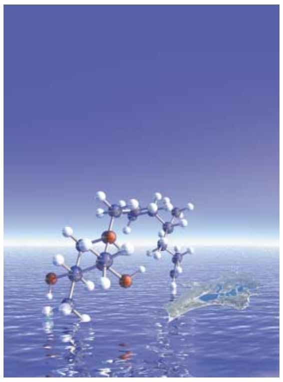
ISSN 1477-0520 OBCRAK(12) 2025–2216(2003)

Organic & Biomolecular Chemistry

FORMERLY PERKIN TRANSACTIONS 1 AND 2

Incorporating Acta Chemica Scandinavica



Cover

See Ivona R. Czuba, Steven Zammit and Mark A. Rizzacasa, page 2044

A model of the marine natural product rottnestol is depicted with an aerial view of Rottnestol Island in the background. Rottnestol was isolated from a sponge which occurs in waters around this island off the SW coast of Western Australia. The total synthesis of rottnestol and the related sponge metabolites raspailols A and B was achieved which allowed for the assignment of the absolute configuration of all these compounds.

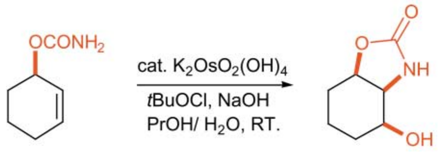
Cover art by J. Dalvean

Chemical biology articles published in this journal also appear in the *Chemical Biology Virtual Journal*: **www.rsc.org/chembiol**

contents

EMERGING AREA

2025 2028



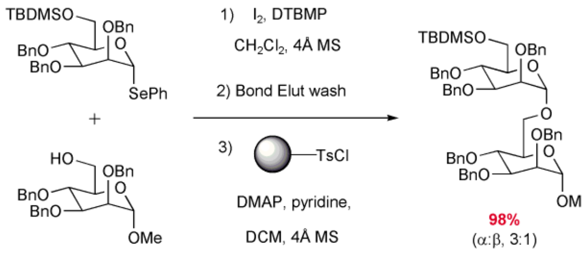
The tethered aminohydroxylation (TA) reaction

Timothy J. Donohoe, Peter D. Johnson and Richard J. Pye

Novel approach towards gaining reliable and predictable regio- and stereocontrol through the use of a tethered carbamate to promote an intramolecular AA reaction.

COMMUNICATIONS

2029 2031



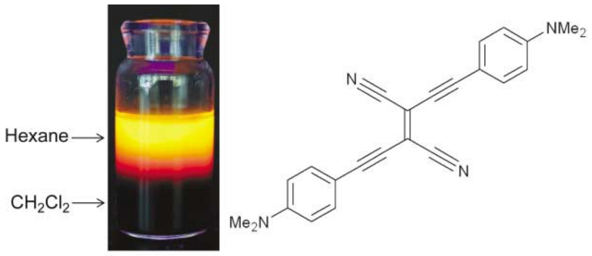
Synthesis of carbohydrate derivatives using solid-phase work-up and scavenging techniques

Rachel N. MacCoss, Paul E. Brennan and Steven V. Ley

Methods to allow the clean preparation of oligosaccharides without conventional column chromatography or an aqueous work-up were investigated.

COMMUNICATIONS

2032 2034

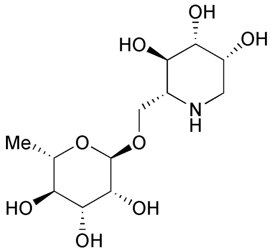


Donor-substituted cyanoethynylethenes: powerful chromophores for opto-electronic applications

Nicolle N. P. Moonen, Robin Gist, Corinne Boudon, Jean-Paul Gisselbrecht, Paul Seiler, Tsuyoshi Kawai, Atsushi Kishioka, Maurice Gross, Masahiro Irie and François Diederich

A series of *N*,*N*-dimethylanilino donor-substituted cyanoethynylethenes (CEEs) has been synthesised. These novel chromophores display an intense intramolecular charge-transfer and a remarkably high two-photon absorption cross-section, which makes them interesting for opto-electronic applications.

