
Preface

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This volume covers the literature of organophosphorus chemistry published in the period from January 2006 to January 2007, and reflects our efforts in recent years to provide a more up to date survey of progress in this topic which continues to generate a vast range of literature. The volume follows the traditional approach, apart from the absence of the usual chapter on mononucleotide chemistry. However, some coverage of this area has been included in David Loake's chapter on nucleotides and nucleic acids and it is hoped that the mononucleotide area will receive a full survey in the next volume. We welcome new authors Professor Gabino Carriedo (Universidad de Oviedo) who has covered phosphazenes and Professor Gerd-Volker Roeschenthaler (Institute of Inorganic & Physical Chemistry, University of Bremen) who has reported on advances in hypervalent phosphorus chemistry.

The use of a wide range of trivalent phosphorus ligands in homogeneous catalysis continues to be a major driver in the chemistry of both traditional P–C-bonded phosphines and also that of trivalent phosphorus acid derivatives. It is interesting to note the increasing use of borane-protected metallophosphide reagents in methods for the synthesis of new phosphines. A study of the synthesis of chiral primary arylphosphines has revealed, surprisingly, that primary phosphines in which the aryl substituent is involved in extended conjugation are significantly more stable to air than are simple phenyl analogues. It seems that many primary arylphosphines are no more sensitive to air than are moderately reactive aldehydes, and that these compounds are much more attractive synthetic precursors than previously supposed. Considerable interest has also been shown in studies of the physicochemical properties of phosphines, in particular the *solution-phase* acidity of compounds containing P–H bonds and new approaches for the prediction of the basicity of phosphines in general. It has been shown that the solvent exerts a profound influence on the basicity of phosphines and that it is not valid to use gas-phase data to interpret the solution-phase basicity of these compounds.

The chemistry of phosphine chalcogenides, phosphonium salts and ylides has also continued to develop and activity in this area remains at a high level. Of note is a growing literature on the use of phosphonium-based ionic liquids as solvents.

Nucleotide chemistry also continues to be a very active area. 2006 saw a further increase in the number of publications relating to modified oligonucleotides. By far the largest single area of research in this field concerns oligonucleotides containing modified nucleobases, with applications ranging from duplex and triplex stabilisation to modified base pairs and analogues prepared to investigate the mechanism of action of a variety of enzymes. The largest section in the review concerns oligonucleotide conjugates, a very diverse field, which includes fluorescent analogues and their applications, molecular beacons, FRET techniques and single molecule studies. Also noted is the rapidly expanding study of nanodevices and nanostructures and a growing interest in the use of metal-chelating pseudonucleosides, which have applications in novel base pairing interactions, in metal catalysis, and in the study of therapeutic reagents such as cisplatin. The structural study of oligonucleotides is another expanding area of research, and each year more complex structures are solved by X-ray crystallography or by NMR. NMR techniques now allow for the study of larger and larger biosystems that include a number of oligonucleotide-peptide structures. In addition, many new techniques are emerging that give global

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structures of biomolecules, such as atomic force microscopy and electron microscopy.

Once again, there has been keen interest in quinquevalent phosphorus chemistry. Studies have been particularly rewarding in the field of stereoselective synthesis—some reactions proceeding in a highly enantioselective manner giving up to 99% ee. Success in the biological areas includes the synthesis of a large number of natural and unnatural phosphates and their phosphonate, phosphinate and fluorinated analogues as well as several inositols and phosphorus analogues of amino acids. Highlights include the total synthesis of the antitumor fostriecin analogue, PD 113.271, cytostatin, and phostactomycin B that show antitumor, antibacterial and antifungal activities. Other syntheses include a novel series of phosphorus-containing C-11-aryl-substituted steroids and several analogues of aryl-substituted fosfidomycin which are superior to fosfidomycin in inhibiting the growth of malaria parasites. Mechanistic studies include phosphate ester hydrolysis and metal-catalyzed reactions. Highlights include the great catalytic potential of chiral phosphoric acids having different functionalized aromatic systems (Brønsted acids) for reactions such as the rhodium catalyzed allylic alkylation of chelated enol phosphates, and the allylation of iminophosphonates using various allylsilanes catalyzed by a copper complex.

Interest in phosphazene chemistry is as keen as ever. A larger range and improved preparative routes to Schwesinger's bases has led to their wider use in synthesis, *e.g.* as catalysts. They are now becoming commercially available. Improvements in the stabilities of phosphazanium cations make them useful as counter cations in basic conditions and for improving anion reactivities such as the 'naked' fluoride ion. Mechanistic studies of the aza-Wittig reaction are assisting the wide use of this reaction in organic synthesis. Staudinger ligation has also received attention furthered by its utilization for making biologically active compounds. The role of phosphazenes in metal catalysis is highlighted by the use of Rh and Ir complexes with ferrocenyl phosphazenes in olefin hydrogenation in almost perfect enantiomeric excess. Better methods for the generation of polyphosphazenes have been developed. Studies of cyclo- and poly-phosphazenes have continued unabated. This has been largely due to their immense range of applications especially as improved materials and biological applications. These include membrane and photonic developments, biosensors, bone composites, electrolyte additives, ion-conducting materials and flame retardants. Their potential as ligands for metal catalysis is only just beginning to be realised.

The interest in hypervalent phosphorus chemistry centres mainly on the boundaries of acyclic, monocyclic and bicyclic phosphorus compounds as well as the interconversion of penta- and hexa-coordinate states. In addition to theoretical studies there have been advances in the use of ^{31}P NMR techniques to investigate the structures of more complex systems, such as phosphoryl transfer enzymes, as well as for investigating complex oxide structures. There have been reviews of stereogenic phosphorus sites and the stereochemistry associated with phosphorane and oxyphosphorane reactions where pentacoordinate transition states or intermediates are often encountered. Consideration of apicophilic, fluxional behavior, bond parameters, and tetra- vs. penta-coordination has shown that the familiar apicophilicity rules give an oversimplified picture. Evidence has been presented that a number of betaines exist in equilibrium with isomeric phosphoranones. The mechanism of ligand rearrangement (pseudorotation) has been an exciting and keenly studied area of pentavalent phosphorus chemistry and we acknowledge the major contribution made by Ivar K. Ugi (1930–2005) who will be especially remembered for his work on the alternative 'Turnstile Rotation' mechanism to the established 'Berry Pseudorotation'.