

Introduction

The "Physical Methods" chapter has not appeared in Organophosphorus Chemistry since volume 19 and our difficulty in finding an author to replace John Tebby is a measure of the wide knowledge and volume of work required. We are delighted that Declan Gilheany from University College, Dublin has now agreed to take on the task from volume 24 and, in his first contribution, to cover the major points from the appropriate literature of the last few years.

Interest in the synthesis and chemistry of phosphines and phosphonium salts continues at a high level. Reports include one describing a sterically protected triarylphosphine which survives heating in peracetic acid for 24 hours! Compounds containing p_{π} -bonded phosphorus continue to be the subject of major interest. The phospho-alkyne CICP has been characterised and it has been shown that simple phospho-alkynes RCP, including that with R=H, can persist in solution for several days. Further evidence is available that, for p_{π} -bonded compounds, the structural effects of hybridisation changes at phosphorus are much more significant than for nitrogen; π -bonding interactions may account for only half of the observed bond shortening.

There have been relatively few truly novel developments in penta- and hexaco-ordinated phosphorus compounds. The emphasis continues to be on cyclic phosphoranes and structural aspects of pentaco-ordinated compounds and a useful review covering X-ray and ^1H n.m.r. investigations of the latter area has appeared. It has been shown that phosphoranes containing five-, six-, and seven-membered rings retain their solid state structures in solution and that the boat conformation is preferred for saturated six-membered rings in apical-equatorial orientations of trigonal bipyramids. The importance of apical-equatorial ring orientations for phosphorinanes appearing as *tbp* intermediates in enzymatic reactions of cyclic AMP analogues has been emphasised.

New developments in phosphine oxide chemistry have been largely confined to the continuing use of stabilised carbanions in synthesis. In view of this we intend to stop covering the area in a separate chapter from Volume 25. With the exception of the phosphine oxide-stabilised carbanion chemistry, which will be reported in "Ylides and Related Compounds", the material now covered in the chapter will be incorporated in chapter 1 together with phosphines and phosphonium salts.

With the notable exception of nucleotide chemistry, highlights in the trivalent- and pentavalent-phosphorus acid areas have not been numerous in the period covered. Olah's demonstration that triisopropyl phosphite can be used as a substitute for Clemmensen/Wolf-Kishner techniques for the reduction of ketones to hydrocarbons is noteworthy, as is the remarkable structure of P_2Se_5 . As noted in the Introduction to Volume 22, the pentavalent phosphorus acid area remains to a large extent in the doldrums. The exceptions to this are in the myo-inositol phosphate and aminophosphonic acid areas, with a rapidly growing interest in the synthesis of peptide-like compounds based on the latter. There has been substantially more activity in phosphonic/phosphinic acid chemistry than in that of phosphoric acids. Hammerschmidt's work on the biosynthesis of natural products having the P-C link, e.g. the role of hydroxyalkylphosphonic acids in fosfomycin and also the biosynthetic pathways to 2-aminoethylphosphonic acid, is worthy of special mention.

Nucleotide chemistry continues to be dominated by the potential use of analogues as chemotherapeutic agents, particularly as anti-HIV drugs. In spite of many problems the anti-sense approach to viral chemotherapy continues to make steady progress and it is likely that anti-viral oligodeoxynucleotides will enter phase-one clinical trials in the near future. Interest in the interaction of nucleic acids with many diverse ligands which bind and cleave DNA has been maintained by the world-wide initiatives in molecular recognition and numerous elegant studies have appeared on this subject.

Reports of theoretical and, especially, mechanistic studies on ylides and phosphonate-stabilised carbanions and their reactions are much reduced this year although these reactions continue to be very extensively used in synthesis. Developments include the increased range of heterocyclic systems synthesised by aza-Wittig reactions, the increased number and complexity of phosphonates used in natural product synthesis and the variety of new methods of introducing fluorinated-alkyl functions.

Activity continues to increase in both basic and applied areas of phosphazene chemistry. Exciting advances in (poly)phosphazene chemistry include anionic initiation of condensation polymerisation of phosphoranamines at modest temperatures, new heterophosphazene polymers and the first interpenetrating network polymer containing a poly(phosphazene) hydrogel which can encapsulate living cells while allowing them to retain biological activity. Finally, an overview of the regio- and stereochemical pathways followed in the reactions of cyclophosphazenes and principles for predicting these pathways has become available.