFP ¹⁵⁸¹; $\text{Hbmppt} = 4\text{-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione}$ ¹⁵⁸²). Some conclusions that may be drawn from these studies include (a) the synergism was attributed to the replacement of solvate water by the added ligand^{1349,1351}; (b) adduct formation was enthalpy and entropy stabilized^{1579,1581}; (c) Hpmbcp –topo showed higher extraction than Hpmbp –topo¹⁵⁸⁰; (d) the extraction properties of Hpmtfp –topo were similar to those of Hpmap ¹⁵⁸¹; and (e) the extraction could be followed by a computer-controlled flow-injection system¹⁵⁸².

A ternary system, Hpmbp – Htta –topo, extracted UO_2^{2+} as $[\text{UO}_2(\text{pmbp})(\text{tta})\cdot(\text{topo})]^{1574}$. This ternary complex is stable, but no improvement in extraction over

Hpmbp-topo was achieved although it showed a higher extraction than Htta-topo. Uranium(IV) was extracted as $[\text{UA}_3\text{CIL}]$ from HCl with Hpmbp-topo in CHCl_3 ¹⁵⁸³.

Extraction of uranium with $\text{R}_3\text{PO}-\text{H}_2\text{dehp}$ (and related compounds). The synergistic extraction of uranium(VI) was carried out using H_2dehp (or related compounds) and R_3PO combinations ($\text{R} = \text{Bu}^n$, *n*-octyl, Ph, isoamyl) as follows: topo- H_2dehp (HA) from $\text{HNO}_3-\text{H}_2\text{SO}_4$ solution¹⁵⁸⁴, $\text{R}_3\text{PO}-\text{H}_2\text{dehp}$ ($\text{R} = \text{Bu}^n$, Ph, isoamyl) from sulphate medium¹⁵⁸⁵⁻¹⁵⁸⁸ and $\text{R}_3\text{PO}-(\text{R}'\text{O})_2\text{P}(\text{O})(\text{OH})$ ($\text{R} = n\text{-butyl}, n\text{-octyl}$; $\text{R}' = n\text{-butyl}$)^{1563, 1589, 1590} from H_2SO_4 solution and topo- $(n\text{-OctO})(\text{Bu}^n\text{O})\text{P}(\text{O})(\text{OH})$ ^{1591a}. The extracted species were normally $[\text{UO}_2\text{A}_2(\text{HA})_2(\text{R}_3\text{PO})]$ ^{1584, 1586, 1590} and $[\text{UO}_2\text{A}_2(\text{R}_3\text{PO})]$ ^{1585, 1589} {HA = H_2dehp or $(\text{R}'\text{O})_2\text{P}(\text{O})\text{OH}$, etc.}. Some other comments are: (a) H_2dehp also extracts HNO_3 to some extent¹⁵⁸⁴; (b) the order of synergistic enhancement appears to be $\text{topo} > (\text{isoamyl})_3\text{PO} > \text{Bu}_3^n\text{PO} > \text{Ph}_3\text{PO} > \text{tbp}$ ^{1563, 1585, 1587-1589}; (c) $\text{Bu}_3^n\text{PO}-\text{H}_2\text{dehp}$ was demonstrated as suitable for the recovery of uranium(VI) from low-grade uranium liquors¹⁵⁸⁸; (d) in CCl_4 , synergism was higher than that in *n*-hexane^{1563, 1589}; and (e) the synergistic extraction was attributed to an adduct formation and not to the replacement of HA molecules¹⁵⁹⁰.

Extraction of uranium with R_3PO -organic acids. Topo fatty acids/aromatic acids have also been used for the extraction of metals. Here the acids act as synergists, although antisnergism was also observed under certain experimental conditions. For instance, in the extraction of uranium(VI) with topo in CCl_4 from aqueous perchlorate medium^{1591b}, benzoic acid acted as a synergist up to a certain acid concentration (0.01 M), but at higher acid concentrations, topo interacts with the acid, thus lowering the topo concentration; the extracted species is $[\text{UO}_2(\text{ClO}_4)(\text{PhCOO})(\text{topo})]$.

Topo- $\text{PhCOOH}-\text{CCl}_4$ offers an excellent method in acidic solution (pH 2.5-3.5) for the separation of uranium from rare earths, which are virtually unextracted by this combination¹⁵⁹² (separation factor 800-2500 for U/rare earths). This method was used for the determination of uranium in rocks and minerals. Topo-salicylic acid showed synergistic extraction of UO_2^{2+} from aqueous NO_3^- , Cl^- or ClO_4^- solutions¹⁵⁹². By contrast, PhCOOH showed synergism up to a certain concentration of NO_3^- ions (and for $> 0.1 \text{ M NaNO}_3$, it showed antisnergism because the benzoate ions cannot compete with NO_3^- in their coordinating ability to uranium(VI). Since the salicylic acid acts as a chelating agent, and forms stable chelates, no antisnergism was observed even at high NO_3^- concentration. There was no extraction of UO_2^{2+} from sulphate solutions.

In the extraction of uranium(VI) with topo in CCl_4 from dilute HNO_3 (pH 1-5)^{1593, 1594} in the presence of aromatic monocarboxylic acids, it was demonstrated that the presence of salicylic acid showed the highest extraction. The method was suitable for the separation of uranium(VI) from rare earths, Y, Th, Zr, Ir and Fe, followed by direct spectrophotometric determination. These elements interfere when uranium(VI) is determined with arsenazo III reagent. At pH ≈ 5 , the *D* values decreased in the order salicylic acid (693) $>$ phenylpropionic acid (363.0) $>$ *o*-chlorobenzoic acid (223) $>$ benzoic acid (93.9) $>$ hydroxycinnamic acid (37.4) $>$ *trans*-cinnamic acid (32.9) $>$ *o*-nitrobenzoic acid (8.4). The action of the acids varied from antagonistic below pH 1.8 to synergistic above pH 2.0. The synergistic effect depends linearly on the p*K* values except for salicylic acid. At low pH, acids are protonated and then interact with topo, lowering its activity when the pH is increased. Organic acids dissociate and transfer to the aqueous phase, forming complexes with UO_2^{2+} .

A series of fatty acids (valeric acid, $\text{Me}(\text{CH}_2)_3\text{COOH}$; capric acid, $\text{Me}(\text{CH}_2)_8\text{COOH}$; pentadecanoic acid, $\text{Me}(\text{CH}_2)_{11}\text{COOH}$; palmitic acid, $\text{Me}(\text{CH}_2)_{10}\text{COOH}$; and margaric acid, $\text{Me}(\text{CH}_2)_{15}\text{COOH}$) acted as synergists (pH > 1.9) during the extraction of UO_2^{2+} with topo in different organic acids¹⁵⁹⁵. Since the dissociation constants of the acids are similar, the corresponding synergistic effect was also similar. An increase in pH increased the synergism, as expected. The chain length did not have any extra effect on

the synergism. The D values decreased in the sequence $C_6H_6 > C_6H_{12} > CCl_4$. The behaviour of xylene and toluene was similar to that of cyclohexane.

Recovery of uranium from wet-process phosphonic acid/ores. The recovery of uranium from wet-process phosphonic acid solutions and ores has received special attention. For effective recovery, uranium must be present in oxidation state VI, and therefore any uranium(IV) present has to be converted into uranium(VI) using an oxidizing agent. Topo- H_2dehp is commonly employed for extraction; however, a few other reagents have also been used.

