

A Specialist Periodical Report

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Organophosphorus  
Chemistry  
Volume 8

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# Organophosphorus Chemistry

Volume 8

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A Review of the Literature published  
between July 1975 and June 1976

Senior Reporter

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# Organophosphorus Chemistry Volume 8

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## Foreword

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The volume of published work in organophosphorus chemistry has again increased, and several Reporters have had great difficulty in keeping within their allotted space. Much, but not all, of the research has been of a routine and predictable nature. The stimulus provided by the discovery of phosphonomycin is still being felt. It would be interesting to know just how many research projects and proposals have been linked, however tenuously, to this phosphorus-containing antibiotic. Six-co-ordinate species are being identified more frequently. Some are remarkably stable and have been isolated, whereas the intermediacy of others in reactions has been inferred from kinetic data. Clearly, much more will be heard of these. Finally, on the instrumental front, Fourier-transform  $^{31}\text{P}$  n.m.r. spectroscopy is proving to be a very powerful tool for the detection and study of unstable intermediates, for example in Arbusov reactions, and one can look forward to the solution of many long-standing problems in organophosphorus chemistry using this technique. We hope to report on some of these in Volume 9.

S. Trippett

# Abbreviations

ADP	adenosine 5'-pyrophosphate
AIBN	bisazoisobutyronitrile
AMP	adenosine 5'-phosphate
ATP	adenosine 5'-triphosphate
CMP	cytidine 5'-phosphate
DBN	1,5-diazabicyclo[4,3,0]non-5-ene
DBU	1,5-diazabicyclo[5,4,0]undec-5-ene
DCC	dicyclohexylcarbodi-imide
DMF	<i>NN</i> -dimethylformamide
DMSO	dimethyl sulphoxide
FAD	flavin-adenine dinucleotide
GDP	guanosine 5'-pyrophosphate
g.l.c.	gas-liquid chromatography
HMPT	hexamethylphosphoric triamide
HMT	hexamethylenetetramine
NAD	nicotinamide-adenine dinucleotide
NADP	nicotinamide-adenine dinucleotide phosphate
NBS	<i>N</i> -bromosuccinimide
NMN	nicotinamide mononucleotide
n.q.r.	nuclear quadrupole resonance
pp <sub>i</sub>	inorganic pyrophosphate
TCNE	tetracyanoethylene
TDAP	tris(dimethylamino)phosphine
TFAA	trifluoroacetic acid
THF	tetrahydrofuran
t.l.c.	thin-layer chromatography
TMPT	trimethylphosphoric triamide
UDPGal	uridine 5'-pyrophosphate galactose
UDPGlc	uridine 5'-pyrophosphate glucose

# Contents

<b>Chapter 1 Phosphines and Phosphonium Salts</b>	<b>1</b>
<i>By D. W. Allen</i>	
<b>1 Phosphines</b>	<b>1</b>
Preparation	1
From Halogenophosphine and Organometallic Reagents	1
From Metallated Phosphines	2
By Addition of P—H to Unsaturated Compounds	5
By Reduction	6
Miscellaneous	8
Reactions	10
Nucleophilic Attack at Carbon	10
Carbonyls	10
Miscellaneous	11
Nucleophilic Attack at Halogen	12
Nucleophilic Attack at Other Atoms	15
Miscellaneous	17
<b>2 Phosphonium Salts</b>	<b>18</b>
Preparation	18
Reactions	21
Alkaline Hydrolysis	21
Additions to Vinylphosphonium Salts	23
Miscellaneous	25
<b>3 Phospholes</b>	<b>27</b>
<b>4 Phosphorins</b>	<b>29</b>
<b>Chapter 2 Quinquecovalent Phosphorus Compounds</b>	<b>31</b>
<i>By S. Trippett</i>	
<b>1 Introduction</b>	<b>31</b>
<b>2 Structure and Bonding</b>	<b>32</b>
<b>3 Acyclic Systems</b>	<b>34</b>

