

Cambridge University Press

978-0-521-29757-8 - Introduction to Phosphorus Chemistry

Harold Goldwhite

Index

[More information](#)

## Index

*Page numbers in italics refer to tables.*

- absolute configuration, phosphonium salt, 56
- adenosine diphosphate, 3
- adenosine triphosphate, 3
- alkylene phosphorane, 60–62
- apicophilicity, 74
- Arbuzov A. E., 1, 54, 55
- basicity
  - hybridization effect, 26–27
  - phosphines, 42–44
- Berry mechanism, 74–75
- bond energy, 94
  - P:N bond, 30
  - P:O bond, 30
  - terms, 83
- bond length, 93
  - bond order correlation, 31–32
- bond order
  - bond length correlation, 31–32
  - vibrational frequency effect, 33
- <sup>13</sup>C nmr, 20–21
- calcium phosphates, 3
- catenated compounds, 68–70
  - C.N.1, 5
  - C.N.2, 6–7
  - C.N.3
    - oxidation, 52–53
    - ozonides, 89
    - reaction mechanism, 50–51
    - stereochemistry, 38–42
    - survey, 7–8
    - synthesis, 37–38
  - C.N.4
    - catenated compounds, 68–70
    - reaction mechanisms, 57–68
    - stereochemistry, 56–57
    - survey, 8
    - synthesis, 54–56
  - C.N.5
    - geometry, 72
- intermediates in C.N.4 reactions, 76–80
  - ligand mobility, 73–75
  - stereochemistry, 72–73
  - survey, 8–9
  - synthesis, 72–73
- C.N.6, 9
- conformational analysis and PH coupling constants, 19
- Coulson, C. A., 33
- coupling constants, 97–98
- Craig D. P., 33
- cyclophosphazenes, 34–36
- cyclopolyphosphates, 69
- cyclopolyphosphines, 82
- dehalogenation, 88
- deoxygenation, 87
- desulfurization, 86
- Dewar M. J. S., 35
- dimethylphosphite, 10
- DIOP, 92
- dioxaphospholane hydrolysis, 76–77
- diphosphane, 37
- diphosphate, 69
- diphosphine, see *diphosphane*
- d*-orbitals and multiple bonding, 33
- E<sub>2</sub> elimination, 57
- electronegativity, 81
- electron spectroscopy, 23–24
- electron spin resonance (esr), 21–22
- eutrophication, 3
- fluoroapatite, 3
- free-radical addition reactions
  - diphosphines, 12
  - PH<sub>3</sub>, 21
  - phosphines, 11
  - phosphites, 11
  - phosphorus halides, 13
- <sup>1</sup>H nuclear magnetic resonance, 19–20

*Index*

112

- Hammett study  
 nucleophilic displacement at P, 58  
 quaternization of phosphines, 45
- HCP, 5  
 bonding, 36  
 hexachlorodisilane reduction, 71  
 history of phosphorus chemistry, 1  
 homogeneous catalyzed hydrogenation, 91  
 HSAB (hard and soft acid base) theory, 46  
 hybridization  
   apicophilicity, 74  
   basicity, 26–27, 43  
   geometry, 26  
   PH coupling constants, 19  
   PP coupling constants, 18  
 hydrogenation, 91
- ion-cyclotron resonance, 23  
 infrared spectroscopy (also see vibrational spectroscopy), 95  
 ionization energy, and basicity, 44
- $^2J_{\text{PCH}}$  and dihedral angle, 20  
 $^1J_{\text{PP}}$ , 18, 19
- Kinnear-Perren reaction, 55
- Liebig, J. von, 2  
 ligands, 46–50  
 lithium tetrahydroaluminate reduction, 70
- mass spectroscopy, 22–23  
 metal phosphide hydrolysis, 37  
 metal-phosphorus bond, 48–50  
 metaphosphate, 64  
   analog, 7  
   intermediate, 64
- Michaelis, A., 1  
 Michaelis-Arbuzov reaction, 54, 55  
 Michaelis-Becker reaction, 10  
 microcosmic salt, 1  
 molecular orbitals, 28  
 multiple bonds, 28–36
- nuclear magnetic resonance (nmr)  
 $^{13}\text{C}$ , 20–21  
 $^1\text{H}$ , 19–20  
 $^{31}\text{P}$ , 17–19
- nomenclature, xi–xiv  
 nucleic acids, 3  
 nucleophilicity of phosphines, 45–46
- oxaphosphetane, 62–63  
 oxiran synthesis, 88–89  
 oxophosphorane, 73, 90  
   in synthesis, 90–91  
 oxidation state, 5  
 oxidative addition to C.N.3, 72
- $^{31}\text{P}$  Chemical shifts, 96  
 $^{31}\text{P}$  nuclear magnetic resonance (nmr), 17–19
- Pauling, L., 33  
 Pauling electronegativity, 81  
 PC bond reactions, 11  
 $\text{PCl}_3$  reaction with alcohols, 85  
 Pearson hard soft acid base (HSAB) theory, 46  
 Perkov reaction, 55  
 pesticides, discovery, 1  
 $\text{PF}_3$  ligand, 47–48  
 phenylsilane reduction, 71  
 $\text{PH}_2\text{F}_3$ , 74  
 phosdrin, 55  
 P-halogen bond reactions, 13  
 P-halogen compounds as halogenating agents, 85–86  
 P-H bond reactions, 10–11  
 phosphabenzene, 6  
   bonding, 36  
   spectra, 36  
 phosphacyanins, 6  
 phosphagens, 65  
   hydrolysis, 66  
 phosphate  
   detergents, 3  
   fertilizers, 2  
   cyclic, hydrolysis, 76  
   hydrolysis, 12  
   minerals, 3  
 phosphazenes  
   cyclic, 34–36, 68  
   linear, 69  
 phosphine ( $\text{PH}_3$ )  
   radical addition to, 21  
   synthetic uses, 37  
 phosphine oxides, chiral, 56  
 phosphines  
   acyl, 40–41  
   basicity, 42–44  
   inversion, 39  
   ion-molecule reactions, 23  
   mass spectra, 22  
   nucleophilicity, 45–46  
   optically active, 38, 39  
   proton affinity, 42, 43  
 phosphino radicals, 22  
 phosphite desulfurization, 86  
 phosphite, dimethyl, 10  
 phosphocreatine, 66  
 phospholes, 40, 41  
 phosphonium salts  
   chiral, 56  
   reactions with nucleophiles, 57–63  
 phosphoramides, hydrolysis, 11, 12  
 phosphorane, 8  
 phosphoranyl radical, 21, 52