A number of workers have described the extraction of uranium(VI) from wet-process phosphonic acid solutions of phosphate ores using H_2dehp -topo¹⁵⁹⁶⁻¹⁶⁰⁸. Some important conclusions drawn are (a) typical yields in uranium recovery from H_3PO_4 and phosphate ores are 95 and 80.8%, respectively¹⁶⁰⁷; however recoveries of >98% and concentration of uranium in H_3PO_4 from $\sim 60 \text{ mg l}^{-1}$ to 7 g l^{-1} was achieved in another study¹⁶⁰⁸; (b) the extracted species was identified as $[UO_2A_2(\text{topo})]^{609}$ ($HA = H_2dehp$); (c) iron present in the uranium-loaded organic layer was removed by placing it in contact with a stream of 30% P_2O_5 - H_3PO_4 ¹⁵⁹⁶⁻¹⁵⁹⁸; (d) the extraction decreased on changing the solvent in the order kerosene > hexane > C_6H_6 > CCl_4 ; and (e) the recovery of uranium from the Itataia wet-process H_3PO_4 involved first reduction of uranium(VI) to uranium(IV) followed by its extraction with octylpyrophosphoric acid in kerosene^{1602,1603,1605,1606}. The organic layer was then stripped with concentrated H_3PO_4 and the uranium(IV) converted to uranium(VI) with an oxidizing agent followed by re-extraction with H_2dehp -topo. The extract was stripped with $(NH_4)_2CO_3$ and the uranium(VI) recovered as a commercial concentrate.

Other reagents used for uranium(VI) extraction are topo and a mixture of H_2dehp and mono- and di-(nonylphenyl) phosphate in kerosene (I)¹⁶¹⁰; topo- $(R_2CHO)_2P(O)(OH)$ ($R = BuOCH_2$) in kerosene (II)^{1611,1612}; dialkylphosphoric acid and mixed phosphine oxides (III)¹⁶¹³; and R_3PO ($R = \text{alkyl}$)¹⁶¹⁴ and bifunctional chelating agents incorporating a phosphine oxide and phosphoric acid diester, *O*-methylhexylphosphine oxide-*O*'-2-ethylhexylphosphoric acid (IV)¹⁶¹⁵. System I gives a recovery of uranium(VI) present to the extent of 0.00092% in H_3PO_4 with >90% efficiency¹⁶¹⁶. System II was superior to H_2dehp -topo ($D = 14.0$ versus 4.2). Iron(III) present showed poor extraction ($D = 0.40$ versus 0.04). Similarly, system III showed a greater extraction efficiency than H_2dehp -topo ($K_{ex} = 31.5$ versus 25.0). System IV appears to be an excellent and superior alternative to H_2dehp -topo for the extraction of uranium(VI)¹⁶¹⁵.

Neptunium. Investigations on the extraction of neptunium(IV) from HNO_3 have involved (a) Ph_3PO in CCl_4 , C_6H_6 or $CHCl_3$ ¹⁶¹⁷, (b) $Hpmbp$ -topo in C_6H_{12} ¹⁶¹⁸ and (c) $Htta-Bu_3^nPO$ ¹⁵⁵⁰. Ph_3PO extracted neptunium as $[Np(NO_3)_4(Ph_3PO)]$ whereas with other reagents the extracted species were $[Np(tta)_2(NO_3)_2(Bu_3^nPO)_2]$, $[Np(tta)_3(NO_3)(Bu_3^nPO)]$ and $[Np(tta)_4]$. $Hpmbp$ -topo could separate neptunium(V) the transplutonium elements, uranium(VI) and the rare earths. In the last two synergistic systems, the synergism was attributed to the ability of neptunium to acquire 8-coordination and not to the replacement of H_2O by topo.

Plutonium(IV, VI). Topo in hexane extracted plutonium(IV) quantitatively (99.5%) from HNO_3 over a range of concentrations (0.3–11.0 M)¹⁶¹⁹; however, the extraction of plutonium(VI) required a lower acidity (0.3–0.7 M HNO_3). Both plutonium(IV) and plutonium(VI) were readily separated from plutonium-amerium mixtures. From HCl solutions, the extraction of both of these was quantitative at 5 M HCl but poor at <5 M HCl. The formation of species of the type $[PuX_4L_2]$ or $[PuX_6L_2]$ ($X = Cl, NO_3$) was suggested.

Plutonium(IV) was extracted from uranium fission products in the presence of $NaNO_3$ using Bu_3^nPO in CCl_4 ¹⁶²⁰ and from HNO_3 solutions with a range of phosphine oxides, $R_2R'PO$ ($R, R' = Me$ to C_8H_{17} , Ph), and observations similar to those for

zirconium–niobium were noted¹³⁶⁶. Use of $\text{Bu}_3^{\text{n}}\text{PO}$ with H_2dehp gave a 50-fold enhanced extraction of plutonium(IV) and plutonium(VI) than with either of these reagents separately¹⁵⁸⁸. $\text{Bu}_3^{\text{n}}\text{PO}$ –Htta in hexane extracted plutonium(IV) synergistically from HNO_3 solutions¹⁵³⁰. Here the synergism was attributed to the ability of the actinides to achieve a coordination number of eight and not to the replacement of H_2O by $\text{Bu}_3^{\text{n}}\text{PO}$ or similar molecules. The formation of $[\text{Pu}(\text{tta})_2(\text{NO}_3)_2(\text{Bu}_3^{\text{n}}\text{PO})_2] \cdot [\text{Pu}(\text{tta})_3(\text{NO}_3)(\text{Bu}_3^{\text{n}}\text{PO})]$ and $[\text{Pu}(\text{tta})_4]$ was observed.

Topo– H_2dehp in kerosene was used to extract plutonium quantitatively from H_2SO_4 solutions (containing NaNO_3 or HNO_3) obtained by acid digestion of plutonium-contaminated waste free from sulphate¹⁶²¹. The presence of H_3PO_4 in the feed did not influence the extraction of plutonium, but uranium(VI), if present, is also extracted. Stripping of the organic phase with $(\text{NH}_4)_2\text{CO}_3$ or 1 M HNO_3 transfers only plutonium to the aqueous layer, leaving uranium(VI) in the organic phase. The extraction of americium(III) as noted above was poor ($K_{\text{ex}} < 1\%$).

Transplutonium elements (TPE). The yield of TPE from the irradiation of plutonium is usually a few percent of the target material. The atom ratio of the fission products, TPE/lanthanides, is Ca 1:10. The separation of lanthanide group elements from TPE is difficult owing to the similarity of their chemical properties. The studies described below provide various methods for the separation of TPE from one another or other elements.

Extraction of TPE with R_3PO alone. Topo in xylene showed poor extraction of americium(III) from HCl but the extraction increased by a factor of 10^5 from LiCl solutions¹⁴⁹⁷. An increase in the concentration of LiCl lowers the water activity, which in turn leads to higher ligation of americium(III) by topo. The extracted species was $[\text{AmCl}_3(\text{topo})_n]$ ($n = 1, 3$, depending on the LiCl concentration). In another study¹⁶²², the separation factors for californium and einsteinium from americium and curium increased with increase in the number of the halide ions in the inner-sphere coordination to the metal with a simultaneous decrease in the degree of complexation in the aqueous phase. Bromide ions showed less inner-sphere coordination than chloride ions.

Topo (in *n*-octane) showed a similar extraction of americium(III) and curium(III) from aqueous nitrate medium ($K_{\text{ex}} = 1.5 \times 10^7 \text{ l}^3 \text{ mol}^{-3}$ for Cm and $2.9 \times 10^7 \text{ l}^3 \text{ mol}^{-3}$ for Am)¹⁶²³. $\text{Bu}_3^{\text{n}}\text{PO}$ in benzene or topo in xylene also extracted curium and americium from aqueous nitrate or HNO_3 solutions^{1498,1499,1623}. The extracted species appeared to be $[\text{M}(\text{NO}_3)_3\text{L}_3]$. It was observed that at constant NO_3^- concentration, the value of D was higher at lower acid concentration. Addition of tbp to the topo solution enhanced the extraction of americium(III) from concentrated HNO_3 ¹⁶²⁴. Tbp was labelled as a modifier. Similar behaviour was noted in the extraction of americium(III) with diaryldialkylcarbamoylmethylphosphine oxide¹⁶²⁵.

