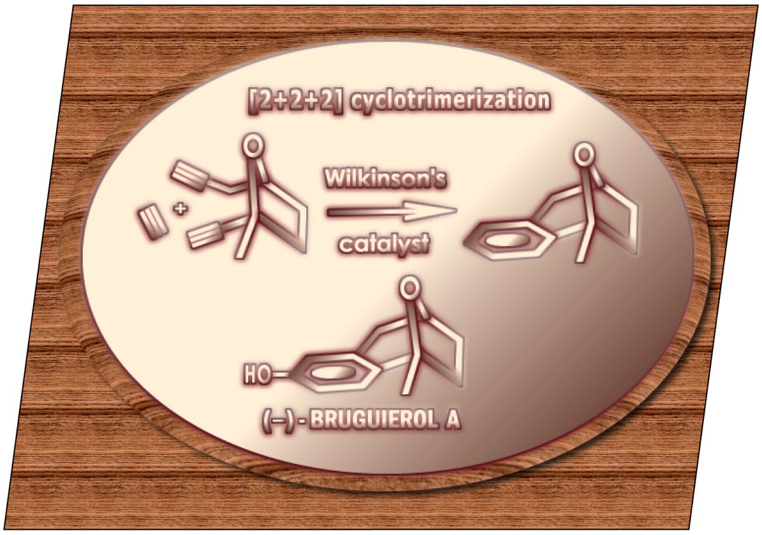
COVER PICTURE

The cover pocture shows the use of a [2+2+2] cyclotrimerization reaction for the construction of strained benzannulated 8-oxabicyclo[3.2.1]octane systems. Wilkinson's catalyst was found to be successful in accomplishing this cross alkyne cyclotrimerization for oxa-bridged bicyclic systems. The first total synthesis of (−)-bruguierol A, that establishes its absolute configuration, was accomplished by employing this approach. Details are discussed in the Short Communication by C. V. Ramana et al. on p. 5483ff.



CONTENTS

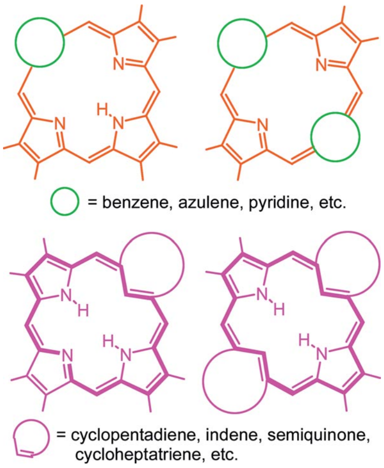
MICROREVIEW

Porphyrin Analogs

T. D. Lash* **5461–5481**

Recent Advances on the Synthesis and Chemistry of Carbaporphyrins and Related Porphyrinoid Systems

Keywords: Porphyrinoids / Azuliporphyrins / Tropiporphyrins / Benziporphyrins / MacDonald and Rothemund reactions



Carbaporphyrins and related systems, where one or more of the usual pyrrolic subunits are replaced by carbocyclic rings such as benzene, azulene, cycloheptatriene, and cyclopentadiene, are now available by well established synthetic methodologies. These important bridged annulenes have a broad range of physical and spectroscopic properties, unusual chemical reactivities and commonly afford stable organometallic derivatives.

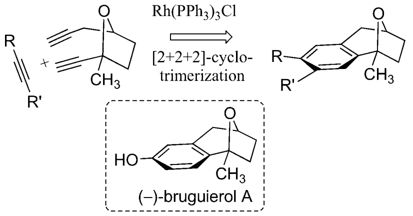
SHORT COMMUNICATIONS

Cyclotrimerisation Reactions

C. V. Ramana,* S. R. Salian,
R. G. Gonnade **5483–5486**

An Expeditious Assembly of 3,4-Benzannulated 8-Oxabicyclo[3.2.1]octane Systems by [2+2+2] Alkyne Cyclotrimerisation: Total Synthesis of (−)-Bruguierol A

Keywords: Total synthesis / Epoxidation / Cyclotrimerisation / Wilkinson's catalyst



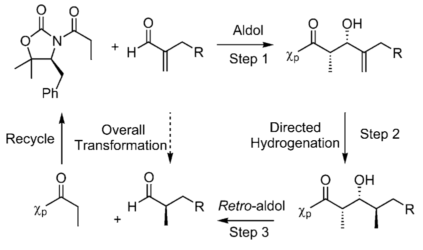
Bridged bicyclic systems by [2+2+2] cyclotrimerisation: Facile construction of benzene-fused 8-oxabicyclo[3.2.1]octane systems by employing a cross alkyne cyclotrimerisation reaction was explored. With this procedure, (−)-bruguierol A was synthesised, and its absolute configuration was established.

