















BELGIUM







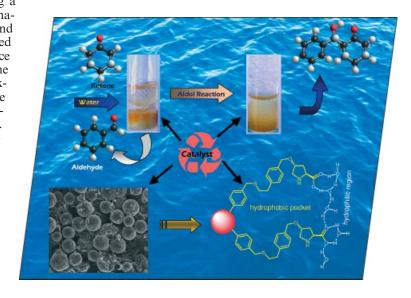




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic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

COVER PICTURE

The cover picture shows the aldol reaction between ketones and arylaldehydes carried out by using a polystyrene-supported L-proline catalyst. This material furnishes aldol products in high yields and stereoselectivities. Screening of solvents showed that these reactions take place only in the presence of water. This solvent effect, coupled with the high stereoselectivities observed, has been explained by the formation of a hydrophobic core in the inner surface of the resin with the hydrophilic proline moiety in the resin/water interface. Such a microenvironment promotes the aldol reaction and increases the stereoselectivity. Recycling investigations have shown that this material can be reused, without loss in conversion and stereoselectivity for, at least, five cycles. This catalyst can be considered a better mimic of natural Class I aldolase enzymes that use an enamine-mediated mechanism in water. Details are discussed in the article by M. Gruttadauria et al. on p. 4688ff. This work is dedicated to Professor Domenico Spinelli on the occasion of his 75th birthday.



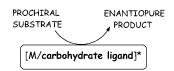
MICROREVIEW

Carbohydrate Ligands

M. Diéguez,* C. Claver,
O. Pàmies* 4621–4634

Recent Progress in Asymmetric Catalysis Using Chiral Carbohydrate-Based Ligands

Keywords: Asymmetric catalysis / Enantioselectivity / Carbohydrate ligands



This review describes the use of the most representative carbohydrate derivative ligands in asymmetric catalysis between 1972 and 2006 (approximately). Particular emphasis is placed on the latest results published in the most active period of this area of research (1998 to January 2007).

SHORT COMMUNICATIONS

Lithiation of Fluorous-Tagged Indole

H. Naka, Y. Akagi, K. Yamada, T. Imahori, T. Kasahara, Y. Kondo* 4635–4637

Fluorous Synthesis of Yuehchukene by α-Lithiation of Perfluoroalkyl-Tagged 1-(Arylsulfonyl)indole with Mesityllithium

Keywords: Fluorous tags / Indole alkaloids / Lithiation / Fluorous solid-phase extraction / Yuehchukene

Mesityllithium was found to be a suitable reagent for the α -lithiation of perfluoro-alkyl-tagged 1-(arylsulfonyl)indole, and the

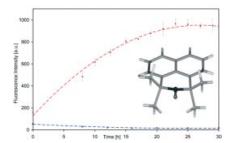
fluorous synthesis of yuehchukene was accomplished efficiently using this method as a key step.

Profluorescent Nitroxides

J. P. Blinco, J. C. McMurtrie, S. E. Bottle* 4638–4641

The First Example of an Azaphenalene Profluorescent Nitroxide

Keywords: Nitroxides / Fluorescence / Polymers / Degradation / Radicals



The synthesis and full characterisation of a new class of profluorescent nitroxides is presented. These nitroxides have applications in materials science where they have been shown to protect polymers by retarding oxidative damage as well as by giving a fluorescent signal indicating the degree of degradation occurring.

Ritter Reaction

R. Sanz,* A. Martínez, V. Guilarte,

J. M. Álvarez-Gutiérrez,

F. Rodríguez 4642-4645

The Ritter Reaction under Truly Catalytic Brønsted Acid Conditions

Keywords: Alcohols / Amides / Ritter reaction / Homogeneous catalysis / Brønsted acids

$$R^{2} = H$$

$$R^{1} = Alk,$$

$$Ar$$

$$Ar$$

$$R^{1}$$

$$R^{1} = R^{2} = Me$$

$$R^{1} = R^{2} = Me$$

$$R^{1} = R^{2} = Me$$

Simple organic acids such as 2,4-dinitrobenzenesulfonic acid (DNBSA) used in catalytic amounts promote the amidation of secondary benzylic alcohols. The reaction is air- and moisture-tolerant and also amenable to large-scale synthesis. Styrene derivatives are obtained when using tertiary benzylic alcohols as starting materials through a formal dimerization process.



