

















CZECH REPUBLIC





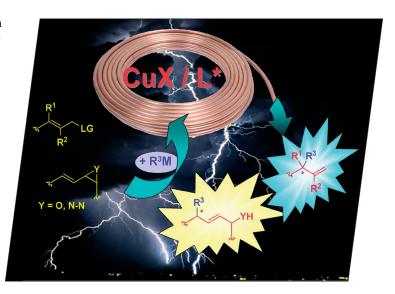




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further EUChemSoc Societies (Austria, Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

The cover picture shows a figurative illustration of the copper-catalytic cycle for the asymmetric allylic alkylation and its powerful stereoselective control over the regio-, chemo- and enantio-selective allylic ring opening of oxiranes or S_N2' displacement of leaving groups. This Microreview by C. A. Falciola and A. Alexakis on p. 3765ff. covers the field from the early stages of diastereoselective procedures to the more recent highly efficient catalytic protocols.



MICROREVIEW

Asymmetric Catalysis

C. A. Falciola, A. Alexakis* ... 3765-3780

Copper-Catalyzed Asymmetric Allylic Alkylation

Keywords: Copper / Allylic compounds / Asymmetric catalysis

$$\mathbb{R}^{M} \xrightarrow{\mathbb{R}^{1}} \mathbb{L}^{G}$$

$$\mathbb{R}^{M} \xrightarrow{\mathbb{R}^{2}} \mathbb{R}^{2}$$

$$Y = 0, N-N, ...$$

$$\mathbb{R}^{M} \xrightarrow{\mathbb{R}^{2}} \mathbb{R}^{2}$$

This review covers the main asymmetric allylic alkylation and ring-opening reactions enabled by copper reagents. This past decade has mostly focused on catalytic procedures giving access to a large diversity of allylic chiral adducts. With the increasing

number of publications on the subject, the scope of the methodologies has broadened to highly substituted substrate patterns, more functionable substrates and a larger range of nucleophilic sources.

SHORT COMMUNICATION

Natural Products

H. V. Kemami Wangun, K. Ishida, C. Hertweck* 3781–3784

Epicoccalone, a Coumarin-Type Chymotrypsin Inhibitor, and Isobenzofuran Congeners from an *Epicoccum* sp. Associated with a Tree Fungus

Keywords: Coumarins / Fungi / Natural products / Polyketides / Protease inhibitors

A new inhibitor of the serine protease α -chymotrypsin, epicoccalone (1), was isolated from an *Epicoccum* sp. associated with the tree fungus *Pholiota squarrosa*. The isolation and structural elucidation of two co-metabolites (2, 3) suggest that the unusual coumarin (1) and the isobenzofuranes (2, 3) share an orsellinic acid derived polyketide biosynthetic pathway.

FULL PAPERS

Peptido-Carbene Complexes



Optically Active (Peptido-carbene)palladium Complexes: Towards True Solid-Phase Combinatorial Libraries of Transition Metal Catalysts

Keywords: Palladium catalysts / Solid phases / Combinatorial chemistry / Chiral catalysts / Carbenes

Peptido-carbenes and their Pd complexes were synthesised on solid support and characterised by NMR and MS data. Solid-phase reactions of peptides containing imidazolium ions in the backbone with BEMP and PdCl₂COD or Pd(OAc)₂ afforded mono- or didentate (carbene)palladium complexes on solid support. These methods are suitable for solid-support combinatorial synthesis of chiral palladium catalysts.



Benzannelated Thienyl Oligomers

$$\begin{array}{c|c} & & \\ & &$$

S S S S S R^2

A ring opening of lactones with Grignard reagents followed by thionation with Lawesson's reagent led to the synthesis of several benzannelated thienyl oligomers.

Results from the optical and electrochemical studies of benzo[c]thiophenes are also presented.

P. Amaladass, J. A. Clement, A. K. Mohanakrishnan* 3798–3810

Synthesis and Characterization of Benzannelated Thienyl Oligomers

Keywords: Lactones / Lawesson's reagent / Benzothiophene / Oligomers / Cyclic voltammetry / Thiophenes

Tautomeric Equilibria

Relative stabilities of various tautomers of compound 1 were investigated in both the gas phase and in water by a series of DFT and ab intio calculations. In addition, the basicity of 1 in aqueous solution was estimated.

$$H_2N$$
 H_2N
 H_2N

Y. Wei, H. Zipse* 3811-3816

Tautomeric Equilibria in 3-Amino-1-(2-aminoimidazol-4-yl)prop-1-ene, a Central Building Block of Marine Alkaloids

Keywords: 2-Aminoimidazole / Tautomeric equilibria / ab initio calculations

OH PPhBu (5–10 mol-%) THF, 25 °C, 1–5 h

80-98% yield, up to 88% ee

The use of bifunctional chiral phosphane Lewis bases in catalytic asymmetric aza-Morita-Baylis-Hillman reactions of *N*sulfonated imines with methyl vinyl ketone affords the corresponding adducts in good-to-excellent yields and moderate-to-good enantioselectivities within a few hours at room temperature.

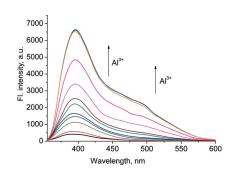
Aza-Morita-Baylis-Hillman Reaction

A Fast Catalytic Asymmetric Aza-Morita—Baylis—Hillman Reaction of *N*-Sulfonated Imines with Methyl Vinyl Ketone in the Presence of Chiral Bifunctional Phosphane Lewis Bases

Keywords: Asymmetric catalysis / Aza—Morita—Baylis—Hillman reaction / Ketones / Lewis bases

Al³⁺ Fluorescent Sensor

Sensor 1 was developed as a fluorescence-enhanced Al³+ sensor with unique dual-channel emissions. The addition of Al³+ to 1 elicits a large fluorescence enhancement by inhibition of a PET channel and also a fluorescence enhancement due to promotion of an emissive excimer channel. The dual-channel fluorescence-enhanced response of the sensor contributes to its high sensitivity and selectivity.



