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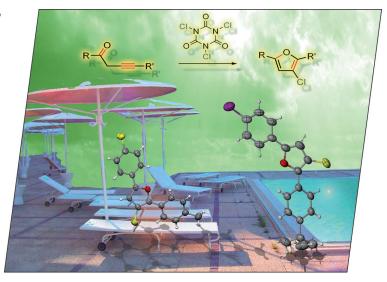




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic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

COVER PICTURE

The cover picture shows an artistic image related to the chlorocyclization reaction with the use of trichloro-s-triazinetrione, which is sold as a chemical for pools. This reagent is a source of electrophilic chlorine that triggers a tandem chlorination/ cylization reaction that yields 3-chlorofurans or 5-chlorofuropyrimidine nucleosides. Details are discussed in the Short Communication by R. Dembinski et al. on p. 3449ff. Cover art by Tomasz Sniady.



MICROREVIEW

Amino Acids

M. I. Calaza, C. Cativiela* 3427–3448

Stereoselective Synthesis of Quaternary Proline Analogues

Keywords: α,α -Disubstituted amino acids / Constrained amino acids / α -Substituted prolines / Diastereoselectivity / Enantioselectivity

This review describes available methods for the diastereoselective and asymmetric synthesis of quaternary prolines. The focus is on the preparation of α -functionalized prolines with the pyrrolidine moiety not embedded in a polycyclic frame. The diverse synthetic approaches are classified according to the bond that is formed to complete the quaternary skeleton.

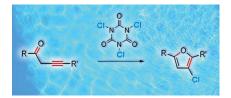
SHORT COMMUNICATIONS

Chlorocyclization



Room-Temperature Electrophilic 5-endodig Chlorocyclization of Alk-3-yn-1-ones with the Use of Pool Sanitizer: Synthesis of 3-Chlorofurans and 5-Chlorofuropyrimidine Nucleosides

Keywords: Alkynes / C–C coupling / Cyclizations / Halogenation / Heterocycles / Ketones / Nucleosides / Trichloroisocyanuric acid



2,5-Disubstituted 3-chlorofurans are accessed in high yields by 5-endo-dig chlorocyclization of 1,4-disubstituted alk-3-yn-1-ones (propargylic ketones) with the use of trichloro-s-triazinetrione (trichloroisocyanuric acid). In a similar manner, chlorocyclization of 5-alkynyl-2'-deoxyuridines produces 5-chlorofuropyrimidine nucleosides.

Ionic Liquids

K. Bica, P. Gaertner* 3453-3456



Metal-Containing Ionic Liquids as Efficient Catalysts for Hydroxymethylation in Water

Keywords: Ionic liquids / Iron / Water chemistry / Hydroxymethylation / Lactones

The iron-containing ionic liquid butylmethylimidazolium tetrachloroferrate (bmim-FeCl₄) proved to be an efficient and recyclable catalyst for the hydroxymethylation of β -keto esters using aqueous formaldehyde and a low catalyst loading of up to 0.1 mol-% without co-solvents or additional surfactants.



Strecker Reaction

In spite of their poor electrophilic character, aldehyde and ketone N,N-dialkylhydrazones react with hydrogen cyanide under extremely mild conditions: room temperature, pure water, and absence of any catalysts or additives. This high reactivity can be explained as a result of the activation of HCN by the dialkylamino lone pair, driving the addition of cyanide to the neighbor C=N bond.

$$\begin{array}{c} N \stackrel{N}{\longrightarrow} R_2 \\ R^1 \stackrel{\longleftarrow}{\longrightarrow} R^2 \end{array} \xrightarrow{\begin{array}{c} TMSCN \text{ or KCN/AcOH} \\ H_2O, \text{ r.t.} \end{array}} \\ \begin{array}{c} HN \stackrel{NR_2}{\longrightarrow} CN \\ 71-94\% \\ R^1 \stackrel{\longleftarrow}{\longrightarrow} CN \\ 71-94\% \\ \end{array}$$

 $R^1, R^2 = Alkyl, aryl; NR_2 = piperidin-1-yl, NMe_2$

E. Marqués-López, R. P. Herrera, R. Fernández,* J. M. Lassaletta* 3457-3460

Uncatalyzed Strecker-Type Reaction of N,N-Dialkylhydrazones in Pure Water



Keywords: Synthetic methods / Hydrazones / Nucleophilic addition / Water / Hydrazino nitriles

Peptidyl Olefins

Optically active γ -hydroxy sulfones to be assembled into peptidyl olefins by the Julia-Kocienski reaction were prepared. Lipase-catalyzed hydrolysis of prochiral diesters introduced optical activity. The se-

quence of the subsequent chemical reactions, either protection-hydrolysis-functionalization or functionalization-hydrolysis-protection, determined the absolute stereochemistry of the product.

