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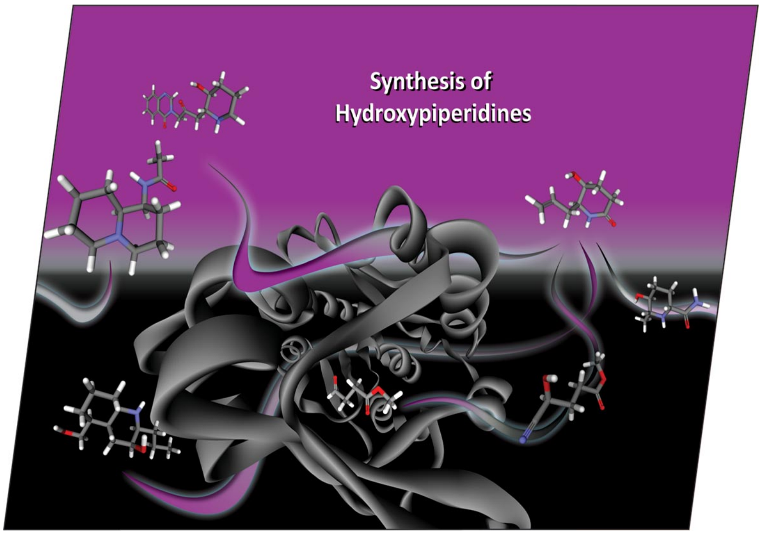
COVER PICTURE

The cover picture shows an artistic impression of the interaction of different types of 3-hydroxypiperidine-containing natural products with an imaginary receptor protein. The 3-hydroxypiperidine motif represents a privileged structural element that occurs in a large variety of biologically relevant compounds displaying a range of activities. Examples include the natural products 3-hydroxypipecolic acid, prosopinine, morusimic acid D, cassine and febrifugine. Enantioselective synthetic strategies to these compounds are presented in the Microreview by F. P. J. T. Rutjes et al. on p. 2831 ff. Cover picture design by Dr. Sander S. van Berkel.



CONTENTS

MICROREVIEW

Hydroxypiperidines

M. A. Wijdeven, J. Willemsen, F. P. J. T. Rutjes* **2831–2844**

The 3-Hydroxypiperidine Skeleton: Key Element- in Natural Product Synthesis

Keywords: Natural products / Nitrogen heterocycles / Alkaloids / Hydroxypiperidines / Febrifugine / Cassine

Natural products keep inspiring organic chemists as a result of their often challenging structures and biological properties. A structural element in many natural products is the 3-hydroxypiperidine scaffold, as occurring in the alkaloids cassine and febrifugine. This account provides an overview of synthetic strategies to the 3-hydroxypiperidine core and natural products containing this moiety.

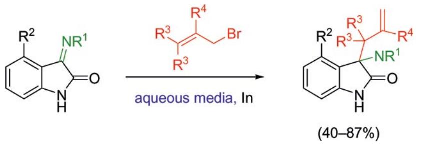
SHORT COMMUNICATIONS

Allylation of Imines

B. Alcaide,* P. Almendros,* C. Aragoncillo **2845–2848**

Indium-Promoted Allylation Reaction of Imino-Isatins in Aqueous Media: Synthesis of Quaternary 3-Aminooxindoles

Keywords: Synthetic methods / Indium / Allylation / Nitrogen heterocycles



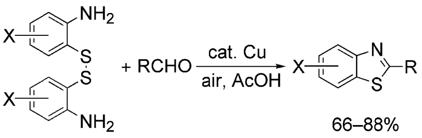
The 3-substituted 3-amino-2-oxindole skeleton is present in various natural products and biologically active compounds. In this paper, the synthesis of quaternary 3-amino-2-oxindoles is described using the allylation and the propargylation reactions of imino-isatins under Barbier conditions in aqueous media.

Cu-Catalyzed Oxidation

J. Hyvl, J. Srogl* **2849–2851**

Copper-Catalyzed Activation of Disulfides as a Key Step in the Synthesis of Benzothiazole Moieties

Keywords: Oxidation / Copper / C-H activation / Disulfides / Imines / N,S heterocycles / Benzothiazole synthesis



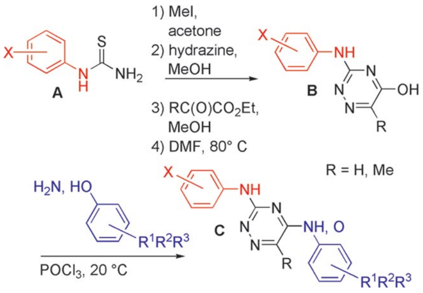
A convenient synthesis of substituted benzothiazoles has been accomplished by way of a copper-catalyzed reaction of aromatic disulfide amines and aldehydes. The process proceeds in a tandem fashion via C–H bond activation, followed by aerobic oxidation of resulting dihydrobenzothiazole intermediate.