W. Lin,* L. Yuan, J. Feng 3821-3825

A Dual-Channel Fluorescence-Enhanced Sensor for Aluminum Ions Based on Photoinduced Electron Transfer and Excimer Formation

Keywords: Sensors / Aluminum / Fluorescence / Coumarins

CONTENTS

Phosphane Organocatalysts

A. Panossian, N. Fleury-Brégeot, A. Marinetti* 3826-3833

Use of Allenylphosphonates as New Substrates for Phosphane-Catalyzed [3+2] and [4+2] Annulations

Keywords: Phosphanes / Organocatalysis / Phosphonates / Allenes / Asymmetric catalysis

Allenylphosphonates react with imines, α,β -unsaturated esters, and enones in Bu₃P-or iBu₃P-promoted reactions to afford pyrrolines, tetrahydropyridines, and cyclopentenes bearing phosphoryl functions.

Enantioselective variants of these cyclization reactions afforded enantiomeric excesses of up to 90% when a chiral phosphepine was used as the catalyst.

$\alpha^{2,2},\beta^3$ -Diamino Acids



Synthesis of $\alpha^{2,2}$, β^3 -Diamino Acids by Double Stereodifferentiation Aldol Addition of Oxazolidinone Enolates to *N*-(*tert*-Butylsulfinyl) Imines

Keywords: Amino acids / Oxygen heterocycles / Nitrogen heterocycles / Diastereoselectivity / Antifungal agents / Peptidomimetics

NH3*O
R

NH3*O
R

NH2
OXAZOIe-1,5-dione
$$de: 100\%$$
 $de: 76-100\%$
 exo

THF/HMPA/-80 °C

 $endo$

Alloc

 R^1HN
 NH_2
 N

Chiral $\alpha^{2,2}$, β^3 -diamino acids were synthesized by double stereoinduction reactions of chiral oxazolidinone enolates with N-sulfinyl aldimines. Among a variety of highly functionalized diamino acids, this highly diastereoselective protocol provides a synthetic route for yet unreported C-glycosyl and α -nucleoside diamino acids.

Dendrimers

S. L. Elmer, S. Man, S. C. Zimmerman* 3845–3851

Synthesis of Polyglycerol, Porphyrin-Cored Dendrimers Using Click Chemistry

Keywords: Azide / Dendrimers / Click chemistry / Biocompatibility / 1,3-Dipolar cycloaddition

Clicking polyglycerol dendrons to a porphyrin core gives dendrimers with molecular weights of approximately 8000 and 16000 and with 64 and 128 allyl ether groups on their periphery, respectively.

Hydrostannations

N. Jena, U. Kazmaier* 3852-3858

Synthesis of Stannylated Allyl- and Vinylphosphonates via Molybdenum-Catalyzed Hydrostannations

Keywords: Allylphosphonates / Cross couplings / Hydrostannations / Molybdenum / Vinylphosphonates

$$\begin{array}{c|c} & & & & & & & & & & & & & & & \\ RO & P & N & & & & & & & & \\ RO & 0 & & & & & & & & \\ RO & 0 & & & & & & & \\ RO & 0 & & & & & & \\ RO & 0 & & & & & & \\ RO & 0 & & & & & & \\ RO & 0 & & & & & & \\ RO & 0 & & & & & & \\ RO & 0 & & & & & & \\ RO & 0 & & & & & & \\ RO & 0 & & & & & & \\ RO & 0 & & \\ RO & 0 & & & \\ RO & 0 & &$$

Syntheses of stannylated allyl and vinylphosphonates by molybdenum-catalyzed hydrostannation of the corresponding propargyl and alkynylphosphonate derivatives proceed with high regioselectivities. The stannylated phosphonates obtained are versatile building blocks for further modifications, such as iodinations or cross coupling reactions.



Ring-Closing Metathesis

A new class of α , β -unsaturated δ -oxacaprolactams was synthesized from imines as starting material. The synthetic procedure

is based on an acyl chloride addition in the first step, followed by a ring-closing metathesis using a ruthenium catalyst. M. Watzke, K. Schulz, K. Johannes, P. Ullrich, J. Martens* 3859–3867

First Synthesis of Bi- and Tricyclic α,β -Unsaturated δ -Oxacaprolactams from Cyclic Imines via Ring-Closing Metathesis

Keywords: Heterocyclic imines / Ring-closing metathesis / Unsaturated caprolactams / Acrylamides / Ruthenium catalysis

Densely Substituted Butadienes

An efficient and stereoselective synthesis of densely substituted 1,3-dienes has been achieved by a domino reaction of Lidimsylate, an 2-(arylmethylidene)-2-phosphonoacetonitriles, an aldehyde and LiOEt involving Michael/Horner—Wadsworth—Emmons/elimination steps.

Sequential Double Olefination of 2-(Arylmethylidene)-2-phosphonoacetonitrile with Dimsyl Lithium and Aldehydes: A Domino Route to Densely Substituted 1,3-Butadienes

Keywords: Domino reactions / Olefination / Michael addition / Elimination

CORRECTION

Keywords: Conducting materials / Annulenes / Polymers / Cyclic voltammetry / UV/Vis spectroscopy

Emerging Prospects for Unusual Aromaticity in Organic Electronic Materials: The Case for Methano[10]annulene

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

^{*} Author to whom correspondence should be addressed.