2035 2037

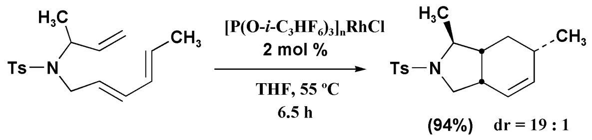


Chemoenzymatic syntheses of (−)-1-deoxymannojirimycin (DMJ) and its naturally occurring 6-*O*-α-L-rhamnopyranosyl glycoside

Martin G. Banwell, Xinghua Ma, Naoki Asano, Kyoko Ikeda and John N. Lambert

The illustrated natural product, a potent α-fucosidase inhibitor, has been prepared by chemoenzymatic means from chlorobenzene.

2038 2040

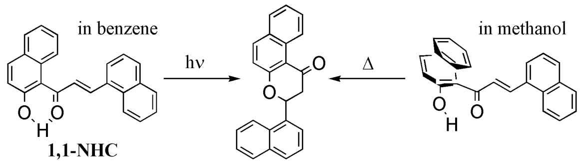


Substrate control of stereoselection in the rhodium(I) catalyzed intramolecular [4 + 2] cycloaddition reaction

Donogh J. R. O'Mahony, David B. Belanger and Tom Livinghouse

Rh(I) catalyzed intramolecular [4 + 2] cycloaddition of representative achiral and chiral enedienes has been shown to proceed with excellent levels of stereoselectivity and in high yield under mild reaction conditions.

2041 2043



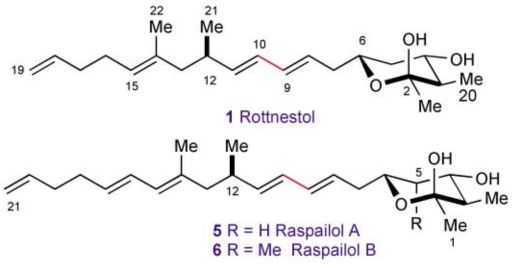
Mechanistic approach to the cyclization reaction of a 2′-hydroxychalcone analogue with light and solvent

Kaoru Kaneda and Tatsuo Arai

A photochemical cyclization reaction of 1-(2′-hydroxy-1′-naphthyl)-3-(1-naphthyl)-2-propen-1-one (**1,1-NHC**) to give a flavanone derivative occurred in benzene, but did not occur in methanol.

ARTICLES

2044 2056



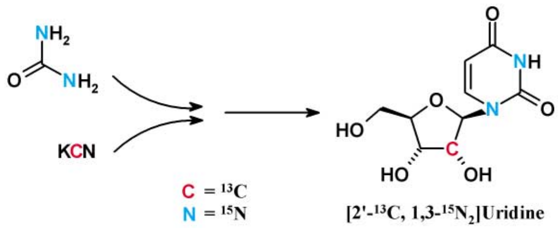
Total synthesis of the marine sponge metabolites (+)-rottnestol, (+)-raspailol A and (+)-raspailol B

Ivona R. Czuba, Steven Zammit and Mark A. Rizzacasa

The asymmetric syntheses of the related marine sponge metabolites (+)-rottnestol (**1**) and (+)-raspailols A (**5**) and B (**6**) are described. The key step in each of these sequences was a Stille coupling to form the C9–C10 bond.

ARTICLES

2057 2062

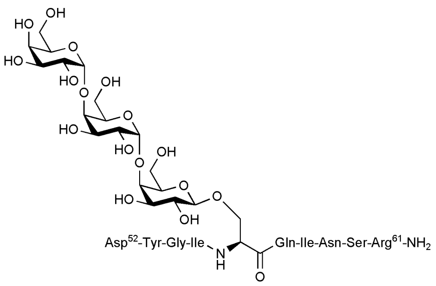


The economical synthesis of $[2'\text{-}^{13}C, 1,3\text{-}^{15}N_2]$uridine; preliminary conformational studies by solid state NMR

Simon G. Patching, David A. Middleton, Peter J. F. Henderson and Richard B. Herbert

The labelled uridine was efficiently synthesised and an intramolecular distance in the crystal structure was measured by solid state NMR.