*Index*

113

- phosphoric esters, hydrolysis, 12  
phosphorous acid  
  diethyl ester, 16  
  dimethyl ester, 10  
phosphorous amides  
  alcoholysis, 11, 12  
  desulfurization, 87  
  oxiran synthesis, 88  
phosphorus  
  abundance, 2  
  atomic energy levels, 25  
  cycle, 3, 4  
  ecology, 2-4  
  economy, 2  
  elemental forms, 5  
  first production, 1  
  group VA comparisons, 81-84  
  history, 1  
  red, 7  
  white, 7  
phosphorus-carbon bonds, multiple, 6  
  reactions, 11  
phosphorus ligands, 46-50  
phosphorus-metal bond, 48-50  
  coupling constants, 49  
phosphorus nmr  
  chemical shift, 18, 96  
  chemical shift standard, 17  
  sensitivity, 17  
phosphorus pentachloride, 8  
phosphorus pentafluoride, 8  
phosphorus trichloride  
  oxidation, 53  
  synthetic uses, 38  
phosphorus trifluoride ligand, 47  
phosphenyl group, infrared spectra, 16, 17  
phostionate, 79  
physical data, 93-94  
PN bond reactions, 11-12  
 $P_4O_{10}$ , 69, 70  
PO bond reactions, 12  
P:O bond, reduction, 12  
polymers, phosphorus-nitrogen, 69  
polyphosphate detergents, 1  
PP bonds, 12, 82  
P:S bond, 13  
  desulfurization, 13  
pseudorotation, 74  
pyrophosphate, 69  
quaternization, 45  
redistribution, 51  
reduction, C.N.4 compounds, 70-71  
rotation barriers, 41, 42  
Saunders, B. C., 1  
Schrader G., 1  
singlet oxygen, 89  
 $S_N(C)$ , 57  
 $S_N(P)$ , 58  
spectroscopic data, 95-98  
Staudinger H., 60, 61  
stereochemistry  
  C.N.3, 38-42  
  C.N.4, 56-57  
  C.N.5, 72-73  
Taft  $\sigma^*$  and basicity, 42  
tetraphosphate, 69  
triarylphosphite dihalides, 86  
triphenyl phosphine  
  in dehalogenation, 88  
  in deoxygenation, 87  
triphenyl phosphine dihalides, 86  
triphenyl phosphite ozonide, 89  
triprophosphate, 69  
turnstile mechanism, 75  
ultraprophosphate, 69  
valence bond, 25  
vibrational spectroscopy, 15-17  
  bond order, 33  
Walden inversion, 67  
Westheimer F. H., 76  
Wilkinson's catalyst, 91  
Wittig G., 61  
  reaction, 61  
ylid, *see* alkylene phosphorane