S. Mirilashvili, N. Chasid-Rubinstein, A. Albeck* 3461-3464

Optically Active y-Hydroxy Sulfone Julia Reagents for the Synthesis of Peptidyl Olefin Peptidomimetics

Keywords: Asymmetric synthesis / Enzymes / Olefination / Stereocontrol / Peptidomimetics

Trifluoromethylation

A novel reagent for the electrophilic trifluoromethylation of carbon nucleophiles is described. The reagent was designed as a trifluorinated version of a Johnson-type methyl-transfer reagent.

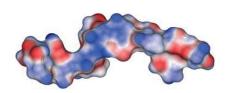
S. Noritake, N. Shibata,* S. Nakamura, T. Toru, M. Shiro 3465-3468

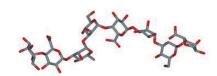
Fluorinated Johnson Reagent for Transfer-Trifluoromethylation to Carbon Nucleophiles

Keywords: Fluorine / Trifluoromethylation / Electrophilic / Sulfur / C-C bond formation

FULL PAPERS

The O-antigen of the major lipopolysaccharide from S. fredii SMH12 displays distinct flexibility around the different glycosidic linkages. NMR spectroscopic measurements unequivocally show that the proton pairs of the different pyranose moieties possess different rotational effective correlation times. Molecular dynamic calculations are in agreement with the NMR spectroscopic data.





Flexibility in Saccharides

F. J. Fernández de Córdoba, M. A. Rodríguez-Carvajal,* F. J. Cañada, P. Teiero-Mateo, A. M. Gil-Serrano,* J. Jiménez-Barbero* 3469-3473

Solution Conformation and Dynamics of the O-Antigen of the Major Lipopolysaccharide from Sinorhizobium fredii

SMH12 Keywords: Conformation analysis / NMR spectroscopy / Molecular dynamics / Lipo-

polysaccharides / Antigens

CONTENTS

Asymmetric Synthesis

P. Etavo, R. Badorrey, M. D. Díaz-de-Villegas,* J. A. Gálvez* 3474-3478

Asymmetric Synthesis of a Novel Conformationally Constrained D-Lysine Analogue with a Piperidine Skeleton

Keywords: Amino acids / Asymmetric synthesis / Lysine / Piperidines / Stereoselectivity

The asymmetric synthesis of a novel, orthogonally protected pipecolic acid-lysine

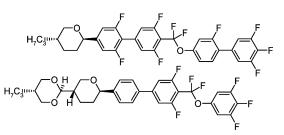
pipecolic acid-lysine chimera chimera in an enantiomerically pure form is reported.

Fluorinated Liquid Crystals

P. Kirsch,* W. Binder, A. Hahn, K. Jährling, M. Lenges, L. Lietzau, D. Maillard, V. Meyer, E. Poetsch, A. Ruhl, G. Unger, R. Fröhlich 3479-3487

Super-Fluorinated Liquid Crystals: Towards the Limits of Polarity

Keywords: Liquid crystals / Oxygen heterocycles / Density functional calculations / Mesogens / Iminoenolates / Chirality



Highly fluorinated liquid crystals with unprecedented polarity were obtained by introducing a tetrahydropyran moiety into their mesogenic core structure. The new materials exhibit an unusually favourable combination of mesophase properties, excellent solubility and low rotational viscosity, which renders them highly attractive for application in fast-switching active matrix LCDs.

Fluorescent Materials

Y. Zhang, P. Starynowicz, J. Christoffers* 3488-3495

Fluorescent Bis(oligophenylylamino)terephthalates

Keywords: Enamines / Cross coupling / Fluorescence / Oligophenylenes / Oxidation / Terephthalates

$$X \longrightarrow NH$$
 CO_2R
 RO_2C $HN \longrightarrow X$ $X = H, CF_3, OMe$
 $R = Et, nOct$

2,5-Diaminoterephthalates with N-biphenylyl, N-terphenylyl and N-quaterphenylyl moieties possess fluorescence properties and have been prepared in two steps by oxidative aminolysis of succinyl succinates with aniline derivatives followed by Suzuki cross-coupling reactions.

