

## *Introduction*

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We welcome the return of the Physical Methods chapter, after an absence of eight years, and in particular the return of John Tebby to the team, together with his new co-author, Robert Slinn. We are confident that the compilation of data in this chapter, ranging across virtually the whole of the organophosphorus area, will be valued by our readers.

Sadly, we regret that Ron Edmundson and Chris Allen have decided to retire as contributors after this volume. Ron took over authorship of the quinquevalent phosphorus acids chapter in volume 7 of this series, and has contributed every year since then! We are now in volume 28. In subsequent volumes, this chapter will be written by Brian Walker. Chris is a relative newcomer, it is a mere 12 years since he first contributed the phosphazene chapter in volume 16! We estimate that between them they have cited over 8,000 papers in their respective chapters. Our thanks to them both for sustained comprehensive and critical writing over a combined total of 34 years. We are delighted that Dr. J. C. van de Grampel from the University of Groningen has agreed to take over authorship of the phosphazene area. As many of you will know Dr van de Grampel is an established, highly respected researcher in the area and contributed to volume 15 as a joint author of what was then a one-off review of 'Cyclic and Polymeric Phosphazenes.'

In the areas covered by Chapter 1, (Phosphines and Phosphonium Salts), a significant increase (ca 20%) in the number of publications, compared to last year, is evident. Although it is particularly difficult to identify significant advances, there is clearly a continuing high level of interest, particularly in the chemistry of phosphines and low coordination number phosphorus compounds, reflecting enormous effort world-wide.

A number of important review articles have appeared in the area of pentacoordinate and hexacoordinate phosphorus chemistry. Robert Holmes has provided an extremely informative comparison of the hypervalency, stereochemistry and reactivity of silicon and phosphorus including the application of the latter to enzyme systems. The coordination chemistry of hydrophosphoranes including the formation of complexes from bicyclic-, tricyclic- and tetracyclic hydrophosphoranes has also been the subject of a comprehensive review with literature coverage to 1995. Numerous metal complexes are mentioned including Rh, Ru, Pd, Co, Fe, Mo, and W and the relevance to asymmetric catalysis is discussed. Neutral six-coordinate compounds of phosphorus, including mono-, di-, tri-, and tetracyclic examples, have also been reviewed.

In the phosphorus(V) acids area, there has been continued interest in the preparation of phosphates from elemental phosphorus, and also of compounds derived from the calixarenes. Apart from these, there has been little of real significance in the phosphate field. A much greater interest has been shown in enantio- or diastereo-selectivity in synthesis and reactivity of phosphonates and

phosphinates. Most interest has been concentrated on hydroxyalkyl and aminoalkyl phosphonates, particularly those compounds containing other functions, especially fluorine. Of considerable interest have been studies of stereoselectivity in the alkylation of phosphorus carbanions, and the reactions between the latter and cyclic alkenones.

The area of nucleotide and nucleic acid chemistry remains buoyant, including the development of new trivalent phosphorus acid derivatives as reagents for nucleotide synthesis. A major area of interest has been the design of modified internucleotide linkages, including nucleoside phosphonates and analogues thereof. One of the most rapidly developing areas continues to be the application of the MALDI mass spectrometric technique to oligonucleotide characterisation.

Overall levels of innovation this year in the area of ylide chemistry are disappointingly low. All the various forms of phosphorus-based olefination continue to be used widely in synthesis and perhaps the relative paucity of new phosphorus chemistry is a reflection on the extent to which these methods have been developed. One area which does continue to expand, and where there is still considerable potential, is the use of phosphorus-stabilised anions in anantioselective and asymmetric synthesis. Warren's continuing use of phosphine oxides and Denmark's excellent contributions to this area are especially worthy of mention.

Activity in the phosphazene area continues along the lines noted in the past few years. In the acyclic area a decrease in applications to synthetic organic chemistry and an increase in the use of these materials as ligands has been noted. In cyclophosphazene chemistry the synthetic elegance of dendrimer systems continues to be explored. Other interesting observations involve the change in isomeric selectivity when reactions occur at interfaces and the crown ether effect of oligooxyethylene substituents in promoting reactions of sodium aryloxides, with cyclophosphazenes. Considerable activity in metallacyclic systems, but very little phospho(thia)zene chemistry, has been noted. One of the noteworthy publications, however, is the isolation and characterisation of a cyclothionylphosphazene which is the largest known inorganic heterocycle. In poly(phosphazene) chemistry emphasis on membranes, ionic conductors and biomedical systems continues. In the latter, exciting work in slow release agents and microspheres has been published.

On the more general matters, it may not be generally appreciated that the sixth edition (1996) of the Heilbron Dictionary of Organic Compounds (and related supplements), published by Chapman and Hall, now includes entries for compounds with P-C bonds, and also some phosphites and phosphates, which initially appeared in the earlier Dictionary of Organophosphorus Compounds, and which have now been up-dated. Useful information on P(III) compounds and some phosphates can also be found in Chapman and Hall's Dictionary of Inorganic Compounds