

Preface

Organophosphorus chemistry continues to generate a very large volume of literature, with no sign of any decline in activity. In this volume, we have increased our period of coverage of the literature, bringing it up to June 2004, in order to try to remedy the increasingly evident problem that our team of writers has in putting together these volumes in a timely manner. Our coverage of the above period is complete apart from the absence of the usual chapter on ylides chemistry. This deficiency, and the fact that this volume will not appear until early 2006, reflect the conflicting pressures which our authors are facing in collecting the information and in finding the substantial time needed to write these usually comprehensive reports. In consequence, it is probable that this volume will be last in the current style. Future volumes are likely to offer a more selective and critical coverage of the area, since the increasing availability of computer-aided literature search facilities makes attempts to provide comprehensive coverage unnecessary.

The period under review has seen the publication of several important books and general reviews. François Mathey has contributed a new book on heterocyclic organophosphorus compounds (*Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Elsevier, 2001) and Louis Quin and Anthony Williams have compiled a valuable new data resource on ^{31}P NMR spectroscopy (*Practical Interpretation of P-31 NMR Spectra and Computer-Assisted Structure Verification*; Advanced Chemistry Development, Toronto, 2004). A review of odd-electron bonds and biradicals in main group element chemistry (H. Grutzmacher and F. Breher, *Angew Chem. Int. Ed.*, 2002, **41**, 4006) contains much that is relevant to organophosphorus chemistry. A special edition of the journal *Phosphorus, Sulfur, Silicon and the Related Elements* (2004, **179**, issue 4–5, 649) was devoted to the proceedings of the Tenth International Symposium on Inorganic Ring Systems held in August 2003 in Vermont, USA and this again contains much relevant material.

Once again, the drive for improved performance in transition metal ion-catalysed processes has continued to stimulate the synthesis of new types of organophosphine and trivalent phosphorus-ester and -amide ligands. Activity in the chemistry of heteroaromatic phosphorus ring systems and low-coordination number p_π -bonded systems has also remained at a high level. New mechanistic insights into the Mitsunobu reaction have been reported, and interest in synthetic applications of Staudinger/Mitsunobu procedures has continued to develop.

The chemistry of phosphonium salts and phosphine chalcogenides has also continued to develop, although no major advances have appeared, doubtless reflecting the maturity of the area.

In the area of mononucleotide chemistry, extensive work has been reported on the chemistry of polyphosphates, in particular that of dinucleoside and

sugar nucleoside pyrophosphates. This reflects the reliability and flexibility of phosphoramidate methods which have been developed over the past few years. Similarly, a wide range of oligonucleotide building blocks, incorporating extensive structural modifications when compared to the natural nucleoside structures, have been described.

The review of polynucleotide chemistry focuses on oligonucleotide modifications, the largest group of which involves novel nucleobases that are used not only for duplex stabilisation and tertiary structures, but find application in understanding the mode of action of other biological molecules, conjugation with small molecules as well as macromolecules, and in nanotechnology devices. Advances also relate to sugar and backbone modifications. Noteworthy emerging areas include templated organic synthesis, and single molecule detection.

The three years since SPR 33 have seen considerable activity in the field of hypervalent phosphorus chemistry especially in the area of hexacoordinate and pseudo-hexacoordinate phosphorus compounds. In this respect, the Holmes' group has made further, substantial contributions to the subject of N, O and S donor interactions at hypervalent phosphorus and the relevance of such interactions to the mechanism of phosphoryl transfer enzymes. The utility of proazaphosphatranes as catalysts (or co-catalysts) has been established by Verkade *et al.* in an impressive range of synthetic procedures and both Kawashima and Akiba have reported outstanding work on bicyclic phosphorane systems, carbaphosphatranes and the relevance of anti-apicophilic phosphorane systems to the mechanism of the Wittig reaction. The Lacour group has detailed the use of C₂-symmetric hexacoordinated phosphate anions for enantiodifferentiation of organic and organometallic cations and last, but not least, Gillespie *et al.* have produced a thought-provoking review on bonding in penta- and hexacoordinated molecules. After 25 years Dennis Hall is retiring as an author to this publication. We thank him for his invaluable contributions.

