























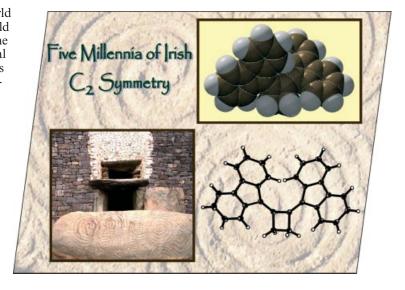




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic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

COVER PICTURE

The cover picture shows the entrance to the World Heritage Site at Newgrange, a 5000-year-old Neolithic passage tomb, situated near Dublin. The background depicts a twofold symmetric spiral engraving on the entrance stone and provides an appropriate motif for the sequential transformation of 9-(trimethylsilylethynyl)-9*H*-fluoren-9-ol, via 3,3-(biphenyl-2,2'-diyl)-1-(trimethylsilyl)allene, into a series of sterically crowded head-to-tail and tail-to-tail silyl-allene dimers with unusually long carbon—carbon and carbon—silicon bonds. Removal of the silyl substituents culminates in the formation of the bis(alkylidene)cyclobutane shown, whose intrinsic C_2 symmetry arises solely from the overlap of fluorenylidene fragments with very large wingspans. Details of this work are described in the article by M. J. McGlinchey et al. on p. 2611 ff.



MICROREVIEWS

Asymmetric Catalysis

Recent Advances in the Catalytic Asymmetric Nitroaldol (Henry) Reaction

Keywords: Henry reaction / Asymmetric catalysis / Nitro compounds / C-C bond formation

$$\begin{matrix} O \\ R \end{matrix} + CH_3NO_2 & \begin{matrix} cat^* \\ \hline [La, Zn, Cu, Co, Mg \\ or \ organocatalyst] \end{matrix} & \begin{matrix} OH \\ R \end{matrix} + NO_2 \end{matrix}$$

The nitroaldol (or Henry) reaction is a valuable C-C bond-forming process that gives rise to synthetically useful intermediates. In recent years, successful promotion of the Henry reaction, with high degrees of

stereocontrol, by chiral catalysts – both metal-based (La, Zn, Cu, Co, Mg) and organocatalysts – has been described. The main advances in this area are presented.

Organocatalysis

R. Marcia de Figueiredo,
M. Christmann* 2575-2600

Organocatalytic Synthesis of Drugs and Bioactive Natural Products

Keywords: Total synthesis / Natural products / Organocatalysis / Medicinal chemistry / Asymmetric synthesis

In the last few years organocatalysis has been a strongly growing branch of asymmetric synthesis. This review discusses recent applications of metal-free catalytic processes in the synthesis of biologically relevant molecules.

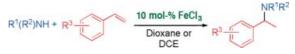
SHORT COMMUNICATIONS

Hydroamination

J. Michaux, V. Terrasson,

S. Marque, J. Wehbe, D. Prim,*

J.-M. Campagne* 2601-2603



Intermolecular FeCl₃-Catalyzed Hydroamination of Styrenes

Keywords: Iron / Hydroamination / Styrenes

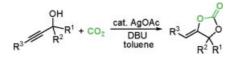
Hydroamination reactions of vinyl arenes with nonnucleophilic nitrogen derivatives catalyzed by FeCl₃ are described. FeCl₃ is

an environmentally friendly and a inexpensive catalyst; the reaction is carried out in the absence of any ligand or cocatalyst.

Cyclic Carbonates

Silver-Catalyzed Incorporation of Carbon Dioxide into Propargylic Alcohols

Keywords: Alkynes / Carbonates / Carbon dioxide fixation / Silver



Catalytic silver acetate and stoichiometric DBU efficiently catalyzed the incorporation of CO_2 into a wide range of propargylic alcohols bearing a terminal or an internal triple bond to afford the corresponding cyclic carbonates in high-to-excellent yields. All the obtained cyclic carbonates were found to be single isomers with the (Z) geometry.



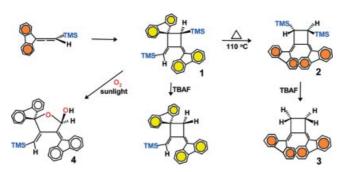
Catalytic Asymmetric Synthesis

Highly enantioselective and catalytic aryl transfer reactions to aromatic aldehydes by using mixed triarylbismuthane and dimethylzinc reagents gave chiral diarylmethanols with up to 97 % ee.

