









FRANCE















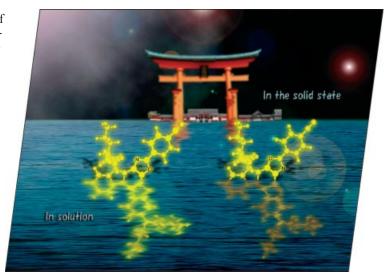




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic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

COVER PICTURE

The cover picture shows photophysical properties of structural isomers of novel benzofuro[2,3-c]oxazolo[4,5-a]carbazole-type (3) and benzofuro-[2,3-c]oxazolo[5,4-a]carbazole-type fluorophores (4), which differ in the position of the oxygen and nitrogen atoms on the oxazole ring. Considerable differences in the absorption and fluorescence spectra were observed between structural isomers both in solution and in the solid state. The background shows the "Itsukushima Shinto Shrine" (in the UNESCO World Heritage List) in Hiroshima, Japan, where the research reported in the article by Y. Harima et al. on p. 3613ff was performed.



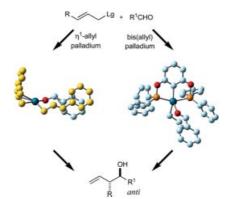
MICROREVIEW

Pd-Mediated Carbonyl Allylation

G. Zanoni,* A. Pontiroli, A. Marchetti, G. Vidari 3599-3611

Stereoselective Carbonyl Allylation by Umpolung of Allylpalladium(II) Complexes

Keywords: Allyl ligands / Umpolung / Allylation / Palladium / Chiral monoligands



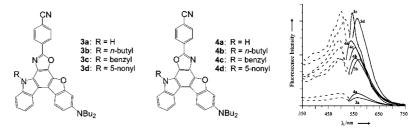
The nucleophilic palladium-mediated allylation of a carbonyl group requires the inversion of the reactivity (umpolung) of the η³-allylpalladium moiety. Stereochemical features are defined by the umpolung conditions: (a) by transmetallation with a more electropositive metal, the stereoselectivity is determined by the rate of $\eta^3 - \eta^1 - \eta^3$ equilibration of the allylpalladium complex; (b) through the intermediacy of an η^1 - or bis-(allylpalladium) complex, the stereoselectivity mainly depends on the nature of the substituents on the allyl fragment. Enantioselectivity can be achieved by using either chiral monophosphanes/phosphoramidite as ligands for palladium or preformed bis-(allylpalladium) systems with one chiral allylic fragment.

FULL PAPERS

Solid-State Fluorescence

Synthesis and Solid-State Fluorescence Properties of Structural Isomers of Novel Benzofuro[2,3-c]oxazolocarbazole-Type Fluorescent Dyes

Keywords: Donor—Acceptor systems / Dyes / Pigments / Fluorescence / Heterocycles / Substituent effects



Structural isomers of novel benzofuro[2,3-c]oxazolocarbazole-type fluorophores (3a and 4a), which differ in the position of oxygen and nitrogen in the oxazole ring, and their N-alkylated derivatives (3b-d and

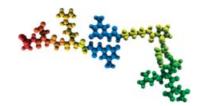
4b-d) have been synthesized, and their absorption and fluorescence properties in solution and in the solid state were evaluated.

Modified Peptides



Convenient Solid-Phase Synthesis of Ureido-Pyrimidinone Modified Peptides

Keywords: Solid-phase synthesis / Modular approach / Peptides / Ureido-pyrimidinone / Supramolecular chemistry / Quadruple hydrogen bonding / Biomaterials



Peptides have been modified with quadruple hydrogen bonding ureido-pyrimidinone moieties to be applied in supramolecular architectures for biomedical applications. A convenient solid-phase synthesis method was developed to functionalize peptide sequences with ureido-pyrimidinone units.



Artificial Carbohydrate Receptors

An acyclic aminonaphthyridine-based receptor shows effective binding of *N*-acetylneuraminic acid (Neu5Ac), the most commonly occurring sialic acid, in competitive solvents such as water/dimethyl sulfoxide.

The receptor is able to form neutral/chargereinforced hydrogen bonds and ion pairs with Neu5Ac, similar to sialic acid binding proteins.

