

# Contents

---

Chapter 1 Phosphines and Phosponium Salts	1
<i>By D. J. H. Smith</i>	
<b>1 Phosphines</b>	1
Preparation	1
From Halogenophosphines and Organometallic	
Reagent	1
From Metallated Phosphines	1
By Reduction	4
Miscellaneous	5
Reactions	7
Nucleophilic Attack on Carbon	7
Activated olefins	7
Activated acetylenes	8
Carbonyls	9
Nucleophilic Attack at Halogen	10
Nucleophilic Attack at Other Atoms	12
Miscellaneous	13
<b>2 Phosponium Salts</b>	15
Preparation	15
Reactions	18
Alkaline Hydrolysis	18
Additions to Vinylphosponium Salts	21
Miscellaneous	24
<b>3 Phosphorins</b>	25
Preparation	25
Reactions	28
<b>4 Phospholes</b>	30
Preparation and Reactions	30
Physical Measurements	32
Chapter 2 Quinquecovalent Phosphorus Compounds	34
<i>By S. Trippett</i>	
<b>1 Ligand Reorganization and Structure</b>	34
<b>2 Acyclic Systems</b>	35

<b>3 Three-membered Ring</b>	37
<b>4 Four-membered Rings</b>	37
<b>5 Five-membered Rings</b>	39
Phospholans and Phospholens	39
1,3,2-Dioxaphospholans	40
1,3,2-Dioxaphospholens	42
1,2-Oxaphospholens	44
1,3,2-Oxazaphospholens	44
1,3,5-Oxazaphospholens	46
Miscellaneous	47
<b>6 Six-membered Ring</b>	49
<b>7 Six-co-ordinate Species</b>	49
<b>Chapter 3 Halogenophosphines and Related Compounds</b>	52
<i>By J. A. Miller</i>	
<b>1 Halogenophosphines</b>	52
Physical Aspects	52
Reactions	53
Electrophilic Attack by Phosphorus	53
Nucleophilic Attack by Phosphorus	56
Biphilic Reactions	56
Miscellaneous Reactions	59
<b>2 Halogenophosphoranes</b>	60
Structure and Bonding	60
Preparation	62
Reactions	63
<b>Chapter 4 Phosphine Oxides, Sulphides, and Selenides</b>	70
<i>By J. A. Miller</i>	
<b>1 Introduction</b>	70
<b>2 Preparation</b>	70
From Secondary Phosphine Oxides or from Phosphinites	70

<i>Contents</i>	vii
By Grignard and Related Reactions	72
By Oxidation of Phosphines	73
By Miscellaneous Routes	76
<b>3 Reactions and Properties</b>	<b>79</b>
<b>Chapter 5 Tervalent Phosphorus Acids</b>	<b>83</b>
<i>By B. J. Walker</i>	
<b>1 Introduction</b>	<b>83</b>
<b>2 Phosphorous Acid and Derivatives</b>	<b>83</b>
Nucleophilic Reactions	83
Attack on Saturated Carbon	83
Attack on Unsaturated Carbon	86
Attack on Nitrogen	98
Attack on Oxygen	99
Attack on Halogen	101
Electrophilic Reactions	103
Rearrangements	105
Cyclic Esters of Phosphorous Acid	105
Miscellaneous Reactions	109
<b>3 Phosphonous and Phosphinous Acids and Derivatives</b>	<b>111</b>
<b>Chapter 6 Quinquevalent Phosphorus Acids</b>	<b>112</b>
<i>By N. K. Hamer</i>	
<b>1 Phosphoric Acid and Derivatives</b>	<b>112</b>
Synthetic Methods	112
Solvolyses of Phosphoric Acid Derivatives	115
Reactions of Phosphoric Acid Derivatives	121
<b>2 Phosphonic and Phosphinic Acids and Derivatives</b>	<b>127</b>
Synthetic Methods	127
Solvolyses of Phosphonic and Phosphinic Esters	130
Reactions of Phosphonic and Phosphinic Acid	
Derivatives	132
Miscellaneous	138

<b>Chapter 7 Phosphates and Phosphonates of Biochemical Interest</b>	
<i>By D. W. Hutchinson</i>	141
<b>1 Introduction</b>	141
<b>2 Mono-, Oligo-, and Poly-nucleotides</b>	141
Mononucleotides	141
Nucleoside Polyphosphates	150
Oligo- and Poly-nucleotides	152
Analytical Techniques and Separation Methods	156
<b>3 Coenzymes and Cofactors</b>	157
Nucleoside Diphosphate Sugars	157
Vitamin B <sub>6</sub> and Related Compounds	158
Other Coenzymes	158
<b>4 Naturally Occurring Phosphonates</b>	160
<b>5 Oxidative Phosphorylation</b>	161
<b>6 Sugar Phosphates</b>	163
<b>7 Phospholipids</b>	164
<b>8 Enzymology</b>	165
<b>9 Other Compounds of Biochemical Interest</b>	167
<b>Chapter 8 Ylides and Related Compounds</b>	170
<i>By S. Trippett</i>	
<b>1 Methylenephosphoranes</b>	170
Preparation	170
Reactions	172
Halides	172
Carbonyls	174
Miscellaneous	179
<b>2 Phosphoranes of Special Interest</b>	181
<b>3 Selected Applications of Ylides in Synthesis</b>	188
Natural Products	188
Macrocyclic Compounds	191
Miscellaneous	192