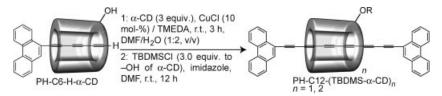
Multicomponent Reactions

The first catalytic four-component reaction of carbonyl compounds (acetals, ketals, or vinyl ethers) with alkyl chloroformate, HMDS and Et₃SiH has been successfully developed to produce alkoxycarbonyl-protected primary amines in the presence of 5 mol-% of an iron(II) salt at room temperature.

Iron-Catalyzed Four-Component Reaction for the Synthesis of Protected Primary Amines

Keywords: Multicomponent reactions / Reductive amination / Carbonyl compounds / Acetals / Primary amines

Stabilization of Oligocarbynes



An effective method to stabilize oligocarbynes as a model for polycarbyne by simultaneous complexation with α -cyclodextrin (α -CD) is described. An oligocarbyne possessing one or two α -CD molecules was

prepared by oxidative coupling reaction of the corresponding triyne in the presence of α -CD. The resulting rotaxanes proved to be stable enough in comparison with the corresponding free oligoynes.

J. Sugiyama, I. Tomita* 4651-4653

Novel Approach to Stabilize Unstable Molecular Wires by Simultaneous Rotaxane Formation — Synthesis of Inclusion Complexes of Oligocarbynes with Cyclic Host Molecules

Keywords: Rotaxane / Cyclodextrin / Inclusion compounds / Carbynes

C-C Bond Formation Reactions

 $R^1 = alkyl$ $R^3 = aryl$ $R^2 = alkyl$ $R^4 = aryl$, alkyl, alkoxy

Cycloalkanes as reagents: A simple FeCl₂-catalyzed C-C bond formation reaction by direct alkylation of activated methylene by using simple alkanes was developed.

Several kinds of alkanes were found to react with phenyl β -ketone ester and diketone compounds to afford alkylated 1,3-dicarbonyl compounds.

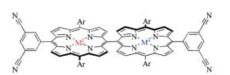
Y. Zhang, C.-J. Li* 4654-4657

Highly Efficient Direct Alkylation of Activated Methylene by Cycloalkanes

Keywords: C-C bond formation / Alkanes / Iron / C-H bond reactions

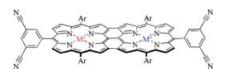
FULL PAPERS

Fused Diporphyrins



meso,meso-linked biaryl type

A change in the metal complexed in a porphyrin macrocycle had a profound influence on the optical and electrochemical properties of porphyrin monomers, biaryltype *meso,meso*-linked diporphyrins, and



meso,meso-β-β, β-β triply linked planar type

planar triply fused diporphyrins. The insertion of mixed-metal ions provides a novel way to tune the electrochemical HOMO–LUMO gap of these systems.

meso,meso-Linked and Triply Fused Diporphyrins with Mixed-Metal Ions: Synthesis and Electrochemical Investigations

Keywords: Diporphyrins / Electrochemistry / UV/Vis spectroscopy / Electrostatic interactions / Conjugation

CONTENTS

[4.4]Cyclophanes

N. Bogdan, I. Grosu,* E. Condamine,

L. Toupet, Y. Ramondenc,

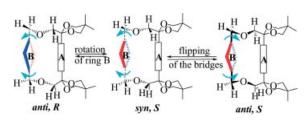
I. Silaghi-Dumitrescu, G. Plé,

E. Bogdan 4674-4687



New [4.4]Cyclophane Diketals, Monoketones, and Diketones: Design, Synthesis, and Structural Analysis

Keywords: Cyclophanes / NMR spectroscopy / Pi interactions / X-ray diffraction / Molecular structures



NMR and molecular modeling investigations of the rotation of the aromatic

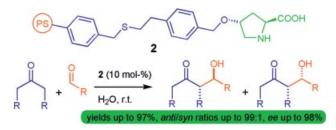
units and the flipping of the chains in new [4.4]cyclophanes are reported.