Temporary Stereocentre

D. G. Niyadurupola, I. R. Davies,
R. Wisedale, S. D. Bull* **5487–5491**

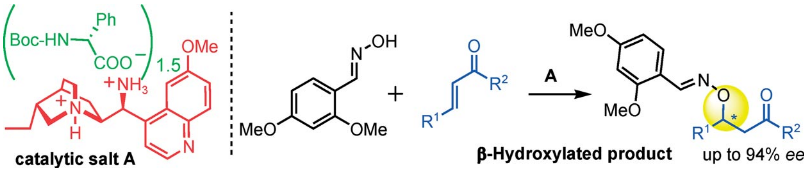
A Temporary Stereocentre Approach for the Stereodivergent Synthesis of Either Enantiomer of α-Methyloctanal

Keywords: Temporary stereocentre / Aldol / Hydrogenation / *retro*-Aldol reaction / Chiral aldehyde



Two for the price of one: A novel three-step aldol/hydrogenation/*retro*-aldol protocol has been developed that employs the same enantiomer of a chiral auxiliary for the stereodivergent synthesis of either enantiomer of α-methyloctanal using a temporary stereocentre approach for stereocontrol.

Asymmetric Organocatalysis



The first organocatalytic asymmetric β-hydroxylation of α,β-unsaturated ketones was accomplished by using commercially available oximes as the O-centered nucleophiles. The use of catalytic primary amine salt **A**, in which both the cation and the anion are chiral, exhibits high reactivity and selectivity for iminium-ion catalysis with enones.

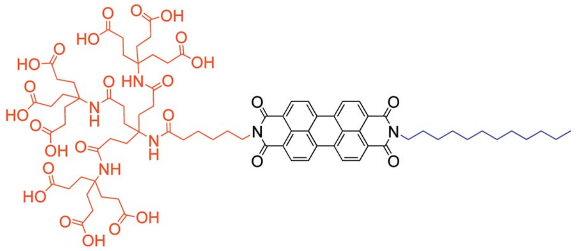
A. Carlone, G. Bartoli, M. Bosco, F. Pesciaioli, P. Ricci, L. Sambri, P. Melchiorre* 5492–5495

Organocatalytic Asymmetric β-Hydroxylation of α,β-Unsaturated Ketones

Keywords: Asymmetric catalysis / Conjugate addition / Ketones / Organocatalysis / Oximes

FULL PAPERS

Water-Soluble Perylenecarboxdiimides



A series of very water-soluble symmetric and asymmetric perylenetetracarboxdiimide ("perylene bisimide", PBI) dyes were synthesized and their aggregation behaviour was characterized by optical spectroscopy and transmission-electron-microscopy (TEM).

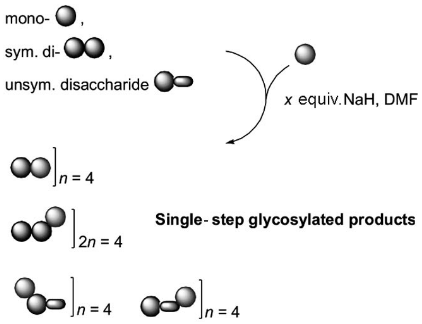
C. D. Schmidt, C. Böttcher, A. Hirsch* 5497–5505

Synthesis and Aggregation Properties of Water-Soluble Newkome-Dendronized Perylenetetracarboxdiimides

Keywords: Perylene / Dendrimers / Amphiphiles / Micelles / Aggregation

Unprotected Acceptor Glycosylations

First single-step random-glycosylation methodology for fully unprotected glycosyl acceptors leading to a variety of regioisomeric glycosides is reported. In such systems conventional glycosylation methods fail. Starting from unprotected nonreducing saccharides, the syntheses of β-glucosylated and β-galactosylated monosaccharides (Glc, Gal), symmetric disaccharides (e.g. α,α-trehaloses) as well as unsymmetric disaccharides (e.g. sucrose) were studied.

