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Organophosphorus Chemistry

Volume 46

Edited by David W. Allen, David Loakes and John C. Tebby

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Organophosphorus Chemistry

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Preface

David Allen,[a] David Loakes[b] and John Tebby[c]

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This volume, no. 46 in the series, (first published in 1970 under the editorship of Professsor Stuart Trippett), covers the literature of organophosphorus chemistry published in the period from January 2015 to January 2016, and continues our efforts to provide an up-to-date survey of progress in this topic which continues to generate a vast amount of research. Once again, we have been unable to secure coverage of the oligo- and poly-nucleotides area and would welcome approaches from prospective authors who might consider taking on this chapter in future volumes. We again welcome to our team of authors Professor Goutam Brahmachari, who has contributed a further guest chapter reviewing progress in green and energy-efficient synthetic approaches in organophosphorus chemistry in 2015, as a follow-up to his previous three year survey published in volume 45 of this series. The continuing vitality of research in phosphorus chemistry was demonstrated at the 21st International Conference on Phosphorus Chemistry, held in Kazan, Russia from June 5–10, 2016. Papers from the 20th International Conference have now been published in a special edition of *Phosphorus, Sulfur Silicon,* 2015, **190**, issue 5–6.

The use of a wide range of tervalent phosphorus ligands in homogeneous catalysis has again continued to be a major driver in the chemistry of both traditional P–C-bonded phosphines and also that of tervalent phosphorus acid derivatives. The application of tertiary phosphines and related compounds as nucleophilic catalysts in the reactions of electrophilic unsaturated systems involved in new synthetic approaches has also continued to grow. The reactions of sterically-crowded arylphosphine-arylboranes (Frustrated Lewis Pair (FLP) systems) in the activation of small molecules such as dihydrogen and carbon dioxide has shown further development and now extends to an increasing number of papers on phosphine adducts of other Lewis acids, notably involving aluminium or zirconium. Whereas long-established topics such as the chemistry of diphosphenes and phosphaalkynes have again received comparatively little study, the chemistry of phosphaalkenes (and related P=C=X compounds), and the less-developed groups of low coordination number phosphorus compounds, in particular phosphenium ions, phosphinidenes, and their complexes with carbenes and metal ions, has again dominated the area.

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In phosphine chalcogenide chemistry, interest in the development of methods for their synthesis, and their applications as new components in opto-electronic devices, has again shown considerable growth. Notable again are efforts to develop catalytic versions of key reactions, *e.g.*, the Wittig, Appel and Mitsunobu reactions, in which the key phosphine reagent is regenerated by *in situ* reduction of the generated phosphine oxide. The chemistry of phosphonium salts and related ylides continues to show remarkable activity, with particular reference to catalytic applications and, in particular, to the synthesis and applications of phosphonium salts as ionic liquids that display higher thermal and electrochemical stabilities compared to related ammonium salts and which also have potential as new solvents in organic synthesis and as stabilisers for nanoparticle systems.

The nucleic acids and nucleotides chapter covers selected papers published in 2015 on chemical synthesis and biological application of modified nucleotides, including data on new approaches in the field of prodrugs and antiviral compounds. Nucleoside phosphates and polyphosphates, as well as their cyclic congeners and covalent adducts with other biomolecules, all play important roles in all living systems, being involved in processes of synthesis of many biophosphates, further recruited in subsequent synthetic or regulatory events. New analogues of nucleotides are devised to meet specific expectations related to the tuning of natural biochemical pathways (including potential medical applications) or to the exploration of metabolic processes at a molecular level. Among synthetic P-modified analogues there are now also methanephosphonates, boranephosphates, phosphoramidates, thiophosphoramidates, and, perhaps less popular, phosphoroselenoates. They are used not only for biochemical mechanistic studies (as enzyme inhibitors or non-hydrolysable substrates, receptor agonists or antagonists), but also as potential drugs or prodrugs with sought-after anticancer, antiviral, or antioxidant activity. There is also a developing field of probes able to detect and quantify natural nucleotides or fluorescently labelled analogues at nanomolar levels.