An Acyclic Aminonaphthyridine-Based Receptor for Carbohydrate Recognition: Binding Studies in Competitive Solvents

Keywords: Molecular recognition / Receptors / Carbohydrates / Supramolecular chemistry / Hydrogen bonds

Nitronyl Nitroxide Synthesis

$$\begin{array}{c|c} OH & O* & O* \\ \hline N & OH & OH \\ \hline OH & OH \\ \hline OH & OH \\ \hline OH & OH & OH \\ \hline OH & OH$$

Cascade reactions Me_3Si -substituted imidazolidine-1,3-diols in $PbO_2/MeOH$ involves the formation of the corresponding nitronyl nitroxides (NN-R) and further elimination of the Me_3Si group. The effi-

ciency of the method is demonstrated by reference to syntheses of NN-C \equiv C-H, NN-C₆H₄-C \equiv C-H, and enamine- and 1,2,3-triazolyl-substituted nitronyl nitroxide.

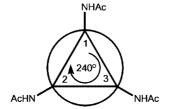
- E. Tretyakov, G. Romanenko, V. Ikorskii,
- D. Stass, V. Vasiliev, M. Demina, A. Mareev, A. Medvedeva, E. Gorelik,

Cascade Reactions of Me₃Si-Substituted Imidazolidine-1,3-Diols with PbO₂, Including Oxidation of the Corresponding Diol and Subsequent Elimination of the Trimethylsilyl Fragment

Keywords: Nitrogen oxides / Cleavage reactions / Oxidation / Protecting groups / Alkynes

Conformational Analysis

A simulation restrained by NOE distances showed that trisialic acid lactone possesses a helical conformation with a *gauche-anti* conformer of exocyclic torsions (ω 7, ω 8) and a skew twist-boat conformer of the lactone was characterized as a repeating unit with n = 1.5.



Conformation of Trisialic Acid Lactone: NMR Spectroscopic Analysis and Molecular Dynamics Simulation

Keywords: Sialic acid / Lactones / NMR spectroscopy / Molecular dynamics / Conformational analysis

Herein, we report the selective synthesis of mono and disaccharide (glucose, xylose and sucrose) derivatives containing unsaturated systems using two different procedures, esterification and Wittig olefination, both under microwave irradiation.

By studying the application of microwave technology, we intend to develop cleaner and more efficient methods for synthesis in an attempt to contribute to sustainable development.

Microwaves in Carbohydrate Synthesis

Selective Synthesis Under Microwave Irradiation of Carbohydrate Derivatives Containing Unsaturated Systems

Keywords: Microwave / Selective methods / Carbohydrates / Esterification / Wittig reactions

CONTENTS

Azasugars

M. I. Attia, M. Timmermann, P. Högger, C. Herdeis* 3669–3675

Design, Synthesis and Biological Activity of Azasugar-Based CD163 Ectodomain Shedding Inhibitors

Keywords: Hydroxamic acid / Azasugar / Wittig reaction / Metalloproteinase

Synthesis of novel homopipecolic acid derivatives containing the hydroxamic acid functionality is reported. The synthesized compounds reveal a significant metalloproteinase CD163 ectodomain shedding inhibitory activity at 1 µm concentration.

Enantiopure Benzhydrylamines

D. Castagnolo, G. Giorgi, R. Spinosa, F. Corelli, M. Botta* 3676-3686

Practical Syntheses of Enantiomerically Pure *N*-Acetylbenzhydrylamines

Keywords: Alkene—alkyne cross-metathesis / Diels—Alder reaction / Benzhydrylamine

Two practical routes for the synthesis of benzhydrylamine derivatives in enantiomerically pure form have been developed. *N*-Acetylbenzhydrylamines can be synthesised in few steps and high yields starting from 1-aryl-1-propargylamines. *N*-Acetyl-

benzhydrylamines have been also converted in both enantiomers of the antifungal agent bifonazole, emphasizing the importance of these compounds as scaffolds for the synthesis of biologically active compounds in enantiopure form.

Axial Chirality in Concave Reagents

O. Winkelmann, D. Linder, J. Lacour,*
C. Näther, U. Lüning* 3687–3697

Chiral Concave Imidazolinium Salts as Precursors to Chiral Concave N-Heterocyclic Carbenes

Keywords: Axial chirality / Carbenes / Chiral anions / Macrocycles / NMR enantio-differentiation / Supramolecular chemistry

An imidazolinium unit as a precursor for an N-heterocyclic carbene has been embedded into a chiral bimacrocyclic concave environment. Axial chirality was achieved using a naphthalene bridgehead.