The extraction of the TPE (Am, Cm, Cf) from nitrate media with trioctylamine nitrate is enhanced by the addition of topo or Ph_3PO in benzene¹⁵⁴². $(\text{R}_3\text{NH})[\text{M}(\text{NO}_3)_4\text{L}]$ and $[\text{M}(\text{NO}_3)_5\text{L}_n]^{2-}$ ($n = 1, 2$) were suggested to be the extracted species. The behaviour of triarylamine–topo for americium, curium, and promethium was similar¹⁶²⁶. The extraction of americium(III) or curium(III) with *N*-benzoyl-*N*-phenylhydroxylamine in CHCl_3 was enhanced after the addition of R_3PO , but the synergistic extraction decreased in the sequence $\text{tbp} > \text{topo} > \text{bipy}$, which is the reverse of the basicity of these donor ligands¹⁵³⁹.

The extraction of americium(III) from 1 M NH_4SCN solution with topo or $\text{Bu}_3^{\text{n}}\text{PO}$ in xylene was increased when a liquid anion exchanger, ASCN (ASCN = thiocyanate form of a quaternary ammonium chloride, Aliquat 336)^{537,1516,1627}, was added. The synergic species were $[\text{Am}(\text{NCS})_4 \cdot \text{A}(\text{topo})_m]$ ($m = 2, 3$) and $[\text{Am}(\text{NCS})_4 \cdot \text{A}(\text{Bu}_3^{\text{n}}\text{PO})_3]$. The separation factors for Am/Eu increased from 2.9 to 6.0 for topo and from 3.3 to 6.2 for $\text{Bu}_3^{\text{n}}\text{PO}$ on addition of ASCN. The greater participation of 5f orbitals in bonding to

TABLE 26. Extraction of metals with bis(tertiary phosphine oxides)

R ₂ P(O)(CH ₂) _n P(O)R ₂				
R	n	Metal	Ref.	
<i>d-Block elements</i>				
<i>n</i> -Octyl	2	Sc(III) ^a	1633, 1634	
<i>n</i> -Octyl	2	Fe(III) ^a	1633–1636	
Ph	1	Fe(III) ^a	1633–1636	
Ph	2–4, 6	Co(II) ^b	1637	
<i>n</i> -Octyl, Ph	1	Y(III) ^a	1638, 1639	
<i>n</i> -Hexyl	1	Zr(IV), Hf(IV) ^{a,c,d}	1640–1642	
<i>n</i> -Octyl	1–6, 8, 10	Mo(VI), Ga(III) ^e	1324, 1325, 1382	
<i>n</i> -Hexyl	1	Nb(III), Ta(III) ^{a,d}	1643	
<i>n</i> -Octyl	2	Ca(II), Al(III) ^c	1633	
<i>n</i> -Hexyl	1	Alkaline earth metals ^c	1644	
<i>f-block elements</i>				
<i>n</i> -Octyl	4	Ce(III) ^{a,f}	1633, 1644	
<i>n</i> -Octyl, Ph	1	Nd(III) ^a	1639	
Ph	2–4, 6	Pm(III), Eu(III), Tm(III) ^b , Am(III), Cm(III), Cf(III)	1637, 1645–1647	
<i>n</i> -Hexyl	1–4	Pr(III), Nd(III), Sm(III) ^{a,c,e} , Tm(III), U(VI)	1648–1654	
Ph, <i>n</i> -octyl	1	Eu(III), Am(III) ^c	1655, 1656	
Ph	1	Ce(III), Eu(III), Am(III), Cm(III) ^g	1657	
Ph, etc.	1	Eu(III), Am(III), Cm(III), Bk(III), Cf(III), Es(III), U(VI) ^a	1658, 1659–1667	
Ph, <i>n</i> -octyl	1	Eu(III), Am(III) ^{a,c}	1534, 1668	
<i>n</i> -Hexyl, 2-ethylbutyl	1	Th(IV) ^a	1669	
<i>n</i> -Butyl, <i>n</i> -octyl, Ph	1,2	Pu(III), Pu(IV), Pu(VI), Pa(V) ^a	1661, 1662	
Ph, <i>n</i> -butyl, <i>n</i> -octyl	1–3	Am(III) ^a	1636, 1670	
Ph	1, 4, 5	Am(III), Cm(III), Cf(III) ^h , etc.	1671	
Ph, <i>n</i> -octyl	2	U(VI) ^a	1672, 1673	
Miscellaneous ligands				
Reagent	R	n	Metal	Ref.
Ph ₂ P(O)CH ₂ P(O)R ₂ (R = octyl)	—	—	Eu(III), Am(III) ^c	1655, 1656, 1674
<i>cis</i> - and <i>trans</i> -R ₂ P(O)CH=CHP(O)R ₂	Ph	—	Mo(VI) ^a	1675
	Ph, <i>p</i> -Tol	—	Eu(III), Am(III), Pu(III), Pu(IV), Pu(VI), Pa(V), U(VI) ^{a,c}	1660–1662, 1668, 1673, 1676, 1678
Ph ₂ P(O)C≡CP(O)Ph ₂	—	—	Pu(III), Pu(IV), Pu(VI), Pa(V), U(VI)	1660, 1662, 1673
Ph ₂ P(O)CH(R')P(O)Ph ₂ (R' = Cl, allyl etc)	—	—	Eu(III), Am(III), Cm(III) ^{a,c} , Bk(III), Cf(III), Es(III), Eu(III), U(VI)	1658, 1668
<i>p</i> -C ₆ H ₄ [CH ₂ P(O)R ₂] ₂ ⁱ	<i>n</i> -Octyl	—	Mo(VI), Ga(III)	1324, 1325, 1382
(continued)				

(continued)

TABLE 26. (continued)

Miscellaneous ligands				
Reagent	R	<i>n</i>	Metal	Ref.
<i>o</i> -, <i>m</i> -, <i>p</i> -C ₆ H ₄ [CH ₂ P(O)Ph ₂] ₂	—	—	Eu(III), U(VI), TPE, Pu(IV), U(IV), etc.	1678, 1679
R ₂ P(O)(CH ₂) _{<i>n</i>} P(O)R ₂ -HA:				
HA = Hbfa, Hpvtfa	Ph	1,2	Zn(II)	1472, 1473
Hbfa	Ph	1,2	Eu(III) ^c	1473, 1515, 1680
Htta	<i>n</i> -Hexyl	1,3,4	Eu(III) ^e	1473, 1515, 1680
Htta	Ph	2	Ln(III) ^b (except Ce, Pm, Er, Lu)	1681
Hpmtfp	Ph	1	La(III), Pr(III), Eu(III) ^c , Ho(III), Yb(III)	1524, 1525
Hpmbp	Ph	1	Am(III) ^a	1677

^a HNO₃.^b LiNO₃-KNO₃ (eutectic, 160 °C).^c HClO₄.^d H₂SO₄.^e HCl.^f HNO₃-H₃DO₄.^g H₃PO₄.^h NaNO₃.ⁱ *p*-xylene- $\alpha\alpha'$ -diylbis(di-*n*-octylphosphine oxide).

americium as compared with europium appears to be responsible for this difference. Americium(III) and curium(III) were extracted as [M(tta)₃(topo)₂] from 0.01 M HCl with Htta-topo in different organic solvents^{1318,1319}. The highest extraction was found with cyclohexane as the diluent and the lowest with CHCl₃. Further, the extraction constant (*K*_{ex}) decreased in the order topo > Ph₃PO > tbp (3320, 7.0 and 0.11, respectively). Htta-Bu₃PO and Hdbm-topo have also been used for the synergistic extraction of americium(III)^{1310,1514}.