The quinquevalent organophosphorus acids chapter describes compounds possessing, in addition to the phosphoryl group P=O, three P–O bonds (phosphates), two P–O bonds and one P–C bond (phosphonates) as well as one P–O and two P–C bonds (phosphinates). In addition, applications of chiral phosphoric acids are described in which they have found use as catalysts in many varied organic reactions. Other aspects include the use of phosphates, and also phosphonates, as reagents for the total synthesis of many biologically active compounds, including, for instance, topsentolide A1 and its stereoisomers, a cytotoxic oxylipin active against human solid tumor cell lines, the natural products (−)-cedarmycins A and B, involving α-alkylidene-γ-butyrolactones prepared *via* a one-pot rhodium(II)-catalysed C–H insertion/olefination sequence of α-diazo-α-(diethoxyphosphoryl)acetates), a synthesis of tamiphosphor (5*S*) and its (5*R*) epimer as a potent neuraminidase inhibitor with IC_{50} and EC values of 2.5 and 31.5 nM against wild-type H1N1 influenza virus and the first total synthesis of serratezomine E and huperzine N from 5-oxodecahydroquinoline and phosphonate reagents.

In the field of five- and six-coordinate phosphorus chemistry, most of the progress has been in revealing reaction mechanisms and especially their role as intermediates in determining stereo-chemical outcomes of reactions. This has been particularly rewarding in biological fields such as the mechanism of selective transfer of phosphorus groups as well as DNA cleavage. It has also been shown that the presence of the hydroxyl group in the 2′ position of ribose in RNA facilitates many transformations in the absence of enzymes by the intervention of intermediates such as cyclic phosphates. Other notable research includes intramolecular N–H bond cleavage of amines by oxidative addition to tricoordinate phosphorus compounds. The reaction proceeds smoothly under mild conditions to give structurally robust phosphorane adducts. The chemistry of hexacoordinated compounds has been mainly limited to the synthesis and modification of diverse perfluoroalkyl fluorophosphates. A number of theoretical studies have also given valuable information in a variety areas.

Phosphazenes continue to be widely studied. Acyclic phosphazenes include various types of iminophosphoranes, dimeric analogues, and various types of cyclophosphazenes, polyphosphazenes and hybrid polymers. The potential applications of these compounds are discussed. Highlights of the research include the preparation of bisphosphazene super bases that can act as ''proton sponges'', a chiral diphosphazene copper complex that catalyses cyclopropanation, and click reactions. The bulk of phosphazene research continues to be on the cyclic systems. This includes some new members of the rare 4-membered cyclophosphazenes and the isolation of P_5–P_9 chlorocyclophosphazenes. Fluorescent dendrimer-like structures have been made from halogenocyclophosphazenes and a Fe^{3+} concentration of 4.8 μM was detected using an azidocyclophosphazene coupled to a rhodamine dye. Cyclophosphazene dendrimers, hexa- and dodeca-porphyrin derivatives and viologen-containing complexes with pseudorotaxanes have been made. A hexa-substituted cyclophosphazene is a plasticizer for starch. Dendrimeric cyclophosphazenes were evaluated as flame retardants and combined with graphite to make anodes for lithium batteries. Composites with montmorillonite are very good flame retardants and a thermally stable tris-spirophosphazene was used to prepare flame-retardant viscose fibres. An abundance of new applications for cyclophosphazene-based ligands includes encapsulating cobalt nanoparticles and reactions with diiron- and dimolybdenum-carbonyls. Rigid bulky co-substituents on polyphosphazenes have given elastomers. Hydrophobic ethoxyphosphazenes are a new class of bio-erodible polymers. Advances in drug delivery include the use of biodegradable microspheres and hollow structures. Dehydration of fructose into 5-hydroxymethylfurfural was achieved by homogeneous catalysis involving phosphazenes. Fluorinated phosphazenes have been shown to improve the thermal and safety performance of lithium–ion battery electrolytes and also to make luminescent ionic liquids. A polymeric fluorinated cyclophosphazene improved the interfacial properties of carbon fibre composites.

Author biographies

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David W. Allen, after gaining his PhD in 1967 at the University of Keele, and following a postdoctoral research fellowship at Cambridge, David W. Allen joined what has become Sheffield Hallam University, where he is now Emeritus Professor. His research interests have centred mainly on the chemistry of phosphorus and arsenic. With more than 50 years of experience in both teaching and research, he has produced nearly 200 scientific publications including original research papers, review articles, and invited book chapters. He has been a contributing author and, more recently, co-editor of the RSC Specialist Periodical Report on Organophosphorus Chemistry since volume 8 of the series.

