

Introduction

After more than a century of activity, organophosphorus chemistry continues to be a lively area of wide international interest as judged by the increasing volume (and the origin) of the literature to be reviewed. However, for this Report, we have experienced some difficulties in securing coverage of all of the traditional areas, notably that of tervalent phosphorus acid derivatives and part of the physical methods chapter. We hope to redress these deficiencies in the next volume (Volume 32), by providing reviews covering two year's literature.

Within the broad area of organophosphine chemistry, increased interest is evident in the application of phosphine–borane adducts in synthesis, and in the structural characterisation of metallophosphides. The maturity of the low coordination number phosphorus area is reflected by the appearance of a book on the subject by Dillon, Mathey, and Nixon.

There is a resurgence of interest in mechanistic and theoretical studies of the Wittig reaction and ylides. One notable ylide investigated structurally is the simplest that can be made, methylene(trimethyl)phosphorane. Linking of independent procedures into 'tandem' reactions is always of interest, and the latest development in the Wittig area is the first tandem Wittig–hydroformylation reaction. Controlled free-radical polymerisation is another topical area, and a number of organophosphorus compounds, including Wittig reagents, have been used to exert 'control' on the polymerisation process. As usual, the synthesis of an ever more complex array of biologically active compounds has been achieved using Wittig procedures. The number of publications in the field of nucleotides and nucleic acids has again risen sharply. Novel oligonucleotide analogues have continued to attract considerable attention and an increase in interest in oligonucleotides incorporating conformationally-locked sugars that have been shown to hybridise to complementary oligonucleotide targets with unprecedented affinity has also been apparent in the literature. Exciting new methodology has been developed for preparing oligoribonucleotides using alternatives to the protecting groups previously employed. The rapid increase in the number of novel modified nucleoside triphosphates can be attributed to the development of techniques for nucleic acid library construction and selection. Such libraries have been utilised in several roles: generating novel nucleic acid reactivity; probing protein–nucleic acid and nucleic acid–nucleic acid interactions; and determining metal ion binding sites. Several new reports of the incorporation of site-specific metal ion binding sites into DNA have been made utilising either novel post-synthetic methodology or a solid-phase Heck-type reaction.

This year saw the 70th birthday and retirement of Professor Robert Holmes, distinguished for his outstanding contributions to hypervalent phosphorus and silicon chemistry, and it is a pleasure to acknowledge the tribute paid to him by the dedication of the July (1998) issue of *Heteroatom Chemistry* to his work. Another major contributor to phosphorus chemistry reached his seventieth birthday in 1999 and the seventh and eighth issues of *Heteroatom Chemistry*, Vol. 10 are fittingly dedicated to Professor Alfred Schmidpeter who provides an 'Essay on Phosphorus Chemistry' at the outset of a series of articles from friends and colleagues throughout the world. In a review dealing with donor interaction by N, O and S atoms at tri-, tetra- and pentacoordinate phosphorus Robert Holmes points out that such interactions give rise to higher coordination and may be highly relevant to enzyme activity. Specifically, phosphate substrates are displaced modestly towards pentacoordinate structures (equivalent to the ground state complex) whereas pentaoxyphosphoranes are displaced more strongly towards octahedral geometry (equivalent to the transition state complex) by a donor interaction, which results in P–O bond weakening and, consequently, higher reaction rates. Similar reasoning leads to the conclusion that coordination of the tyrosyl carbonyl group with the pentacoordinate transition state in the activation of tyrosine by tyrosyl-tRNA synthetase enhances reactivity.

Biological aspects of quinquevalent phosphorus acid chemistry, quite separate from nucleotide chemistry, continue to increase in importance. Tetra-coordinate phosphorus compounds are a major source of transition state analogues for the generation of abzymes, *etc.* A wide variety of natural and unnatural phosphates, especially those of carbohydrates, and their phosphonate and phosphinate, particularly fluorinated, analogues have been synthesised, usually with some biologically-related purpose. The synthesis of extremely complex natural carbohydrate phosphates and unnatural analogues has rapidly developed, and the synthesis and biological properties of inositol phosphates, phosphatidylinositols and related compounds have again been particularly active areas. The interest in phosphorus analogues of all types of amino acids continues. The importance of enantiomeric and asymmetric synthesis is illustrated in many of the reports and the synthesis, and use of chiral phosphorus(V) amides as chiral catalysts, features in many publications. Interest in approaches to easier and safer nerve gas hydrolysis continues. Acylphosphonates have substantial potential as synthetic intermediates and investigations of their synthesis and reactions have increased. A number of thorough mechanistic studies of reactions involving a variety of tricoordinate phosphorus(V) compounds as reactive intermediates have appeared.

The first example of a phosphide in a variation of the Staudinger reaction led to the formation of a phosphonium diylide. Intramolecular aza-Wittig reactions have facilitated heterocyclic ring extensions with reports on the use of a chiral ylide to prepare diastereomeric α -aminoesters as well as new reagents for electrophilic amination leading to pyridopyrimidines. The number and variety of applications for phosphazenes continues to expand in a remarkable manner. A number of uses for phosphazenes as bases are reported

as well as for phosphazanium cations as catalysts. Several heterocubanes and some new dendrimers have been characterised. High yields of cyclophosphazenes bearing macrocyclic polyether substituents have been achieved and an example of self-assembling cyclophosphazenes is reported. Polymeric phosphazenes with useful surface properties and further examples of sols, electrolytes and membranes have been described. Such properties have found useful applications in medicine, for example fluoroalkoxy derivatives as coatings for blood contacting devices.

Novel analysis of the ESR linewidth in TR-ESR experiments has been used for the measurement of addition constants and structural relationships of phosphinoyl radicals. The line width is not affected by spin-polarisation processes, easing determination of rate constant. The first examples of crystal structures of lithiated organophosphorus enamines have been reported