Heterocyclic Chemistry

R. Leenders,* J. Heeres, D. Vandenput, R. Zijlmans, J. Guillemont, P. Lewi **2852–2854**

3-(Arylamino)-1,2,4-triazin-5-one: A Novel Synthesis and Its Use

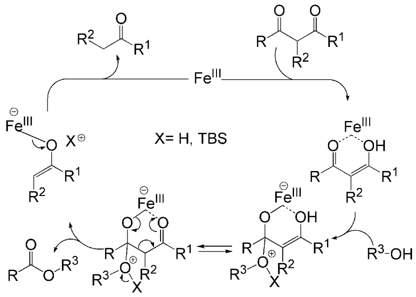
Keywords: Nitrogen heterocycles / Medicinal chemistry / Antiviral agents



An optimized synthesis of 1,2,4-triazines **B** and coupling with anilines and phenols to give **C** is described.

Retro-Claisen Condensation

An iron(III) salt catalyzed retro-Claisen condensation between an alcohol and a 1,3-diketone was investigated. The mechanism involves the formation of a metal-induced six-membered cyclic transition state and cleavage of the $C_{sp^2}-C_{sp^3}$ bond. Regioselective esterification and one-pot conversion of silyl ethers into esters with good yields was observed.



C. B. Rao, D. C. Rao, D. C. Babu, Y. Venkateswarlu* 2855–2859

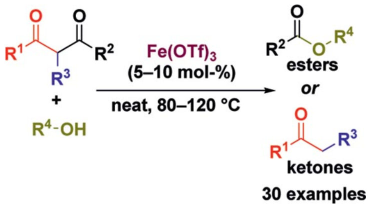
Retro-Claisen Condensation with Fe^{III} as Catalyst under Solvent-Free Conditions

Keywords: Iron / Cleavage reactions / Esters / Regioselectivity / Retro reactions

FULL PAPERS

Iron-Mediated C–C Bond Cleavage

A simple and efficient $Fe(OTf)_3$-catalyzed reaction of 1,3-diketones and alcohols is described. Variously substituted esters or ketones are obtained in high yield through direct carbon–carbon bond cleavage by retro-Claisen condensation under solvent-free conditions. Tandem carbon–carbon bond formation of the 1,3-dicarbonyl compounds followed by carbon–carbon bond cleavage is also demonstrated.



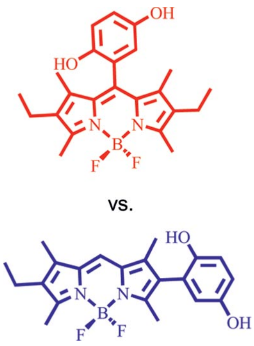
S. Biswas, S. Maiti, U. Jana* 2861–2866

An Efficient Iron-Catalyzed Carbon–Carbon Single-Bond Cleavage via Retro-Claisen Condensation: A Mild and Convenient Approach to Synthesize a Variety of Esters or Ketones

Keywords: Iron / Nucleophilic addition / Cleavage reactions / Esters / Ketones

Photochemistry

The synthesis of 2-substituted aryl-Bodipy derivatives is described. The ^{19}F NMR is highly sensitive to the oxidation state of the directly attached aromatic; small changes in molar volume can retard the free rotation. Time-resolved studies on the hydroquinones is interpreted as electron transfer occurring from the hydroquinone unit to the first-excited singlet (S_1) state of the Bodipy center.



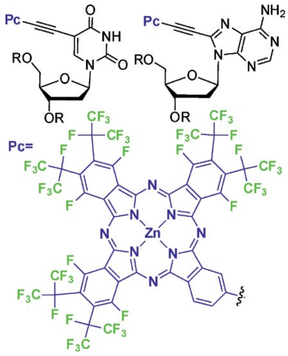
A. C. Benniston,* G. Copley, H. Lemmetyinen,* N. V. Tkachenko 2867–2877

Off the Back or on the Side: Comparison of *meso* and 2-Substituted Donor-Acceptor Difluoroborondipyrromethene (Bodipy) Dyads

Keywords: Dyes / Luminescence / Fluorescence / Electrochemistry / Photochemistry / Electron transfer

Fluorinated Drugs

Deoxyribonucleoside-appended perfluoroisopropyl-substituted zinc phthalocyanines have been efficiently synthesized. Photophysical investigations and preliminary biological experiments with the conjugates have revealed interesting properties that make them suitable for use in the photodynamic therapy of cancer.



