

AUSTRALIAN JOURNAL OF CHEMISTRY

AN INTERNATIONAL JOURNAL FOR CHEMICAL SCIENCE

RESEARCH FRONT: ORGANIC-08

Foreword

ORGANIC-08 Research Highlights

S. G. Pyne

Aust. J. Chem. **2009**, 62, 603–604.

This special issue of *Australian Journal of Chemistry* includes reviews and research papers by some of the plenary and invited lecturers at the 23rd RACI Organic Division Conference, ORGANIC-08, which was held at Wrest Point, Hobart, Tasmania, in December 2008. The topics covered exemplified the diversity of the discipline and gives readers a glimpse of some of the exciting developments happening in the fascinating area of organic chemistry.

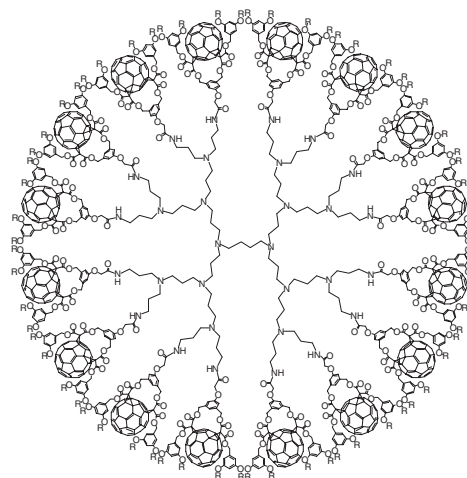
Reviews

Synthesis and Properties of Fullerene-Rich Dendrimers

*Michel Holler, Jean-François
Nierengarten*

Aust. J. Chem. **2009**, 62, 605–623.

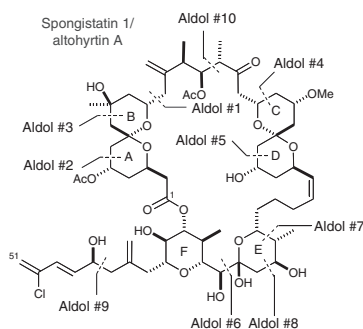
Because of their peculiar electronic properties, fullerene derivatives are attractive building blocks for dendrimer chemistry. In this review, the most recent developments on the molecular engineering of fullerene-rich dendrons and dendrimers are presented to illustrate the current state-of-the-art of fullerene chemistry for the preparation of new dendritic materials.



Recent Advances in the Total Synthesis of Polyketide Natural Products as Promising Anticancer Agents

Ian Paterson, Alison D. Findlay

Aust. J. Chem. **2009**, 62, 624–638.



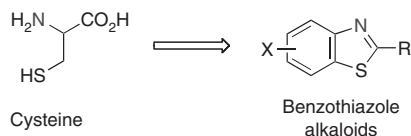
Recent advances in the development of aldol-based synthetic routes to bioactive polyketide natural products are discussed. Representative total syntheses of important anticancer polyketides from the authors' laboratory include dolastatin 19, spirangien A, reidispongionolide A, and spongistatin 1/altohyrtin A.

Naturally Occurring Nitrogen–Sulfur Compounds. The Benzothiazole Alkaloids

Lucille Le Bozec,
Christopher J. Moody

Aust. J. Chem. **2009**, 62, 639–647.

Nature produces a number of compounds that contain both nitrogen and sulfur, and a subset of these interesting terrestrial and marine natural products are the benzothiazoles. Benzothiazole alkaloids are relatively rare in Nature, but they encompass a range of fascinating molecules including firefly luciferin, and more complex molecules such as the thiazo-rifamycins and the dercitin-kuanoniamine family. This short review highlights their isolation, their possible biosynthesis from cysteine, and in a few cases, their chemical synthesis.



Rapid Communications

Organoiodine-Catalyzed Oxidative Spirocyclization of Phenols using Peracetic Acid as a Green and Economic Terminal Oxidant

Yutaka Minamitsuji, Daishi Kato,
Hiromichi Fujioka, Toshifumi Dohi,
Yasuyuki Kita

Aust. J. Chem. **2009**, 62, 648–652.