Preferential Enrichment

M. Horiguchi, S. Yabunaka, S. Iwama, E. Shimano, Z. Lepp, H. Takahashi, H. Tsue, R. Tamura* 3496-3505

Case Study on the Effects of Molecular Structure on the Mode of Polymorphic Transition Inducing Preferential Enrichment

Keywords: Chiral resolution / Polymorphism / Symmetry breaking / Chirality

(±)-1a, X=Cl, n = 1(±)-2a, X=CI, n = 2(±)-**1b**, X=Br, n = 1(±)-**2b**, X=Br, n = 2(±)-1c, X=I, n = 1 (\pm) -2c, X=I, n=2 (\pm) -1d, X=Me, n=1 (\pm) -2d, X=Me, n=2 A series of new compounds (\pm) -1 and (\pm) -2 were prepared, and their preferential enrichment experiment was performed. As a result, $(\pm)-1a-c$ showed preferential enrichment, whereas (\pm) -1d and (\pm) -2a-d failed to show this phenomenon. These experimental results and each mode of polymorphic transition occurring during crystallization are reported.



Dynamic Kinetic Resolution

The combination of salicylaldehyde-catalyzed racemization with lipase-catalyzed ester hydrolysis allows dynamic kinetic

resolution of various α-amino acid esters to access a-amino acids in high yield and optical purity.

Dynamic Kinetic Resolution of α-Amino Acid Esters in the Presence of Aldehydes

Keywords: Kinetic resolution / Biocatalysis / Enzymes / Racemization / Amino acids

Three-Component Reactions

ArCHO +
$$\frac{NH_2}{n}$$
 $\frac{1}{5}$ mol-% $\frac{1}{2}$ THF $\frac{1}{n}$ $\frac{1}{3}$ $\frac{1$

A mild, efficient, and general method for the synthesis of benzo[f]quinoline and benzo[a]phenanthridine derivatives by a

three-component reaction of arenecarbaldehyde, naphthalen-2-amine, and cyclic ketone using iodine as catalyst is described.

An Efficient Method for the Synthesis of Benzo[f]quinoline and Benzo[a]phenanthridine Derivatives Catalyzed by Iodine by a Three-Component Reaction of Arenecarbaldehyde, Naphthalen-2-amine, and Cyclic Ketone

Keywords: Benzo[f]quinoline / Benzo[a]phenanthridine / Iodine / Cycloketone / Multicomponent reactions / Heterocycles

Multi-Component Reaction

A novel and convenient one-pot multicomponent reaction leading to polyfunctional tetrahydropyrimidine analogues is disclosed. During this domino reaction four C-N bonds are formed in one step. The yields are moderate-to-good. The products are interesting nitrogen heterocycles containing α - and β -amino acid blocks.

M. Zhang, H.-F. Jiang* 3519-3523

A New Multicomponent Reaction Catalyzed by a Lewis Acid Catalyst: Convenient Synthesis of Polyfunctional Tetrahydropyrimidines

Keywords: Lewis acids catalysis / Multicomponent reactions / One-pot synthesis / Tetrahydropyrimidine / Heterocycles

Aryl Cyanides

An environmentally friendly Pd/C-PEG-H₂O system was developed for the cyanation of aryl halides under microwave irradiation. A wide range of substrates were demonstrated to undergo the reaction sequence. There is no phosphorus- or nitrogen-containing ligand or solvent involved, and this reaction can be carried out without the protection of an inert atmosphere.

$$Ar - X \xrightarrow{Pd/C, K_4[Fe(CN)_6] \cdot 3H_2O} Ar - CN$$

G. Chen, J. Weng, Z. Zheng, X. Zhu, Y. Cai, J. Cai, Y. Wan* 3524-3528

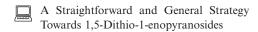
Pd/C-Catalyzed Cyanation of Aryl Halides in Aqueous PEG

chemistry / Microwaves / Sustainable chem-

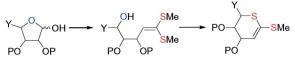
CONTENTS

Thiosugars

M. Buchotte, M. Muzard, R. Plantier-Royon* 3529-3534



Keywords: Carbohydrates / Thiosugars / Ketene dithioacetal / Cyclization / Olefination



Y = H or CH₂OP, P = protecting group

An efficient route to a new class of thiosugar derivatives, 1,5-dithio-1-enopyranosides, has been achieved in a two-step sequence from easily available aldofuranoses. The synthesis is based on the intramolecular nucleophilic substitution of an activated hydroxy group by a sulfur atom of a ketene dithioacetal function.