2063 2069

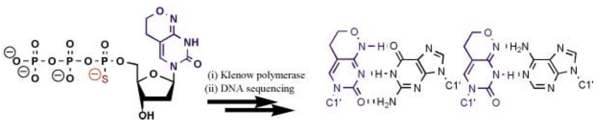


Influence of saccharide size on the cellular immune response to glycopeptides

Mickael Mogemark, Thomas P. Cirrito, Petter Sjölin, Emil R. Unanue and Jan Kihlberg

Synthesis and evaluation of a trigalactosylated peptide may explain why glycopeptides having large saccharides are not recognized by T cells.

2070 2074

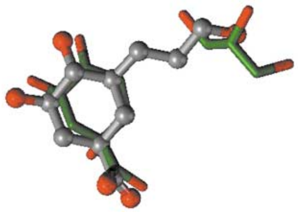


Recognition of base-pairing by DNA polymerases during nucleotide incorporation: the properties of the mutagenic nucleotide dPTPαS

Victoria H. Harris, Clifford L. Smith, W. Jonathan Cummins, Alan L. Hamilton, David P. Hornby and David M. Williams

A convenient qualitative assay for studying nucleotide incorporation which reveals for the first time a potential role for the minor tautomeric forms of the natural DNA bases in base misinsertion (substitution mutagenesis) during replication.

2075 2083

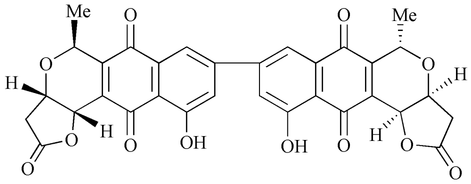


Design, synthesis and evaluation of bifunctional inhibitors of type II dehydroquinase

Miguel D. Toscano, Martyn Frederickson, David P. Evans, John R. Coggins, Chris Abell and Concepción González-Bello

The separate binding features of glycerol and a known inhibitor were combined in the design of a series of novel inhibitors of type II dehydroquinase.

2084 2095

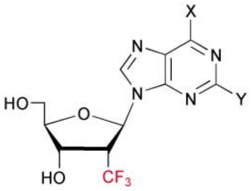


Suzuki–Miyaura homocoupling of naphthyl triflates using bis(pinacolato)diboron: approaches to the biaryl skeleton of crisamicin A

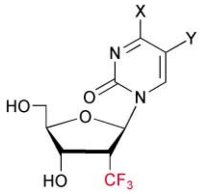
Margaret A. Brimble and Michelle Y. H. Lai

The homocoupling of naphthyl triflates to binaphthyls has been achieved providing the first examples of the use of a Suzuki–Miyaura coupling using bis(pinacolato)diboron and $PdCl_2$(dppf) to effect homocoupling of aryl triflates to biaryls.

2096 2102



11 (X = NH$_2$, Y = H)
12 (X = OH, Y = NH$_2$)



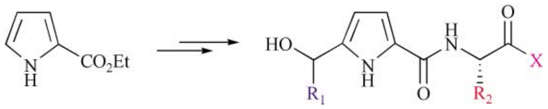
17 (X = OH, Y = H)
18 (X = OH, Y = CH$_3$)
19 (X = NH$_2$, Y = H)

Synthesis and antiviral evaluation of 2′-deoxy-2′-*C*-trifluoromethyl β-D-ribonucleoside analogues bearing the five naturally occurring nucleic acid bases

Frédéric Jeannot, Gilles Gosselin and Christophe Mathé

2′-Deoxy-2′-*C*-trifluoromethyl-β-D-ribonucleosides have been synthesized. Unfortunately, none of these compounds show significant antiviral activity against HIV, HBV and several RNA viruses.