B. Das, E. Tokunaga, M. Tanaka, T. Sasaki, N. Shibata* 2878–2884

Perfluoroisopropyl Zinc Phthalocyanines Conjugated with Deoxyribonucleosides: Synthesis, Photophysical Properties and In Vitro Photodynamic Activities

Keywords: Fluorine / Fluorescence / Phthalocyanines / DNA / Photocytotoxicity / Photodynamic therapy

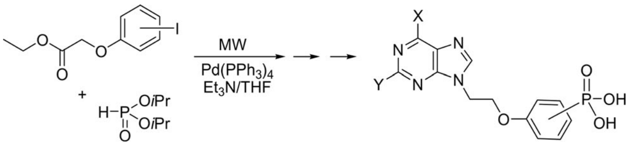
CONTENTS

Nucleoside Arylphosphonates

D. Hocková,* M. Dračínský, A. Holý **2885–2892**

Synthesis and Properties of a Novel Type of Acyclic Nucleoside Phosphonates: 2-(Purin-9-yl)ethoxyphenylphosphonic Acids

Keywords: Nucleotides / Nucleosides / Phosphorus / Cross-coupling



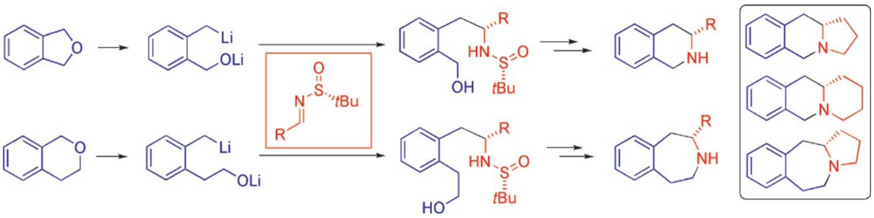
Acyclic nucleoside phosphonates with various purine bases and a built-in arylphosphonate moiety have been prepared by a microwave-assisted cross-coupling reaction as the key step. Their pK_a values, as a key parameter of pharmacokinetic properties, were determined by ^{31}P NMR titration studies and their biological activities were evaluated.

Organolithium Chemistry

D. García, F. Foubelo,* M. Yus* **2893–2903**

Reductive Ring-Opening of Phthalan and Isochroman: Application to the Stereoselective Synthesis of Tetrahydroisoquinolines and Tetrahydrobenzazepines

Keywords: Lithium / Lithiation / Zincates / Diastereoselectivity / Hydrolysis / Nitrogen heterocycles / Sulfinylimines



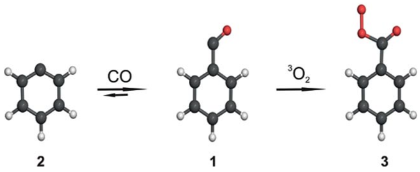
Differently substituted tetrahydroisoquinolines and -benzazepines have been prepared with high stereoselectivity starting from phthalan and isochroman, respectively, and a chiral *N-tert*-butylsulfinylimine in a strategy of two one-pot processes: reductive ring-opening lithiation of the starting heterocycle and subsequent reaction with the chiral imine and cyclisation of the resulting amino alcohol derivative.

Matrix Isolation of Radicals

A. Mardyukov, W. Sander* **2904–2909**

Matrix Isolation and IR Characterization of the Benzoyl and Benzoylperoxy Radicals

Keywords: Radicals / Matrix isolation / IR spectroscopy



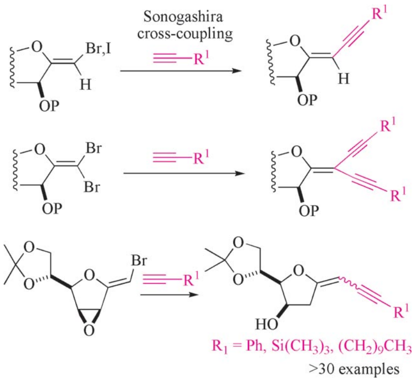
The benzoyl radical **1** can be synthesized in argon matrices by the thermal reaction of the phenyl radical **2** with CO. The formation of **1** from **2** and CO is photochemically reversible. The benzoyl radical **1** can react with molecular oxygen in the matrix to produce the benzoylperoxy radical **3**. The radical **1**, **2** and **3** play an important role in the combustion of aromatic hydrocarbons.

