



SVENSA

SWEDEN









EUChemSoc









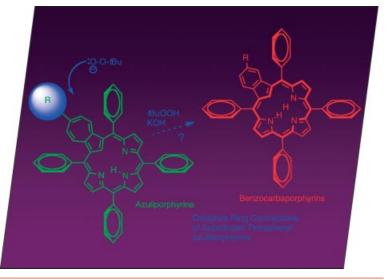




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic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

COVER PICTURE

The cover picture shows the oxidative ring contraction of tetraphenylazuliporphyrins to give benzocarbaporphyrins. Bulky substituents on the azulene moiety influence the regioselectivity but do not inhibit this unusual chemistry. Details are discussed in the article by J. A. El-Beck and T. D. Lash on p. 3981ff.



MICROREVIEW

Anionic Polysaccharides

L. J. van den Bos, J. D. C. Codée,

R. E. J. N. Litjens, J. Dinkelaar,

H. S. Overkleeft,

G. A. van der Marel* 3963-3976

Uronic Acids in Oligosaccharide Synthesis

Keywords: Carbohydrates / TEMPO / Oxidation / Glycosylation / Uronic acids

HO
$$OP^2$$
 glycosylation OP^2 OP^2

This microreview covers some general strategies for the preparation and incorporation of uronic acid residues in anionically charged oligosaccharides. Two distinct

strategies can be recognized: (1) glycosylation followed by oxidation, and (2) oxidation of the monosaccharide building blocks followed by glycosylation.

SHORT COMMUNICATION

Copper-Catalyzed Domino Reactions

Copper-Catalyzed Synthesis of 2,3-Disubstituted Indoles

Keywords: Indoles / Copper catalyst / BINOL / Domino reactions / One-pot synthesis

2,3-Disubstituted indoles were formed starting from 2-iodoaniline and β-keto

esters by a copper-catalyzed domino reaction.

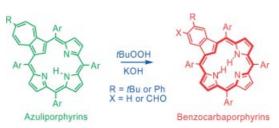
FULL PAPERS

Carbaporphyrinoid Chemistry

J. A. El-Beck, T. D. Lash* 3981-3990

Synthesis and Reactivity of 2³-tert-Butyland 2³-Phenyltetraarylazuliporphyrins: an Analysis of the Effect of Bulky Substituents on Oxidative Ring Contractions to Benzocarbaporphyrins

Keywords: Carbaporphyrinoids / Azulene / Aromaticity / Cope rearrangement / Metalations



Tetraarylazuliporphyrins with 2^3 -tert-butyl- or 2^3 -phenyl substituents were found to undergo oxidative rearrangements with tBuOOH and KOH to give substituted

benzocarbaporphyrins. The data indicate that these reactions are triggered by nucleophilic attack at the positions adjacent to the azulene substituents.



Organoiron Intermediates



The configurational stability of reactive intermediates derived from ethylcyclobuta-diene–Fe(CO)₃ by the formal abstraction of a hydride ion, a hydrogen atom or a proton from the pseudobenzylic position

was investigated theoretically (DFT, Becke3LYP), and rotational barriers for rotation around the exocyclic C-C bond were probed experimentally.

Stereospecific Side Chain Activation in Cyclobutadiene – Fe(CO)₃ Chemistry: A Theoretical and Experimental Study on the Structure and Configurational Stability of Cationic, Radical and Anionic Intermediates

 $\begin{tabular}{ll} \textbf{Keywords:} & Organoiron & compounds / \pi \\ Complexes / Density & functional & calculations / Reactive & intermediates / Stereospecificity / S_N1 reactions \\ \end{tabular}$

Receptor – Anion Interactions

A series of colorimetric and ratiometric chemosensors containing the pyrrolecar-boxamide functionality have been developed and employed for probing receptor—anion interactions. The nature of the individual probe—anion interactions can be defined by a combination of spectroscopic techniques including ¹H NMR spectroscopy, UV/Vis absorption and fluorescence spectroscopy



Probing Receptor—Anion Interactions by Ratiometric Chemosensors Containing Pyrrolecarboxamide Interacting Sites

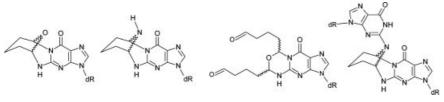
Keywords: Receptors / Fluorescent probes / Molecular recognition / Anions

DNA Alkylation by Glutaraldehyde

R. Olsen, J. Backman, P. Molander, K. D. Klika,* L. Kronberg* ... 4011-4018

Identification of Adducts Formed in the Reactions of 2'-Deoxyguanosine and Calf Thymus DNA with Glutaraldehyde

Keywords: DNA alkylation / Nucleobases / Glutaraldehyde / NMR spectroscopy

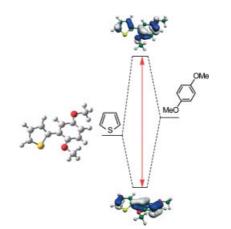


Glutaraldehyde, a widely used industrial chemical that has found to be mutagenic in bacteria and mammalian cells, reacts with 2'-deoxyguanosine to form six adducts suf-

ficiently stable to be isolated by semi-preparative LC and identified by UV absorbance and ¹H and ¹³C NMR spectroscopic and mass spectrometric studies.