<b>4 Four-membered Rings</b>	<b>35</b>
<b>5 Five-membered Rings</b>	<b>36</b>
Phospholens	36
1,2-Oxaphospholans	37
1,3,2-Dioxaphospholans	37
1,3,2-Dioxaphospholens	39
1,3,2-Oxazaphospholidines	41
Miscellaneous	44
<b>6 Six-membered Rings</b>	<b>46</b>
<b>7 Six-co-ordinate Species</b>	<b>46</b>
<b>Chapter 3 Halogenophosphines and Related Compounds</b>	<b>50</b>
<i>By J. A. Miller</i>	
<b>1 Halogenophosphines</b>	<b>50</b>
Physical and Structural Aspects	50
Preparation	51
Reactions with Simple Alkenes and Aromatic Compounds	52
Reactions in which Phosphorus is Electrophilic	53
Biphilic Reactions	54
Miscellaneous Reactions	58
Silyl- and Related Phosphines	59
<b>2 Halogenophosphoranes</b>	<b>61</b>
Physical and Structural Aspects	61
Preparation of Phosphoranes from Phosphorus(III) Compounds	62
Preparation of Phosphoranes by Exchange Methods	64
Reactions of Phosphoranes	65
Synthetic Uses of Phosphine-Halogenocarbon Reactions	68
Miscellaneous	70
<b>Chapter 4 Phosphine Oxides and Sulphides</b>	<b>71</b>
<i>By J. A. Miller</i>	
<b>1 Preparative Aspects</b>	<b>71</b>
<b>2 Addition Reactions of <math>R_3P(X)H</math></b>	<b>76</b>
<b>3 Reactions involving P—C Bond Cleavage</b>	<b>78</b>
<b>4 Reactions at X in the <math>P=X</math> Group</b>	<b>79</b>

<b>5 Reactions of the Side-chain</b>	<b>80</b>
<b>6 Miscellaneous Physical and Structural Aspects</b>	<b>82</b>
<b>Chapter 5 Tervalent Phosphorus Acids</b>	<b>84</b>
<i>By B. J. Walker</i>	
<b>1 Introduction</b>	<b>84</b>
<b>2 Phosphorous Acid and its Derivatives</b>	<b>84</b>
Nucleophilic Reactions	84
Attack on Saturated Carbon	84
Attack on Unsaturated Carbon	86
Attack on Nitrogen	91
Attack on Oxygen	92
Attack on Halogen	93
Electrophilic Reactions	95
Rearrangements	97
Cyclic Esters of Phosphorous Acid	98
Miscellaneous Reactions	99
<b>3 Phosphonous and Phosphinous Acids and their Derivatives</b>	<b>100</b>
<b>Chapter 6 Quinquevalent Phosphorus Acids</b>	<b>102</b>
<i>By R. S. Edmundson</i>	
<b>1 Synthetic Methods</b>	<b>102</b>
General	102
Phosphoric Acid and its Derivatives	104
Phosphonic and Phosphinic Acids and their Derivatives	109
<b>2 Reactions</b>	<b>114</b>
General	114
Reactions of Phosphoric Acid and its Derivatives	117
Reactions of Phosphonic and Phosphinic Acid Derivatives	124
<b>3 Structure</b>	<b>131</b>
<b>Chapter 7 Phosphates and Phosphonates of Biochemical Interest</b>	<b>133</b>
<i>By D. W. Hutchinson</i>	
<b>1 Introduction</b>	<b>133</b>



<b>2 Coenzymes and Cofactors</b>	134
Nicotinamide Nucleotides	134
Flavin Coenzymes	135
Pyridoxal Phosphate	135
Thiamine Phosphates	137
<b>3 Sugar Phosphates</b>	137
<b>4 Phospholipids</b>	141
<b>5 Phosphonates</b>	142
<b>6 Oxidative Phosphorylation</b>	143
<b>7 Enzymology</b>	144
Enzyme Mechanisms	144
Miscellaneous Enzymes	146
Phosphoproteins	147
<b>8 Other Compounds of Biochemical Interest</b>	147
<b>Chapter 8 Nucleotides and Nucleic Acids</b>	151
<i>By J. B. Hobbs</i>	
<b>1 Introduction</b>	151
<b>2 Mononucleotides</b>	151
Chemical Synthesis	151
Cyclic Nucleotides	158
Affinity Chromatography	159
<b>3 Nucleoside Polyphosphates</b>	160
Chemical Synthesis	160
Affinity Labelling	165
Prebiotic Models	167
<b>4 Oligo- and Poly-nucleotides</b>	168
Chemical Synthesis	168
Enzymatic Synthesis	171
Sequencing	173
<b>5 Analytical Techniques and Physical Methods</b>	174
Separation and Quantitation	174
Structure Probes	176