Bicyclic Hemiaminal Synthesis

C. Ménard-Moyon, R. J. K. Taylor* 3698-3706

Stereoselective Syntheses of the Octahydropyrano[2,3-b]pyridine DE Core of 'Upenamide via a Stannous Chloride-Induced Deacetalisation—Cyclisation Procedure

Keywords: 'Upenamide / Hemiaminal / Stannous chloride / Deacetalisation—cyclisation process / Aza-annulation

Two stereoselective syntheses of the octahy-dropyrano[2,3-b]pyridine DE hemiaminal core of the macrocyclic alkaloid 'upen-amide are described. The aza-annulation is stereoselective affording a single stereo-

isomer having the same relative configuration as in the natural product. An asymmetric synthesis of the octahydropyrano-[2,3-b]pyridine ring system is also disclosed.

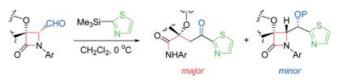


Asymmetric Synthesis

B. Alcaide,* P. Almendros,*
M. C. Redondo 3707-3710

N1-C4 β-Lactam Bond Cleavage in the 2-(Trimethylsilyl)thiazole Addition to β-Lactam Aldehydes: Asymmetric Synthesis of Spiranic and Tertiary α-Alkoxy-γ-keto Acid Derivatives

Keywords: Aldehydes / Asymmetric synthesis / Cleavage reactions / Lactams / Spiro compounds



The reaction between spiranic- or 3-substituted-3-alkoxy-β-lactam aldehydes and 2-(trimethylsilyl)thiazole (TMST) gave as major products conformationally con-

strained α -alkoxy- γ -keto amides, which can be considered both as aldols as well as Passerini-type products, by N1-C4 β -lactam bond cleavage.

Neodymium Organyls

S. F. Kirsch,* C. Liébert 3711-3717

Neodymium(III)-Mediated Reformatsky-Type Reactions of α -Halo Ketones with Carbonyl Compounds

Keywords: Neodymium / Aldol reactions / Lanthanides / Enolates

In a neodymium(III) iodide induced process, α -bromo ketones 1 and aldehydes 2 are effectively converted into aldol products 3 by using NdI₃ at 23 °C in CH₂Cl₂.

The analogous reaction in the presence of NdBr₃/NaI at 50 °C in THF favors the formation of corresponding aldol-Tishchenko products 5.

Efficient Blue-Light Emitters

Synthesis and Emitting Properties of the Blue-Light Fluorophores Indolizino[3,4,5-ab]isoindole Derivatives

Keywords: Indolizino[3,4,5-*ab*]isoindole / Fluorescence / Electrochemistry / Molecular orbitals

Cycloadditions of indolizine derivatives with benzyne provide an efficient access to indolizino[3,4,5-ab]isoindole derivatives with diverse structural features. An investigation of their molecular structures, fluorescence and electrochemical properties shows that some of the synthesized compounds are promising blue-light emitters for OLED devices.

Cascade Metathesis Reactions

E. Groaz, D. Banti, M. North* 3727-3745

Synthesis of Cyclic and Macrocyclic Ethers Using Metathesis Reactions of Alkenes and Alkynes

Keywords: Oxygen heterocycles / Mediumring compounds / Macrocycles / Metathesis / Ruthenium

Cyclohexene derivatives bearing allylic or propargylic ethers undergo alkene and enyne metatheses without involvement of the cyclohexene unit. In contrast, the strained alkene within related norbornene

derivatives does participate in a metathesis cascade, and by use of a suitable substrate, alkyne, enyne and alkene metatheses can all be carried out consecutively in a one-pot process.

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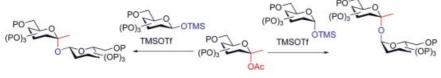
Ionic Liquids

A wide range of the title compounds was prepared in a two-step reaction from tetraalkylureas, triflic anhydride, and *sec*amines. The majority of the hexaalkylguanidinium triflates are room-temperature ionic liquids, which were characterized for their melting point, glass transition temperature, viscosity, and refractive index. H. Kunkel, G. Maas* 3746-3757

Hexaalkylguanidinium Trifluoromethanesulfonates – A General Synthesis from Tetraalkylureas and Triflic Anhydride, and Properties as Ionic Liquids

Keywords: Guanidinium salts / Ionic liquids / Solvent properties / Amines / Urea, tetrasubstituted

Stereoselective Glycosidation



Ketoside-type analogues of trehalose were synthesized stereoselectively by using α -selective O-glycosidation of ketose. α -Ketopyranosyl α -aldopyranosides and α -keto-

pyranosyl β -aldopyranosides were synthesized and full deprotection of them was achieved.

Development of Ketoside-Type Analogues of Trehalose by Using α-Stereoselective O-Glycosidation of Ketose



Keywords: Carbohydrates / Glycosylation / Trehalose / Ketose

If not otherwise indicated in the article, papers in issue 21 were published online on July 3, 2007