



























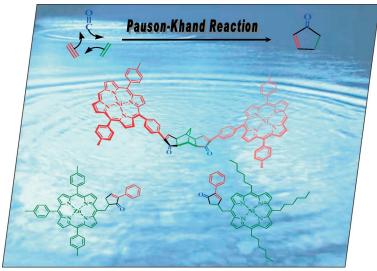




A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

The cover picture shows the products of the intermolecular Pauson-Khand reaction of meso-substituted porphyrins. In addition to various monomers, this method offers easy access to porphyrin dimers with well-defined stereochemistries. Details are discussed in the article by S. Horn and M. O. Senge from Trinity College Dublin on p. 4881ff.



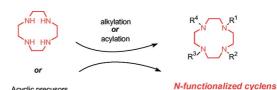
MICROREVIEW

Functionalized Cyclens

M. Suchý, R. H. E. Hudson* 4847-4865

Synthetic Strategies Toward N-Functionalized Cyclens

Keywords: Cyclen derivatives / Lanthanide chelation / Contrast agents



Acyclic precusors

Cyclen (1,4,7,10-tetraazadodecane) is a widely used building block in the synthesis of many important molecules with applications spanning MRI contrast agents,

fluorescent probes and heavy metals sensors. This review describes the various synthetic methodologies employed for the preparation of N-functionalized cyclens.

SHORT COMMUNICATIONS

Iron-Catalyzed Epoxidation

B. Bitterlich, K. Schröder, M. K. Tse, M. Beller* 4867-4870

An Improved Iron-Catalyzed Epoxidation of Aromatic and Aliphatic Olefins with Hydrogen Peroxide as Oxidant

Keywords: Epoxidation / Alkenes / Iron / Hydrogen peroxide / Homogeneous catalysis

in situ Fe catalyst COOH FeCl₃·6H₂O t-amyl alcohol 15 examples yields up to 96% соон

A practical method for the iron-catalyzed epoxidation of aromatic and aliphatic olefins is described. The iron catalyst system is generated in situ from iron trichloride hexahydrate, pyridine-2,6-dicarboxylic acid

(H₂pydic), and benzylamines. Both aliphatic and aromatic olefins are oxidized in high yield and selectivity in the presence of hydrogen peroxide as the terminal oxidant.

Amino Acid Synthesis

T. Andreassen, L.-K. Hansen, O. R. Gautun* 4871-4876

Diastereoselective Synthesis of Heteroaromatic Glycine Derivatives

Keywords: Aromatic heterocycles / Electrophilic substitution / Sulfinimine / Diastereoselectivity / Glycine derivatives

Optically active heteroaromatic glycine derivatives are prepared in moderate-to-good yield from a TMSOTf promoted addition of an N-tert-butanesulfinyl α-imino ester to five-membered aromatic heterocycles. Diastereoselectivities up to 99% were observed.

Selective Oxidation

T. M. A. Shaikh, A. Sudalai* ... 4877-4880

WO₃/70% TBHP/Aqueous NaOH: An Efficient Catalytic Combination for the Selective Oxidation of Methylarenes and Alkyl Aryl Ketones to Benzoic Acids

Keywords: Tungsten / Oxidation / Arenes / Ketones / Benzoic acids

 $R^1 = R^2 = CI$, Br, F, NO_2 , Me, OMe, etc.

been described. Alkylarenes are oxidized to either benzylic alcohol or ketones whether

An efficient catalytic method for the C-H oxidation of methylarenes and C-C bond cleavage of alkyl aryl ketones to the corresponding benzoic acids in good yields has

base is used or not.

R = alkyl

vield = 83-94%



FULL PAPERS

Porphyrin Chemistry

$$\begin{array}{c} Co_2(CO)_8 \\ \hline \\ Ni \\ \hline \end{array}$$

Porphyrins containing alkenyl- and alkynyl-substituents at the meso position can be used as precursors for the intermolecular Pauson-Khand reaction. A variety of cyclopentenyl-substituted porphyrins can be synthesised in moderate to good yields. Porphyrin dimers can be obtained with well-defined stereochemistry via a two-step double Pauson-Khand reaction in nearly quantitative yield.

S. Horn, M. O. Senge* 4881-4890

The Intermolecular Pauson-Khand Reaction of meso-Substituted Porphyrins

Keywords: Porphyrins / Pauson-Khand reaction / Intermolecular reactions / Cyclizations / Porphyrin dimers

Gold Catalysis

Benzylic stereocentres in dihydroisoindoles can be prepared by 1,2-induction in enantiomerically pure imino sulfoxides in combination with gold-catalysed ring-closure.