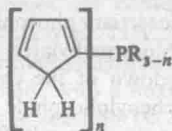
<b>Chapter 9 Ylides and Related Compounds</b>	<b>177</b>
<i>By D. J. H. Smith</i>	
<b>1 Methylene phosphoranes</b>	<b>177</b>
Preparation	177
Structure	179
Reactions	179
Aldehydes	179
Ketones	181
Other Carbonyl Compounds	183
Organometallics	184
Miscellaneous	186
<b>2 Phosphoranes of Special Interest</b>	<b>187</b>
<b>3 Selected Applications of Ylides in Synthesis</b>	<b>190</b>
Heterocycles	190
Pheromones	193
Prostaglandins	194
Carbohydrates	195
Carotenoids	196
Non-Benzenoid Aromatic Compounds	198
<b>4 Selected Applications of Phosphonate Carbanions</b>	<b>199</b>
General	199
Natural Products	202
<b>Chapter 10 Phosphazenes</b>	<b>204</b>
<i>By R. Keat</i>	
<b>1 Introduction</b>	<b>204</b>
<b>2 Synthesis of Acyclic Phosphazenes</b>	<b>204</b>
From Amines and Phosphorus(v) Halides	204
From Azides and Phosphorus(III) Compounds	206
Other Methods	208
<b>3 Properties of Acyclic Phosphazenes</b>	<b>213</b>
Halogeno-derivatives	213
Amino-, Alkyl, and Aryl derivatives	214
<b>4 Synthesis of Cyclic Phosphazenes</b>	<b>219</b>

<b>5 Properties of Cyclic Phosphazenes</b>	<b>220</b>
Halogeno-derivatives	220
Amino-derivatives	221
Alkoxy- and Aryloxy-derivatives	223
Alkyl and Aryl derivatives	227
<b>6 Polymeric Phosphazenes</b>	<b>227</b>
<b>7 Phosphazenes as Fire Retardants</b>	<b>229</b>
<b>8 Molecular Structures of Phosphazenes Determined by X-Ray     Diffraction Methods</b>	<b>230</b>
<b>Chapter 11 Photochemical, Radical, and Deoxygenation Reactions</b> <i>By R. S. Davidson</i>	<b>232</b>
<b>1 Photochemical Reactions</b>	<b>232</b>
<b>2 Phosphinidenes and Related Species</b>	<b>233</b>
<b>3 Radical Reactions</b>	<b>234</b>
<b>4 Deoxygenation and Desulphurization Reactions</b>	<b>240</b>
<b>5 Deselenation Reactions</b>	<b>247</b>
<b>Chapter 12 Physical Methods</b> <i>By J. C. Tebb</i>	<b>248</b>
<b>1 Nuclear Magnetic Resonance Spectroscopy</b>	<b>248</b>
Biological Applications	248
Chemical Shifts and Shielding Effects	249
Phosphorus-31	249
$\delta_P$ of $P^I$ compounds	249
$\delta_P$ of $P^{III}$ compounds	250
$\delta_P$ of $P^{IV}$ compounds	250
$\delta_P$ of $P^V$ and $P^{VI}$ compounds	252
Carbon-13	252
Hydrogen-1	253
Studies of Equilibria and Shift Reagents	253
Pseudorotation	254
Non-equivalence, Inversion, and Medium Effects	255

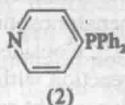
Spin-Spin Coupling	255
$J_{PP}$ and $J_{PM}$	256
$J_{PC}$	257
$J_{PC_nH}$	258
$J_{PNH}$	259
$J_{PXCH}$	259
N.Q.R. Studies	259
<b>2 Electron Spin Resonance Spectroscopy</b>	260
<b>3 Vibrational Spectroscopy</b>	262
Band Assignment and Structure Elucidation	262
Stereochemical Aspects	263
Studies of Bonding	264
<b>4 Microwave Spectroscopy</b>	264
<b>5 Electronic Spectroscopy</b>	264
Absorption	264
Photoelectron	265
<b>6 Rotation</b>	266
<b>7 Diffraction</b>	266
X-Ray	266
Electron	269
<b>8 Dipole Moments, Permittivity, and Polarography</b>	269
<b>9 Mass Spectrometry</b>	271
<b>10 <math>pK_a</math> and Thermochemical Studies</b>	272
<b>11 Chromatography and Surface Properties</b>	274
G.l.c.	274
T.l.c.	274
Paper Chromatography	274
Column Chromatography	274
<b>Author Index</b>	276