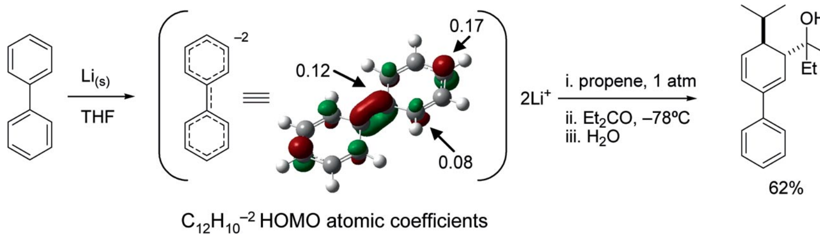


A. Steinmann, J. Thimm, J. Thiem* 5506–5513

First Direct Glycosylation of Unprotected Nonreducing Mono- and Disaccharides

Keywords: Combinatorial chemistry / Glycosylation / Single-step reactions / Sacharides

Reactivity of Arene Dianions



Dianions derived from arenes of high reduction potential (biphenyl, naphthalene) and $Li_{(s)}$ can carbometallate alkenes in an intermolecular fashion. This reaction runs at room temperature to afford partially dearomatized alkylated aryl anions that are susceptible to further functionalization by electrophilic capture.

C. Melero, A. Guijarro,* V. Baumann, Á. J. Pérez-Jiménez, M. Yus* 5514–5526

Carbolithiation of Simple Terminal and Strained Internal Alkenes by the Naphthalene and the Biphenyl Dianion: New Modes of Reactivity of Highly Reduced Organic Species in Solution

Keywords: Arene dianion / Dearomatization / Intermolecular carbolithiation / Lithium

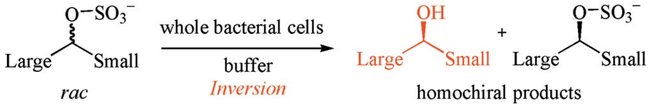
CONTENTS

Enantioselective Biohydrolysis

P. Gadler, K. Faber* **5527–5530**

Highly Enantioselective Biohydrolysis of *sec*-Alkyl Sulfate Esters with Inversion of Configuration Catalysed by *Pseudomonas* spp.

Keywords: Enzymes / Inversion of configuration / Enantioselectivity / Biohydrolysis / Biocatalysis



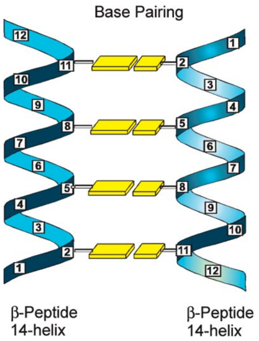
Highly enantioselective biohydrolysis of *rac*-*sec*-alkyl sulfate esters by *Pseudomonas* spp. proceeded with strict inversion of configuration.

β-Peptide Helix Recognition

A. Weiß, U. Diederichsen* **5531–5539**

Uniformly Nucleobase-Functionalized β-Peptide Helices: Watson–Crick Pairing or Nonspecific Aggregation

Keywords: Base pairing / β-Peptides / Helical structures / Molecular recognition / Peptide nucleic acids (PNA) / Self-assembly



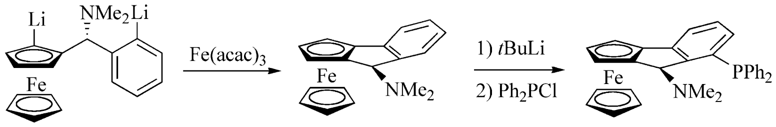
Functionalization of β-peptide helices with nucleobases allows three-dimensional organization of these secondary structure elements. Using helices uniformly functionalized with one kind of nucleobase a Watson–Crick preference for recognition was shown. If Watson–Crick pairing cannot be realized quite stable complexes were formed based on nonspecific interactions.