A Highly Enantioselective and Catalytic Aryl Transfer Reaction Using Mixed Triarylbismuthane and Dialkylzinc Reagents

Keywords: Arylation / Asymmetric synthesis / Bismuth / Catalysis / Zinc

FULL PAPERS



Thermolysis of the head-to-tail silyl-allene dimer 1 yields the tail-to-tail isomer 2. Desilylation of 2 furnishes 3, which retains its C_2 symmetry because of the overlapping

adjacent fluorenylidene moieties. The juxtaposition of bulky substituents in 1 results in long C-C and C-Si bonds that are readily cleaved in air to form the lactol 4.

Overlapping Fluorenylidenes

E. V. Banide, B. C. Molloy, Y. Ortin, H. Müller-Bunz, M. J. McGlinchey* 2611–2622

From Allenes to Tetracenes: A Synthetic and Structural Study of Silyl- and Halo-Allenes and Their Dimers

Keywords: Allenes / Dimerizations / Long bonds

Asymmetric allylation and reduction of imines in the presence of chiral *N*-formylproline derivatives as well as different additives is reported. The role of the second formamide moiety in the activator is shown to be crucial to bring about the enhancement of the reaction rate and enantioselectivity in the allylation reaction.

Allylation and Reduction of Imines

C. Baudequin, D. Chaturvedi, S. B. Tsogoeva* 2623-2629

Organocatalysis with Chiral Formamides: Asymmetric Allylation and Reduction of Imines

Keywords: Chirality / Formamides / Organocatalysis / Allylation / Reduction

Molecular Electronics

The synthesis of a series of cruciform molecules like 1, consisting of a terminally sulfur-functionalized oligophenylene-ethynyl rod of various length and a transversal oligophenylene push-pull system, is reported. These new cruciform structures are expected to display electric field-dependent transport properties in nanoscale junctions.

A. Błaszczyk, M. Fischer, C. von Hänisch, M. Mayor* 2630-2642

The Synthesis of Molecular Rods with a Transversal Push-Pull System

Keywords: Push-pull system / Molecular rods / Cruciform / Sonogashira coupling / Suzuki coupling

CONTENTS

N/O-Aryl Coupling

M. Egger, X. Li, C. Müller, G. Bernhardt, A. Buschauer,*

B. König* 2643-2649

Tariquidar Analogues: Synthesis by Cu^I-Catalysed N/O-Aryl Coupling and Inhibitory Activity against the ABCB1 Transporter

Keywords: Cross-coupling / Medicinal chemistry / Lipophilicity

A synthetic route to tariquidar analogues as ABCB1 transporter inhibitors is presented. Starting from anthranilic acid, a central building block was prepared that can be converted into various tariquidar analogues by Cu^I-catalysed N/O-aryl coupling reactions. The new compounds show significant inhibitory activity against the ABCB1 transporter.

Catalytic Nazarov Cyclization

I. Walz, A. Bertogg,

A. Togni* 2650-2658

Cationic Vanadium(IV) Complexes as Efficient Catalysts for Nazarov Cyclizations

Keywords: Electrocyclic reactions / Homogeneous catalysis / Vanadium / Schiff bases

Nazarov cyclizations of dialkenyl ketones bearing α -ester groups are efficiently catalyzed by a vanadium(IV) species generated

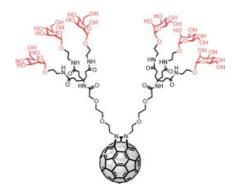
from the corresponding dichlorido(salen)-vanadium(IV) complex, upon in-situ activation with AgSbF₆.

Fullerene Sugars

H. Kato, C. Böttcher, A. Hirsch* 2659-2666

Sugar Balls: Synthesis and Supramolecular Assembly of [60]Fullerene Glycoconjugates

Keywords: Sugars / Mannose / Dendrimers / Fullerenes / Self-assembly / Micelles



A fullerene glycoconjugate containing six deprotected sugar building blocks was synthesized. The amphiphilic nature of this very water-soluble fullerene derivative with its cone-shaped structure forces the formation of small supramolecular sugar balls with an extremely narrow size distribution of around 4 nm.

