The EUChemSoc Societies

have taken the significant step into the future by merging their traditional journals,























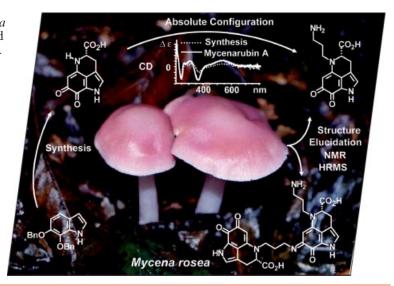


EUChemSoc

to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

The cover picture shows the mushroom Mycena rosea whose fruiting bodies contain two new red pyrrologuinoline alkaloids named mycenarubin A and B. So far, pyrroloquinoline alkaloids are mainly known from marine sources. The new secondary metabolites have been detected by means of a comparative HPLC profiling of the fruiting bodies and the mycelial cultures. The absolute configuration of the mycenarubins was established by a stereoselective synthesis of the model compound (S)-4-carboxydamirone C and comparison of its CD spectrum with the CD spectra of the mycenarubins. Details are discussed in the article by S. Peters and P. Spiteller on p. 1571 ff.

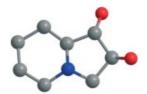


MICROREVIEW

Enzyme Inhibitors

(+)-Lentiginosine, a Potent and Selective Inhibitor of Amyloglucosidase: Synthetic Efforts and Disputes on Its Absolute Configuration

Keywords: Indolizidine / Alkaloids / Imino sugars / Cycloaddition / Molecular dynamics



(+)-Lentiginosine is a selective and potent inhibitor of amyloglucosidase. This Microreview focuses on the isolation, the biological assays, the total syntheses and the molecular dynamic studies of this alkaloid, which allowed the assignment of its absolute configuration.

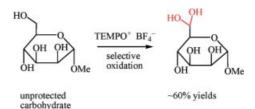
SHORT COMMUNICATION

Oxidation of Carbohydrates

T. Breton, G. Bashiardes,* J.-M. Léger, K. B. Kokoh 1567–1570

Selective Oxidation of Unprotected Carbohydrates to Aldehyde Analogues by Using TEMPO Salts

Keywords: Aldehydes / Oxidation / TEMPO / Carbohydrates



The selective transformation of the primary 6-hydroxy function of carbohydrates to the corresponding aldehyde provides a useful intermediate for numerous applications, but in all cases selective protection/deprotection of all the remaining positions is

devised and employed to selectively introduce the modification at the 6-position. We describe herein the only selective oxidation of the primary 6-hydroxy function to the corresponding aldehyde in anomerically methylated carbohydrates.

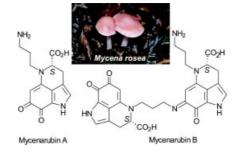
FULL PAPERS

"Marine-Type" Alkaloids

S. Peters, P. Spiteller* 1571-1576

Mycenarubins A and B, Red Pyrroloquinoline Alkaloids from the Mushroom *Mycena rosea*

Keywords: Alkaloids / Configuration determination / Fungi / Natural products / Pyrroloquinolines

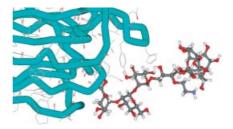


Mycenarubins A and B, two new red pyrroloquinoline alkaloids, have been detected by comparative HPLC profiling in the fruiting bodies of the mushroom *Mycena rosea*. Unlike all pyrroloquinoline alkaloids known so far, the mycenarubins each possess a carboxylic group at C-4, supporting the hypothetised biosynthetic origin of pyrroloquinoline alkaloids from L-tryptophan.



Mannose Oligosaccharides

NMR experiments show that mannose oligosaccharides are recognized by banana lectin through a conformational selection process.



C. Clavel, A. Canales, G. Gupta, F. J. Cañada, S. Penadés,* A. Surolia,* J. Jiménez-Barbero* 1577–1585

NMR Investigation of the Bound Conformation of Natural and Synthetic Oligomannosides to Banana Lectin

Keywords: Mannose oligosaccharides / NMR spectroscopy / Molecular dynamics / Banana lectin / Molecular recognition

 $R = BnCH_{2}-, (CH_{3})_{2}CH-, (CH_{3})CHCH_{2}-, C_{6}H_{11}CH_{2}-$

₂– syn-oxazine

anti-oxazine

An efficient procedure for synthesizing oxazines was developed by the palladium(0)-catalyzed intramolecular cyclization of a benzamide through a π -allylpalla-

dium(II) complex. Unlike other palladiumcatalyzed reactions, the temperature was found to be a key factor in determining the stereochemistry of the oxazine.