2103 2110

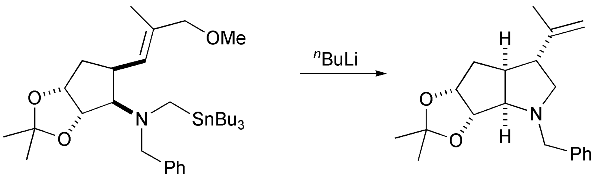


Ring-deactivated hydroxyalkylpyrrole-based inhibitors of α-chymotrypsin: synthesis and mechanism of action

Derek C. Martyn, Andrea J. Vernall, Bruce M. Clark and Andrew D. Abell

C2-Acylated hydroxyalkylpyrroles extended in the C-direction with an amino acid or dipeptide have been shown to inhibit α-chymotrypsin, the potency of which is somewhat dependent upon R^2 and X and to a lesser extent R^1.

2111 2119

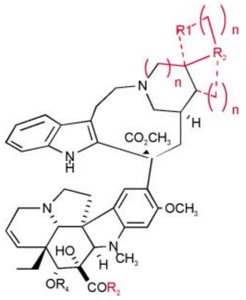


Intramolecular carbolithiation reactions for the preparation of 3-alkenylpyrrolidines

Iain Coldham, Kathy N. Price and Richard E. Rathmell

Tin–lithium exchange allows the formation of α-amino-organolithium species that undergo anionic cyclization onto allylic ethers to give 3-alkenylpyrrolidines.

2120 2136

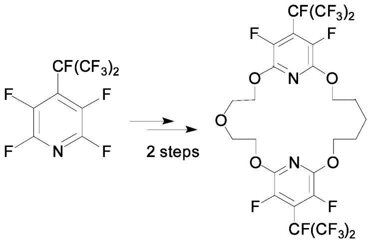


Syntheses and biological evaluation of vinblastine congeners

Martin E. Kuehne, William G. Bornmann, Istvan Markó, Yong Qin, Karen L. LeBoulluec, Deborah A. Frasier, Feng Xu, Tshilundu Mulamba, Carol L. Ensinger, Linda S. Borman, Anne E. Huot, Christopher Exon, Fred T. Bizzarro, Julia B. Cheung and Susan L. Bane

Total syntheses of 62 congeners of vinblastine allowed structure–activity optimization to 1000′ VLB cytotoxicity to L1210 tumor cells.

2137 2147



Polyhalogenated heterocyclic compounds. Macrocycles from perfluoro-4-isopropylpyridine

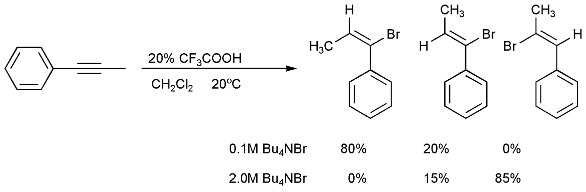
Richard D. Chambers, Philip R. Hoskin, Alan R. Kenwright, Ali Khalil, Paul Richmond, Graham Sandford, Dmitrii S. Yufit and Judith A. K. Howard

Flexible methodology for the synthesis of macrocycles from perfluorinated heterocycles is described.

2148 2151

Regiochemical variation in the electrophilic addition of HBr to 1-phenylprop-1-yne

Hilton M. Weiss, Kim M. Touchette, Frantz Andersen and David Iskhakov

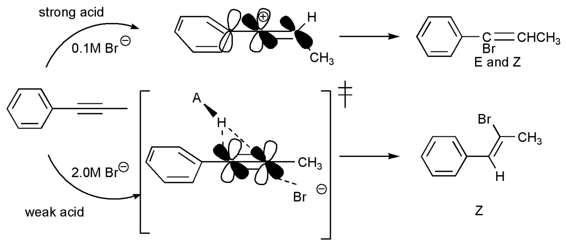


In strongly acidic solutions, conjugated aryl alkynes containing low concentrations of bromide ion, undergo protonation to form resonance stabilized vinyl cations. In less acidic solutions containing higher concentrations of nucleophile, a concerted mechanism becomes dominant in which the less polarized transition state causes an increased proportion of anti-Markovnikov product.

