



























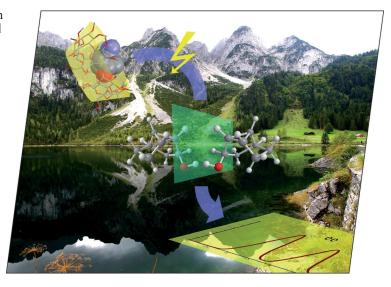




A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further members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

COVER PICTURE

The cover picture shows the photochemical reaction of a diazirine encapsulated in the inherently chiral cavity of a cyclodextrin. The generated carbene affords intramolecular insertion products. For the first time for carbene reactions, products are imprinted, though modestly, with handedness derived from the cyclodextrins. Details are discussed in the article by U. H. Brinker et al. on page 5907ff. The authors thank Mr. Michael Abraham for the photograph in the cover picture. The background shows the Vorderer Gosausee, Salzkammergut, Upper Austria. Large parts of the region were listed as a World Heritage Site in 1997.



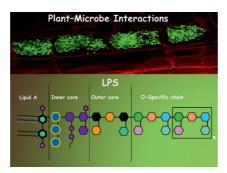
MICROREVIEW

Microbial Glycolipids

A. Molinaro*, M.-A. Newman, R. Lanzetta, M. Parrilli 5887-5896

The Structures of Lipopolysaccharides from Plant-Associated Gram-Negative Bacteria

Keywords: Lipopolysaccharides / Immunochemistry / Plant-associated bacteria / Glycolipids / Innate immunity / Structure elucidation



Gram-negative bacterial lipopolysaccharides are amphiphilic glycoconjugates present in almost all Gram-negative bacteria. The elucidation of their structures is crucial for understanding of the biological processes in which these microbes are involved. This review provides a comprehensive overview of the currently available plant pathogenic microbial lipopolysaccharide structures and substructures.

SHORT COMMUNICATIONS

Copper Catalysis

G. Shen, X. Lv, W. Bao* 5897-5901



Synthesis of *N*-Substituted-2-Aminobenzothiazoles by Ligand-Free Copper(I)-Catalyzed Cross-Coupling Reaction of 2-Haloanilines with Isothiocyanates

Keywords: Copper / Fused-ring systems / Domino reactions / Cross-coupling / Heterocycles

$$R^{1} \stackrel{\text{II}}{\underset{\text{I(Br)}}{\text{II}}} + R^{2} \stackrel{\text{NCS}}{\underset{\text{NCS}}{\text{NCS}}} \frac{\text{Cul (15 mol-\%), N}_{2}}{\text{K}_{2}\text{CO}_{3}, \text{DMSO, 115 °C, 24h}} R^{1} \stackrel{\text{II}}{\underset{\text{II}}{\text{II}}} \times N \stackrel{\text{R}^{2}}{\underset{\text{NH}}{\text{NH}}}$$

X = CH, $N R^2 = alkyl$, aryl, or acyl

A novel and efficient formation of *N*-substituted-2-aminobenzothiazoles by a ligand-free copper(I)-catalyzed one-pot cascade process was developed. Various *N*-substituted-2-aminobenzothiazoles, which

might be potentially applicable in the pharmaceutical and biochemical areas, were conveniently synthesized in moderate to excellent yields.

La(III)-Catalyzed Cross-Coupling

S. N. Murthy, B. Madhav, V. P. Reddy, Y. V. D. Nageswar* 5902-5905



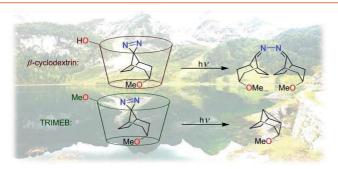
Lanthanum(III) Oxide as a Recyclable Catalyst for the Synthesis of Diaryl Sulfides and Diaryl Selenides

Keywords: Cross-coupling / Selenium / Sulfur / Lanthanum / Sustainable chemistry

 ${\rm La_2O_3}$ as a new and efficient recyclable catalyst in coupling various aryl halides with aromatic/alkyl thiols and dipheny diselenide in combination with KOH as a base and DMEDA as a ligand in DMSO at 110 °C is reported.



FULL PAPERS



The outcome of reactions of an entrapped diazirine is highly dependent on the molecular reactor used. While in β -cyclodextrin azine formation is clearly favored, in the permethylated reactor exclusively intramolecular 1,3-C-H insertion takes place.

Due to supramolecular photochirogenesis of achiral carbene precursors within the chiral cavities, for the first time for carbene reactions one enantiomer of products is slightly favored.

