

Preface

The literature of organophosphorus chemistry remains buoyant, activity in the area continuing at a high level. As has been the case in recent years, we have again encountered problems in securing new authors for some areas, and this has inevitably led to delays in publication. For this volume, we are pleased to welcome Dr Aleksandra Skowrońska and her colleague Dr Richard Bodalski, from the Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz and the Technical University in Lodz, respectively, who have provided a two-year survey of the literature relating to the chemistry of quinquevalent phosphorus acids. In this volume, the usual chapter on penta- and hexa-coordinated phosphorus compounds is missing, the reason being that the volume of literature in this area has declined significantly and the author feels that a two-year coverage would now be more appropriate. We hope that the first biennial review of this area will appear in volume 35 in due course.

July 4–9 2004 saw the first ICPC to be held in Britain. The Conference was held in the International Conference Centre in Birmingham and despite the high cost, it was well attended and attracted chemists, as usual, from all corners of the globe. Papers on synthesis and reactions were popular, ligand and medicinal chemistry were also strong and there were many good contributions in organometallic, applications and theoretical areas. An excellent presentation on the next 2007 ICPC conference, which will be held in Xiamen City, China, indicated that there will be a wide choice of cultural activities.

The drive for improved performance in transition metal ion-catalysed processes continues to stimulate the synthesis of new types of chiral phosphine and related chiral trivalent phosphorus ester and amide ligands. Activity has also remained high in the chemistry of heteroaromatic phosphorus ring systems and low-coordination number p_{π} -bonded systems. Also noteworthy are the developing applications of organophosphines in the Mitsunobu and Staudinger protocols in general synthetic chemistry.

As would be expected, synthetic applications of the Wittig and related reactions continue to dominate the literature relating to phosphorus-based ylides. Nevertheless, fundamental studies of the structure, bonding and reactivity of these compounds continue to appear.

In the mononucleotide area, the development of new protecting groups for the synthesis of oligoribonucleotides, particularly on solid supports, continues to be a major effort, as does interest in the synthesis of new antiviral and antitumour nucleoside analogues. The number of publications relating to oligo- and polynucleotide chemistry has continued to grow, the two most dominant research

areas being new base analogues and NMR solution structures, these being driven by advances in chemistry and NMR methodology. Other newly developing areas are the synthesis of oligonucleotides attached to metal and glass surfaces, and of oligonucleotide-conjugates.

Over the two year period covered there have been some impressive advances in many areas of quinquivalent phosphorus chemistry. New and improved synthetic procedures include the use of iodophosphates, P-nitrosophosphates, amidophosphates and a PhS^+ reagent for generating POP bonds. Amongst various isotopic labelling studies, a novel route to ^{32}P labelled compounds has been described. Mechanistic studies of reactions concerning phosphate ester hydrolysis continue to be reported and it has been shown that increased rates of phosphorylation can be achieved by facilitating an AE mechanism with the formation of phosphene intermediates. The importance of enantiomeric and asymmetric synthesis using chiral phosphorus (V) reagents is highlighted, which includes the use of a wide range of organometallic reagents and intermediates. There have been reports on enzyme enantioselective hydrolysis.

A large number of natural and unnatural phosphates, including carbohydrates and their phosphonate and phosphinate analogues, as well as many inositols, have been synthesized, usually with some biologically related purpose. The synthesis of phosphorus analogues of all types of amino acids, phospho- and phosphono-peptides and some glucosyl phosphates has also been developed. Several phosphorylated C_{60} fullerenes have been made and the first asymmetric PC bond formation under heterogeneous conditions has been described. Fluorinated phosphonates have also received much attention.

The phosphazide intermediate in the Staudinger synthesis of phosphazenes has been isolated by the use of sterically demanding reagents. There has been much attention to the preparation of multidentate phosphazene ligands and their complexation with a wide variety of metals. Many of the complexes are cyclic and some caged. An unusual ferrocenylboron complex consists of a planar four membered BNB ring. Deprotonated methylene groups of bis (aminophosphorano)methanes have been used to form carbon metal bonds. There has been a range of studies on the use of phosphazenes as catalysts for polymerisations. Non-ionic phosphazene bases have been found to be excellent catalysts for Michael addition reactions. Reviews on the incorporation of phosphazenes in complexes and polymers have appeared and some interesting preferences for geminal substitution rather than 1,3 substitution in tricyclophosphazenes have been reported. Compounds which incorporate crown ether structures show an interesting variety of affinities for alkali metal ions. Recent developments in polyphosphazene chemistry have been reviewed, including thionyl phosphazenes. Polyphosphazenes have also been used in the synthesis of light-emitting polymers as well as in the synthesis of a variety of membranes.

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