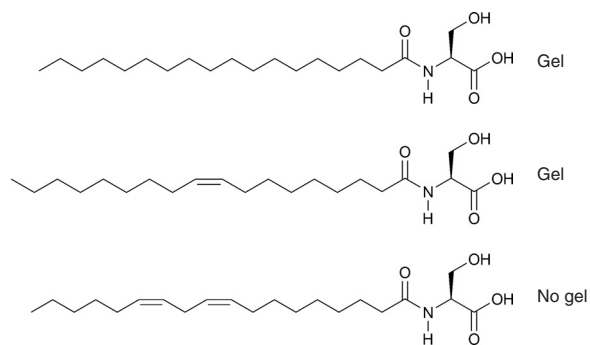
Hypervalent iodine reagents are widely recognized as mild, safe, and environmentally friendly new organocatalysts. The use of peracetic acid as a green and economical terminal oxidant in fluoroalcohol solvents could provide a practical iodoarene-catalyzed oxidation of phenols. In this catalytic approach, acetic acid and water were the only co-products.

The Effect of Unsaturation on the Formation of Self-Assembled Gels from Fatty Acid L-Serine Amides and their Cytotoxicity Towards Caco-2 Cancer Cells

Li Yun Grace Lim, Yingying Su,
Filip Braet, Pall Thordarson

Aust. J. Chem. **2009**, 62, 653–656.

While all showing relatively low cytotoxicity towards Caco-2 cancer cells, the fatty acid L-serine amides reported here differ in their ability to form self-assembled gels, with increased unsaturation in the fatty acid component adversely affecting their ability to aggregate into self-assembled gels.



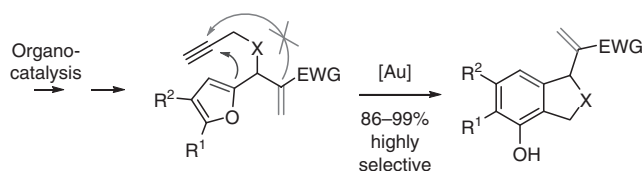
Full Papers

Gold Catalysis: Chemoselective Indolin Synthesis in the Presence of Acrylate Units

A. Stephen K. Hashmi,
Sebastian Wagner, Frank Rominger

Aust. J. Chem. **2009**, 62, 657–666.

Combining an aza-Morita–Baylis–Hillman reaction and a gold-catalyzed phenol synthesis, indolines functionalized with Michael acceptors in the side chain have been prepared. In the last step, the alkyne activated by the gold catalyst chemoselectively reacts with the electron-rich alkene only and ignores the second equidistant but electron-poor alkene.

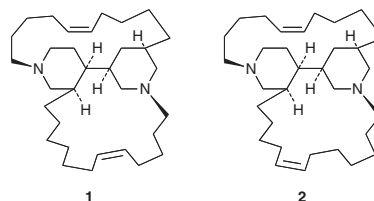


The Absolute Configurations of Haliclonacyclamines A and B Determined by X-Ray Crystallographic Analysis

I. Wayan Mudianta, Mary J. Garson,
Paul V. Bernhardt

Aust. J. Chem. **2009**, 62, 667–670.

X-Ray crystallography establishes that the marine alkaloids (–)-haliclonacyclamine A **1** and (+)-haliclonacyclamine B **2** each have the configuration C2 (*R*), C3 (*R*), C7 (*R*), and C9 (*R*). The alkaloids appear to be enantiomerically pure and may derive from a polyketide-derived precursor via *endo* selective Diels–Alder cyclization and ring opening.