Htta-topo in cyclohexane has been exploited for the separation of traces of americium(III) from other rare earths or actinide congeners in HNO₃ media¹⁶²⁸. The method involved prior oxidation of americium(III) to americium(V) using aqueous peroxodisulphate solution. Americium(V) remained in the aqueous phase, whereas the other elements (e.g. Ce, Eu, Cm, Pm) were extracted. Interestingly, the Cm/Am separation factor depended on the concentration of the oxidant, being 2187 for 0.05 M (NH₄)₂S₂O₈ vs 389 for 0.25 M (NH₄)₂S₂O₈. This decrease in the separation factor was attributed to the coordination of curium(III) by the peroxodisulphate ions. The *D* values for the elements extracted decreased in the order Cm > Ce > Pm > Eu (105, 89.5, 76.3 and 63.7, respectively). The separation of americium(III) from Ce, Eu, U, Np, Pu, Cm, Bk and Cf was effected with Hpmbp-topo in C₆H₁₂¹⁶²⁹ in a similar way to that described for Htta-topo¹⁶²⁸. The extraction of americium(III), curium(III), californium(III) and berkelium with Hpmbp-R₃PO varied with R in the sequence^{1630,1631} topo > Ph₃PO > Bu₃PO > Ph₃PS. A comparative study^{1631,1632} of the extraction of TPE with β -diketones and pyrazolones along with topo showed an extraction sequence Hbfa < Htta < Hpmdbp < Hpmbp. Interestingly, the extraction of americium(III) from HClO₄ by 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-thione (HA) in

benzene was undetectable; however, the addition of topo led to the synergistic extraction as $[\text{AmA}_3(\text{topo})_2]$ with a selectivity of 68 for americium over europium¹⁵²⁹. Finally, mono-2-ethylhexylphosphoric acid–topo in toluene extracted americium(III) from HCl, but the synergism was lower than that for thulium, yttrium, and europium¹⁵³³.

b. Extraction with di-tertiary phosphine oxides. This section describes the liquid–extraction chemistry of di-tertiary phosphine oxides. A previous review in this area gives an excellent account of their solvent extraction properties³⁶. For a balanced treatment, a summary of various extraction systems is given in Table 26, from which some interesting conclusions can be drawn:

- Generally, the metals were extracted as $[\text{Sc}(\text{NO}_3)_3\text{L}_2]$, $[\text{Y}(\text{NO}_3)_3\text{L}_2]$, $[\text{MoO}_2\text{LCl}_2]$, $[\text{GaCl}_3\text{L}_m]$ ($m = \frac{1}{2}$ or 1), $[\text{ZnA}_2\text{L}]$, $[\text{M}(\text{NO}_3)_3\text{L}_n]$ $\text{M} = \text{Ce}, \text{Nd}, \text{Pm}, \text{Eu}, \text{etc.}; n = 1-3$, $[\text{Th}(\text{NO}_3)_4\text{L}_2]$, $[\text{ML}_m(\text{ClO}_4)_3]$ ($m = 2, 3; \text{M} = \text{Eu}, \text{Am}$), $[\text{UO}_2(\text{NO}_3)_2\text{L}]$ and $[\text{MA}_3\text{L}]$, ($\text{M} = \text{La}, \text{Eu}, \text{etc.}; \text{HA} = \beta\text{-diketone or pyrazolone}$).
- Di-tertiary phosphine oxides are better extractants than monotertiary phosphine oxides, probably owing to the chelate effect and the more hydrophobic environments created by the bulky organophosphorus moieties of the bidentate ligands.
- dpmO_2 and $\text{cis-R}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{R}_2$ ($\text{R} = \text{Ph}, p\text{-Tol}$) are for superior extractants to other bidentate ligands. There is no clear relationship between the extraction efficiency and chain length, although ligands with smaller numbers of CH_2 groups generally showed higher extraction.
- $\text{trans-Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$ and $\text{Ph}_2\text{P}(\text{O})\text{C}\equiv\text{CP}(\text{O})\text{Ph}_2$ are poor extractants in comparison with the bidentate ligands discussed above¹⁶⁷³.
- When a phenyl or aryl group on phosphorus is replaced with an alkyl group such as butyl, hexyl, octyl or ClCH_2CH_2 , PhCH_2 , the extraction decreases. This difference is attributed to aryl stabilization, which is an entropy effect^{1638,1682,1683}. Further, the introduction of electron-withdrawing substituents on phosphorus leads to a decrease in extraction and vice versa^{1684,1685}.
- The extraction of a metal in the presence of H_3PO_4 was low, owing to possible complexation of the metal ion together with extensive hydration of the complex. Generally, the extraction decreased in the sequence $\text{HNO}_3 \approx \text{HClO}_4 > \text{HCl} > \text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4$.
- Using $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ and hydroxyethylenediphosphoric acid¹⁶⁸⁶, a separation factor for Am/Fe of $> 10^4$ (from HNO_3) was achieved, making the quantitative separation of the two possible.
- Stability constant data on TPE with $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$ ($n = 1, 4, 5$) revealed that the order of extraction of the metals was $\text{Am} > \text{Cm} \gg \text{Cf}$ ¹⁶⁷¹. Further bidentate phosphine oxides with branched groups were most effective for the extraction of TPE¹⁶⁸⁷.
- The replacement of hydrogen in the methylene of dpmO_2 by other atoms or groups such as allyl, Cl or *n*-dodecyl lowered the extraction¹⁶⁵⁸.
- $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_4\text{P}(\text{O})\text{Ph}_2$ was shown to possess a separation factor for Eu/Am of $> 10^4$ in the molten state¹⁶³⁷; other ligands also showed a higher extraction of lanthanides over actinides.
- $\text{R}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{R}_2$ ($\text{R} = n\text{-hexyl}, 2\text{-ethylbutyl}$) showed quantitative extraction of thorium(IV) from nitrate media¹⁶⁶⁹.
- Uranium(VI) and Protactinium(IV) were separated from cerium(III) in acidic solution using $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}(\text{R})\text{P}(\text{O})\text{Ph}_2$ ¹⁶⁸⁸. For $\text{R} = \text{Me}$, a maximum separation factor for plutonium(IV)/uranium(VI) was achieved from 1M HNO_3 . Curium(III), cerium(III) and europium(III) were poorly extracted. Addition of H_2dehp had no effect.

- m. The replacement of PO with SO (sulphoxide) was shown to lower the extraction. For example, for the extraction of europium(III) and americium(III) ¹⁶⁵⁹ the extraction capacity decreased in the order PO-PO > PO-SO > SO-SO.
- n. *o*- and *m*-C₆H₄(CH₂P(O)Ph₂)₂ were shown to possess high degrees of specificity, which in turn depended on the size of the metal ion¹⁶⁵⁸. The *O*-substituted isomer was highly selective for uranium(VI) (U/Am separation factor = 10⁵), whereas the *m*-substituted isomer was selective for americium(III) and was 3 × 10³ times better than the *o*-substituted isomer.

c. *Extraction with poly-tertiary phosphine oxides.* Only a few investigations of the use of poly-tertiaryphosphine oxides have been made. The ligands used and the metals extracted are {Ph₂P(O)CH₂}₂P(O)R (R = Ph, OH, OEt) for zirconium(IV) and hafnium(IV)^{1689,1690} and 1,3,5-C₆H₃{CH₂P(O)Ph₂}₃, 1,2,4,5-C₆H₂{CH₂P(O)Ph₂}₄ and 2,3,5,6-C₆H₂{CH₂P(O)Ph₂}₄ for TPE, uranium(VI) and europium(III)^{1658,1678}. It was observed that these ligands did not provide any enhanced extraction over bidentates, probably owing to steric factors.

d. *Extraction with mono- and di-tertiary phosphine sulphides/selenides.* Extraction studies on tertiary phosphine sulphides or selenides are few²¹ compared with the extensive work reported on tertiary phosphine oxides. Bu₃PS quantitatively extracted silver(I) from H₂O and HNO₃ media^{1691,1692,1693}, gold(III) from HNO₃¹⁶⁹² and mercury(II) from 0.1 M HCl and HNO₃ media^{1691,1692}. Extraction of other metals such as copper(II), zinc(II), lead(II) and bismuth(III) was poor (*D* < 0.56)^{1691,1692}. Using Bu₃PS and Oct₃PS, more than 95% recovery of mercury(II) from waste waters and waste solids was achieved¹⁶⁹⁵. In a study with Cl⁻ or SCN⁻ media, the formation of [HgX₂L_{*n*}] (*n* = 1, 2; L = Bu₃PS, Oct₃PS, X = Cl, SCN)¹⁶⁹⁴ was established.

n-Oct₃PS showed high levels of extraction of silver(I), mercury(II) and palladium(II) from HNO₃ media¹⁶⁹⁵. From HCl media extraction of mercury(II) was less (*D* = 10 600 vs 586) and gold(III) showed high extraction (*D* = 6280)¹⁶⁹⁵. Increasing the HCl concentration enhanced the extraction of gold(III) and lowered that of mercury(II). Extractions of palladium(II), platinum(IV), molybdenum(VI) and selenium(IV) from HCl were poor or nil (platinum)¹⁶⁹⁵.