Organocatalysis

M. Gruttadauria,* F. Giacalone,

Hydrophobically Directed Aldol Reactions: Polystyrene-Supported L-Proline as a Recyclable Catalyst for Direct Asymmetric Aldol Reactions in the Presence of Water

Keywords: Alcohols / Enantioselectivity / Ketones / Organocatalysis / Polymers



A polystyrene-supported L-proline material has been prepared and used as a catalyst in direct asymmetric aldol reactions, with high yields and stereoselectivities. The catalyst works only in the presence of water, and this material can be reused, without loss in levels of conversion and stereoselectivity, for at least five cycles.

Spirolactones



Investigating Direct Access to 2-Oxospiro-[4.5]decanones via 6π -Electrocyclisation

Keywords: 2-Oxospiro[4.5]decan-1-one / Spirolactones / Microwave irradiation / Electrocyclic reactions / Calculations

Known methods to construct the spiro-γ-lactone motif seen in some natural products (e.g. clerodanes) are somewhat limited and usually involve multiple functional group interconversions. A novel synthetic

approach to this system utilising 6π -electrocyclisation has been identified and associated density functional calculations performed.

Selective Hydroformylation

K. Hamza, J. Blum* 4706-4710

Highly Selective Hydroformylation of Vinylarenes to Branched Aldehydes by [Rh(cod)Cl]₂ Entrapped in Ionic Liquid Modified Silica Sol-Gel

Keywords: Hydroformylation / Catalyst recycling / Ionic liquids / Rhodium / Silica sol-gel / Branched aldehydes

The catalytic hydroformylation of vinylarenes to branched aldehydes in an unusually highly selective fashion is described. The catalyst system consists of a mixture of [Rh(cod)Cl]₂ and Na[Ph₂P-3-C₆H₄SO₃] co-

entrapped within a silica sol-gel matrix modified with ca. 5% of 1-butyl-3-[3-(trimethoxysilyl)propyl]imidazolium chloride. The immobilized catalyst is leach-proof and recyclable.



Probe for Photoaffinity Labeling

Benzoic acid 22 is a novel tag-free chemical probe for photoaffinity labeling. In a proofof-concept study ester 23 was irradiated in methanol. The derived insertion product could be fished out by a click reaction with an azide.

Design and Synthesis of a Tag-Free Chemical Probe for Photoaffinity Labeling

Keywords: Photoaffinity labeling / Click chemistry / Triazoles / 1,3-Dipoles / Diazirines / Nitrogen heterocycles

DNA Binders

 $R = -(CH_2)_3NMe_2$: $\Delta T_m = 10.8 \,^{\circ}C$; $R = -(CH_2)_4NHCO(CH_2)_3$

An aminoalkyl-substituted acridiziniumbased intercalator is more selective for abasic sites in DNA than the tailor-made intercalator-adenine conjugates, as shown

by a comparison of the denaturation temperatures of oligonucleotides with and without an abasic site.

Targeting Abasic Sites in DNA by Aminoalkyl-Substituted Carboxamidoacridizinium Derivatives and Acridizinium-Adenine Conjugates

Keywords: Nitrogen heterocycles / Acridizinium / Adenine / DNA recognition / Abasic DNA

Depending on the relative configuration of the starting bicyclic ketones (cis or trans), either linear or angular indole annulation takes place.

Regioselective Indole Annulation

C. L. Diedrich, W. Frey, J. Christoffers* 4731-4737

Linear versus Angular Fischer Indole Annulation: Relative Configuration Determines Regioselectivity

Keywords: Annulation / Indole derivatives / Heterocycles / Regioselectivity / Carbazole derivatives

Functionalized Nanodiamonds

As [121]tetramantane is stick-shaped it would be highly desirable to utilize apically bis-functionalized derivatives for a wide range of applications. However, these compounds are not readily accessible through direct methods. We report here C-H-bond functionalization-isomerization sequences to bis-apical products for this and related diamondoid hydrocarbons.