Carbenes within Cyclodextrins

J.-L. Mieusset, G. Wagner, K.-J. Su, M. Steurer, M. Pacar, M. Abraham, U. H. Brinker* 5907-5912

Supramolecular Photochirogenesis with Carbenes Entrapped in Cyclodextrins

Keywords: Diazirines / Carbenes / Cyclodextrins / Supramolecular chemistry / Chiral induction

X ONH2 HO ON NH2 HO OR N CONH2 X = N₃. NH₂, OB0 inosine R = Me, Bu, Bn

Inosine has been used as the starting material for the versatile preparation of two series of AICAR analogues in which the reference compound was modified either at the 2'- or the 5'-position of the

ribose moiety. The target compounds are useful tools for the study of AICAR anticancer activity and for addressing issues in the field of metabolic studies in which AICAR is extensively used.

Nucleoside Analogues

A. Bracci, G. Colombo, F. Ronchetti, F. Compostella* 5913-5919

2'-O-Alkyl Derivatives and 5'-Analogues of 5-Aminoimidazole-4-carboxamide-1-β-D-ribofuranoside (AICAR) as Potential Hsp90 Inhibitors

Keywords: Antitumor agents / Ribonucleosides / Metabolism / Inhibitors

BODIPY Dves

The facile synthesis of dichloropyrimidinyl-BODIPY dyes is reported. These dyes show excellent reactivity towards nucleophilic aromatic substitution and transition-metal-catalysed reactions, while retaining outstanding spectroscopic properties.

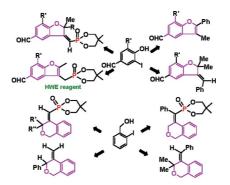
V. Leen, F. Schevenels, J. Cui, C. Xu, W. Yang, X. Tang, W. Liu, W. Qin, W. M. De Borggraeve, N. Boens, W. Dehaen* 5920-5926

Synthesis and Substitution of 8-(4,6-Dichloropyrimidin-5-yl)-BODIPY

Keywords: Fluorescent probes / Nucleophilic substitution / Palladium-catalysed reactions / Dyes/pigments

Allenylphosphonates

Regioselective coupling of allenylphosphonates and phenyl allenes with functionalized iodophenols (in polyethylene glycol, PEG-400), 2-iodobenzoic acid, and 2-iodobenzyl alcohol under palladium catalysis was investigated. Utility of some of the products in Horner—Wadsworth—Emmons reaction (e.g., in the synthesis of Obovaten analogues) was explored.



M. P. Pavan, M. Chakravarty, K. C. Kumara Swamy* 5927-5940

Pd-Catalyzed Reactions of Allenylphosphonates and Related Allenes with Functionalized 2-Iodophenols, 2-Iodobenzoic Acid, and 2-Iodobenzyl Alcohol Leading to Functionalized Benzofurans, Isocoumarins, and Benzopyrans

Keywords: Allenes / Fused-ring systems / Phosphorus / Oxygen heterocycles / PEG medium / Palladium

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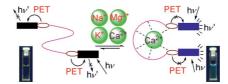
Calcium Ion Steered Foldamer

P. Ashokkumar, V. T. Ramakrishnan, P. Ramamurthy* 5941-5947



Specific Ca^{2+} Fluorescent Sensor: Signaling by Conformationally Induced PET Suppression in a Bichromophoric Acridinedione

Keywords: Sensors / Calcium / Fluorescence / Electron transfer / Photophysics / Acyclic polyethers



A specific photoinduced electron transfer (PET)-based fluorescence sensor for Ca^{2+} was designed. This sensor comprises an acyclic polyether-linked acridinedione bichromophore, the conformation of which can change from linear to pseudocyclic upon complexation with Ca^{2+} . This results in the suppression of the PET process and allows selective Ca^{2+} detection.

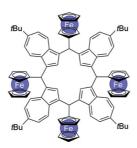
Azulene Chemistry

T. Shoji,* J. Higashi, S. Ito,* K. Toyota, T. Iwamoto, N. Morita* 5948-5952



Synthesis and Properties of Ferrocenylmethylene-Bridged Calix[4]azulene and a New Example of Bis(1-azulenyl)ferrocenylmethylium Ion

Keywords: Azulene / Calixarenes / Carbocations / Electrochemistry / UV/Vis spectroscopy



Ferrocenylmethylene-bridged calix[4]azulene derivative 3 and bis(1-azulenyl)ferrocenylmethane derivative 4 were obtained by the reaction of 6-tert-butylazulene (6) with ferrocenecarbaldehyde (7) in acetic acid. The new bis(1-azulenyl)ferrocenylmethylium ion 5+ was also generated by the hydride abstraction reaction of the corresponding hydro derivative 4 with DDQ.