Bu₃PS and di-2-ethylhexylphosphoric acid in Varsol DX-364 quantitatively extracted silver(I) or palladium(II) from dilute H₂SO₄¹⁶⁹⁷. The extraction using Bu₃PS in toluene from HNO₃ media was also quantitative¹⁶⁹⁷. Similarly, Pr₃PS is highly selective for silver(I), from acidic sulphate solutions containing copper(I) and zinc(II)¹⁶⁹⁸. Ph₃PS in CHCl₃ was also used for the extraction of silver(I) deposited on electrodes¹⁶⁹⁹. Bu₃PS in toluene or a mixture of Bu₃PS, 2-ethylhexanol (or *p*-nonylphenol)^{1700,1701} and di-*n*-hexyl sulphide extracted palladium(II) from HCl solutions ¹⁷⁰²⁻¹⁷⁰⁴ containing Pd, Pt, Rh and Ni. In the absence of the alcohol or phenol, precipitates are formed. The formation of [PdCl₂L_{*n*}] (*n* = 1, 2) was identified¹⁷⁰⁰⁻¹⁷⁰¹.

n-Oct₃PSe is a very suitable extractant for palladium(II), the *D* value being > 10³ versus (C₁₀H₂₁)₂(C₈H₁₇)PS or (C₉H₁₉)₂(C₁₀H₂₁)PS (*D* ≈ 500)¹⁷⁰⁵. *D* values for platinum(II), rhodium(I) and iridium(I) were low. However, in another study, Bu₃PS and Ph₃PS were used for the recovery of the fission product rhodium from aqueous HNO₃¹⁷⁰⁶.

Rhenium(VII) showed higher extraction with *n*-Oct₃PE in the sequence *n*-Oct₃PO > *n*-Oct₃PS > *n*-Oct₃PSe¹⁷⁰⁷.

Studies on di-tertiary phosphine sulphides are limited^{1699,1708,1709}. However, these reagents were found to be more efficient extractants for silver(I) and mercury(II) than Ph₃PS ligands^{1699,1708,1709}.

2. Reversed-phase chromatography

Reversed-phase chromatography (RPC) is another useful technique for the separation of metals. Here a paper or a resin acts as a solid phase which is soaked with a suitable organophosphorus reagent. Investigations in this area are few compared with liquid-liquid separations.

a. d-Block elements. Zirconium(IV) was recovered from HNO_3 solution by sorption on macroporous styrene-divinylbenzene resin saturated with Bu_3PO . The extraction was increased by the use of a solid extractant, eliminating loss of the reagent¹⁷¹⁰.

Tantalum(V) (in traces) was selectively removed from a niobium extract ($\text{Nb } 76.3 \text{ g l}^{-1}$, $\text{Ta } 0.08 \text{ g l}^{-1}$)¹⁷¹¹ containing tantalum and other metal ions in addition to HF , NH_3 , K^+ or H_2SO_4 , by sorption with topo fixed on porous polypropylene beads. The spent sorbent was regenerated by eluting the tantalum into an aqueous solution containing NH_4^+ , K^+ or HF .

Noble metals (Rh , Pd , Pt , Au , Ir) were separated and determined by paper and column reversed-phase chromatography using tris(2-ethylhexyl)phosphine oxide as the extracting agent¹⁷¹². Topo has been used to remove cobalt(II) from cations sorbed on anion-exchange resins¹⁷¹³. Ruthenium(III) was equilibrated between a 2 M HCl phase and a solid phase consisting of R_3PO ($\text{R} = \text{n-butyl}$ or octyl) on Kieselguhr¹⁴¹⁴. Addition of *n*-octanol or cyclohexanol lowered the extraction of ruthenium(III) due to hydrogen-bonded interaction with R_3PO .

b. Main Group elements. Gallium(III) was separated from 2–6 M HCl solutions of a number of binary and multi-component mixtures with topo as a stationary phase on a silica gel column¹⁷¹⁴. The method was suitable for the separation of trace amounts of gallium from bauxite samples. Similarly, selenium(IV) and tellurium(IV) were extracted from 4–6 M HCl solution and separated from several elements with topo fixed on a resin as the stationary phase¹⁷¹⁵.

Various alkali metals were separated from each other, e.g. Li from Na , Be from Mg , using methylenebis(di-*n*-hexylphosphine oxide) as the stationary phase in RPC (paper and column)¹⁷¹⁶.

c. Lanthanides and actinides. The distribution of rare earth elements (Ce , Nd , Eu and Gd), Am and Cm between dilute HNO_3 and isopentyldialkylphosphine oxide-solid resin sorbent was studied under static and dynamic conditions¹⁷¹⁷. The separation factors $\text{Cm/Ce} = 500$, $\text{Cm/Nd} = 260$, $\text{Cm/La} = 250$, $\text{Cm/Eu} = 14$ and $\text{Cm/Gd} = 14$ indicate the possibility of group separation of TPE and rare earth elements. Separation of TPE and rare earths from palladium was also studied.

A series of rare earths were separating using methylenebis{di(2-ethylhexyl)phosphine oxide} as the stationary phase in RPC¹⁷¹⁸. The separation factors were higher in HNO_3 than in HClO_4 or HCl solutions. Lanthanum, cerium, thorium and uranium were recovered from HNO_3 solution by sorption on macroporous divinylbenzene saturated with phosphine oxides such as Bu_3PO ¹⁷¹⁰. Various rare earth impurities present in traces in Sc_2O_3 were separated with topo as a stationary phase in RPC prior to their determination by inductively coupled plasma atomic emission spectrometry (ICP-AES)¹⁷¹⁹. Similarly, methylenebis(di-*n*-hexylphosphine oxide) and topo were used as the stationary phases in RPC to separate the rare earths from each other¹⁷¹⁶. The *D* values generally increase as the charge to radius ratio of the unhydrated cation increases.

Uranium and thorium were separated from H_3PO_4 solutions by trialkylphosphine oxide (R_3PO , R groups containing C_7 or C_8 atoms) fixed on Levextrel resin¹⁷²⁰. The separation of uranium(VI) from solutions using topo and polyurethane foam is efficient and specific¹⁷²¹. A desorption method was investigated which recovered 77.3% of the

uranium and 94% of the topo from an ore. The absorption and desorption steps are fairly specific for uranium, although other actinides could interfere.

A column of glass beads coated with tri-*m*-tolylphosphine oxide adsorbed uranium from partially digested urine¹⁷²²; the recovery was 73%. Uranium(VI) was transported from acidic media with topo as a liquid membrane supported on a microporous polymer in the form of a flat sheet or tube¹⁷²³; the uranium(VI) was extracted as $[\text{UO}_2(\text{NO}_3)_2\text{L}_2]$.

The recovery of plutonium even at trace levels from nitric acid waste was best carried out with topo sorbed on Amberlite XAD-4 resin as compared with the use of *tbp*, dihexyl-*N,N*-diethylcarbamoylmethylphosphine oxide or octylphenyl-*N,N*-diisobutylcarbamoylmethylphosphine oxide^{1724,1725}. Topo on Dowex 1-X4 (50–100 mesh) was found to be superior to Amberlite XAD-4 for the recovery of plutonium¹⁷²⁶.