Piotr Bałczewski studied chemistry at the Technical University of Łodź. MSc/PhD theses (P/S/Si and cyclopentanoid chemistry) were with Prof. M. Mikołajczyk at the Centre of Molecular and Macromolecular Studies (CM&MS), Polish Academy of Sciences (PAS), Łódź. Doctoral studies at the Warsaw PAS, Institute of Organic Chemistry, then a postdoctoral period at Manchester University (UK) in alkaloid chemistry (Prof. J. A. Joule) led to habilitation and appointment as full professor at CM&MS PAS, Łódź. He currently leads materials research groups at CM&MS PAS, Łodź and the J. Długosz University in Częstochowa, and is currently Vice-President of the Polish Chemical Society.

Goutam Brahmachari After receiving his PhD in 1997 at Visva-Bharati University (India), Goutam Brahmachari joined his alma mater the very next year and currently holds the position of a full professor of chemistry since 2011. Research interests of his group include green chemistry, organic synthesis and medicinal chemistry of natural products, as well as artificial compounds. With more than 18 years of experience in both teaching and research, he has produced nearly 160 scientific publications including original research papers, review articles, books and invited book chapters in the fields of natural products and green chemistry. He has authored/edited 18 books and more than 30 book chapters so far published by internationally reputed major presses. He is the Series Editor of the Elsevier Book Series '*Natural Product Drug Discovery*'. Prof. Brahmachari is a Who's Who in the World-2015 & 2016 Listee, and also a recipient of Academic Brilliance Award-2015 (Excellence in Research).

Mário J. F. Calvete received his Industrial Chemistry diploma from the University of Coimbra in 2000 and his PhD in Natural Sciences–Organic Chemistry in 2004, from Eberhard Karls University of Tuebingen, Germany, with Prof. Dr h. c. Michael Hanack. After a two-year stay at Tuebingen as a postdoctoral fellow in Industry/University, he returned to Portugal for a postdoctoral stay at the University of Aveiro. In 2010 he was appointed as Auxiliary Researcher at the University of Coimbra. He is also Invited Auxiliary Professor and his current research interests are tetrapyrrolic macrocycle design and other heterocyclic ligands and their uses in homogeneous/heterogeneous catalysis and theranostics. He has published *ca.* 60 peer-reviewed papers in international journals, one book and 5 book chapters.

Rui M. B. Carrilho obtained his degree in Chemistry in 2006 at the University of Coimbra, where he received his Master diploma in Advanced Chemistry in 2008. He concluded his PhD in Macromolecular Chemistry in 2014, focused on the synthesis of phosphorus ligands and organometallic complexes for homogeneous catalysis, in the University of Coimbra (Portugal) and the University of Pécs (Hungary). During 2014, he worked as a researcher in pharmaceutical spin-off Luzitin S. A., on the development of new drugs for use in diagnosis (PDD) and photodynamic therapy (PDT). Since 2015, he has worked as a post-doctoral fellow in University of Coimbra (Portugal) and in University Rovira i Virgili (Tarragona, Spain), on the study of sustainable catalytic processes for carbon dioxide activation. He is the author of 15 peer-reviewed papers and 4 book chapters.

Vadapalli Chandrasekhar obtained his PhD degree in 1982 from the Indian Institute of Science, Bangalore and postdoctoral work at the University of Massachusetts, Amherst, MA. After briefly working at the Research and Development section of the Indian Petrochemicals Corporation at Vadodara, as a Senior Research Officer, he joined the Department of Chemistry at the Indian Institute of Technology Kanpur in 1987 where he has been a full professor since 1995. He served as the Head of the Department of Chemistry, IIT Kanpur (2008–10), and as the Dean of Faculty Affairs, IIT Kanpur (2011–12). He also worked at the Tata Institute of Fundamental Research, Centre for Interdisciplinary Sciences, Hyderabad, as a Senior Professor and Dean (2012–14). Currently he is the Director, National Institute of Science Education and Research (NISER), Bhubaneswar, India. His research interests are in the area of molecular materials, inorganic rings and polymers, main-group organometallics, and polynuclear metal assemblies. He has been a recipient of the S. S. Bhatnagar Award of the Council and Scientific Industrial Research, India, and the Friedrich-Wilhelm-Bessel Research Award of the Alexander von Humboldt Foundation, Germany. He is an elected Fellow of the Indian Academy of Sciences, Bangalore, the National Academy of Sciences, Allahabad, the Indian National Science Academy, and the Academy of Sciences of the Developing World, Trieste, Italy.