## 1 Phosphines

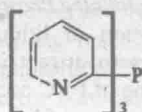
**Preparation.**—From *Halogenophosphine and Organometallic Reagents.* The cyclopentadienylphosphines (1) have been obtained from the reaction of cyclopentadienylthallium with chlorophosphines in ether.<sup>1</sup> Diphenyl(4-pyridyl)phosphine (2) is prepared from 4-pyridyl-lithium and chlorodiphenylphosphine,<sup>2</sup> and an improved procedure for the synthesis of tri-(2-pyridyl)phosphine (3) from 2-pyridyl-lithium and phosphorus trichloride has been reported.<sup>3</sup>



(1) R = Me or Ph; n = 1 or 2

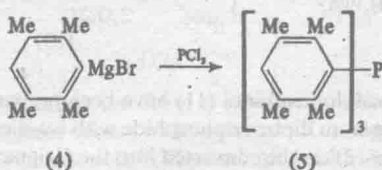


(2)



(3)

Treatment of phosphorus trichloride with an excess of the Grignard reagent (4) leads to the sterically hindered phosphine (5).<sup>4</sup> A sample of <sup>14</sup>C-labelled triethylphosphine has been synthesized from <sup>14</sup>C-labelled ethylmagnesium iodide and phosphorus trichloride.<sup>5</sup> The reaction of chlorodiphenylphosphine with the Grignard



(4)

(5)

reagent derived from 2,2'-dibromobiphenyl in THF solution leads to the diphosphine (6), which is dehydrogenated by various rhodium complexes to form *trans*-2,2'-diphenylphosphinostilbene (7).<sup>6</sup>

<sup>1</sup> F. Mathey and J.-P. Lampin, *Tetrahedron*, 1975, 31, 2685.

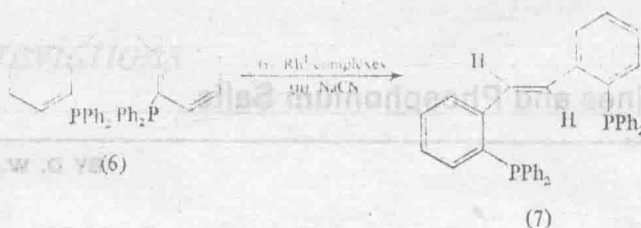
<sup>2</sup> M. A. Weiner and P. Schwartz, *Inorg. Chem.*, 1975, 14, 1714.

<sup>3</sup> R. K. Boggess and D. A. Zatko, *J. Coordination Chem.*, 1975, 4, 217.

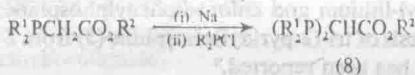
<sup>4</sup> B. I. Stepanov, A. I. Bokanov, A. B. Kudryavtsev, and Yu. G. Plyashkevich, *J. Gen. Chem. (U.S.S.R.)*, 1975, 44, 2312.

<sup>5</sup> M. Kanska and S. Drabarek, *Nukleonika*, 1974, 19, 977 (*Chem. Abs.*, 1975, 83, 10270).

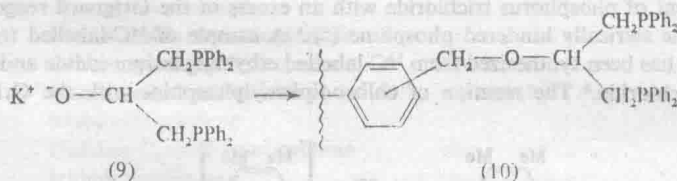
<sup>6</sup> M. A. Bennett, and P. W. Clark, *J. Organometallic Chem.*, 1976, 110, 367.