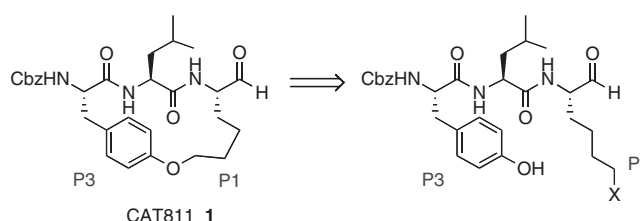


Efficient Large-Scale Synthesis of CAT811, a Potent Calpain Inhibitor of Interest in the Treatment of Cataracts

Matthew A. Jones, James M. Coxon,
Stephen B. McNabb, Janna M.
Mehrtens, Nathan A. Alexander,
Seth Jones, Hongyuan Chen,
Clémence Buisan, Andrew D. Abell

Aust. J. Chem. **2009**, 62, 671–675.

A high-yielding, short, and scalable synthesis of a potent calpain 2 inhibitor (CAT811) is reported. The key step in the sequence involves an intramolecular macrocyclization of a 6-iodonorleucine residue to the side chain of tyrosine. This compound is currently under evaluation as a potential treatment of cataracts.

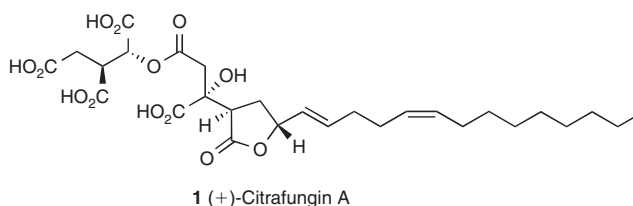


Formal Total Synthesis of (+)-Citrafungin A

Sammi Tsegay, Helmut Hügel,
Mark A. Rizzacasa

Aust. J. Chem. **2009**, 62, 676–682.

The formal total synthesis of the fungal GGTase I inhibitor (+)-citrafungin A **1** is described. The key steps include a selective vinyl anion addition of the anion derived from iodide **10** to the lactone **9** and lactonization/selective deprotection of the allylic alcohols **8** and **23** to afford the citrafungin lactone. Esterification with the isocitrate **6** afforded citrafungin A tetra-*t*-butyl ester **5** which completed the formal total synthesis.

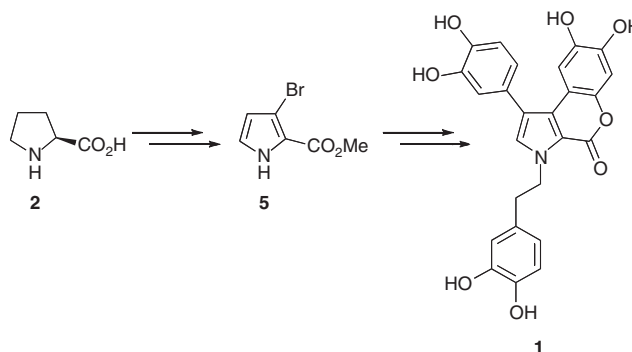


A Total Synthesis of the Marine Alkaloid Ningalin B from (S)-Proline

Katrin Hasse, Anthony C. Willis,
Martin G. Banwell

Aust. J. Chem. **2009**, 62, 683–691.

The marine alkaloid ningalin B (**1**) has been prepared in seven steps from pyrrole **5**, a readily available derivative of (*S*)-proline (**2**).

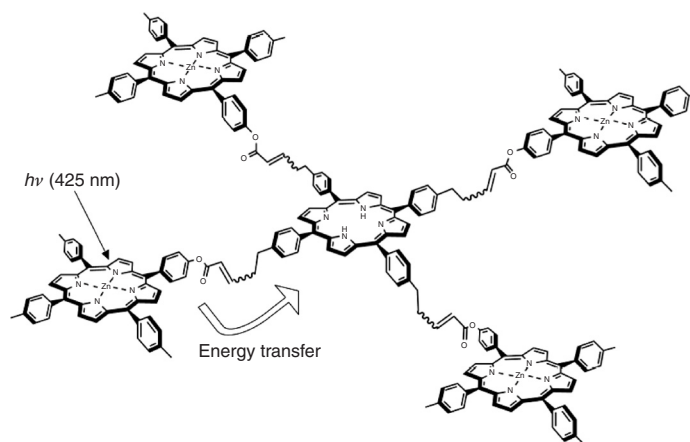


Synthesis and Photophysical Properties of a Conformationally Flexible Mixed Porphyrin Star-Pentamer

Toby D. M. Bell, Sheshanath V. Bhosale, Kenneth P. Ghiggino, Steven J. Langford, Clint P. Woodward

Aust. J. Chem. **2009**, 62, 692–699.