A. S. K. Hashmi,* S. Schäfer, J. W. Bats, W. Frey, F. Rominger 4891-4899

Gold Catalysis and Chiral Sulfoxides: Enantioselective Synthesis of Dihydroisoindol-4-ols

Keywords: Alkynes / Furans / Gold / Isoindoles / Sulfoxides / Sulfones

Catalytic Asymmetric Synthesis

The stereoselective total synthesis of several members of the styryllactone family was achieved efficiently from a common intermediate prepared by using a catalytic asymmetric inverse-electron-demand hetero-Diels-Alder/allylboration sequence.

A. Favre, F. Carreaux,* M. Deligny, B. Carboni 4900-4907

Stereoselective Synthesis of (+)-Goniodiol, (+)-Goniotriol, (-)-Goniofupyrone, and (+)-Altholactone Using a Catalytic Asymmetric Hetero-Diels-Alder/Allylboration Approach

Keywords: Lactones / Total synthesis / Asymmetric catalysis / Cycloaddition / Boron

Nickel Nanoparticles

Nickel nanoparticles have been found to activate primary alcohols used for the α alkylation of ketones or in indirect aza-Wittig reactions. For the first time Ni is employed in both reaction types as a potential alternative to noble-metal-based catalysts. Reactions are carried out under mild conditions in the absence of any ligand, hydrogen acceptor or base.

F. Alonso,* P. Riente, M. Yus* 4908-4914

Alcohols for the α-Alkylation of Methyl Ketones and Indirect Aza-Wittig Reaction Promoted by Nickel Nanoparticles

Keywords: Alcohols / Ketone alkylation / Hydrogen transfer / Nickel nanoparticles / Aza-Wittig reactions

CONTENTS

Nucleotide Chemistry

C. Lam, C. Hipolito, D. M. Perrin* 4915–4923

Synthesis and Enzymatic Incorporation of Modified Deoxyadenosine Triphosphates

Keywords: Nucleotides / Heterocycles / SELEX / Bioorganic chemistry / DNA / Enzymes

Several deoxyadenosine triphosphates containing modifications at the 8-position have been synthesized. Incorporation assays were performed for these modified residues with many commercially available DNA polymerases.

Zinc Homologation

A. Abramovitch, I. Marek* 4924-4931

Zinc Homologation – Elimination Reaction of α -Sulfinyl Carbanions as a New Route to Olefins

Keywords: Zinc / Carbenoids / Sulfur / Carbanions / Alkenes / Elimination / Rearrangement

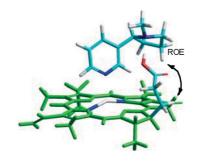
 $\alpha\text{-Lithiosulfinyl}$ carbanions react either intermolecularly, after transmetalation into organocopper derivatives in an $S_N2\text{-type}$ process, with zinc carbenoids or intramolecularly by higher-order zincates through a tandem zinc homologation— $\beta\text{-elimination}$ reaction into the corresponding alkenes.

Host-Guest Systems

J. S. Kavakka, S. Heikkinen, J. Helaja* 4932–4937

Zn Pyropheophorbide *a*: A β-Face Selective Nicotine Receptor

Keywords: Host-guest systems / NMR spectroscopy / Supramolecular chemistry / Receptors



Nicotine binds to Zn pyropheophorbide a in a receptor-like manner to form a 1:1 complex with β -face diastereomeric configuration, as evidenced by ¹H NMR, ROESY and DOSY spectroscopic experiments and molecular modelling DFT B3LYP calculations at the 6-31G* level.

Allocolchicines

F.-D. Boyer, I. Hanna* 4938-4948

Synthesis of New Allocolchicinoids with Seven- and Eight-Membered B-Rings by Enyne Ring-Closing Metathesis

Keywords: Allocolchicines / Enyne / Ringclosing metathesis / Cycloheptenes / Cyclooctenes / Diels—Alder reactions

Total syntheses of allocolchicines with a seven- or eight-membered B-ring and the C-ring ester functionality at the C10 or C11 positions are reported. The main features included the elaboration of the AB bicyclic

ring system by an enyne RCM reaction. A subsequent Diels—Alder/aromatization sequence afforded the set of functionalized ring-C allocolchicinoids with high regioselectivity.