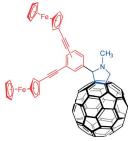
Photoinduced Electron Transfer

L. Pérez, D.-M. Shafiqul Islam, Y. Araki, P. de la Cruz, F. Cardinali, O. Ito,*

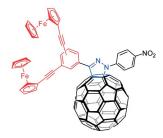
F. Langa* 3535-3543

Photoinduced Electron Transfer in Branched Bis(ferrocenylacetylene)-C₆₀ Systems: Influence of the Nature of Conjugation

Keywords: Fullerenes / Electron transfer / Metallocenes



Four new branched 3,4- and 3,5-bis(ferrocenylacetylene)phenyl-C₆₀ molcules have been prepared. In these systems, a photoinduced charge-separation efficiently takes place. The lifetimes of the CS states were



evaluated to be ca. 10 ns, which are shorter than those of the similar dyads with phenylenevinylene linkage, suggesting higher electron-hole conductivity through the phenylacetylene linkage.

Fungal Meroterpenoids

M. Lang, A. Mühlbauer, E. Jägers, W. Steglich* 3544-3551

Studies on the Biosynthesis of Bovilactone-4,4 and Related Fungal Meroterpenoids

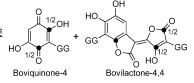
Keywords: Natural products / Meroterpenoids / Mushrooms / Biosynthesis / Isotopic labelling

OH Suillus OH Suillus
OAC
$$CO_2H$$
Suillin

 $\bullet = ^{13}C$ -label

GG = Geranylgeranyl

The first step in the biosynthesis of boviquinone-4, bovilactone-4,4 and suillin in *Suillus* species is the geranylgeranylation of 3,4-dihydroxybenzoic acid at the 2-position. Feeding experiments with ¹³C-



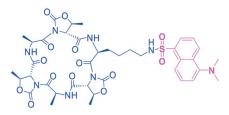
labelled biosynthetic intermediates showed that boviquinone-4 acts as building block for the bovilactone-4,4 dilactone unit, whereas the catechol component originates from deacetylsuillin.

Pseudopeptides

G. Angelici, R. Tresanchez Carrera, G. Luppi, C. Tomasini* 3552–3558

The Design and Synthesis of Dansyl-Containing Cyclic Pseudopeptides

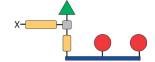
Keywords: Chiral pool / Chromophores / Coupling reactions / Cyclization / Peptides



Six cyclic pseudopeptides with the general formula cyclo-(L-AA-D-Oxd) $_n$ [where AA is an α -amino acid, D-Oxd is trans-(4R,5S)-4-carboxy-5-methyloxazolidin-2-one and n=3, 4] have been designed and efficiently synthesized in the liquid phase in good overall yields. Furthermore the dansyl unit (dansyl = 5-dimethylamino-1-naphthylsulfonyl) was introduced into the side-chain.



A versatile synthetic approach is described for the functionalization of tripodal scaffold molecules on solid support. Intrinsic problems related to the attachment of tripodal scaffolds to a resin are discussed and solutions are provided.



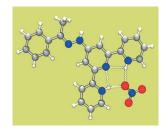
Tripodal Scaffolds on Solid Support

Functionalization of Tripodal Scaffold Molecules on Solid Support

Keywords: Tripodal structures / Multivalency / Solid-phase synthesis / Scaffold molecules / Oligopeptides

Terpyridine Chemistry

Four 4'-hydrazone derivatives of 2,2':6',2"-terpyridine with differing *N*- and *C*-substitution in the R'NN=CRPh unit are reported; protonation studies and solution behaviour of the products are complemented by crystal structures of the neutral compounds and their mono- and diprotonated derivatives.



J. E. Beves, E. C. Constable,*
C. E. Housecroft,*
M. Neuburger, S. Schaffner,
J. A. Zampese 3569–3581

4'-Hydrazone Derivatives of 2,2':6',2"-Terpyridine: Protonation and Substituent Effects

Keywords: Hydrazone / Protonation / Rotamers / 2,2':6',2"-Terpyridine

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

If not otherwise indicated in the article, papers in issue 19 were published online on June 18, 2008

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