Piotr Guga, a resident of Lodz, Poland, received his M.S. in 1981 from Technical University of Lodz (on peptide chemistry) and Ph.D. in 1991 from Centre of Molecular and Macromolecular Studies, PAS, Lodz, under the supervision of Professor Wojciech J. Stec (chemistry and stereochemistry of phosphorothioate analogs of nucleic acids). During 1992–1993, he carried out his postdoctoral work at R&D Department of Applied Bioosystems (Foster City, CA) working on automated sequencing of proteins from the C-terminus. His research interests are in the fields of synthesis and structural features of P-stereodefined analogs of oligonucleotides. He has published more than 70 research papers.

György Keglevich was born in 1957 and graduated from the Technical University of Budapest in 1981 as a chemical engineer. He was awarded the ''*Doctor of Chemical Science*'' degree in 1994, in the subject of organophosphorus chemistry. He has been the *Head of the Department of Organic Chemistry and Technology* since 1999. He is a P-heterocyclic chemist. He also deals with environmentally friendly chemistry: MW chemistry, phase transfer catalysis and the development of new catalysts. He is the author or co-author of *ca.* 450 papers (the majority of which appeared in international journals). He is the member of the Editorial Board of *Heteroatom Chemistry* and *Phosphorus, Sulfur and Silicon, and the Related Elements.* He is Associate Editor for *Letters in Drug Design and Discovery and Current Organic Synthesis,* Regional Editor for *Current Organic Chemistry,* co-Editor-in-Chief for *Letters in Organic Chemistry* and *Current Catalysis, and* Editor-in-Chief for *Current Green Chemistry.*

Anna Dorota Maciaszek, a resident of Lodz, Poland, received her M.S. in 1991 from the Technical University of Lodz (on catalysis) and PhD in 2012 from Centre of Molecular and Macromolecular Studies, PAS, Lodz, under the supervision of Piotr Guga (chemistry and stereochemistry of phosphoroselenoate analogs of nucleic acids). Her research interests are in the field of synthesis and structural features of P-stereodefined analogs of oligonucleotides. She has published 18 research papers.

Ramakirushnan Suriya Narayanan completed his B.Sc. and M.Sc. in Chemistry from Madurai Kamaraj University, Tamil Nadu, India. After completing an M.Sc. in 2006, he joined the research group of Prof. V. Chandrasekhar as a PhD student at the chemistry department, Indian Institute of Technology Kanpur, Kanpur, India. After completing the PhD work in 2012, he moved to TIFR Centre for Interdisciplinary Sciences, Hyderabad as Research Associate. Subsequently he worked as a Postdoctoral Researcher with Prof. A. Roodt, Department of Chemistry, University of the Free State, Bloemfontein, South Africa. He is currently a research associate at the National Institute of Science Education and Research (NISER), Bhubaneswar. His research interests include Inorganic Rings, Cages and Clusters.

Marco Noè obtained his PhD at Università Ca Foscari Venezia with Alvise Perosa in 2012. He was then Endeavour Research Fellow at the University of Sydney under the supervision of Prof. Thomas Maschmeyer. Later on he joined the group of Prof. Pericas as Marie Skłodowska Curie Fellow. Marco's research focusses on sustainable chemistry, working on the development of new chemical processes using green solvents and reagents. More recently he dedicated his efforts to the field of the exploitation of renewable feedstocks.

Romana Pajkert obtained a MSc degree in Chemistry at Adam Mickiewicz University in Poznan (Poland) under supervision of Prof. Henryk Koroniak. Afterwards she pursued her PhD research at the same university. In 2009 she joined the group of Prof. Gerd-Volker Röschenthaler at the University of Bremen and then at the Jacobs University as a postdoctoral fellow where she focused on investigations on the chemistry of fluorinated phosphonates, bisphosphonates as well as *N*-heterocyclic carbene complexes of hypervalent phosphorus fluorides. Among them, her research interests include the design and synthesis of novel luminescent metal complexes for OLED application.