Palladium-Catalyzed Oxazine Formation

J.-E. Joo, K.-Y. Lee, V.-T. Pham, W.-H. Ham* 1586–1593

Stereoselective Intramolecular Oxazine Formation by a π -Allylpalladium Complex Catalyzed by Pd 0

Keywords: Stereoselective synthesis / Chiral oxazine / Catalysis / Amino alcohol / Palladium / Synthetic methods

Three Component Syntheses

de up to 78% yield up to 82%

Three component allylation reactions of aldehydes, amines, and allyltributylstannanes to afford homoallylic amines in good yield and stereoselectivity were achieved in aqueous media catalyzed by Brønsted acids.

Regio- and Diastereoselective Three-Component Syntheses of Homoallylic Amines in Aqueous Media Catalyzed by Brønsted Acids

Keywords: Aqueous media / Allylation / Multicomponent reactions / Amines

Synthetic Methods

$$R^{2}$$

$$X$$

$$R^{3}$$

$$R^{4}$$

$$R^{2}$$

The synthesis of polysubstituted quinoline derivatives without the use of ketones is easily accomplished with RuCl₂(dmso)₄ as

a catalyst. The high yields obtained in this new procedure could favor its use in many other quinoline syntheses.

RuCl₂(dmso)₄ Catalyzes the Solvent-Free Indirect Friedländer Synthesis of Polysubstituted Quinolines from Alcohols

Keywords: Annulation / Homogeneous catalysis / Hydrogen transfer / Ruthenium / Synthetic methods

CONTENTS

Envne Metathesis

M.-A. Virolleaud, O. Piva* 1606-1612

Tandem Sequential Ring-Closing Metathesis/Diels-Alder/Cross-Metathesis: Formation of Polycyclic Compounds by a New Three-Component Reaction

Keywords: Ring-closing metathesis / Cycloaddition / Tandem reaction / Crossmetathesis / Enynes

$$\begin{array}{c|c}
\hline
& RCM \\
\hline
& n = 0,1
\end{array}$$

$$\begin{array}{c|c}
\hline
& RCM \\
\hline
& N \\
& N \\
\hline
& Ph
\end{array}$$

$$\begin{array}{c|c}
\hline
& CM \\
& N \\
& N \\
& Ph
\end{array}$$

A new three-component reaction has been devised that combines the formation of a 1,3-diene by ring-closing metathesis, a Diels-Alder process and finally a crossmetathesis reaction between a vinyl group generated during the first step and an alkene introduced in the middle.

1,1'-Biaryl Synthesis

M. Solinas, R. E. Meadows, C. Wilson, A. J. Blake, S. Woodward* 1613-1623

Efficient Synthesis of 2-Methyl Derivatives of 1,1'-Bi[2-naphthol] and 1,1'-Bi[2-phenols]

Keywords: Axial chirality / Biaryl compounds / Binaphthyl compounds / Silicon / Phosphorus

1 ex. BINOL

A succinct route to monomethyl 1,1'-binaphthyl and biphenyl species 1 is presented together with their directed lithiation and reaction with subsequent electrophiles.

Ring-Chain Tautomerism

T. Delaine, V. Bernardes-Génisson, J.-L. Stigliani, H. Gornitzka, B. Meunier, J. Bernadou* 1624-1630

Ring-Chain Tautomerism of Simplified Analogues of Isoniazid-NAD(P) Adducts: an Experimental and Theoretical Study

Keywords: Tautomerism / Hemiamidal / Computer chemistry / Isoniazid / Tuberculosis

keto-amide form

Isoniazid-NAD(P) adducts are potent inhibitors of key reductases that are involved in Mycobacterium tuberculosis cell wall biosynthesis. Analogues of these adducts were prepared and the observed tautomeric ring-chain equilibrium was experimentally and theoretically studied in sight of further design and syntheses of antituberculosis drugs.

Mushroom Pigments

B. Koch, W. Steglich* 1631-1635

Meroterpenoid Pigments from Albatrellus flettii (Basidiomycetes)

Keywords: Natural products / Meroterpenoids / Mushrooms / Quinones / Furans

The structure of albatrellin suggests its biosynthesis from the monomeric meroterpe-

noids grifolin and cristatic acid, a sequence, which could also be performed in vitro.



Synthesis of Heterocycles

In a convenient noble-metal-catalyzed process, 2-alkynyl-2-hydroxy carbonyl compounds are effectively converted into spirocyclic 3(2H)-furanones and 3-pyrrolones. The cascade reactions likely proceed through a 5-endo-dig heterocyclization, followed by a 1,2-migration. The scope and limitations of the novel reactions are shown in the preparation of 22 3(2H)-furanones and 10 3-pyrrolones.