Over the two year period covered, there have been impressive advances in several areas of P(V) chemistry. For example, biological aspects of quinquavalent phosphorus acids chemistry continue to increase in importance. A wide variety of natural and unnatural phosphates including inositols, lipids, some carbohydrates and their phosphonates, phosphinates and fluorinated analogues have been synthesized. Highlights include the asymmetric synthesis of phosphates, access to enantiomerically pure α -fluorinated phosphonate mimetics and a fluorescent porphyrin conjugate. Special attention has been paid to the synthesis of phosphorus analogues of all types of amino acids and some peptides. Numerous investigations of phosphate ester hydrolysis and related reactions continue to be reported. They include fluorescent monitoring probes and control of stereoselectivity of enzymatic hydrolysis of phosphonates. There have been interesting studies of phosphate complexation with lanthanide, zinc and copper complexes, the latter involving host-guest concepts. Interest in approaches to easier detoxification of insecticides continues. A number of new and improved stereoselective synthetic procedures have been elaborated.

Notable were highly enantioselective additions of N-phosphonyl imines with dialkyl zinc or hydroxyketones and a one-pot reaction of alkynylzirconocenes with alkynyl phosphazenes and zinc carbenoids to give single isomer cyclopropylphosphonamides. The importance of enantioselective and dynamic kinetic asymmetric transformations is illustrated in many publications. Other interesting reports cover the use of phosphoramidates for the synthesis of allylic amines as well as the first example of C–P cleavage of α -aminophosphono acids using periodate.

Two books have appeared on phosphazene chemistry reflecting its continuing wide development. There has been keen interest in acyclic phosphazenes and the ever-useful Staudinger reaction has been employed to produce novel tricyclic oxazoles, linear oligophosphazenes, as well as a series of aryloxypolyphosphazenes with potential for producing dendrimeric structures. Phosphoranimines have been prepared in high yields and their use in aza-Wittig reactions has paved the way for the preparation of a wide variety of natural products. A novel *N*-trimethylsilylphosphoranimine cationic salt has been prepared in which the NP bond approaches that of a triple bond. The basicity of a number of phosphazene bases (P1–P4) in the gas phase has been calculated and it was found that Bu^t-P4 was by far the strongest phosphazene base (even stronger than Verkade's superbase). It was used in UV-vis spectrophotometric titrations of acids and in various synthetic procedures. Thus Et-P2 was utilised in the asymmetric synthesis of disubstituted *N*-tosyl aziridines whereas Bu^t-P2 reacted with *O*-acyl hydroxamic acid derivatives to yield 2,3-dihydro-4-isoxazole carboxylic esters. Bu^t-P1, Et-P2 or BEMP has been used to solubilise α -amino acids to facilitate the synthesis of peptides. Other applications include dehydrochlorination, polymer modifiers, host-guest reactions and the tribology of phosphorylated carbon-coated surfaces, enhanced conductivity and fuel cell membranes. Various networks have been prepared by radical polymerization using phosphazenes as crosslinking reagents and a polyphosphazene has been utilised in bucky ball chemistry. Biomedical applications include membrane separations, biodegradable polymers and controlled drug release experiments.

In conclusion, we would thank our team of contributors for their efforts in writing for these volumes in recent years. As noted above, this volume may represent the end of an era which has extended over more than 35 years, the first volume having appeared in 1970 under the editorship of Professor Stuart Trippett. It would be a serious omission in writing this preface if we failed to note the passing of Professor Leopold Horner (1911–2005) who contributed so much to the development of organophosphorus chemistry, particularly to the development of routes to chiral phosphines and, of course, to the Horner modification of the Wittig reaction.

D.W. Allen and J.C. Tebby