2152 2156

The concerted addition of HBr to aryl alkynes; orthogonal pi bond selectivity

Hilton M. Weiss, Kim M. Touchette, Sarah Angell and Jihan Khan

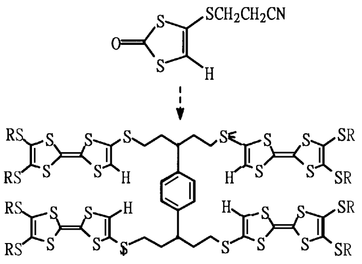


In a weakly acidic solution, the addition of HBr to 1-phenylprop-1-yne produces predominantly the anti-Markovnikov product. We conclude that this is due to the concerted addition occurring on the acetylenic π bond orthogonal to the extended aromatic π system.

2157 2159

Novel electron donors containing multi-TTF units: synthesis and electrochemical properties

Lei Zou, Wei Xu, Xiangfeng Shao, Deqing Zhang, Quanrui Wang and Daoben Zhu



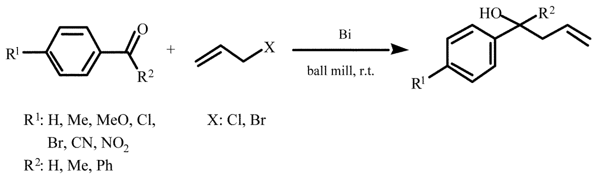
3a-b

New multi-TTF systems were derived from 4-(2-cyanoethylthio)-1,3-dithiole-2-one.

2160 2163

Noticeable facilitation of the bismuth-mediated Barbier-type allylation of aromatic carbonyl compounds under solvent-free conditions

Shinobu Wada, Nobuyuki Hayashi and Hitomi Suzuki

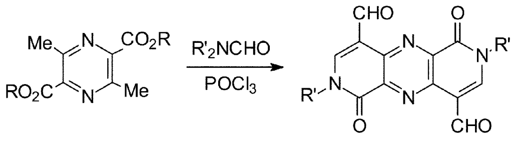


When milled together with bismuth shot in the presence of allyl halide, aromatic aldehydes and ketones undergo a Barbier-type allylation to afford the corresponding homoallyl alcohols in moderate to good yield.

2164 2167

DOTTADs – readily made novel metal ligands with multivariant functionality – trans-DOTTADs and semi-DOTTADs

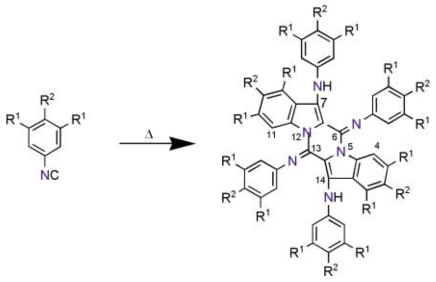
Andrea Arany, Otto Meth-Cohn, István Berhés and Miklós Nyerges



trans-DOTTADs

Two new ligand systems related to the previously described DOTTADs have been generated in a simple one step reaction.

2168 2172

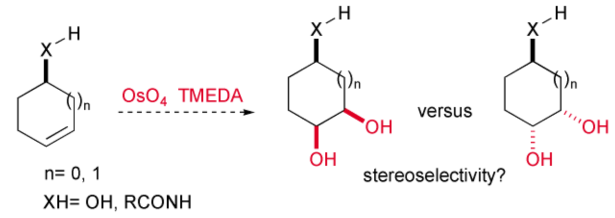


Thermal oligomerisation of aryl isocyanides: formation of pyrazino[1,2-*a*:4,5-*a*′]diindoles and indigo diarylimines

Jan C. A. Boeyens, Leanne M. Cook, Yunxiang Ding, Manuel A. Fernandes and David H. Reid

Heating aryl isocyanides at 130–150 °C gives aryl isocyanide hexamers based on the pyrazino[1,2-*a*:4,5-*a*′]diindole system.