The synthesis of a porphyrin star-pentamer bearing a free-base porphyrin core and four zinc(II) metalloporphyrins is described. Photoexcitation of the zinc porphyrin chromophores leads to significant energy transfer to the central free-base porphyrin. Photophysical studies suggest the efficiency of this process is affected by the configuration of the interacting porphyrins.

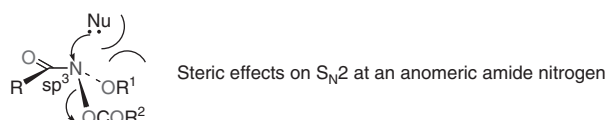


S_N2 Substitution Reactions at the Amide Nitrogen in the Anomeric Mutagens, *N*-Acyloxy-*N*-alkoxyamides

Katie L. Cavanagh, Stephen A. Glover, Helen L. Price, Rhiannon R. Schumacher

Aust. J. Chem. **2009**, 62, 700–710.

Anomeric amides with two heteroatoms at nitrogen are pyramidal with little amide resonance. Mutagenic *N*-acyloxy-*N*-alkoxyamides with a leaving group at nitrogen undergo S_N2 reactions at nitrogen that, like α-haloketones, are subject to steric effects β to the reactive centre but not on the leaving group.

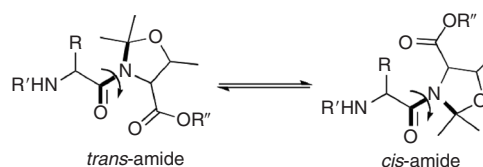


Solid-State and Solution-Phase Conformations of Pseudoproline-Containing Dipeptides

Jack K. Clegg, James R. Cochrane, Nima Sayyadi, Danielle Skropeta, Peter Turner, Katrina A. Jolliffe

Aust. J. Chem. **2009**, 62, 711–719.

The conformations of 14 threonine-derived pseudoproline-containing dipeptides (including four *D*-*allo*-Thr derivatives) have been investigated by NMR. In all cases, the major conformer present in solution is that in which the amide bond adopts a *cis*-configuration. In the solid state, two dipeptides adopt a *trans*-amide conformation while a third adopts a *cis*-amide conformation.

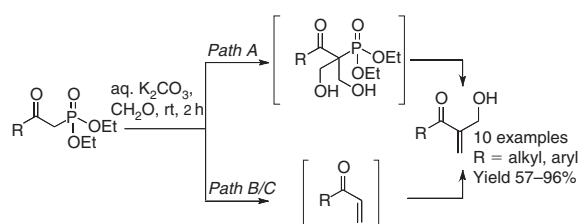


A Synthetic and Computational Investigation into the Direct Synthesis of α-Hydroxymethylated Enones from β-Keto Phosphonates

Sarah J. Ryan, Christopher D. Thompson, David W. Lupton

Aust. J. Chem. **2009**, 62, 720–727.

The one step conversion of β-keto phosphonates that bear alkyl, aryl, and α,β-unsaturation into the corresponding α-hydroxymethylated enones has been achieved using a Villiéras Homer–Wadsworth–Emmons reaction with formaldehyde. The mechanism and viability of three pathways (A, B, and C) were investigated, and the reaction appears to involve a Schlosser–Corey type dialkylation pathway (A).



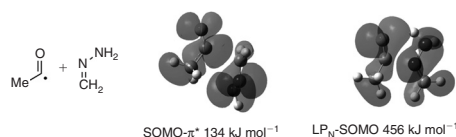
Full Papers

Ab Initio Studies of Carbonyl Radical Additions to Hydrazone Systems

Sara H. Kyne, Carl H. Schiesser

Aust. J. Chem. **2009**, 62, 728–733.

