

A union formed by chemical societies in Europe (ChemPubSoc Europe) has

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



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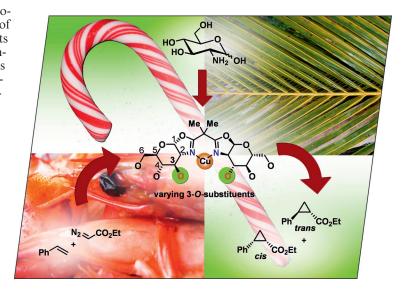


NETHERLANDS

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 various uses for carbohydrates in nature: Chitin in the exoskeleton of crustaceans (lower left corner), cellulose in plants (upper right corner) and as the energy-storage compound sucrose in plants, which ultimately makes its way into sweets such as candy canes. In the laboratory, carbohydrates can be transformed into interesting and versatile tools for stereoselective synthesis such as chiral ligands for asymmetric catalysis. The article by M. M. K. Boysen et al. on p. 997ff describes carbohydrate-based bis-(oxazoline) ligands. These sweets for catalysis were successfully fine-tuned for asymmetric cyclopropanation reactions by the introduction of O-substituents with varying steric and electronic properties. The authors thank Anja Glinschert for her help with the cover design. Financial support of the German Research VolkswagenFoundation Foundation, Fonds der Chemischen Industrie is gratefully acknowledged.



MICROREVIEW

Catalytic Hydrogenolysis

E. Thiery, J. Le Bras, J. Muzart* 961–985

Reactivity versus Stability of Oxiranes under Palladium-Catalyzed Reductive Conditions

Keywords: Palladium / Homogeneous catalysis / Heterogeneous catalysis / Oxygen heterocycles / Epoxides / Hydrogenolysis / Cleavage reactions / Alcohols

$$R^1 O R^3$$
 Pd catalyst $R^1 O R^3$
 H_2 or hydride species $R^2 O R^3$

The palladium-catalyzed hydrogenolyses of epoxides are reviewed according to the structure of the substrates and reducing agents. The regio-, stereo-, and chemoselectivities of the reactions are discussed, as are the mechanisms.

SHORT COMMUNICATIONS

Asymmetric Oxidation



Catalytic Asymmetric Oxidation of Heteroaromatic Sulfides with *tert*-Butyl Hydroperoxide Catalyzed by a Titanium Complex with a New Chiral 1,2-Diphenylethane-1,2diol Ligand

Keywords: Asymmetric catalysis / 1,2-Diphenylethane-1,2-diol / Chiral sulfoxides / Oxidation / Titanium

Catalytic asymmetric oxidation of sulfides attached to nitrogen-containing heterocyles to chiral sulfoxides with *tert*-butyl hydroperoxide and a chiral titanium complex, formed in situ from Ti(*i*PrO)₄, chiral 1,2-

diphenylethane-1,2-diol **3c** and water, was achieved. The chiral sufoxides were obtained in high yield (97%) with excellent enantiomeric excess of up to 98% *ee*.

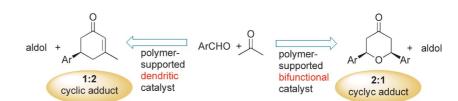
Supported Organocatalysis

L. Tuchman-Shukron, T. Kehat, M. Portnoy* 992-996



Cyclic 2:1 and 1:2 Aldehyde-to-Acetone Byproduct Adducts in Aldol Reactions Promoted by Supported Proline-Incorporated Catalysts

Keywords: Supported catalysts / Organocatalysis / Domino reactions / Aldol reactions / Cyclizations



Cyclic 2:1 and 1:2 aldehyde/acetone adducts are formed as significant byproducts when the aldol reaction is catalyzed by supported bifunctional proline/triscarbamate guanidine or dendritic proline catalysts.

These adducts, unprecedented in the context of the aldol reaction, are most probably formed through a multistep domino mechanism.



FULL PAPERS

Carbohydrate bis(oxazoline) ligands with 4,6-benzylidene acetals and 3-O substituents of varying size and electronic properties were prepared and tested in asymmetric cyclopropanation, revealing a strong dependence of enantioselectivity on steric demand and electronic properties of the 3-O residue. Also, a great influence of the pyranose conformation was observed.