2173 2186

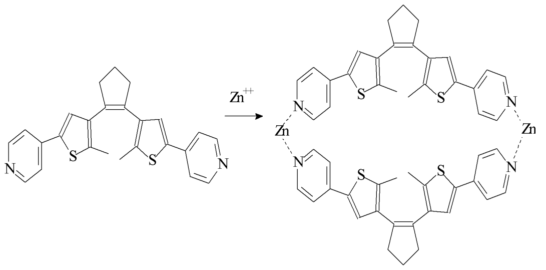


Scope of the directed dihydroxylation: application to cyclic homoallylic alcohols and trihaloacetamides

Timothy J. Donohoe, Lee Mitchell, Michael J. Waring, Madeleine Helliwell, Andrew Bell and Nicholas J. Newcombe

In order to define the substitution patterns that facilitate directed dihydroxylation, a variety of cyclic homoallylic alcohols and amides have been synthesised. This methodology will be useful in synthetic applications.

2187 2191

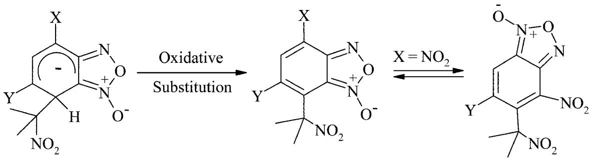


Enhanced photochromism of 1,2-dithienylcyclopentene complexes with metal ion

Bing Qin, Rongxia Yao, Xueli Zhao and He Tian

Photocyclization quantum yield is found to be increased by the complexation of a zinc ion with a new pyridine-tethered photochromic compound.

2192 2199

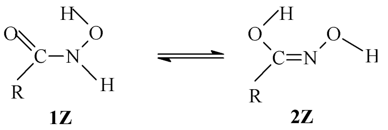


σ-Complex formation and oxidative nucleophilic aromatic substitution in 4-nitro-2,1,3-benzoxadiazoles

Régis Goumont, Emmanuel Jan, Mieczyslaw Makosza and Francois Terrier

A clear relationship between the oxidation potential and the thermodynamic stability of the σ-adducts, is highlighted.

2200 2206



R=H,CH3, C2H5

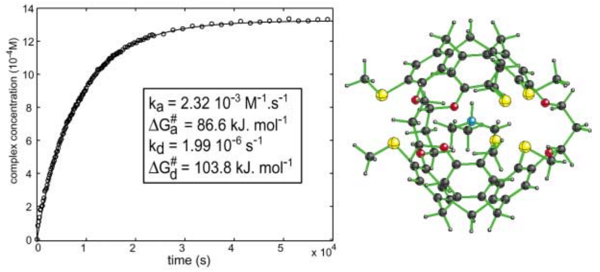
Conformational behavior of some hydroxamic acids

Rita Kakkar, Rajni Grover and Preeti Chadha

The interconversion of the keto (**1*Z***) and iminol (**2*Z***) tautomers of a series of hydroxamic acids and their rotational barriers have been studied theoretically.

ARTICLES

2207–2216



Kinetic and thermodynamic consequences of the substitution of SMe for OMe substituents of cryptophane hosts on the binding of neutral and cationic guests

Chantal Garcia, Delphine Humilière, Nathalie Riva,
André Collet and Jean-Pierre Dutasta

Cryptophane-E acts as a carcerand when changing from OMe to SMe substituents and the kinetics and thermodynamics of encapsulation of neutral and ammonium guests are dramatically changed.

CONFERENCE DIARY

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Dates, venues and contact details of forthcoming events.

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