Topo supported on a microporous polyethylene (Microthene) was used to separate uranium from radium-226 present in phosphorites and their industrial derivatives¹⁷²⁷. Trialkylphosphine oxide–GDX-301 resin separated uranium from acidic solutions of pH 5.8–6.2¹⁷²⁸. Htta–topo extracted uranium, neptunium and plutonium from the waste water of a nuclear plant; the extract was passed over active carbon, which led to their separation by adsorption¹⁷²⁹. A liquid membrane system consisting of H_2dehp –topo on Escaid 100 extracted uranium from H_3PO_4 ¹⁷³⁰. The emulsifier Paranox was used at 3% in a solution containing 5 M H_3PO_4 and 5 g l^{−1} of iron(II) at 45 °C. In a continuous process treating 5 l min^{−1} of H_3PO_4 , the recovery of uranium was >90%. Divinylbenzene copolymer resin impregnated with H_2dehp –topo selectively adsorbed uranium from wet-process H_3PO_4 solutions¹⁷³¹. Uranium was recovered from wet-process H_3PO_4 by extraction with a liquid membrane with H_2dehp –topo showing a synergistic effect¹⁷³².

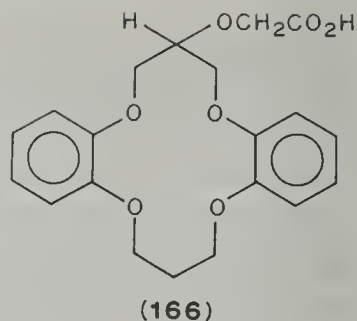
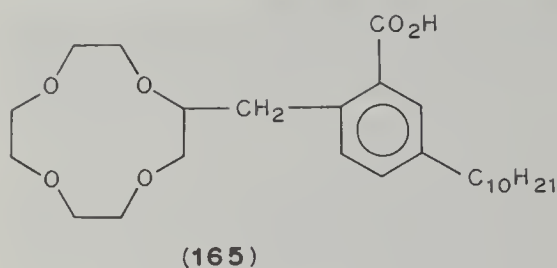
Recently, sorption of europium and actinides was carried out by means of octylphenyl-*N,N*-diisobutylcarbamoylmethylphosphine oxide loaded on silica¹⁷³³.

3. Ion-selective electrodes

a. Alkali and alkaline earth elements. Topo acted as a neutral lithium carrier in a lithium ion-selective electrode membrane¹⁷³⁴. Thus, when topo was used with 1% potassium tetrakis (*p*-chlorophenyl)borate in *o*-nitrophenyl octyl ether–PVC membrane, the electrodes exhibited a nearly Nernstian response with an Li/Na selectivity of 1:60, better than that achieved with previous electrode sensors. Further, topo dramatically improved the Li/Na selectivity of a 14-crown-4 electrode and was used for analysing diluted serum samples. The addition of topo and lipophilic $\text{Bu}_4^+\text{BF}_4^-$ to a PVC membrane lithium ion-selective electrode (based on synthesized non-cyclic neutral carriers) showed an increased selectivity for lithium over the other alkali metal ions¹⁷³⁵. The selectivity coefficient ($\log k_{\text{Li,M}}$) increased from 1.5 to 2.2 for Li^+ over Na^+ and from 2.0 to 3.0 for Li^+ over K^+ . The results obtained are of practical use in developing lithium ion-selective electrodes, as the proposed additives exert positive effects on several kinds of non-cyclic lithium-selective carriers in PVC matrix ion-selective electrodes.

PVC membranes made from ether carboxylic acid ionophores (crowns) (**165** or **166**) and potassium tetrakis(*p*-chlorophenyl)borate, with or without topo as additive, when coated on the tips of silver wires and combined with flow-injection analysis showed increased selectivity¹⁷³⁶. Membranes made from **165** and topo showed increased selectivity for K over Na, Rb, Cs and Sr at low contents of phenylborate and decreased selectivity for K over Li, Ca and Mg at high contents of phenylborate; however, topo enhanced the selectivity of potassium over the cations examined, excluding lithium. For membranes of **166**, the addition of topo decreased the selectivity for Cs over Rb, K, Na, Li and Mg, whereas the selectivity was increased over Ca and Sr.

The selectivity characteristics of ion-selective electrodes, especially Ca^{2+} ion-selective electrodes based on $\text{R}_2\text{PXP}(\text{O})\text{R}_2\{\text{X} = \text{CH}_2, \textit{o}\text{-C}_6\text{H}_4(\text{CH}_2)_2, \text{R} = \text{alkyl, Ph or Toly}\}$



have been studied using several plasticizing agents with different dielectric constants such as dioctyl phthalate and dibutylphthalate¹⁷³⁷. The selectivity depends on the concentration of lipophilic anion in the membrane. An electrode based on tetratolyl-*o*-xylylenediphosphine dioxide¹⁷³⁸ was best for Ca^{2+} . Using the *meta*- in place of the *ortho* isomer made it possible to develop a calcium ion-selective electrode with a high magnesium selectivity, ($K_{\text{Ca/Mg}} = 1.8 \times 10^{-5}$)¹⁷³⁹.

b. Main Group elements. Trace antimony(III) in water was preconcentrated by electrolytic deposition on a topo-modified wire electrode before its determination by atomic absorption spectrometry (AAS)¹⁷⁴⁰. Various metal ions and organic compounds did not interfere. In another study, antimony(III) in water was determined by potentiometric stripping analysis with a topo-modified glassy carbon electrode¹⁷⁴¹. Improvements in the characteristics of the electrode depend on the complex absorbing property of the thin film on the surface of the modified electrode. Such modified electrodes show good reproducibility and sensitivity.

In cyclic voltammetric experiments, a gold film electrode modified with a film of topo in a PVC matrix showed that the electrode is useful for highly selective determinations of a number of metals, namely antimony, bismuth and lead¹⁷⁴².

c. Transition elements. Technetium-(IV) and -(VII) were concentrated from 3 M HCl by complexing them with topo applied as a thin layer to a glassy carbon electrode¹⁷⁴³⁻¹⁷⁴⁴. After an enrichment time of 10 min, about 1.8×10^{-8} M technetium(VII) could be determined using differential-pulse cathodic stripping voltammetry. Technetium(IV) produces a peak near that of technetium(VII) and can therefore be used for a rough estimation of the technetium(VII)/technetium(IV) ratio.

A gold film electrode modified with a film of topo in a PVC matrix showed that the electrode is useful for the highly selective determination of chromium, iron, mercury and uranium¹⁷⁴². Down to 0.02–50 ppm of mercury in environmental samples (e.g. river sediments) can be determined with good precision and accuracy. A topo-modified mercury electrode was used for the preconcentration of cadmium(II) by immersing the electrode in cadmium(II) solution prior to its determination by cyclic voltammetry¹⁷⁴⁵. A topo-coated glassy carbon electrode was used for the voltammetric determination of uranyl ions after preconcentration on a topo layer¹⁷⁴⁶. The method was fairly selective for UO_2^{2+} because the topo layer electrochemically masked some metal ions which gave reduction waves at a glassy carbon electrode without a topo coating. A mercury film electrode modified with a film of topo in a PVC matrix was used for the galvanostatic stripping determination of bismuth in copper alloys¹⁷⁴⁷. The method is simple, selective and rapid, but tin(IV) interferes (the detection limit was 0.002–0.5% of bismuth).

In a recent study, organotransition metal complexes were used as selective surfaces for the reversible detection of SO_2 with a piezoelectric crystal sensor¹⁷⁴⁸. For instance, $[\text{Mn}(\text{OPPh}_3)_4(\text{SO}_2)_2\text{I}_2]$ was identified as a candidate coating for the reversible detection

of SO₂ on piezoelectric crystal sensors. A specified copper complex acts as a reversible coating for the detection of SO₂ in the range 10–1000 mg l⁻¹.

