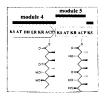
Chemical Society Reviews

Volume 25 Issue 5 Pages 297–370 October 1996



Specificity and Versatility in Erythromycin Biosynthesis By Rembert Pieper, Camilla Kao, Chaitan Khosla, Guanglin Luo and David E. Cane (pp. 297–302)

6-Deoxyerythronolide B synthase is a modular polyketide synthase consisting of three large, multienzyme proteins with at least 28 distinct active sites that together catalyse the formation of 6-deoxyerythronolide B, the parent macrolide of the medicinally important erythromycin family of broad spectrum antibiotics. The combined use of molecular genetic and enzyme mechanistic tools has provided exciting new insights into the organization and function of these fascinating catalysts and allowed the rational generation of novel 'unnatural' natural products.



Environmentally Friendly Catalytic Methods By James H. Clark and Duncan J. Macquarrie (pp. 303-310)

The use of supported reagents as catalysts in liquid phase organic reactions can provide 'clean' alternatives to many traditional and environmentally unacceptable reagents and catalysts. Mesoporous support materials can give the best balance between reactivity and selectivity. Successful applications are diverse and include various acidcatalysed reactions such as Friedel-Crafts reactions, halogenations and nitrations, selective oxidations and basecatalysed carbon-carbon bond forming reactions.

Designing New Lattice Inclusion Hosts By Roger Bishop (pp. 311-320)

Massimo Olivucci and Michael A. Robb (pp. 321-328)

from the Franck-Condon region to the photoproduct valleys.

The discovery of new lattice inclusion hosts traditionally has been an exciting but entirely serendipitous branch of chemistry. Although crystal lattice arrangements of organic molecules still cannot be predicted by computation, our rapidly-developing understanding of molecular packing, intermolecular attractions, and crystal engineering techniques, is rapidly changing this situation. This article surveys major synthetic approaches currently being employed in the design of new lattice inclusion compounds, and attempts to describe how and why these compounds operate as host-guest systems in terms of their supramolecular chemistry.

Modern experiments and quantum chemical computations show that low lying potential energy surface crossings (conical and singlet-triplet intersections) are a general feature of photochemically relevant excited states. This review focuses on the computational and experimental investigation of the efficiency of internal conversion at a surface crossing, the competition with fluorescence when an excited state barrier is present, and the relationship

between the molecular structure at the intersection and structure of the photoproducts. It is shown that single or successive low-lying intersections provide the bottlenecks controlling the evolution of a photoexcited molecule

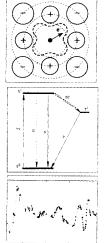
Glutamate and 2-Methyleneglutarate Mutase: From Microbial Curiosities to Paradigms for

Potential Energy Surface Crossings in Organic Photochemistry By Fernando Bernardi,

prefulvene



Coenzyme B₁₂-dependent Enzymes By Wolfgang Buckel and Bernard T. Golding (pp. 329–338) Glutamate mutase and 2-methyleneglutarate mutase are coenzyme B_{12} -dependent enzymes that catalyse carbon-skeleton rearrangements of their substrates. These reactions are initiated by homolysis of the coenzyme's cobalt–carbon σ -bond. This gives cob(11)alamin and 5'-deoxyadenosyl radical, which abstracts a hydrogen atom from a substrate molecule. The resulting substrate-derived radical rearranges to a product-related radical, possibly by a fragmentation-recombination mechanism involving, for glutamate mutase, an acrylate molecule and glycinyl radical as intermediates. Evidence for this remarkable process derives from spectroscopic investigations (EPR), isotopic labelling and model studies.



1800

220

'Covalent' Effects in 'Ionic' Systems By Paul A. Madden and Mark Wilson (pp. 339-350)

Many materials which might be thought 'ionic', on the basis of the electronegativity difference between the elements involved, exhibit non-ionic (or 'covalent') structural features. Electronic structure investigations reveal the key concept that the properties of ions and their interactions are crucially influenced by their local coordination environment and that this gives a many-body character to the interionic forces. Simulations with suitable interaction models show that a wide range of 'covalent' behaviour may be accurately recovered within an ionic model.

Non-porphyrin Photosensitisers in Biomedicine By Mark Wainwright (pp. 351-360)

Conventional drugs used in the photodynamic therapy of cancer (PDT) are porphyrins or porphyrin congeners such as chlorins, phthalocyanines etc. Natural and synthetic alternatives to porphyrins are available which exhibit improved photoactivity in terms of singlet oxygen quantum efficiency, increased maximum wavelength and intensity of absorption. In addition, differences in structure and/or electronic charge can lead to intracellular tumour localisation and sites of action such as mitochondria, lysosomes etc., rather than destruction of tumour vasculature. Non-porphyrin antibacterials and antivirals are also under development.

Nitrous Acid and Nitrite in the Atmosphere By Gerhard Lammel and J. Neil Cape (pp. 361–370)

Nitrous acid is a minor trace gas, yet has an important influence on OH concentrations in the troposphere. Gas phase concentrations in both rural and urban air are larger than predicted from laboratory studies of homogeneous or heterogeneous chemistry. A better understanding of the mechanisms which produce nitrous acid in the atmosphere will lead to improved models of nitrogen oxide and OH chemistry, particularly in polluted air.

Articles that will appear in forthcoming issues include

Scanning Transitiometry Stanislaw L. Randzio

Inhibitors of Glycosphingolipid Biosynthesis Thomas Kolter and Konrad Sandhoff

The Chemistry of the Semiconductor Industry Sean O'Brien

An Odyssey from Stoichiometric Carbotitanation of Alkynes to Zirconium-catalysed Enantioselective Carboalumination of Alkenes Ei-ichi Negishi and Denis Y. Kondakov

Photo- and Redox-active [2]Rotaxanes and [2]Catenanes Andrew C. Benniston

Artificial β-Sheets James S. Nowick, Eric M. Smith and Mason Pairish

Dynamic Resolutions in Asymmetric Synthesis S. Caddick and K. Jenkins

The Role of Short-lived Oxygen Transients and Precursor States in the Mechanisms of Surface Reactions; a Different View of Surface Catalysis **M. W. Roberts**

Shining Light on Catalysis John Evans

The Science and Humanism of Linus Pauling (1901-1994) Stephen F. Mason

Electronic Spectroscopy of Carbon Chains John P. Maier