Carbohydrate-Based Ligands

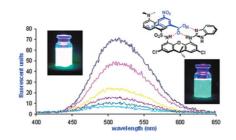
T. Minuth, M. Irmak, A. Groschner, T. Lehnert, M. M. K. Boysen* ... 997–1008

Sweets for Catalysis – Facile Optimisation of Carbohydrate-Based Bis(oxazoline) Ligands

Keywords: Asymmetric catalysis / Carbohydrates / Ligand design / N ligands

DNB Acid Fluorescent Sensor

The daxabe receptor is able to complex carboxylic acids and several anions, with considerable changes in the fluorescence and NMR spectra. This receptor acts as a fluorescent sensor for this interesting type of analyte.



F. M. Muñiz, V. Alcázar, L. Simón, C. Raposo, E. Calle, J. R. Morán* 1009–1015

Daxabe – A Xanthene-Based Fluorescent Sensor for 3,5-Dinitrobenzoic Acid and Anions

Keywords: Fluorescent probes / Amino acids / Receptors / Sensors / Molecular recognition / Complex quenching

o-Quinodimethanes

In their ring-opened form 2-hydroxybenzo-cyclobutenone ethylene dithioacetals are excellent dienes in [4+2] cycloaddition chemistry.

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2-Hydroxybenzocyclobutenone Ethylene Dithioacetals as Precursors of Highly Substituted 1,4-Dihydronaphthalenes

Keywords: Quinodimethanes / Alkynes / Cycloaddition / Electrocyclic reactions / Regioselectivity

Molecular Moulds

Synthesis of two complementary building blocks is described. The self-assembly and moulding properties of these landers will be used to construct nanosized electronic circuits.

R. Barattin, A. Gourdon* 1022-1026

Synthesis of Two Complementary Molecular Moulds

Keywords: Arenes / Molecular devices / Molecular electronics / Self-assembly

CONTENTS

Polycyclic Quinolines

A. Arcadi, G. Abbiati, F. Marinelli,* E. Rossi, M. Verdecchia 1027–1031

Sequential 1,3-Dipolar Cycloaddition of Nitrones to β -(2-Aminophenyl) α , β -Ynones and Cyclocondensation: A New Entry to the Isoxazolino[4,5-c]quinoline Ring

Keywords: Alkynones / Nitrones / Heterocycles / Cycloaddition / Polycycles

$$\begin{array}{c} & & & & \\ & & & \\ R^1 & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & &$$

The reaction of nitrones with β -(2-aminophenyl) α , β -ynones in toluene at reflux temperature affords *cis*-fused isoxazolino-quinolines in moderate-to-high yields. This sequential process takes place through

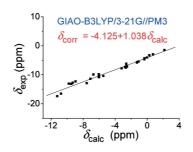
regioselective 1,3-diploar cycloaddition of the nitrone to the triple bond followed by condensation between the amino and carbonyl groups.

Fullerenes

G.-W. Wang,* P. Wu, Z.-G. Tian 1032–1041

Endohedral 1H NMR Chemical Shifts of H_{2^-} , H_2O - and NH_3 -Encapsulated Fullerene Compounds: Accurate Calculation and Prediction

Keywords: Fullerenes / Density functional calculations / Semiempirical calculations / NMR spectroscopy



The GIAO-B3LYP/3-21G//PM3 method has been established as a rapid and accurate method for calculating and predicting the endohedral ^{1}H NMR chemical shifts of H_{2} -, H_{2} O- and NH_{3} -encapsulated fullerene compounds.

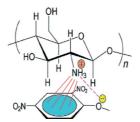
Chemomechanical Motions

K. Kato, H.-J. Schneider* 1042-1047



Supramolecular Interactions in Chitosan Gels

Keywords: Supramolecular structures / Gels / Chemomechanical motion / Polymers / Cooperative effects / Logic gates



Selective size changes of chitosan gels are triggered by complexation with anionic effector molecules, mostly due to water uptake or release. Significant enantioselectivity is observed with aromatic tartaric acid derivatives. Cooperativity between different effectors leads to logic AND gate functions. Smaller particles enhance the speed and sensitivity of the chemomechanical effect significantly.