[2+2]Photocycloaddition

M. Le Liepvre, J. Ollivier, D. J. Aitken* 5953-5962

Synthesis of Functionalized Bicyclo[3.2.0]-heptanes – a Study of the [2+2] Photocycloaddition Reactions of 4-Hydroxycyclopent-2-enone Derivatives

Keywords: Cycloaddition / Carbocycles / Enones / Photochemistry

4-Hydroxycyclopenten-2-one derivatives undergo intermolecular [2+2] photocycloaddition reactions with various alkenes to give mixtures of *exo-* and *endo-*bicyclo-[3.2.0]heptan-2-ones. In contrast, the intramolecular version of the reaction provides a single tricyclic compound, leading to an enantiomerically pure, highly functionalized dihydroxy ketone.

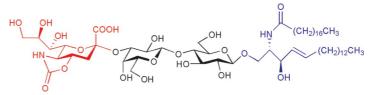
Ganglioside Synthesis

G.-w. Xing,* L. Chen, F.-f. Liang 5963-5970



Facile Synthesis of Tumor-Associated Carbohydrate Antigen Ganglioside GM₃ from Sialic Acid, Lactose, and Serine

Keywords: Carbohydrates / Amino acids / Sialic acids / Antitumor agents / Antigens / Sphingolipids



Ganglioside GM₃ is considered as an important tumor-associated carbohydrate antigen, which can be used in the development of tumor vaccine. In this study, a facile and convergent synthetic strategy for

GM₃ was developed, and the preparation of three building blocks started from the most readily available compounds sialic acid, lactose, and L-serine.



Copper Catalysis

$$R = OMe$$
, OEt, NHMe, Ph $R^1 = Me$, Ph, OEt

Functionalised 5-methylisoxazoles have been synthesised directly from activated nitro compounds by a copper-catalysed process. The method is simple, versatile and tolerant towards diverse functional groups, offering a valid alternative to the use of unfriendly chloroximes as nitrile oxide precursors.

Base- and Copper-Catalysed Condensation of Primary Activated Nitro Compounds with Enolisable Compounds

Keywords: Nitro compounds / Isoxazoles / Organocatalysis / Copper / Enols

Solid-State Fluorescence

The crystals of phenanthro[9,10-d]imidazole-type fluorescent host 1 exhibit drastic fluorescence enhancement behaviour with

a redshift in the emission maximum upon enclathration of various carboxylic acids.

Drastic Solid-State Fluorescence Enhancement Behaviour of Phenanthro[9,10-d]-imidazole-Type Fluorescent Hosts upon Inclusion of Carboxylic Acids

Keywords: Dyes/Pigments / Clathrates / Carboxylic acids / Structure elucidation / Fluorescence

The allylic amination of enantiomerically pure carbonates with 4-substituted benzylamines afforded dehydro- β -amino esters and dehydro- β -amino amides derived from glycine by a S_N2' mechanism. The reaction performed with 4-aminobenzylamine allowed useful precursors of RGD mimetics to be obtained, whose ability to inhibit cell adhesion was very promising.

Dehydro-β-amino Acids

G. Cardillo,* A. Gennari, L. Gentilucci, E. Mosconi, A. Tolomelli,*

S. Troisi 5991-5997

Dehydro- β -amino Acid Containing Peptides as Promising Sequences for Drug Development

Keywords: Amino acids / Enzymes / Chiral resolution / Peptidomimetics / Chemoselectivity / Regioselectivity

Cyclopropylamines

Enantiomerically pure cyclopropylboronic esters were utilised in the synthesis of the corresponding cyclopropylamines by two different routes. One approach — application of a C-B to C-N conversion, thus also expanding the synthetic potential

of trifluoroborates and dichloroboranes — was further developed for the synthesis of tranylcypromine, as well as for a key building block of belactosin A.

J. Pietruszka,* G. Solduga 5998-6008

Enantiomerically Pure Cyclopropylamines from Cyclopropylboronic Esters

Keywords: Cyclopropane / Boron / Asymmetric synthesis / Amines / Natural products

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Enantioselective Epoxidation

J. M. Vega-Pérez,* M. Vega Holm, M. L. Martínez, E. Blanco,

F. Iglesias-Guerra* 6009-6018

Synthesis of New Chiral Ketones from D-Glucose Derivatives and Their Use in the Enantioselective Epoxidation of Arylalkenes

> Keywords: Chiral ketones / Carbohydrates / Asymmetric catalysis / Chiral dioxiranes / Epoxidation / Asymmetric synthesis

$$R^1$$
 R^2
 R^3
 R^3
 R^3
 R^3
 R^3
 R^3
 R^3

The synthesis of two new chiral ketones from carbohydrate derivatives is described. The epoxidation reactions of a range of arylalkenes have been developed.