4. Miscellaneous applications

a. Extractive and direct determination of metals. This section covers some applications not discussed earlier. The only application in which organophosphorus reagents have been used for direct determination without extraction is in the determination of palladium and rhodium using Ph₂PCH₂CH₂P(O)Ph₂ and {Ph₂P(O)CH₂CH₂}₂P(O)Ph. Metals such as platinum, iridium, copper, nickel and cobalt did not interfere¹⁷⁴⁹. Mono-phosphine oxide formed 1:2 and 1:4 complexes and tris-phosphine oxide formed 1:2 complex with palladium. Rhodium formed 1:6 and 1:3 complexes respectively. Topo-mibk extracted trace metals (Ag, Bi, Cd, Pb, Se, Te, Sn and Zn) present in steels and superalloys as their iodo complexes prior to their determination by AAS¹⁷⁵⁰. Similarly, this extractant separated Cu, Zn, Mo, Ag, Cd, In, Sn, Sb, Te, Tl, Pb and Bi from the matrix of geological samples which were subsequently determined by AAS¹⁷⁵¹.

A series of elements, Cd, Mn, Pb, Co, Ni and Cu, were quantitatively separated and concentrated from sea water using a low concentration of topo-1,1,1-trifluoro-4-mercapto-4(2-thienyl) but-3-en-2-one in cyclohexane¹⁷⁵² before their determination by AAS. Topo-dithizone in ethyl benzoate extracted Cd, Ni, Fe, V, Cu, Pb, Zn, Ti, Al, Zr and Co simultaneously¹⁷⁵³. The method can be used for the preconcentration of trace metals from natural waters prior to determination. Topo-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl octane-4,6-dione in dodecane extracted several metals from aqueous chloride solutions^{1754a}.

Using topo-Hhfa and Triton X-100, simultaneous determination of terbium, samarium and europium was carried out^{1754b}. Topo was used for the separation of rare earth elements and yttrium from geological samples followed by their determination using ICP-AES^{1754c}.

b. Fluorimetric determinations and related applications. Organophosphorus reagents have played a significant role in fluorescence; accordingly, this section briefly discusses analytical and related applications based on fluorescence.

Htta-topo has been used for the determination of europium and samarium by laser-excited fluorimetry^{1756,1757} (emission line 619 nm for Eu and 650 nm for Sm). The detection limits were 0.2–10 ppb Eu and 0.1–1 ppm Sm. A flow-injection spectrofluorimetric¹⁷⁵⁷ method was developed for the determination of terbium(III) based on solubilizing its ternary complex with topo and pivaloyltrifluoroacetone in a micellar solution of nona (oxyethylene) dodecyl ether at pH 3.5. Excitation and fluorescence wavelengths of 310 and 611 nm were used. The accuracy and reproducibility are good up to 16 µg l⁻¹ of terbium(III). No interference from a 20-fold excess of rare earths tested was observed.

Fluorescent paint compositions containing fluorine-containing β-diketone and alkylphosphine complexes of europium or terbium are useful for commercial displays¹⁷⁵⁸. Thus [Eu(HFA)₃(topo)] complex was mixed with ABS-100 paint and a thinner to give a composition which was screen-printed onto an acrylic plate and dried. The print showed bright-red fluorescence on UV irradiation.

B. Catalytic Applications

Most of the catalytic applications pertain to complexes of tertiary phosphine oxides and are discussed here. The applications of complexes of tertiary phosphine chalcogenides, which are few, were described in a recent review²¹.

TABLE 27. Metal complexes as catalysts

Catalyst	Applications	Ref.
<i>d-Block elements</i>		
A		
(i) $[\text{TiCl}_4(\text{OPPh}_3)]$	In pinacol rearrangement of benzpinacol For preparation of polybut-1-ene foam from but-1-ene at 80 °C It oxidized tetralin and cyclohexene at 20 °C in the presence of Me_3COOH to give tetralone and cyclohex-2-enone, respectively. Adamantane and cyclohexane also oxidized to alcohols, etc. Safe to handle compared with $[\text{CrO}(\text{O}_2)_2\text{L}]$ ($\text{L} = \text{pyridine-}N\text{-oxide}$) Used for the dimerization of alkenes such as C_2H_4 Used for the dimerization, polymerization and copolymerization of ethylene and propylene	59
(ii) $\text{TiCl}_3\text{-Ph}_3\text{PO-AlCl}_3$		1759a
(i) $[\text{CrO}(\text{O}_2)_2(\text{OPPh}_3)]$		1759b
B		
(ii) $[\text{CrCl}_2(\text{NO})_2(\text{OPPh}_3)_2]$, $[\text{CrCl}_3(\text{OPPh}_3)_3]$	Used in the metathesis of olefins such as pent-2-ene Used in disproportionation of pent-2-ene to hex-3-ene and but-2-ene. Activity comparable to other known catalysts; corresponding $[\text{W}(\text{NO})\text{Cl}_3(\text{OPPh}_3)_2]$ showed lower activity Used in epoxidation of alkenes. Activity was comparable to that of $[\text{Mo}(\text{O}_2)(\text{acac})_2]$ Used in epoxidation of cyclohexene, dpeO_2 showed higher activity over Ph_3PO or even other neutral ligands such as 1,10-phenanthroline Used in epoxidation of alkenes Used for oxidation of Ph_3P to Ph_3PO (a) Used for oxidation of Ph_3P to Ph_3PO by O_2 . Bromo or thiocyanato complex showed the highest effect. The oxidation in MeCN is quantitative and selective at 30–70 °C under atmospheric pressure of O_2 . For $\text{X} = \text{NCS}$, reduction of iron(III) to iron(II) takes place with oxidation of Ph_3P to Ph_3PO . The reduction rate depends on iron(III) to Ph_3P ratio. Order of activity: $\text{NCS} > \text{I} > \text{Br} > \text{Cl}$ (b) Selective catalyst for organic compounds Used in the dimerization of dialkenes	1760, 1761
(iii) $[\text{CrCl}_2\text{L}_2]$, $[\text{CrCl}_2\text{L}_2(\text{NO})_2]$, $[\text{CrCl}_3\text{L}_3]$ and $[(\text{CrCl}_3\text{L}_2)_2]$ ($\text{L} = \text{Bu}_3\text{PO}$, Ph_3PO) and RAIX_2		1762a
(iv) $[\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{OPPh}_3)_2]$ or $[\text{Mo}(\text{N})\text{Cl}_3(\text{OPPh}_3)_2]$ and EtAlCl_2		185, 1762b
(v) $[\text{Mo}(\text{NO})\text{Cl}_3(\text{OPPh}_3)_2]$ and EtAlCl_2		180, 181, 1763–1767
(vi) $[\text{MoCl}_n(\text{NO})_{4-n}\text{L}_2]$ ($\text{L} = \text{Ph}_3\text{PO}$, $n = 1-3$)		1768, 1769
(vii) $[\text{MoO}_2\text{Cl}_2(\text{OPPh}_3)_2]$ and $[\text{MoO}_2\text{Cl}_2(\text{dpeO}_2)]$		1770
(viii) $[\text{MO}(\text{O}_2)_2(\text{OPR}_3)_2]$ ($\text{M} = \text{Mo}, \text{W}$)		175
(i) $[\text{Fe}(\text{OPPh}_3)_4(\text{I}_3)_2]$	1771	
(ii) $[\text{FeX}_3(\text{OPPh}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$)	278, 302, 303, 1772–1775	
C		
(iii) $[\text{M}(\text{NO})_2(\text{R}_3\text{PO})\text{X}]$ ($\text{M} = \text{Fe}, \text{Co}$; $\text{R} = \text{alkyl or aryl}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$)	1776 1785	