N,P-Ferrocenyl Ligands

S.-i. Fukuzawa,* M. Yamamoto,
M. Hosaka, S. Kikuchi **5540–5545**

Preparation of Chiral Homoannularly Bridged N,P-Ferrocenyl Ligands by Intramolecular Coupling of 1,5-Dilithioferrocenes and Their Application in Asymmetric Allylic Substitution Reactions

Keywords: Asymmetric catalysis / Asymmetric synthesis / N,P ligands / Chirality / Allylation / Annulation



Chiral homoannularly bridged ferrocene, which was prepared by Fe(acac)$_3$-mediated intramolecular coupling of 1,5-dilithioferrocene, underwent *ortho* lithiation of the benzene ring, and the resulting lithiated species was trapped with Ph$_2$PCl to afford a chiral N,P ligand. Its palladium-catalyzed allylic substitution with 1,3-diphenyl-2-propenyl acetate proceeded with high enantioselectivities.

Sesquiterpenoids

T. Opatz,* H. Kolshorn, J. Birnbacher,
A. Schüffler, F. Deininger,
T. Anke **5546–5550**

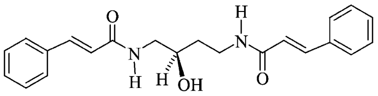
The Creolophins: A Family of Linear Triquinanes from *Creolophus cirrhatus* (Basidiomycete)

Keywords: Terpenoids / Natural products / Structure elucidation / NMR spectroscopy

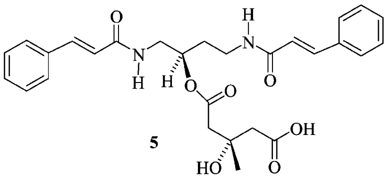
Five novel linear triquinanes, the creolophins A, B, C, D, and E, were isolated from culture filtrates of the tooth fungus *Creolophus cirrhatus.* Presumably during workup, creolophin E dimerized to form neocreolophin, an unusual decacyclic 1,4-dioxepin-6-one. Both monomer and dimer exhibit a cytotoxic effect against several tumor cell lines.

Bioactive Natural Compounds

The isolation of two new cinnamic acid bisamides from the fruiting bodies of the gilled mushroom *Pholiota spumosa* is reported. The absolute configuration of the 2-hydroxyputrescine unit was inferred from the total synthesis of compound **4**. Pholiotic acid (**5**) exhibited antitumour activity on human prostate cancer cells.



4



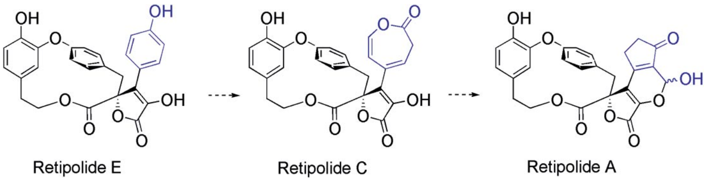
5

M. Clericuzio,* S. Tabasso, J. A. Garbarino, M. Piovano, V. Cardile, A. Russo, G. Vidari .... **5551−5559**

Non-Phenolic Dicinnamamides from *Pholiota Spumosa*: Isolation, Synthesis and Antitumour Activity

Keywords: Natural products / Cinnamic acid / Amides / Structure elucidation / Total synthesis / Prostate cancer

Fungal Macrolides



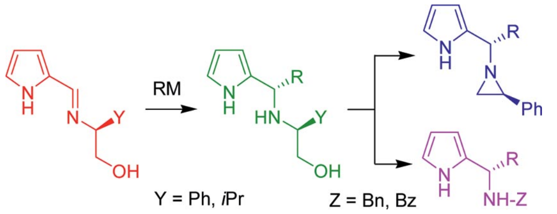
Fruit bodies of *Retiboletus* species contain several unique spiro-macrolactones. The structures of these compounds suggest their formation from a hypothetical precursor, retipolide E, which was synthesized and subsequently isolated from the mushroom extract. In the biosynthetic conversion of retipolide E into retipolide C an oxidative ring enlargement of a 4-hydroxyphenyl group into a 2(3*H*)-oxepinone residue takes place. Retipolide C may then rearrange into the main metabolite, retipolide A, via an intramolecular *O*/*C*-acyl shift.