π -Conjugated Oligomers

Small-sized model $\pi\text{-conjugated}$ oligomers with a non-covalent S-O interaction, mainly electrostatic, have been prepared from thienylene and dimethoxyphenylene units. UV/Photoelectron spectroscopy and DFT studies carried out both in the solid state and in the gas phase show that these oligomers are strongly conjugated: a small inter-ring angle \varPhi , a large interaction energy ΔE^π and a small HOMO-LUMO gap were observed.



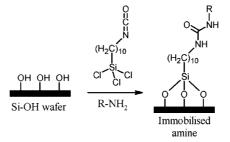
How to Build Fully π -Conjugated Architectures with Thienylene and Phenylene Fragments

Keywords: Sulfur heterocycles / Noncovalent interactions / Photoelectron spectroscopy / Density functional calculations

Immobilisation of Biomolecules

Reaction of Isocyanate-Functionalised Silicon Wafers with Complex Amino Compounds

Keywords: Surface chemistry / Monolayers / Peptides / DNA / Helicene



A monolayer of isocyanate was synthesised at the surface of an oxidised silicon wafer. This monolayer was used to graft different biomolecules and a helicene derivative possessing a primary NH_2 group.

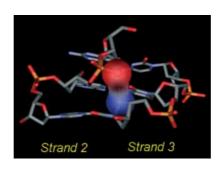
Chemically Modified Oligonucleotides

A. Mayer,

C. J. Leumann* 4038-4049

Pyrrolidino DNA with Bases Corresponding to the 2-Oxo Deletion Mutants of Thymine and Cytosine: Synthesis and Triplex-Forming Properties

Keywords: Oligonucleotides / Pyrrolidino DNA / Antigene agents / Dual recognition / Nucleoside analogues



Thymine and cytosine 2-oxo deletion mutants were incorporated into pyrrolidino DNA and their triplex binding properties analyzed. The observed destabilization clearly highlights their importance in the base-recognition process, irrespective of the underlying sugar unit.

Pinacol Coupling

A. Clerici, C. Greco, W. Panzeri, N. Pastori, C. Punta, O. Porta* 4050-4055



Reductive Coupling of Aromatic Aldehydes Promoted by an Aqueous TiCl₃/tBuOOH System in Alcoholic Cosolvents

Keywords: Radical chemistry / Titanium / Aldehydes / Reductive dimerization / Substituent effects

$$tBuOOH + RCH_2OH$$
 $Tiiu, H^{\dagger}$
 $Tiiv, H_2O$
 $tBuOH + R-CHOH$
 $Tiiv, H_2O$
 Ar
 OH
 OH
 $25-95\%$

The *tert*-butoxyl radical, generated by the aqueous Ti^{III}/TBHP system, abstracts an H atom from alcoholic cosolvents (EtOH,

iPrOH), leading to α-hydroxyalkyl radicals that reduce aromatic aldehydes to the corresponding 1,2-diols.

Supramolecular Assemblies

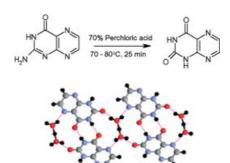
S. Goswami,* A. C. Maity,

H.-K. Fun* 4056-4064



One-Step Synthesis of Lumazine and Xanthine: First Co-Crystal of Lumazine and Perchloric Acid with a Unique Monohydrated Hydronium Ion $(H_5O_2^+)$ Mediated Supramolecular Assembly of the Lumazine Dimer

Keywords: Pterins / Lumazine / Perchloric acid / Supramolecular chemistry / Hydrogen bonds



The perchloric acid mediated synthesis of lumazine derivatives from pterins and xanthine from guanine is reported along with the novel supramolecular assembly of lumazine dimers in co-crystal 21 through bridging with a ${\rm H_5O_2}^+$ unit.



Boron-Mediated Aldol Reactions

favoured in diethyl ether

The regioselectivity of the boron-mediated aldol reactions of 2-(1,3-dioxolan-2-yl)ethyl ethyl ketones depends on both substrate structure and solvent and can be inverted with synthetically useful levels of selectivity (Chx = cyclohexyl).

favoured in pentane

Solvent- and Structure-Dependent Regioselectivity in the Boron-Mediated Aldol Reaction of 2-(1,3-Dioxolan-2-yl)ethyl Ethyl Ketones

Keywords: Aldol reactions / Boron / Regioselectivity / Ketones / Solvent effects

Asymmetric Synthesis

Reactions between α-isocyanoacetamides and aldehydes can be performed at low temperature in the presence of stannous chloride to furnish oxazoles in good to excellent yields. In the presence of the chiral

catalyst [Sn-(R)-Ph-PyBox](OTf)2, the reaction between the chelating aldehyde 2g and 1a afforded the corresponding 5-aminooxazole 3g in good yield and enantioselectivity.