Helical Cyclopropane Derivatives

A. de Meijere,* K. Rauch, B. Schrader,

F. Brackmann, R. Pfoh, S. Rühl, Y. Katoh,

Y. Okamoto, M. D. Wodrich,

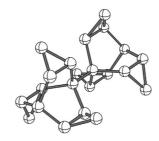
C. Corminboeuf.

P. R. Schreiner 1048-1052



1,1'-Bis(trishomobarrelenyl) – Synthesis and Chiroptic Properties

Keywords: Chirality / Density functional calculations / Helical structures / Oligocyclic cyclopropane derivatives / Small ring systems

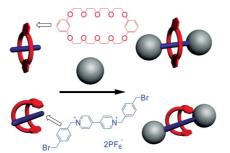


(+)- and (-)-1,1'-bi(endo,exo,syn-pentacyclo[3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecyl) [1,1'-bi(trishomobarrelenyl)], prepared along with the *meso*-diastereomer, exhibit significantly enhanced molar optical rotations due to the presence of three helically arranged 1,2-dicyclopropylethane units in their skeletons.



Crown Ether Rotaxanes

The first bis(*m*-phenylene)-32-crown-10/paraquat [2]rotaxane was synthesized by the threading-followed-by-stoppering strategy. The successful preparation of this [2]rotaxane showed unambiguously that pseudorotaxane-type complexation, rather than the previously reported taco-complex-type complexation, exists for complexation between bis(*m*-phenylene)-32-crown-10 and paraquat derivatives in solution.



A Bis(*m*-phenylene)-32-crown-10/Paraquat [2]Rotaxane



Keywords: Rotaxanes / Crown compounds / Nanostructures / Paraquats / Pseudorotaxanes / Taco complexes

Fluorination

Difluorinated (racemic) analogues of amicetose and rhodinose were prepared from trifluoroethanol by metallated difluoroenol acetal chemistry. Sharpless asymmetric epoxidation followed by epoxide ring-opening with an unusual nucleophilic fluoride source allowed enantiomerically highly enriched and selectively protected monofluoro analogues to be prepared.

$$n=2$$
 FOH

 $P=1 \text{ or } 2$ $P=1$

OH

OH

OH

Fluorinated Analogues of Amicetose and Rhodinose – Novel Racemic and Asymmetric Routes



Keywords: Synthetic methods / Carbohydrates / Fluorination / Diastereoselectivity / Epoxidation

Alkaloid Total Synthesis

The total synthesis of (\pm) -quebrachamine is described, using a formal [3+2] dipolar cycloaddition between a functionalized nitrile and donor-acceptor cyclopropane as the synthetic approach to the indole core.

An efficient chloroacetamide photocyclization was also utilized in the construction of the synthetically challenging nine-membered ring.

Total Synthesis of (±)-Quebrachamine via [3+2] Cycloaddition and Efficient Chloroacetamide Photocyclization



Keywords: Total synthesis / Natural products / Alkaloids / Nitrogen heterocycles / Cycloaddition / Donor-acceptor cyclopropane / Photocyclization

Supported Chiral Auxiliaries

(*R*)-4-Methyl-1-nonanol, the sex pheromone of the yellow mealworm, was synthesized by using non-cross-linked polystyrene supported oxazolidinone as a chiral auxil-

iary in an overall yield of 41.8% over seven steps with a high enantiomeric excess of 98%.

Stereoselective Synthesis of Sex Pheromone (*R*)-4-Methyl-1-Nonanol: Non-Cross-Linked Polystyrene Supported Oxazolidinone as a Chiral Auxiliary

Keywords: Chiral auxiliaries / Heterocycles / Michael addition / Pheromones

CONTENTS

Analogues of Nucleotides

P. Doláková,* M. Dračínský, J. Fanfrlík, A. Holý 1082–1092

Synthesis of Analogues of Acyclic Nucleoside Diphosphates Containing a (Phosphonomethyl)phosphanyl Moiety and Studies of Their Phosphorylation

Keywords: Antiviral agents / Nucleotides / Phosphorylation / dUTPase

The synthesis and chemical and biological properties of acyclic nucleoside (phos-

phonomethyl)phosphinates and their phosphate counterparts are reported.

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

If not otherwise indicated in the article, papers in issue 6 were published online on February 2, 2009

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