Preface

David Allen[a] and John Tebby[b]
DOI: 10.1039/b818914p

This volume covers the literature of organophosphorus chemistry published in the period from January 2007 to January 2008, and continues our efforts in recent years to provide a more up to date survey of progress in this topic which, once again, has generated a vast amount of research, particularly in the chemistry of nucleic acids and nucleotides, although other areas, *e.g.*, phosphine and phosphorane chemistry, have seen a small reduction in activity. The volume sees the welcome return of coverage of the area of mononucleotide chemistry by Marie Migaud (Queen's University, Belfast), who has provided a two-year survey of the 2006 and 2007 literature. We also welcome Professor Irina Odinets (Nesmeyanov Institute of Organoelement Chemistry, Moscow) who has covered phosphonium salts and related ylides, and also Professor Piotr Balczewski and Dr Agnieszka Bodzioch (Centre of Molecular and Macromolecular Studies, Lodz, Poland) who have reviewed quinquevalent compounds.

The use of a wide range of tervalent phosphorus ligands in homogeneous catalysis has continued to be a major driver in the chemistry of both traditional P–C-bonded phosphines and also that of tervalent phosphorus acid derivatives. Perhaps the most remarkable finding in these areas is the ability of a combination of sterically-crowded arylphosphine–arylboranes to cleave molecular hydrogen to form phosphonium hydridoborate salts that have the ability to reduce carbonyl groups. The use of phosphonium salts as ionic liquids is the subject of increasing interest, with many new applications being reported. In phosphine chalcogenide chemistry, the synthesis of enantioenriched phosphine oxides has attracted considerable attention.

Ligand development in the tervalent phosphorus acid area includes a useful review on asymmetric catalysts using chiral carbohydrate-derived phosphinites, phosphites and phosphoramidites. There have also been reviews on the synthesis of phosphonopeptides, the use of zirconium reagents for the synthesis of a variety of linear and cyclic phosphinite ligands, the preparation of macrocyclic compounds by employing pnictogen(III)–nitrogen cyclic compounds, and also applications of macrocyclic compounds possessing tetrathiafulvalene units.

There has been good coverage of traditional quinquevalent phosphorus acid chemistry such as new P(V) reagents, new synthetic approaches, enantioselective syntheses, the use of chiral reagents, and the total syntheses of natural and synthetic biologically active compounds. The chemistry of new materials includes optoelectronics and fluorescent compounds, used mainly as probes in medicinal chemistry. There has been greater use of P(V)-containing cyclic

[a] *Biomedical Research Centre, Sheffield Hallam University, Sheffield, UK S1 1WB*
[b] *Division of Chemistry, Faculty of Sciences, Staffordshire University, Stoke-on-Trent, UK ST4 2DE*

compounds, especially those of aromatic and heteroaromatic character, due to developments in new ionic, radical and dipolar cyclisation reactions as well as cross-coupling methodologies. A shift of interest towards the synthesis of phosphoryl-substituted cyclic compounds, especially those containing 3-, 5- and 6-membered rings with O, N, and S heteroatoms, has also been noted.

Notable developments in nucleotide chemistry during this period include the broadening of protide chemistry and major advances made in the chemistry of polyphosphate nucleosides and dinucleotides. We have seen yet another increase in the number of publications in the field of modified oligonucleotides and many new analogues have been synthesized in order to explore new applications. Growing interest is being shown in developments in nanotechnology involving oligonucleotide conjugates. Another growth area is single molecule studies, which can be used to observe the motion, folding and dynamics of oligonucleotides as well as their interactions with other biomolecules. New techniques for detecting and analyzing nucleic acid structures of increasing complexity are also being developed.

In hypervalent phosphorus chemistry there have been studies on properties and mechanisms. The interconversion of penta- and hexa-coordinated states continues to attract interest due to their involvement as intermediates (or transition states) in biological phosphorylation. Fluorinated derivatives are popular and methods of preparation that avoid the use of toxic phosphorus oxofluorides as starting materials have been investigated. New bidentate ligands based on decafluoro-3-phenyl-3-pentanol have been applied to the synthesis of P–H spirophosphoranes. Methods for the synthesis of spirophosphoranes and a variety of pentacoordinated phosphorus compounds, including myo-inositol derivatives, have been described as well as the synthesis and resolution of a novel chiral hexacoordinated phosphate that behaves as an enantiopure anionic N-ligand. The first example of a compound containing pentacoordinated silicon and phosphorus atoms was reported and a hexacoordinate phosphate anion has been shown to control the conformation of tropos ligands bound to a metal centre.

The versatile reactivity and uses of phosphoranimines have been reflected in numerous patents and many reviews. Reviews include the formation of N and P donor-stabilized cations, fundamental synthetic methods for the preparation of phosphazene polymers and the synthesis, macromolecular architecture, formulation behaviour and activity of various types of polyphosphazene adjuvants including microencapsulation systems and stable linear organophosphazene homo- and co-polymers. Phosphazene bases and organometallic phosphazene derivatives continue to be of special interest. The keen interest in cyclophosphazene chemistry includes reports on bonding, the synthesis of inclusion compounds, dendrimers, cationic derivatives, ligands to form metal-complexes, multifunctional nucleophilic cyclophosphazenes, and nontoxic alternatives to quantum dots for (bio)imaging. Very stable film-forming cyclophosphazene-polymers have been synthesised and a general approach to surface functionalisation of silicon-based materials with selected substituents has been devised. There have been significant advances in a large range of potential biological uses of polyphosphazenes.