Asymmetric Lewis Acid Catalyzed Addition of Isocyanides to Aldehydes - Synthesis of 5-Amino-2-(1-hydroxyalkyl)oxazoles

Keywords: Asymmetric synthesis / Chiral catalyst / Isocyanide / α-Isocyanoacetamide / Multicomponent reaction / Oxazole / Passerini reaction

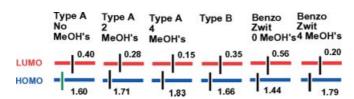
Multicomponent Reactions

Palladium-catalyzed reactions of methylenespiropentane with aryl iodides containing an internal hydroxymethyl or aminomethyl group, in a cascade consisting of six individual steps lead to 3,4-dimethylene-5,6benzotetrahydrooxepines and -azepines, respectively, which undergo Diels-Alder reactions with subsequently added dimethyl fumarate.

A Two-Step, Three-Component Queuing Cascade Leading to Dihydrobenzoxepine and Dihydrobenzazepine Derivatives

Keywords: π -Allylpalladium species / Benzazepine / Benzoxepine / Bicyclopropylidene / Methylenespiropentane

Photochemistry



The zwitterion vs. diradical nature of the S0 intermediate in photochemical enone and dienone rearrangements has been assessed by experimental and computational means. In this study we report a number of new reactions and their mechanisms in

both ground and excited states. Natural orbital analyses are used in one approach. Charge and electron density distribution are used in another. Explicit inclusion of solvent is demonstrated to be important.

Organic Photochemical Rearrangements of Triplets and Zwitterions; Mechanistic and **Exploratory Organic Photochemistry**

Keywords: Zwitterions / Diradicals / Photochemistry / Rearrangements / Computation

CONTENTS

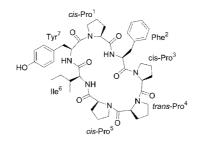
Marine Natural Products

G. Schmidt, A. Grube,

M. Köck* 4103-4110

Stylissamides A-D - New Proline-Containing Cyclic Heptapeptides from the Marine Sponge *Stylissa caribica*

Keywords: Marine natural products / Mass spectrometry / NMR spectroscopy / Peptides



Stylissamide B

The structural analysis of four new cyclic proline-rich heptapeptides from the sponge *Stylissa caribica* using a combination of spectroscopic methods (NMR, MS, and MSⁿ) is described. One of the peptides, stylissamide B, contains the unusual sequence Pro-Pro-Pro, and stylissamide D shows the inverse sequence of stylisin 1.

Ultrasonic Condensation Reactions

M. L. Docampo, R. F. Pellón,*

A. Estevez-Braun,

A. G. Ravelo 4111-4115

Ultrasound-Promoted Reaction of 2-Chlorobenzoic Acids and Aliphatic Amines

Keywords: Ullmann condensation / Copper / Catalysis / Ultrasound / Aliphatic amines



50-88 % yield (Conventional conditions) 72-97 % yield (Ultrasonic irradiation)

An improvement to the use of DMF as a solvent for the condensation of 2-chlorobenzoic acids with aliphatic amines by using a copper catalyst was described.

This condensation reaction could also be achieved under ultrasonic irradiation, allowing high yields and reducing the reaction time to minutes.

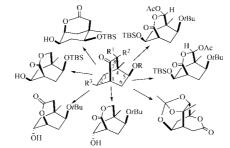
Sterodefined Cyclohexanes

L. Finet, M. Dakir, I. Castellote,

S. Arseniyadis* 4116-4123

Baeyer-Villiger Oxidation of the Bicyclo-[2.2.2]octanone System Revisited: Searchehing for a Modular Construction of Heavily Substituted Cyclohexanes Based on *m*-CPBA Mediated Selective Oxygen Insertion

Keywords: Domino reactions/ Baeyer—Villiger oxidation / Quaternary centers / Configuration reversal / Ring-system interchange



Migration preferences upon Baeyer—Villiger oxidation of a bicyclo[2.2.2]octanone framework were investigated, demonstrating that the nature of substituents at C2 and C8 strongly influence the sense of oxygen insertion.

CORRECTION

K. Neumann, A. Abdel-Lateff,

A. D. Wright, S. Kehraus, A. Krick,

G. M. König* 4125

Novel Sorbicillin Derivatives with an Unprecedented Carbon Skeleton from the Sponge-Derived Fungus *Trichoderma* Species

Keywords: Natural products / Sorbicillin derivatives / Structure elucidation / Trichodermanones / Configuration determination

If not otherwise indicated in the article, papers in issue 23 were published online on July 19, 2007