N. A. Fokina, B. A. Tkachenko, A. Merz, M. Serafin, J. E. P. Dahl, R. M. K. Carlson, A. A. Fokin,*

P. R. Schreiner* 4738-4745

Hydroxy Derivatives of Diamantane, Triamantane, and [121]Tetramantane: Selective Preparation of Bis-Apical Derivatives

Keywords: Cage compounds / Diamondoids / Hydroxylation / Isomerization / Nanostructures

CONTENTS

Cross-Conjugated Molecules

C. A. van Walree,* B. C. van der Wiel. L. W. Jenneskens, M. Lutz, A. L. Spek, R. W. A. Havenith,

J. H. van Lenthe 4746-4751

On the Structure of Cross-Conjugated 2,3-Diphenylbutadiene

Keywords: Conformation analysis / ab initio calculations / Conjugation / Hyperconjugation



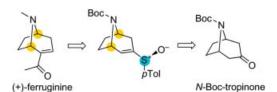
The cross-conjugated compound 2.3-diphenylbutadiene unexpectedly possesses a structure with an s-gauche butadiene moiety. Calculations show that this structure is primarily dictated by conjugation and hyperconjugation phenomena.

Tropane Alkaloids

R. Piccardi, P. Renaud* 4752-4757

Formal Synthesis of (+)- and (-)-Ferruginine

Keywords: Alkaloids / Tropanes / Sulfoxides / Desymmetrization / α,β-Unsaturated sulfones / Conjugate addition



A formal synthesis of the naturally occurring (+)-ferrugine and of its enantiomer starting from the commercially available tropinone is reported. The desymmetrization of tropinone was achieved through formation of diastereomeric unsaturated sulfoxides using the Andersen procedure. Introduction of the acetyl C(2) side chain was achieved by conjugate addition of lithiated ethyl vinyl ether to an unsaturated sulfone.

Modified Nucleosides

U. Chiacchio, A. Corsaro, D. Iannazzo, A. Piperno, G. Romeo, R. Romeo, M. G. Saita, A. Rescifina* 4758-4764

Synthesis of Methyleneisoxazolidine Nucleoside Analogues by Microwave-Assisted Nitrone Cycloaddition

Keywords: 1,3-Dipolar cycloaddition / Nucleosides / Microwave irradiation / Semiempirical calculations

$$\begin{array}{c}
B \\
C = C = C \\
H
\end{array}$$

$$\begin{array}{c}
H \\
O \\
CH_2OH
\end{array}$$

$$\begin{array}{c}
O \\
B = SEM-Thy, Ac-Cyt \\$$

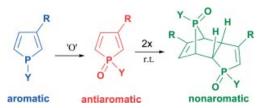
Conformationally locked N,O-nucleoside analogues were synthesized by exploiting allenic nucleobases as dipolarophiles in nitrone 1,3-dipolar cycloadditions.

Quantification of Antiaromaticity

Z. Mucsi*, G. Keglevich 4765-4771

Why are Phosphole Oxides Unstable? The Phenomenon of Antiaromaticity as a Destabilizing Factor

Keywords: Phosphole oxide / ab initio DFT calculations / Antiaromaticity / Aromaticity scale

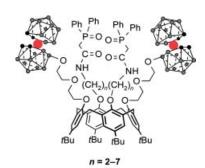


The significant antiaromaticity of phosphole oxides is responsible for their unexpected instability.



Calixarenes and Carboranes

The combination of two cobalt bis(dicarbollide) ions and two CMPO functions at the narrow rim of a calix[4]arene produces extractants with extremely high efficiency for lanthanides and actinides. The distribution coefficients (>100 for 10^{-5} M solutions) are unprecedented. Similar values are found for a 1:1 mixture of a tetra-Cosan- and a tetra-CMPO-calix[4]arene.



- L. Mikulášek, B. Grüner,* C. Dordea,
- V. Rudzevich, V. Böhmer, J. Haddaoui,
- V. Hubscher-Bruder, F. Arnaud-Neu,
- J. Čáslavský, P. Selucký 4772-4783

tert-Butyl-calix[4]arenes Substituted at the Narrow Rim with Cobalt Bis(dicarbollide)(1-) and CMPO Groups — New and Efficient Extractants for Lanthanides and Actinides



Keywords: Calixarenes / Carboranes / CMPO / Actinides, Lanthanides / Liquid-liquid extraction / Complexation

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