The reaction of halogenophosphines with esters of trialkylstannylacetic acids gives a general route to compounds containing the  $-\text{P}(\text{CH}_2\text{CO}_2\text{R})_n$  grouping.<sup>7</sup> Diphosphinoacetic acid esters (8) can be prepared from the monophosphino-esters by treatment with sodium and dialkylchlorophosphines.<sup>8</sup>



**From Metallated Phosphines.** The synthesis of polymeric tertiary phosphines based on the reaction of lithium diphenylphosphide with chloromethylated polystyrenes continues to attract interest.<sup>9,10</sup> Considerable breakdown of the carbon-carbon back-bone of PVC occurs on reaction with lithium diphenylphosphide in THF, and only oligomers of low molecular weight result.<sup>11</sup> The potassium salt (9) reacts with chloromethylated polystyrene to form the polymeric-diphosphine (10).<sup>12</sup>



The  $\omega$ -chloroalkyldiphenylphosphines (11) have been prepared by the reaction of equimolar quantities of sodium diphenylphosphide with  $\alpha\omega$ -dichloroalkanes. Whereas the phosphine (11;  $n = 3$ ) can be converted into the Grignard reagent (12), which reacts with dimethylchlorophosphine to form the unsymmetrical diphosphine (13), the Grignard reagent (14) undergoes a  $\beta$ -elimination reaction to regenerate diphenylphosphide ion.<sup>13</sup>

<sup>7</sup> M. A. Kakli, G. M. Gray, E. G. Delmar, and R. C. Taylor, *Synth. React. Inorg. Metal-Org. Chem.*, 1975, **5**, 357.

<sup>8</sup> Z. S. Novikova, S. Ya. Skorobogatova, and I. F. Lutsenko, Russ. P. 497307 (*Chem. Abs.*, 1976, **84**, 122038).

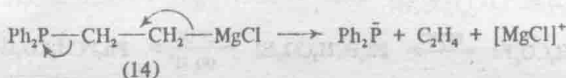
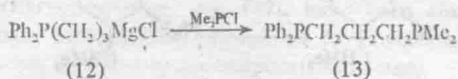
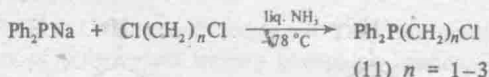
<sup>9</sup> E. Bayer and V. Schurig, *Angew. Chem. Internat. Edn.*, 1975, **14**, 493.

<sup>10</sup> J. Basset, R. Mutin, G. Descotes, and D. Sinou, *Compt. rend.*, 1975, **280**, C, 1181.

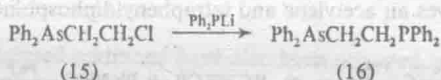
<sup>11</sup> K. A. Abdulla, N. P. Allen, A. H. Badran, R. P. Burns, J. Dwyer, C. A. McAuliffe, and N. D. A. Toma, *Chem. and Ind.*, 1976, 273.

<sup>12</sup> I. Tkatchenko, *Compt. rend.*, 1976, **282**, C, 229.

<sup>13</sup> S. O. Grim and R. C. Barth, *J. Organometallic Chem.*, 1975, **94**, 327.

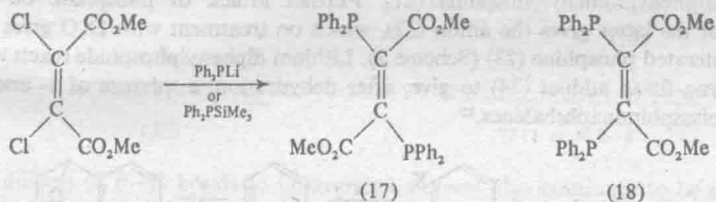


Similarly, the chloroalkylarsine (15) (obtained from lithium diphenylarsenide and 1,2-dichloroethane) reacts with lithium diphenylphosphide to form the mixed phosphine-arsine (16).<sup>14</sup>



Organosilylphosphines are conveniently prepared by cleavage of alkyldiarylphosphines with lithium in THF, followed by treatment with chlorotrimethylsilane,<sup>15</sup> and tris(trimethylsilyl)phosphine has been prepared from the reaction of chlorotrimethylsilane with a mixture of sodium and potassium phosphides.<sup>16</sup>

The product of the reaction between lithium diphenylphosphide (or trimethyldiphenylphosphine) and dimethyl 2,3-dichloromaleate has been shown to be the fumarate (17)<sup>17</sup> and not (as previously supposed)<sup>18</sup> the expected maleate (18).