K. Justus, R. Herrmann, J.-D. Klamann, G. Gruber, V. Hellwig, A. Ingerl, K. Polborn, B. Steffan, W. Steglich* .... **5560−5572**

Retipolides − Unusual Spiromacrolactones from the Mushrooms *Retiboletus retipes* and *R. ornatipes*

Keywords: Natural products / Retipolides / Macrolactones / Spiro compounds / Oxepinones / Basidiomycetes

Chiral Pyrrole Derivatives



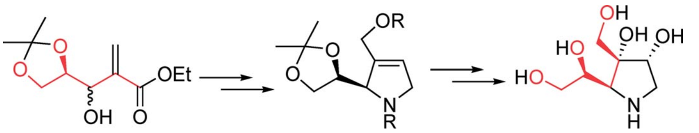
The addition of organometallic reagents to chiral 2-pyrroleimines was exploited to prepare optically pure 1-[1-(2-pyrrolyl)alkyl]aziridines and 1-[1-(2-pyrrolyl)alkyl]amines.

G. Alvaro, R. Di Fabio, A. Gualandi, D. Savoia* .... **5573−5582**

Asymmetric Synthesis of 1-(2-Pyrrolyl)alkylamines by the Addition of Organometallic Reagents to Chiral 2-Pyrroleimines

Keywords: Amines / Asymmetric synthesis / Imines / Organometallic reagents / Pyrrole

Glycosidase Inhibitors



Two pyrrolidine-based imino sugars have been synthesized from sugar-derived Baylis−Hillman adduct in an efficient manner. These azasugars are found to be moderate glycosidase inhibitors.

V. Ramana Doddi, Y. D. Vankar* .... **5583−5589**

Synthesis of Pyrrolidine-Based Imino Sugars as Glycosidase Inhibitors

Keywords: Regiospecific amination / Ring closing metathesis / Diastereospecific dihydroxylation

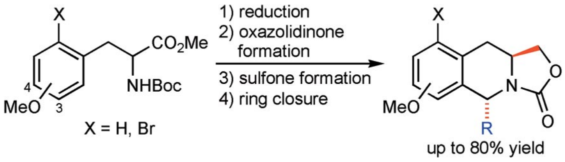
CONTENTS

Substituted Tetrahydroisoquinolines

S. Tusseschläger, A. Baro, S. Laschat,*
W. Frey **5590–5602**

Synthesis of Tyrosine-Derived Tetrahydroisoquinolines by Lewis Acid Catalyzed Cyclization of *N*-(Phenylsulfonyl)alkyloxazolidinones

Keywords: Amino acids / Bromine / Protecting groups / Debromination / Oxazolidinones / Regioselectivity



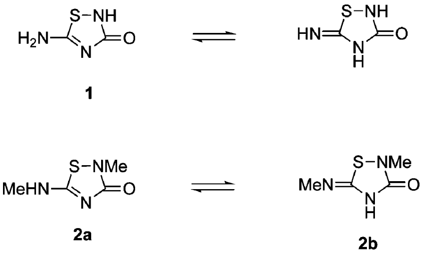
A series of tyrosine-derived tetrahydroisoquinolines with various substituents in the 5-position was prepared. Intermediate oxazolidinones were converted into amido sulfones, which selectively cyclize under acid catalysis to the *trans* configured target compounds, as determined by X-ray crystal structure analysis.

Thiadiazole Tautomerism

A. Encinas, A. Castro, N. E. Campillo,
J. A. Páez* **5603–5608**

The Tautomerism of 5-Amino-3-oxo-1,2,4-thiadiazole: An Experimental and Theoretical Study

Keywords: Nitrogen heterocycles / Sulfur heterocycles / Tautomerism / Density functional calculations



A study of the tautomerism in the 5-amino-3-oxo-1,2,4-thiadiazole system was performed in the gas phase by density functional theory and local density functional methods. The theoretical study in solution was carried out by using several continuum solvation models. UV spectrophotometry was used to unambiguously establish the tautomeric form in aqueous solution.

CORRECTION

B. Alcaide,* P. Almendros,*
T. Martínez del Campo **5609**

Allene Substitution-Controlled Switching of Dimerization to Cycloisomerization in the Pd^{II}-Catalyzed Reaction of Terminal α-Allenones

Keywords: Allenes / Cyclization / Heterocycles / Palladium / Substituent effects