SQMG Analogues

M. Dangate, L. Franchini, F. Ronchetti, T. Arai, A. Iida, H. Tokuda,

D. Colombo* 6019-6026

Short Regioselective Chemoenzymatic Synthesis and Biological Evaluation of 1-O-Acyl-2-O-(β-D-sulfoquinovopyranosyl)-snglycerols

Keywords: Glycolipids / Enzyme catalysis / Antitumor agents

The synthesis of the new sulfoquinovosylmonoacylglycerol analogues 1a-c, based on 2-O-(β-D-glucopyranosyl)-sn-glycerol, is reported. Key steps were the regioselective lipase-mediated acylation of the tosylate 4

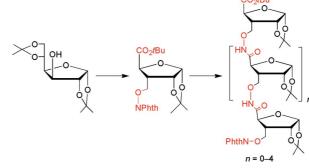
and the final Oxone® oxidation of the unprotected thioacetates 7a-c. The analogues 1a−c were active when tested in the EBV-EA in vitro assay for antitumor promoters.

Carbohydrate Chemistry

Y. Gong, H. Sun, J. Xie* 6027-6033

Synthesis of Oligosaccharide Mimetics with Glycoaminoxy Acids

Keywords: Aminoxy acids / Carbohydrates / Oligosaccharides / Oligomerization / Synthetic methods



Novel furanoid glycoaminoxy acid derivatives have been prepared from di-O-isopropylidene-D-glucose. Careful control of the deprotection conditions allowed us to

synthesize homo-oligomers containing up to six sugar units as a new type of oligosaccharide mimetics.

Nickel Nanoparticles

F. Alonso,* P. Riente. M. Yus* 6034-6042

Wittig-Type Olefination of Alcohols Promoted by Nickel Nanoparticles: Synthesis

of Polymethoxylated and Polyhydroxylated Stilbenes

Keywords: Alcohols / Olefination / Nickel / Nanoparticles / Wittig reactions

R¹ OH + Ph₃P
$$=$$
 R²

R¹ = aryl, alkyl, R² = aryl

R¹ = aryl, R² = alkyl

NiNPs (1 equiv.)

THF, reflux

R¹ $=$ R²

30–99%
29 examples

Nickel nanoparticles were found to activate primary alcohols, as phosphorus vlide partners, in a novel Wittig-type olefination reaction. A wide range of alkenes were prepared from both semi- and nonstabilised ylides. The methodology was applied to the synthesis of a variety of polymethoxylated and polyhydroxylated stilbenes, such as resveratrol, DMU-212 and analogues.



Sulfur Transfer Reagents

A new and simple route for the synthesis of thioesters starting from carboxylic acids and alcohols is reported by using tetrathiomolybdate as the key sulfur transfer reagent. Thioesters were obtained in good to moderate yield depending on the steric crowding around the alcohol.

R = aryl (or) alkyl group R' = alkyl group P. Gopinath, R. S. Vidyarini,

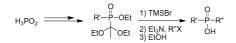
S. Chandrasekaran* 6043-6047

Synthesis of Thioesters by Simultaneous Activation of Carboxylic Acids and Alcohols Using PPh₃/NBS with Benzyltriethylammonium Tetrathiomolybdate as the Sulfur Transfer Reagent

Keywords: Carboxylic acids / Alcohols / Synthetic methods / Sulfur / Molybdenum

Phosphinic Acid Synthesis

A novel synthesis of unsymmetrical dialkylphosphinic acids under mild conditions starting from the protected acid P—H synthon is described. From alkylated H-phosphinates, a "one-pot" methodology based on the sila-Arbuzov reaction easily afforded the dialkylphosphinic acids. This mild methodology is applicable to the synthesis of a dialkylphosphinic acid that exhibits an amino functionality.



C. Fougère, E. Guénin, J. Hardouin, M. Lecouvey* 6048-6054

Rapid and Efficient Synthesis of Unsymmetrical Phosphinic Acids R'P(O)OHR''



Keywords: Phosphinic acids / Phosphorus / Peptidomimetics / Amines / Organophosphorus chemistry

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

If not otherwise indicated in the article, papers in issue 33 were published online on November 3, 2009

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