D	(i) $[\text{CoI}_2(\text{OPPh}_3)_2]$ (ii) $[\text{Co}(\text{NO}_3)_2(\text{OPPh}_3)_2]$ and Et_3Al (iii) $[\text{Rh}(\text{hdmg})_2(\text{O}_2)\text{L}]$ ($\text{L} = \text{Ph}_3\text{PO}$; $\text{H}_2\text{dmg} = \text{dimethylglyoxine}$) and $\text{NaBH}_4 - \text{NaOH}$ (iv) $[\text{Rh}(\text{CO})_2(\text{acac})(\text{topo})]$	Used in reductive carbonylation of MeOH to MeCHO Used for the hydrogenation of butadiene or isoprene Used for preparing cyclododecane and in hydrogenation reactions	1777 1780 1778, 1789
E	(v) $[\text{Rh}(\text{cod})(\text{L})][\text{ClO}_4]$ ($\text{L} = \text{dpmO}_2, \text{dpeO}_2$) (i) $[\text{NiCl}_2\text{L}_2]$ ($\text{L} = \text{Ph}_2\text{EtPO}$, etc.) (ii) $[\text{NiCl}_2(\text{OPR}_3)_2]$ ($\text{R} = \text{Bu}, \text{Ph}$) and EtAlCl_2 (iii) $[\text{NiX}_2(\text{OPR}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$; $\text{R} = \text{alkyl or aryl}$) (iv) $[\text{Ni}(\text{NO})\text{LX}]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}; \text{L} = \text{R}_3\text{PO}$) (v) $[\text{NiX}_2\text{L}_2]$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{Bu}_3\text{PO}, \text{Bu}_2\text{PhPO}$, etc.)	Used for hydroformylation and oxidation of aldehydes, E.g., C_2H_4 was converted to EtCHO which then gave EtCO_2H , $(\text{EtCO})_2\text{O}$ and some Et_2CO Used for reduction of cyclohexene and acetophenone Used for hydrosilylation of alkenes by alkylchlorosilanes Used for dimerization of alkenes Used for hydrosilylation of alkenes ($\text{RCH}=\text{CH}_2$, $\text{R} = \text{hexyl, pentyl}$). Alkyl catalysts were more effective than aryl catalysts Used for dimerization of conjugated dialkenes Used for preparing organosilanes from reaction hydrosilanes and alkenes at $100-120^\circ\text{C}$	1781 961 392, 1782 1783 1784 1785 1786
F	Copper(II)- R_3PO complex	Used in the preparation of carbonic esters	1787
G	$\text{AlCl}_3 - \text{Ph}_3\text{PO}$ complex	<i>Main Group elements</i> (a) Used for the preparation of poly(oxazolidones) from phenyl isocyanate and phenyl glycidyl ether (b) Used in synthesis of model 2-oxazolidone and poly(oxazolidones) involving terpolymerization of (3-vinylphenylazo)methylmalodinitrile, (3-vinylphenylazo)phenyl sulphide or 1-(3-vinylphenylazo)-1,1-diphenylmethyl acetate with methylmethacrylate and butane-1,4-diol dimethylacrylate Used as latent cross-linking catalysts for the manufacture of flexible polyurethane foam with good heat resistance (up to 140°C in air)	1788 1789
H	(i) $[\text{Bu}_2\text{SnX}_2] - \text{Ph}_3\text{PO}$ ($\text{X} = \text{Cl}, \text{NCS}$) (ii) $[\text{Bu}_3\text{SnI}(\text{Bu}_3\text{PO})]$	Used in the addition of CO_2 to oxetone giving trimethylene carbonate. $\text{Bu}_2\text{SnI}_2(\text{Bu}_3\text{PO})$ showed no activity. Hence the coordination mode of ligands and the stability of the complexes are important	1790 1791

TABLE 27. (continued)

	Catalyst	Applications	Ref.
I	(i) $[\text{SbF}_3\text{L}_n]$ ($n = 2$ for Ph_3PO and 1 for dpmO_2)	Used for polycondensation of the monomer forming non-discoloured poly(ethylene terephthalate), which is useful as thermoplasts for fibres, yarns and films	1792a
	(ii) $[\text{SbX}_3\text{L}]$ $\{\text{X} = \text{Cl, F};$ $\text{L} = \text{R}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{R}_2;$ $\text{R} = \text{Me, Pr}^i, \text{Ph}; n = 1, 2\}$	Used for polymerizations, oligomerizations and oxidations	1792b
	(iii) $[\text{SbCl}_5(\text{OPPh}_3)]$	Used for pinacol rearrangement of benzpinacol	59
J	(i) $[\text{LiBr}(\text{OPPh}_3)]$	<i>s-Block elements</i> Used for rearrangement of epoxides to carbonyl compounds. Thus 1-methylcyclohexene epoxide was converted into 1-methylcyclopentane-1-carboxaldehyde	1793
	(ii) $[\text{LiClO}_4(\text{OPPh}_3)]$	Showed similar catalytic properties, but the products were different. Thus 1-methylcyclohexene gave 2-methylcyclohexanone and a small amount of 1-methylcyclopentane-1-carboxaldehyde	1793

Table 27 describes various metal complexes of phosphine oxides which have been used as catalysts for various organic reactions. It can be seen that complexes of the d-block elements have generally been used, whereas complexes of the main group elements have been used comparatively little and only a few s-block element complexes have been used. There is no complex of an f-block element whose catalytic properties have been explored. From Table 27 it can be seen that a variety of organic reactions have been catalysed and that in some cases phosphine oxide complexes were superior to other known catalysts. Examples given in Table 27 and those in the previous review²¹ provide further scope for organic reactions which can be studied using metal complexes of phosphine oxides or chalcogenides.

VI. CONCLUSIONS

From this survey of the literature, it is apparent that the coordination chemistry of tertiary phosphine oxides, sulphides and selenides has been extensively studied; the work on phosphine telluride chemistry is limited, however. Further, the work on mono-tertiary phosphine oxides, sulphides and selenides is much greater than that on di- and poly-tertiary phosphine oxides and chalcogenides. However, it should be pointed out that the coordination chemistry of di- and poly-tertiary phosphine oxides and chalcogenides will continue to attract attention, particularly in opening up new areas where anionic ligands of the type $\{R_2P(E)\}_2CH^-$ and $\{R_2P(E)\}_3C^-$ and unsymmetrical phosphorus ligands such as $R_2P(CH_2)_nP(E)R_2$ and $R_2P(S)(CH_2)_nP(Se)R_2$ ($E = O, S, Se$; $R = \text{aryl or alkyl}$) can be used. Their coordination chemistry is rich in NMR spectroscopy and interesting from the point of view of both metal-ligand bonding and the formation of homo- and hetero-polymetallic complexes. A new ligand, the neutral methanide $Ph_2P(S)CHPh_2Me$, discussed in connection with the gold chemistry of phosphine chalcogenides¹²²¹, is likely to attract attention on a significant scale in view of its interesting bonding properties.

It may be noted that most of the coordination chemistry of these ligands reported so far has been with transition metals, while Main Group and s-group elements have been poorly studied, with a few exceptions such as tin-bis(phosphine oxide) chemistry. Further studies may be expected for various complexes mentioned in the text.

Apart from coordination chemistry of tertiary phosphine oxides, these ligands have been used (a) for the extraction of metals (liquid-liquid separation), (b) in reversed-phase chromatography for the separation of metals (c) in ion-selective electrodes, (d) for extractive and direct determination of metals and (e) for the fluorimetric determination of metals. Complexes of these ligands have also been used in the catalysis of several organic compounds. Similarly, tertiary phosphine chalcogenides find use in these areas but to only a very small extent. However, great scope exists for the development of the metal extraction chemistry (and related areas) of tertiary phosphine chalcogenides.

VII. ACKNOWLEDGEMENTS

The author thanks Randhir Singh, Pushvinder Kaur, Dr Kuldip Singh and Dr Maninderjeet Kaur for their help in collecting literature in part related to Section II.A. He is also grateful to his wife for bearing patience and to his children for preliminary help. Library facilities provided by the Guru Nanak Dev University and Delhi University are also gratefully acknowledged.

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