

Introduction to Volume 33

The flow of papers on the chemistry of organophosphorus compounds shows no sign of slackening off, and keeping pace with developments is a major task for our Reporters. We are pleased that Dr David Loakes, of the Laboratory for Molecular Biology, Cambridge, has joined our team, and, as we hoped, has provided a two-year survey of the literature on polynucleotide and nucleic acid chemistry, (July 1999–June 2001), thereby making up for the deficiencies of Volume 32 on these topics. A two-year coverage of progress in the chemistry of quinquivalent phosphorus acids is also presented. However, once again we are unable to provide specific coverage of ‘Physical Methods’ in this volume. The XVth International Conference on Phosphorus Chemistry was held in Japan in 2001, resulting in a very considerable volume of conference papers and posters which appeared in *Phosphorus, Sulfur and Silicon, and Related Elements* in the summer of 2002 (Vol 177, parts 6–7 (June) and 8–9, (August)).

As in recent years, the synthesis of new chiral phosphines and related chiral trivalent phosphorus esters and amides continues to be a major preoccupation, being driven by the need for improved performance in metal-catalysed processes. It is very pleasing to note that two of the recipients of the 2001 Nobel Prize for Chemistry, William S. Knowles, and Ryoji Noyori, are honoured for their work in the synthesis and application in catalysis of chiral phosphine ligands. Interest in the structures of metallo-organophosphide systems, noted in the previous volume, has continued to develop. The chemistry of heteroaromatic ring systems, notably that of phospholes, and of low coordination number p_{π} -bonded compounds, also remain active areas.

The primary emphasis of most published work on the Wittig reaction, and its counterparts, continues to be applications in synthesis. A potentially useful advance in this area is the use of ionic liquids as a medium for Wittig reactions. Developments in the coordination chemistry of ylide derivatives, particularly iminophosphanes, continue apace and show that these compounds afford a diverse range of metal complexes.

In the mononucleotide area, the past year has been highlighted by the development of novel phosphate-protecting groups and their use in nucleotide and chiral nucleoside thiophosphate chemistry. Concise methodologies have been described for cost effective syntheses of oligonucleotide building blocks, and the collection of unnatural nucleotides reported to have been synthesised has been considerably expanded.

The number of publications on oligonucleotides continues to increase, with many new applications. Advances in NMR techniques are enabling a growing

number of oligonucleotide structures to be solved in solution. Also reported are developments in internucleotide linkages and sugar modifications, leading to a variety of new structures. Conjugation to oligonucleotides is also a rapidly developing field. Interest in DNA microarrays and the attachment of oligonucleotides to solid surfaces is developing, as is the generation of catalytically active DNA and RNA aptamers.

Biological aspects of quinquivalent phosphorus acid chemistry, quite separate from nucleotide chemistry, continue to increase in importance and tetracoordinate phosphorus compounds continue to be a major source of transition state analogues for the generation of abzymes, *etc.* Since the reaction pathways for peptide bond hydrolysis and phosphate ester hydrolysis are quite different, *i.e.* tetrahedral and trigonal bipyramidal transition states, respectively, it has seemed unlikely that a single active site in an enzyme could catalyse both reactions. The number of reports of the synthesis of natural and unnatural sugar phosphates, particularly as probes for the investigation of enzyme mechanisms, continues to increase, as does activity in all aspects of inositols and related materials. Although applied in other areas, the use of monomethyl polyethylene glycol as the polymer support to allow either solid-phase or solution-phase chemistry to be carried out, depending on the solvent employed, is worth noting. The number and breadth of reports of synthetic studies relating to phosphatidylinositols and related structures has increased markedly. Numerous investigations of phosphate ester hydrolysis and exchange reactions continue to be reported. The importance of enantiomeric and asymmetric synthesis is illustrated in many reports and the synthesis, and use as chiral catalysts, of chiral phosphorus (V) amides features in many publications. Dynamic kinetic asymmetric transformation (DYKAT) of racemates has been applied to the asymmetric synthesis of D-myo-inositol 1,4,5-triphosphate. Interest in approaches to safer nerve gas hydrolysis continues and a new method of detection for fluorophosphorus nerve poisons has been reported. Phosphotriesterase (PTE) from *Pseudomonas diminuta* catalyses the hydrolysis of organophosphorus pesticides and nerve gases with rate enhancements of up to 10¹² and it has now been shown that the bridging ligand in the active site of Zn-substituted phosphotriesterase is hydroxide rather than water.

The year has produced some consolidation in the field of hypervalent phosphorus chemistry in the form of two reviews, the first dealing with the reactions of trico-ordinate phosphorus compounds with fluorinated 1,3-diketones or trifluoroacetylphenols and the second covering chiral, P,N-bidentate ligands which afford catalysts on coordination with rhodium and palladium. A section in the second review deals with coordination of hydridophosphoranes with platinum or palladium (*vide infra*), a topic that was reviewed earlier. A review has also appeared on small ring compounds containing highly coordinated Group 14 elements (Si, Sn and Ge) and, by analogy with phosphorus chemistry, many of these compounds contain the Martin ligand, known to stabilize hypervalent systems.

Several reviews have been published on polyphosphazenes. In addition to reports on new methods of synthesis and new polymers, some being very stable,

there has been a great deal of work reported on organometallic aspects. Ring opening polymerization of thf may or may not include phosphazene residues. High yields of graft polymers *via* radical polymerization have been obtained. Advances continue to be made on the Staudinger reaction, and other methods of synthesizing phosphazenes, including microwave methods and further applications of the P = N bond in organic synthesis, have been described. There is a new method for the generation of alkali metal phosphazides and an investigation of their catalytic use for the ring opening polymerisation of ϵ -caprolactam. A molecular modelling approach for cyclophosphazenes has been described and *ab initio* calculations have indicated the lack of importance of *d*-orbitals.

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