Fluorinated Heterocycles

V. De Matteis, O. Dufay, D. C. J. Waalboer, F. L. van Delft, J. Tiebes, F. P. J. T. Rutjes* 2667–2675

An Improved Ring-Closing Metathesis Approach to Fluorinated and Trifluoromethylated Nitrogen Heterocycles

Keywords: Ring-closing metathesis / Fluorinated heterocycles / Trifluoromethylated heterocycles / Sulfonamides / Trifluoromethylated pyrrole

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The synthesis of partially unsaturated fluorinated and trifluoromethylated nitrogen heterocycles via RCM as the key step is described. Furthermore, modification of this pathway gave rise to a trifuoromethylated pyrrole derivative.



Dipolar Cycloadditions

Dipolar cycloaddition reactions of azomethine ylides provide a short, stereoselec-

tive route to the tetracyclic ring system of a number of indole alkaloids.

Intramolecular Dipolar Cycloaddition Reactions to Give Substituted Indoles – A Formal Synthesis of Deethylibophyllidine

Keywords: Cycloadditions / Azomethine ylides / Alkaloids / Pyrrolidines / Indoles

Cationic Rhodium(I) Catalysts

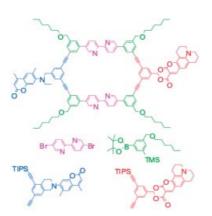
Hydrogenated, cationic, Rh(I)/bisphosphane complexes are highly active catalysts for the isomerization of secondary propargylic alcohols to α,β -enones. Mechanistic studies revealed that the isomerization proceeds through intramolecular 1,3- and 1,2-hydrogen migration pathways.

 R^1 = aryl, Ligand = rac-BINAP, (CH₂Cl)₂, 80 °C R^1 = alkenyl, Ligand = dppe, (CH₂Cl)₂, 80 °C R^1 = alkyl, Ligand = dcpe, CH₂Cl₂, 25 °C

Cationic Rhodium(I)/Bisphosphane Complex-Catalyzed Isomerization of Secondary Propargylic Alcohols to α,β -Enones

Keywords: Alcohols / Alkynes / Catalysis / Homogeneous / Isomerization / Rhodium

A flexible route to shape-persistent macrocycles based upon a collection of building blocks is reported. An easy introduction of several different functional units at predetermined positions as well as the obtainment of cycles in high isolated yields were accomplished by copper-free Sonogashira cross-coupling reactions and gel-permeation chromatography.



Shape-Persistent Macrocycles

J. Sakamoto,

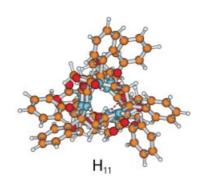
A. D. Schlüter* 2700-2712

Shape-Persistent Macrocycles: A Synthetic Strategy that Combines Easy and Site-Specific Decorations with Improved Cyclization Efficiency

Keywords: Repetitive synthesis / Molecular scaffolds / Coumarin / Cross-coupling / Molecular devices / Synthesis design

Foldamers

A novel class of foldamers containing (S)- β^3 -homophenylglycine and D-4-carboxy-oxazolidin-2-one residues in alternate order is reported. The experimental conformational analysis proved that these oligomers fold into ordered structures and theoretical calculations suggest a helix with 11-membered hydrogen-bonded rings as the preferred secondary structure type.



G. Angelici, G. Luppi, B. Kaptein, O. B. Broxterman, H.-J. Hofmann,

C. Tomasini* 2713–2721

Synthesis and Secondary Structure of Alternate α,β -Hybrid Peptides Containing Oxazolidin-2-one Moieties

Keywords: Hybrid peptides / Foldamers / Amino acids / Ab initio calculations

CONTENTS

Molecular Recognition



Tertiary Amide Rotation in a Nanoscale Host

Keywords: Molecular recognition / Encapsulation / Rotational barrier / Self-assembly / Coalescence method



A self-assembled cylindrical capsule provides a nanoscale environment that significantly affects the rotation rate of tertiary amides depending on their size and geometry.

If not otherwise indicated in the article, papers in issue 15 were published online on April 27, 2007