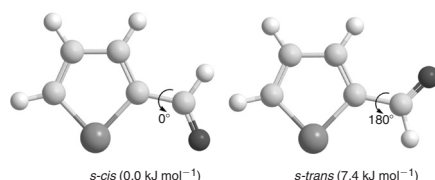
Acyl and oxyacyl radicals react with hydrazones with interesting orbital interactions. DFT calculations reveal dominant SOMO- π^* interactions during attack at the C-end of the π -bond, and LP_N-SOMO interactions at the N-end. These radicals are nucleophilic in their reaction at the carbon-end, while electrophilic at the nitrogen of the π -bond.

**Conformational Analysis of 2-Formylselenophene by Means of ¹³C-¹H, ¹³C-¹³C, and ⁷⁷Se-¹H Spin-Spin Coupling Constants**

Yury Yu. Rusakov, Leonid B. Krivdin, Natalia V. Istomina, Ekaterina P. Levanova, Galina G. Levkovskaya

Aust. J. Chem. **2009**, 62, 734–738.

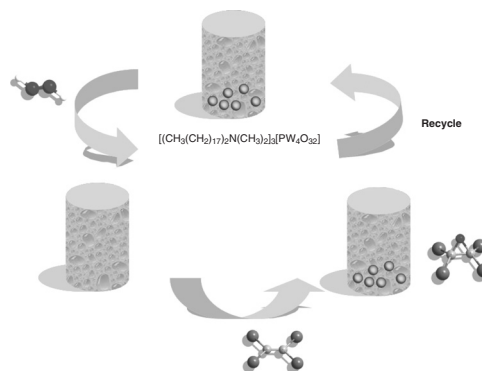
Theoretical energy-based conformational analysis, experimental measurements and high-level *ab initio* calculations of ¹³C-¹H, ¹³C-¹³C, and ⁷⁷Se-¹H spin-spin coupling constants of 2-formylselenophene show that it predominantly adopts the *s-cis* conformation. Most of the spin-spin coupling constants, especially vicinal ⁷⁷Se-¹H couplings, demonstrate remarkable stereochemical behaviour with respect to the internal rotation of the formyl group, and this is of major importance in stereochemical studies of the related selenium-containing compounds.

**Synthesis of Epoxides Catalyzed by a Halide-Free Reaction-Controlled Phase-Transfer Catalytic System: [(CH₃(CH₂)₁₇)₂N(CH₃)₂]₃[PW₄O₃₂]/H₂O₂/Dioxan/Olefin**

Yong Ding, Baochun Ma, Dejie Tong, Hui Han, Wei Zhao

Aust. J. Chem. **2009**, 62, 739–746.

The epoxidation of alkenes was successfully catalyzed by a recyclable and a halide-free reaction-controlled phase-transfer catalytic system: [(CH₃(CH₂)₁₇)₂N(CH₃)₂]₃[PW₄O₃₂]/H₂O₂/dioxan/olefin. This new catalytic system not only is capable of catalyzing homogeneous epoxidation of alkenes with unique reaction-controlled phase transfer characters, but also avoids the use of chlorinated solvents.



Focus

Hydrogen Peroxide and Molecular Iodine: a Very Useful Reagent System

Sabrina B. Ferreira

Aust. J. Chem. **2009**, 62, 747.

The H₂O₂/I₂ mixture is an environmentally safe and inexpensive reagent in keeping with the concept of 'green' chemistry. The preparation and several organic synthetic applications of this multipurpose reagent system are presented, including the iodofunctionalization of various ketones, 1,3-dicarbonyl derivatives, activated aromatic molecules, and alkenes, as well as the formation of cyclopentyl units by ring contraction of *o*-quinones. Overall, the tandem reagent H₂O₂/I₂ is an easily handled, readily available and stable system, convenient for 'green' chemical approaches to various transformations of organic compounds.