Cross-Coupling of Halo-*exo*-Glycals

A. M. Gómez,* A. Barrio, A. Pedregosa, C. Uriel, S. Valverde, J. C. López* **2910–2920**

Sonogashira Couplings of Halo- and Epoxy-Halo-*exo*-Glycals: Concise Entry to Carbohydrate-Derived Enynes

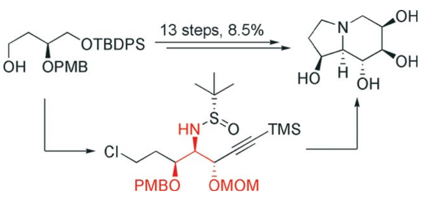
Keywords: Carbohydrates / Glycals / Palladium / Cross-coupling / Enynes



Furanose- and pyranose-derived mono- and dihalo-*exo*-glycals undergo Sonogashira cross-coupling reactions to give carbohydrate-derived enynes in a completely stereoselective manner. On the other hand, a furanose-derived 2,3-anhydro-bromo-*exo*-glycal yielded isomeric, *Z*/*E*, 2-deoxyenynes.

Synthesis of (+)-6-*epi*-Castanospermine

The total synthesis of (+)-6-*epi*-castanospermine in 13 steps and 8.5% yield from known diprotected (*S*)-1,2,4-butanetriol, readily available from cheap (*S*)-malic acid, has been achieved by the highly stereoselective formation of a *syn,anti* acetylenic 2-amino-1,3-diol triad and subsequent ring-closing metathesis/dihydroxylation.

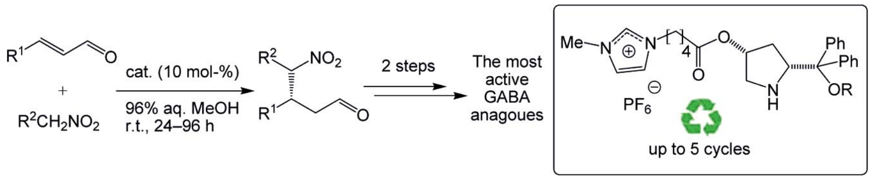


J. Louvel, C. Botuha, F. Chemla,*
E. Demont, F. Ferreira,
A. Pérez-Luna **2921–2926**

Asymmetric Total Synthesis of (+)-6-*epi*-Castanospermine by the Stereoselective Formation of a *syn,anti* Acetylenic 2-Amino-1,3-diol Stereotriad

Keywords: Alkaloids / Zinc / Asymmetric synthesis / Chiral auxiliaries / Sulfinylimines

Organocatalysis



Ionic liquids with (*S*)- or (*R*)-diphenylprolinol units were used as catalysts in the Michael addition of nitroalkanes to α,β-enals. Adducts with the (*S*)- or (*R*) configuration were obtained in high yields (up to 95%) and with high *ee* values (up to 99%) The immobilized catalysts were used five times without a decrease in yield or *ee* values.

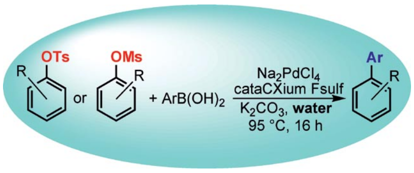
O. V. Maltsev, A. S. Kucherenko,
I. P. Beletskaya, V. A. Tartakovsky,
S. G. Zlotin* **2927–2933**

Chiral Ionic Liquids Bearing *O*-Silylated α,α-Diphenyl (*S*)- or (*R*)-Prolinol Units: Recoverable Organocatalysts for Asymmetric Michael Addition of Nitroalkanes to α,β-Enals

Keywords: Asymmetric catalysis / Organocatalysis / Michael addition / Ionic liquids / Supported catalysts

Aqueous Suzuki–Miyaura Coupling

Aryl toluenesulfonates (Ar-OTs) or aryl methanesulfonates (Ar-OMs) undergo facile Suzuki cross coupling reaction in water using a water-soluble, disulfonated fluorenylphosphane (cataCXium Fsulf) and Na_2PdCl_4 at low catalyst loading of 0.25–0.5 mol-%.



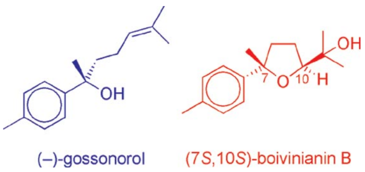
J. Pschierer, H. Plenio* **2934–2937**

Suzuki–Miyaura Coupling of Aryl Tosylates and Mesylates in Water

Keywords: C-C coupling / Palladium / Water / Suzuki–Miyaura reactions / Phosphanes

Asymmetric Synthesis

The first enantioselective syntheses of (−)- and (+)-gossonorol have been achieved, demonstrating the utility of a novel approach to enantiopure tertiary benzylic alcohols; epoxidation of (−)-gossonorol followed by acid-catalysed cyclisation gave (7*S*,10*S*)- and (7*S*,10*R*)-boivinianin B.