<i>Contents</i>	ix
<b>4 Selected Applications of Phosphonate Carbanions</b>	<b>194</b>
<b>5 Ylide Aspects of Iminophosphoranes</b>	<b>197</b>
<b>Chapter 9 Phosphazenes</b>	<b>200</b>
<i>By R. Keat</i>	
<b>1 Introduction</b>	<b>200</b>
<b>2 Synthesis of Acyclic Phosphazenes</b>	<b>200</b>
From Amides and Phosphorus(v) Halides	200
From Azides and Phosphorus(III) Compounds	202
Other Methods	205
<b>3 Properties of Acyclic Phosphazenes</b>	<b>207</b>
Halogeno-derivatives	207
Alkyl and Aryl Derivatives	210
<b>4 Synthesis of Cyclic Phosphazenes</b>	<b>213</b>
<b>5 Properties of Cyclic Phosphazenes</b>	<b>217</b>
Halogeno-derivatives	217
Amino-derivatives	219
Alkoxy- and Aryloxy-derivatives	222
Alkyl and Aryl Derivatives	223
<b>6 Polymeric Phosphazenes</b>	<b>225</b>
<b>7 Molecular Structures of Phosphazenes Determined by</b>	
X-Ray Diffraction Methods	226
<b>Chapter 10 Photochemical, Radical, and Deoxygenation Reactions</b>	
<i>By R. S. Davidson</i>	228
<b>1 Photochemical Reactions</b>	<b>228</b>
<b>2 Phosphinidenes and Related Species</b>	<b>229</b>
<b>3 Radical Reactions</b>	<b>230</b>
Structure	231
$\alpha$ -Cleavage Reactions	232
$\beta$ -Scission Reactions	233

Relative Ease of $\alpha$ - and $\beta$ -Scission Reactions	234
Other Aspects of the Chemistry of Phosphoranyl Radicals	234
<b>4 Deoxygenation Reactions</b>	<b>238</b>
Ozone and Ozonides	238
Molecular Oxygen	239
Hydroperoxides and Peroxides	239
Oxaziridines and Oxadiazoles	240
Sulphoxides	241
Mono- and Poly-sulphides and Elemental Sulphur	242
N-Oxides, Nitroso- and Nitro-compounds	243
 Chapter 11 Physical Methods	 247
<i>By J. C. Tebby</i>	
<b>1 Nuclear Magnetic Resonance Spectroscopy</b>	<b>247</b>
Chemical Shifts and Shielding Effects	247
Phosphorus-31	247
$\delta_P$ of P <sup>II</sup> compounds	248
$\delta_P$ of P <sup>III</sup> compounds	248
$\delta_P$ of P <sup>IV</sup> compounds	250
$\delta_P$ of P <sup>V</sup> compounds	252
Isotope effects on $\delta_P$	253
Carbon-13	253
Hydrogen-1	254
Studies of Equilibria, Reactions, and Solvent Effects	254
Pseudorotation	256
Restricted Rotation	258
Inversion, Non-equivalence, and Configuration	259
Spin-Spin Coupling	260
<i>J</i> (PP) and <i>J</i> (PM)	261
<i>J</i> (PC)	262
<sup>1</sup> <i>J</i> (PH)	263
<i>J</i> (PC <sub><i>n</i></sub> H)	264
<i>J</i> (PXC <sub><i>n</i></sub> H)	266
Relaxation Times, Paramagnetic Effects, and N.Q.R. Studies	268
<b>2 Electron Spin Resonance Spectroscopy</b>	<b>269</b>
<b>3 Vibrational Spectroscopy</b>	<b>270</b>
Stereochemical Aspects	273
Studies of Bonding	274

<i>Contents</i>	xi
<b>4 Microwave Spectroscopy</b>	275
<b>5 Electronic Spectroscopy</b>	275
<b>6 Rotation and Refraction</b>	278
<b>7 Diffraction</b>	279
<b>8 Dipole Moments, Conductance, and Polarography</b>	282
<b>9 Mass Spectrometry</b>	284
<b>10 pK and Thermochemical Studies</b>	287
<b>11 Surface Properties</b>	289
<b>Author Index</b>	290