

Introduction

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The volumes of Annual Reports, Section B offer a selective overview of advances in some aspects of organic chemistry, taken from the primary literature published over the previous year or two, with chapters written by experts in each field.

This year, coverage of advances in organometallic chemistry over the last year or so includes a first contribution by Paul Davies, focusing on catalytic use of metal species for organic synthesis, especially in the areas of metathesis and noble metal catalysis.

Highlights of total syntheses of natural products published during 2007 are ably reported for the first time by Yvette Jackson and Nadale Downer-Riley, concentrating on the key strategic steps of each synthesis. The chapter is organised according to the biological activity of the natural products.

Recent advances in synthetic methodology are covered in several chapters. Ben Buckley discusses organocatalytic methods in his second contribution to *Annual Reports*, in a chapter organized according to the reaction type, and highlights progress achieved in 2007 towards the development of highly enantioselective systems. A number of the elegant natural product architectures that may be prepared by these organocatalytic processes are also described. Steven Nolan and Fabien Boeda provide a further overview of recent advances in the use of N-heterocyclic carbenes (NHCs) as ligands for transition metal-mediated transformations, including an analysis of the performance and scope in catalysis of NHC ligands. David Carbery and Barrie Marsh cover advances in oxidation and reduction methodology, where advances include enantioselective titanium-catalysed epoxidation of unactivated alkenes, iron-catalysed epoxidation of alkenes that uses hydrogen peroxide as stoichiometric oxidant, the first effective catalytic chiral peracid epoxidation reaction, and an organocatalytic aziridination process. Robert Stockman discusses heterocyclic chemistry in his seventh contribution on this topic, concentrating on the synthesis of heterocycles. Highlights include a ruthenium salen catalyst which is able to form aziridines in high enantioselectivities from sulfonyl azides and *cis*-alkenes, an ingenious sulfoxonium ylide mediated transformation of 2,3-aziridin-1-ols into 3-hydroxypyrrolidines, an isonitrile-mediated three-component coupling of imines, acyl chlorides and electron-deficient alkynes to form fully substituted pyrroles, a method for the conversion of terminal alkenes into

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isoxazolidines, and a general strategy for the formation of large rings by the coupling of an alkyne, an alcohol or amine, and tosyl azide, that is able to form up to 17-membered rings in excellent yields. Advances in free radical methodology are described by Gareth Rowlands; significant developments include the use of radicals in cross coupling chemistry, new C–H activation strategies, transition metal-catalysed radical couplings, and the development of fascinating new catalytic enantioselective radical reactions involving a combination of radical chemistry with enamine catalysis. Paul Taylor and James Apps cover advances in heteroatom chemistry, including the organic chemistry of phosphorus, sulfur, selenium, tellurium and silicon, particularly heteroatom-mediated carbon–carbon bond formation, and the formation of carbon–heteroatom bonds. In his fourth article on the topic, biological catalysis in synthetic organic chemistry is reported by Gideon Grogan.

In other chapters, Andy Wilson continues his commentary on the more significant developments in supramolecular chemistry. His chapter is organized into three sections covering molecular recognition, structure and assembly, and functional systems.

Bioinspired organic chemistry is addressed by Simon Webb and Robert Mart, in a chapter that includes short sections on bioinspired materials and bioinspired approaches to preventing amyloid plaque formation. Highlights in this review include: switchable antisense PNA that targets Zebrafish genes to give phenotype changes in Zebrafish embryos, a new method for screening ion channels directly from SDS-PAGE gels, a ‘chemical tongue’ that can detect metabolites in food products, and synthetic polypeptides that engage in simple enzyme-like catalysis.

A chapter on marine natural products by Bob Hill focuses on those with unusual structures or interesting biological activities, and is organised by biogenetic origin, from polyketides, terpenoids, alkaloids and peptides.

After a gap of some years, it is good to see a chapter on Computational Organic Chemistry, and Steven Bachrach provides a comprehensive, but readable update on this fast-developing topic. Among many themes, he sounds a warning about over-reliance on the density functional models that have become the workhorse of the modern organic chemist, considers the recent controversy on the origin of bond strengths in alkanes, and presents the arguments about tunnelling in 1,5-hydrogen shifts.

We also welcome Douglas Neckers with a contribution on Organic Photochemistry. His report highlights the tremendous growth in photo-responsive materials and probes, and covers the extension of photochemistry to the topical field of nanoparticles and nanochemistry. The more traditional areas of reactive intermediates and photocatalysis are included, while multiphoton photochemistry looks to be an area that will attract much attention.

Dean Tantillo and Jeehiun Lee continue their contribution on pericyclic reaction mechanisms. Of particular interest are the findings that alkynyl-boronates are relatively electron-rich dienophiles, that an α -alkynyl substituent enhances the reactivity of an enone dienophile, and that

preorganisation as a result of encapsulation facilitates cycloaddition of normally unreactive aromatic diene components. They present mounting evidence for a radical mechanism for many [1,3] alkyl shifts, and point out the synthetic potential of pericyclic cascades.

Jim Tanko's chapter lists the different hydrogen atom transfer mechanisms and discusses instances of each. The application of radical chemistry to a surprisingly wide range of organic chemistry is also covered in this chapter, including an enantioselective α -allylation of an aldehyde. Recent developments to improve reactions mediated by the ubiquitous tributyltin hydride also feature.

Mark Edgar provides his second report on NMR, and provides updates on improvements in sensitivity and speed, and on solid-state NMR. Of interest to many will be his report on simulation and calculation of spectra, including automated structure verification.

Victor Chechik has again provided a chapter on reactivity in organised assemblies. He described numerous systems; for example, a dendrimer functionalised with up to sixteen zinc ions shows clear evidence of cooperative catalysis of phosphate ester cleavage. The subtle chemistry of the interface zone is presented, for example, benzoic acid, when adsorbed onto graphite is less acidic, but on glassy carbon is more acidic.

For some years now, the major field of polar reaction mechanisms has been absent from Annual Reports. This year we welcome AnnMarie O'Donoghue and Chukwuemeka Isanbor who contribute this chapter covering mostly the years 2005–07. Among the many highlights are a report of the isolation of an amide and its tautomeric enol, determination of barriers for carbanion-carbocation combination, and direct measurement by mass spectrometry of kinetic isotope effects in gas phase S_N and E reactions. The chapter also covers ongoing studies on acyl transfer at carbon, phosphorus and sulfur.