J. T. Binder, B. Crone, S. F. Kirsch,*
C. Liébert, H. Menz 1636–1647

Synthesis of Heterocyclic Systems by Transition-Metal-Catalyzed Cyclization-Migration Reactions — A Diversity-Oriented Strategy for the Construction of Spirocyclic 3(2*H*)-Furanones and 3-Pyrrolones

Keywords: Platinum / Gold / Domino reactions / Cyclizations / Heterocycles

5 mol-% Ph₃PAuNTf₂ r.t., DCM, 24 h 3 equiv. 44%

Reactions of pyrrole derivatives with methyl vinyl ketone in the presence of gold(III) and gold(I) catalysts do not give selective hydroarylation products. Instead, highly substituted pyrrole derivatives are obtained.

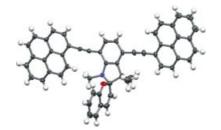
Gold-Catalyzed Hydroarylation

A. S. K. Hashmi,* R. Salathé, W. Frey 1648–1652

Gold Catalysis: Selectivity Problems in Hydroarylations with Pyrroles

Keywords: Alkynes / Gold / Homogeneous catalysis / Hydroarylation / Pyrroles

Structural solid-phase and solution-phase properties of two pyrene-spiropyran molecular dyads are described. Each dyad comprises a 1,1'-[indole-4,6-diylbis(ethyne-2,1-diyl)]bis(pyrene) backbone, with the bis(pyrene) and spiropyran units adopting a T-shaped arrangement.



Solid Phase and Solution Phase Structural Characterization of Pyrene-Based, T-Shaped Molecular Dyads

Keywords: Pyrene / Spiropyran / Isomerization

β-Turn Mimetics

Photochromics

A new set of β -turn mimetics incorporating a bicyclic turn inducer was achieved by utilisation of stereoselective solid-phase multicomponent Petasis reactions. Use of arylboronic acids provided chemical diversity at position i + 1, whilst additional

variety was introduced at the cleavage stage, thus providing a tool for the generation of libraries of β -turn mimetics as privileged structures in combinatorial chemistry.

Synthesis and Conformational Analysis of Constrained β -Turn Mimetics Incorporating a Bicyclic Turn Inducer by Use of the Petasis Three-Component Reaction on Solid Phase

Keywords: Peptidomimetics / Scaffold / Amino acids / Solid-phase synthesis

CONTENTS

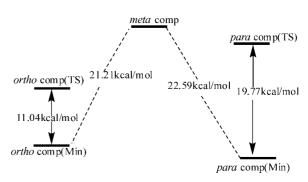
Aromatic Planarity

W.-Q. Li, W. Q. Tian,* J.-K. Feng,* Z.-Z. Liu 1669–1677



Does the Planar Aromatic Phosphorus Analogue of Pyridone Exist?

Keywords: Aromaticity / Planarity / Phosphanyl ketone/ Phosphorus heterocycles



The structural and electronic properties of the tautomers of phosphanyl ketones were investigated. ELF has been successfully employed to determine the electronic structure of these molecules. NICS analysis reveals that their planar conformations are aromatic.

Palladium Catalysis

A. Begouin, S. Hesse,* M.-J. R. P. Queiroz, G. Kirsch* 1678–1682

Palladium-Catalyzed Buchwald-Hartwig Coupling of Deactivated Aminothiophenes with Substituted Halopyridines

Keywords: Cross-coupling / Nitrogen heterocycles / Sulfur heterocycles / Amines / Suzuki coupling

$$\begin{array}{c} R^1 & CO_2Me \\ R^2 & NH_2 & CS_2CO_3 \\ & X = Br, I, CI \\ & R = H, X \end{array} \qquad \begin{array}{c} R^1 & CO_2Me \\ & ArB(OH)_2 \\ & Pd(OAc)_2 \\ & PPh_3 \end{array} \qquad \begin{array}{c} R^2 & NH \\ & R^2 & NH \end{array}$$

The palladium-catalyzed Buchwald-Hartwig coupling of deactivated aminothiophenecarboxylates with differently substituted halopyridines was performed for the first time by using Pd(OAc)₂, Xantphos as the ligand, and Cs₂CO₃ as the base. Some

bromo monoaminated pyridine derivatives, obtained by Buchwald-Hartwig coupling, were further used in the Suzuki coupling of aryl boronic acids bearing electron-withdrawing or electron-donating groups.

If not otherwise indicated in the article, papers in issue 9 were published online on March 2, 2007