K. Abecassis,
S. E. Gibson* **2938–2944**

Synthesis of (+)- and (−)-Gossonorol and Cyclisation to Boivinianin B

Keywords: Asymmetric synthesis / Natural products / Alcohols / Chiral base / Chromium

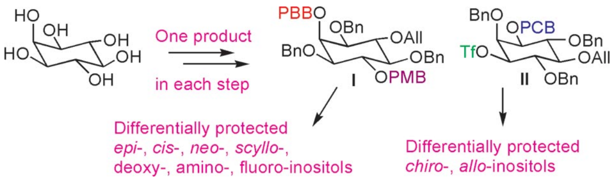
CONTENTS

Un-Parallel(ed) Protection

R. C. Jagdhane,
M. S. Shashidhar* 2945–2953

💻 Orthogonally Protected Cyclohexanehexols by a "One Reaction – One Product" Approach: Efficient Access to Cyclitols and Their Analogs

Keywords: Alkylation / Cyclitols / Inositol / Protecting groups / Regioselectivity



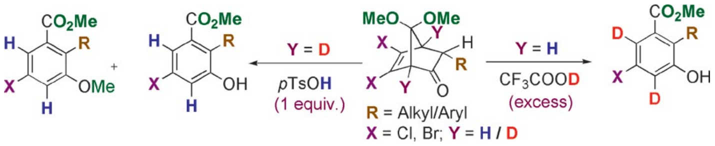
Knowledge of the role of metal ions during the *O*-substitution of inositol hydroxy groups paved the way for the efficient preparation of orthogonal (un-parallel) protected *myo*-inositols. Six isomeric inositols and their analogs could be accessed by starting from the differentially protected *myo*-inositols **I** and **II**.

Reaction Mechanism

F. A. Khan,*
S. Choudhury 2954–2970

💻 An Efficient Synthesis of Substituted *meta*-Halophenols and Their Methyl Ethers: Insight into the Reaction Mechanism

Keywords: Oxidation / Ketones / Grob-type fragmentation / *meta*-Halophenols / Reaction mechanisms



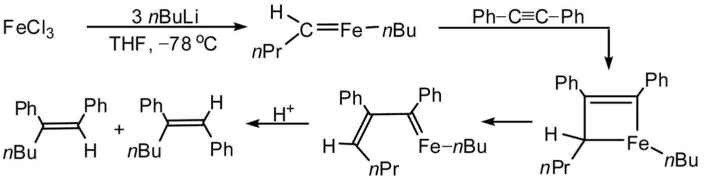
The halogen atoms attached to the sp^2-carbon atom in dihalonorbornyl ketones are lost in a one-pot Grob-type fragmentation/aromatization process, to afford *meta*-halophenol derivatives. Equally interesting is the observation that hydrogen atoms in the *ortho*/*para* positions in the products are derived from the acid used, thus allowing facile deuterium incorporation. Mechanistic details are discussed.

Iron(III)–Carbene Intermediates

J. J. Eisch,* J. U. Sohn,
E. J. Rabinowitz 2971–2977

Novel Alkylidenating Agents of Iron(III) Derivatives by Base-Mediated α,μ-Dehydrohalogenation and Their Chemical Trapping by Cycloaddition

Keywords: Iron(III)–alkylidene complexes / Alkyliron(III) derivatives / α,μ-Dehydrohalogenation / Lithiation / Cycloaddition



The interaction of $FeCl_3$ in THF with 3 equiv. of *n*BuLi at –78 °C led in 80% yield to a iron–carbenes of the type *n*Bu-Fe=CH*n*Pr, which was trapped by cycloadditions with such substrates as alkynes and nitriles. The further reaction of $FeCl_3$ with $PhCH_2MgCl$ offers hope that ligand-stabilized iron–carbenes of the Grubbs type may be isolable.

CORRECTION

L. Peng, X.-Y. Xu, L.-L. Wang,
J. Huang, J.-F. Bai, Q.-C. Huang,
L.-X. Wang* 2978

Noyori's Ts-DPEN Ligand: Simple yet Effective Catalyst for the Highly Enantioselective Michael Addition of Acetone to Nitroalkenes

Keywords: Organocatalysis / Michael addition / Asymmetric synthesis / Amines

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* Author to whom correspondence should be addressed.

💻 Supporting information on the WWW (see article for access details).