Nucleophilic displacement of halide ion from a saturated carbon atom by alkali-metal diphenylphosphide reagents occurs with inversion of configuration at carbon, as is found in normal  $\text{S}_{\text{N}}2$  displacements.<sup>19</sup> Thus menthyl chloride or bromide gives the *neo*-menthyldiphenylphosphine (19).

An improved procedure has been reported for the synthesis of the C-functionalized tertiary phosphine (20), based on the reaction of potassium diphenylphosphide with ethyl chloroacetate.<sup>20</sup>

<sup>14</sup> K. K. Chow and C. A. McAuliffe, *Inorg. Chim. Acta*, 1975, 14, 5.

<sup>15</sup> R. Appel and K. Geisler, *J. Organometallic Chem.*, 1976, 112, 61.

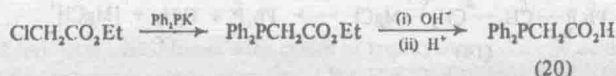
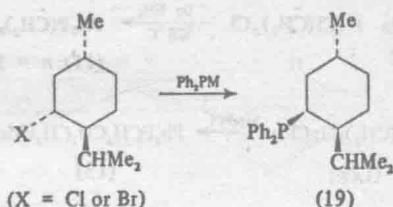
<sup>16</sup> G. Becker and W. Hoelderich, *Chem. Ber.*, 1975, 108, 2484.

<sup>17</sup> D. Fenske and J. Löns, *Chem. Ber.*, 1975, 108, 3091.

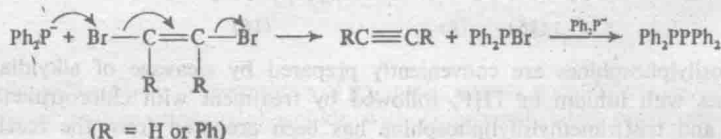
<sup>18</sup> H. J. Becher, D. Fenske, and E. Langer, *Chem. Ber.*, 1973, 106, 177.

<sup>19</sup> A. M. Aguiar, C. J. Morrow, J. D. Morrison, R. E. Burnett, W. F. Masler, and N. S. Bhacca, *J. Org. Chem.*, 1976, 41, 1545.

<sup>20</sup> T. Jarolim and J. Podlahova, *J. Inorg. Nuclear Chem.*, 1976, 38, 125.

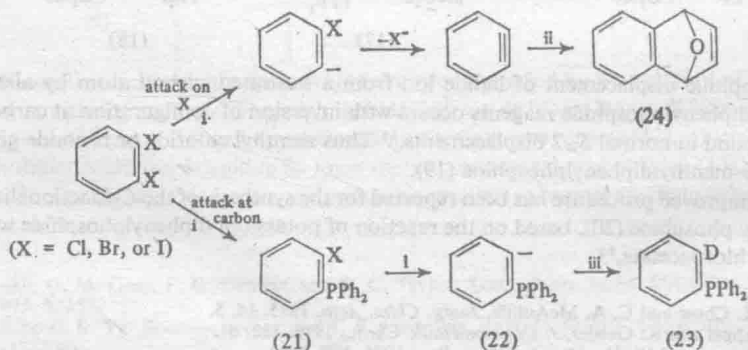


Two reports of the hitherto little documented attack of organophosphide anions on halogen have appeared. Addition of 1,2-dibromoalkenes to lithium diphenylphosphide in THF gives an acetylene and tetraphenyldiphosphine<sup>21</sup> (Scheme 1).



Scheme 1

In the corresponding reactions of *o*-dihalogenobenzenes, attack on halogen, leading to the generation of benzyne, competes with attack at carbon, leading to the *o*-halogenophenyldiphenylphosphine (21). Further attack of phosphide on the halogen of the latter gives the anion (22), which on treatment with D<sub>2</sub>O gives the *ortho*-deuterated phosphine (23) (Scheme 2). Lithium diphenylphosphide reacts with the benzyne-furan adduct (24) to give, after dehydration, a mixture of 1- and 2-diphenylphosphinonaphthalenes.<sup>22</sup>