Mariette M. Pereira obtained her PhD in Organic Chemistry in 1992 at the University of Coimbra and worked as Fellow Assistant Researcher at the University of Liverpool in 1993 and University Autónoma de Barcelona from 1997–1998. She has been Associate Professor with Habilitation at the University of Coimbra since 2007 and Director of Chemistry Research Laboratory of Luzitin Lda, a pharmaceutical spin-off, until 2015. Her current research interests are the synthesis of chiral binaphthyl based ligands for the development of asymmetric catalysts for carbonylation tandem reactions and development of sensitizers based on tetrapyrrolic macrocycles for biomedicinal applications and environmental catalysis. She has published *ca.* 120 peer-reviewed papers in international journals, 2 books, and 6 book chapters and is the inventor of 2 patents.

Alvise Perosa (FRSC) obtained his PhD as a Fulbright Scholar at Case Western Reserve University with A. J. Pearson in 1996. He was Endeavour Research Fellow at the University of Sydney in 2007 and is currently associate professor of organic chemistry at the University Ca' Foscari Venice. He sits on the Editorial advisory boards of the journals Green Chemistry and ACS Sustainable Chemistry and Engineering. Alvise's research focusses on green chemistry with emphasis on multiphase catalysis, ionic liquids, bio-based molecules and green feedstocks and reagents.

Professor Gerd-Volker Röschenthaler received his Dr rer. nat. in Inorganic Chemistry from the University of the Saarland, Saarbrücken (Germany) in 1971. In 1972 he moved to the Technical University of Braunschweig (Germany) to work with Professor Reinhard Schmutzler where he got his his ''Habilitation'' (Dr rer. nat. habil.) in 1982. During this time he spent several months as a visiting scientist with Professor Alan MacDiarmid, University of Pennsylvania, Philadelphia (USA). In 1978 he became Professor at the University of Bremen (Germany) and in 2009 Professor of Chemistry at Jacobs University Bremen. He served as a Visiting Professor at the University of Utah, Salt Lake City (USA), the Hebrew University of Jerusalem and the Israel Institute of Technology (Technion), Haifa (Israel). His main research interests are focused on organofluorine and organophosphorus chemistry. In 2012 he was awarded the Honorary Fellowship of the Technion, where he is serving as a member of the Board of Governors. Since 2016 he is Concurrent Professor at the University of Nanjing, Nanjing (China). He chaired the 18th Int. Symposium on Fluorine Chemistry 2006 in Bremen and the Bremen Fluorine Days 2016.

Maurizio Selva earned his *Laurea* degree in Industrial Chemistry (cum Laude) at the University Ca' Foscari Venezia, in 1989. After covering positions as Assistant Professor (1993–2002) and Associate Professor (2002–2015), in 2015, he was appointed full Professor of Organic Chemistry at the Department of Molecular Sciences and Nanosystems (DMSN) at the University Ca' Foscari Venezia. Research interests of Prof. Selva are in the field of Green Chemistry, specifically on the implementation of eco-friendly syntheses with clean reagents and solvents including dialkyl carbonates, dense CO_2 and ionic liquids. Maurizio Selva is the Author of 102 scientific papers, 10 patents and 11 book chapters (current h-index 31).

Joanna Skalik graduated from the Jan Długosz University in Częstochowa, Faculty of Mathematics and Natural Sciences (2008). She received her PhD with distinction at the Center of Molecular and Macromolecular Studies, Polish Academy of Sciences (CMMS, PAS) (2015). Since 2008, she has been a member of the scientific staff in the group of Prof. Piotr Bałczewski at the Department of Heteroorganic Chemistry, CMMS, PAS. She is a co-author of several patents, original and review articles, and chapters in books (*Organophosphorus Chemistry*, RSC, Vols. 40–42, 44, 46). She is actively involved in the realization of Polish national and European research projects.

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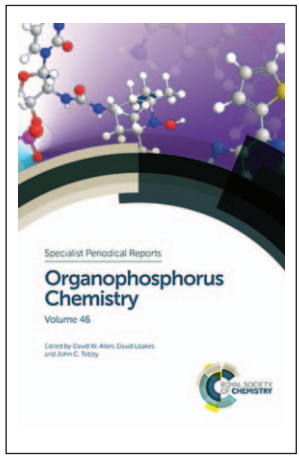

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A selection of organophosphorus molecules. Image reproduced by permission of Dr David Loakes.

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