Cyclopropane Ring Opening

Catalyzed by NHCs, readily available formylcyclopropane 1,1-diesters can undergo domino redox esterification/cyclization with salicylaldehydes to give coumarins in moderate to excellent yield. D. Du, Z. Wang* 4949-4954

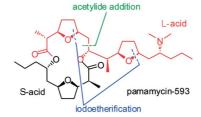
N-Heterocyclic Carbene-Catalyzed Domino Reactions of Formylcyclopropane 1,1-Diesters: A New Synthesis of Coumarins

Keywords: Cyclopropanes / N-Heterocyclic carbenes / Umpolung / Domino reac-

tions / Coumarins

Antibiotics

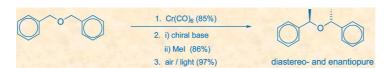
The L-acid fragment of pamamycin-593 and de-N-methylpamamycin-579, strong aerial mycelium-inducers of *Streptomyces alboniger*, was synthesized using a *cis*-selective iodoetherification and nucleophilic addition of cerium acetylide to aldehyde as the key steps.



Synthesis of the L-Acid (C1-C18) Fragment of Pamamycin-593 and De-*N*-methylpamamycin-579

Keywords: Pamamycins / Antibiotics / Synthesis design / Iodoetherification / Cerium acetylide

Asymmetric Synthesis



The stereocontrolled synthesis of four C_2 symmetric ethers has been achieved using

a chiral base/arene chromium tricarbonyl activation approach.

A Stereocontrolled Approach to Ethers with Two α Stereocentres

Keywords: Alkylation / Asymmetric synthesis / Chiral base / Chromium / Ether compounds

The total synthesis of L-(+)-swainsonine, a QH, OH M. A. Alam, A. Kumar,

potent and specific inhibitor of naringinase, was achieved in 14 steps in 17% overall yield by starting from D-(+)-glucose. The syntheses of six unnatural indolizidine azasugars are also reported, two of which were found to be good glycosidase inhibitors at micromolar concentrations.

Total Synthesis of L-(+)-Swainsonine and Other Indolizidine Azasugars from D-Glucose

Y. D. Vankar* 4972-4980

Keywords: Nitrogen heterocycles / Azasugars / Epoxides / Nucleophilic substitution

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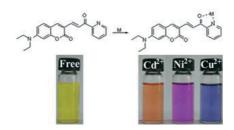
Chromogenic Sensors

W. Lin,* L. Yuan, X. Cao, W. Tan, Y. Feng 4981-4987



A Coumarin-Based Chromogenic Sensor for Transition-Metal Ions Showing Ion-Dependent Bathochromic Shift

Keywords: Sensors / Transition metals / N,O ligands / Charge transfer / Coumarins



Compound 1 was rationally designed and synthesized as a new chromogenic sensor for transition-metal ions, and it showed ion discrimination by exhibiting different extents of bathochromic shifts: 118 nm for Cu^{2+} , 80 nm for Ni^{2+} , and 55 nm for Cd^{2+} .

Temporary Bridge

A. Michaut, S. Miranda-García,

J. C. Menéndez, Y. Coquerel,*

J. Rodriguez* 4988-4998



Stereoselective Synthesis of Bicyclo[4.2.1]nonanes - a Temporary-Bridge Approach to Cyclooctanoids

Keywords: Bicycles / Domino reactions / Fragmentation / Metathesis



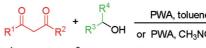
Break, re-build and re-break! A domino ring-cleavage/ring-reconstitution strategy allowed for the synthesis of cis-α, γ-disubstituted cyclopentanones, precursors of bicyclo[4.2.1]nonanes, following an olefinmetathesis cyclization with excellent regioand stereocontrol. An additional fragmentation step of the cyclopentanone in the bicyclo[4.2.1]nonane products opens a route to densely functionalized eight-membered

Benzylation

G.-W. Wang,* Y.-B. Shen, X.-L. Wu 4999-5004

Phosphotungstic Acid Catalyzed Direct Benzylation of β-Dicarbonyl Compounds

Keywords: Phosphotungstic acid / Benzylation / Alcohols / B-Dicarbonyl compounds / Atom-economical reactions



 $R^1 = CH_3$, aryl; $R^2 = CH_3$, aryl, OEt R³ = aryl, trans-PhCH=CH; R⁴ = CH₃ Ph

12-Phosphotungstic acid was used as an efficient, ecofriendly, and air- and moisturestable catalyst to promote the direct substitution of the hydroxy group of benzylic and allylic alcohols with various β-dicarbonyl

compounds. This powerful protocol for carbon-carbon bond-forming reactions provides monoalkylated dicarbonyl compounds in high yields with great efficiency.

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

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