Reagents: i, Ph<sub>2</sub>P<sup>-</sup>; ii, furan; iii, D<sub>2</sub>O

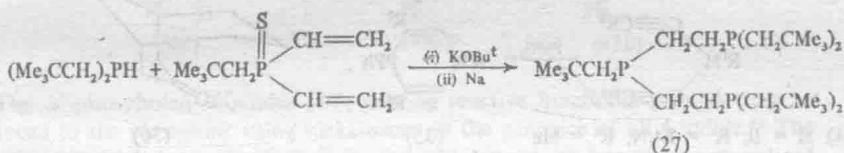
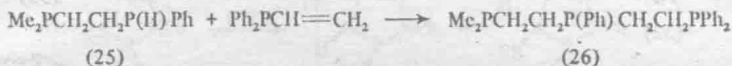
Scheme 2

<sup>21</sup> D. G. Gillespie and B. J. Walker, *Tetrahedron Letters*, 1975, 4709.

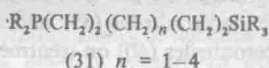
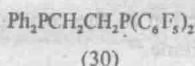
<sup>22</sup> D. G. Gillespie, B. J. Walker, D. Stevens, and C. A. McAuliffe, *Tetrahedron Letters*, 1976, 1905.



**By Addition of P—H to Unsaturated Compounds.** This route continues to be exploited for the synthesis of polydentate tertiary phosphine ligands. Thus base-catalysed addition of diphenylvinylphosphine to the secondary phosphine (25) affords (26).<sup>23</sup> Neopentylpolytertiaryphosphines, *e.g.* (27), have been similarly prepared<sup>24</sup> by addition of primary or secondary phosphines to vinylphosphines (or the related phosphine sulphides, followed by a desulphurization step).



Free-radical-catalysed additions have also been reported, and provide a genuine alternative to the more familiar base-catalysed addition routes. Thus the secondary diphosphine (28) readily adds to diphenylvinylphosphine in the presence of AIBN to give (29).<sup>25</sup> Similarly, addition of di(pentafluorophenyl)phosphine to diphenylvinylphosphine affords<sup>26</sup> the diphosphine (30). Sequential addition of silanes and secondary phosphines to terminal  $\alpha\omega$ -dienes under the influence of u.v. light affords the silylalkylphosphines (31), which may be anchored *via* silicon to the surface of inorganic oxides and used as polymeric catalysts.<sup>27</sup>



Addition of P—H bonds to unsaturated systems also continues to be used as a route to heterocyclic systems. Thus base-catalysed cyclization of the phosphine (32) [prepared by the addition of methyl methacrylate (2 moles) to phenylphosphine], followed by subsequent hydrolysis and decarboxylation, affords the phosphorinanone (33). The phosphorinanone system is also directly accessible by the addition of phenylphosphine to divinyl ketones.<sup>28</sup> The radical-initiated addition of phenylphosphine to dialkynyl systems (34) gives the heterocyclohexadienes (35).<sup>29,30</sup> The stereochemistry of the addition of phenylphosphine to cyclo-octa-2,7-dienone to give

<sup>23</sup> R. B. King, J. A. Zinich, and J. C. Cloyd, jun., *Inorg. Chem.*, 1975, 14, 1554.

<sup>24</sup> R. B. King, J. C. Cloyd, jun., and R. H. Reimann, *J. Org. Chem.*, 1976, 41, 972.

<sup>25</sup> D. L. Dubois, W. H. Meyers, and D. W. Meek, *J.C.S. Dalton*, 1975, 1011.

<sup>26</sup> I. Macleod, L. Manojlović-Muir, D. Millington, K. W. Muir, D. W. A. Sharp, and R. Walker, *J. Organometallic Chem.*, 1975, 97, C7.

<sup>27</sup> A. A. Oswald, L. L. Murrell, and L. J. Boucher, *Preprints Div. Petrol. Chem., Amer. Chem. Soc.*, 1974, 19, 155, 162 (*Chem. Abs.*, 1975, 83, 198 225, 1976, 84, 105 685).

<sup>28</sup> I. N. Azerbaev, B. M. Butin, and Y. G. Bosyakov, *J. Gen. Chem. (U.S.S.R.)*, 1975, 45, 1696.

<sup>29</sup> H. O. Berger and H. Noeth, *Z. Naturforsch.*, 1975, 30b, 641.

<sup>30</sup> G. Märkl, D. Matthes, A. Donaubaue, and H. Baier, *Tetrahedron Letters*, 1975, 3171.