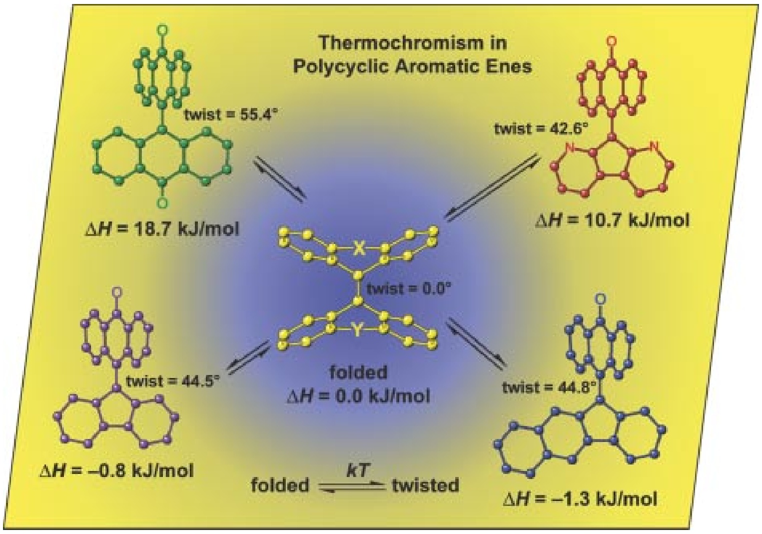
EurJOC
European Journal
of Organic Chemistry

COVER PICTURE

The cover picture shows the phenomenon of thermochromism, i.e. a reversible, temperature-dependent change in color in polycyclic aromatic enes (PAEs). The yellow room-temperature folded conformations represented by the central structure exist in unimolecular equilibria with the deep-colored twisted conformations: bianthrone, green; 1,8-diazafluorenylideneanthrone, red; fluorenylideneanthrone, purple; benzo[*b*]fluorenylideneanthrone, blue. The PAEs under study exhibit thermochromic behavior at room temperature, having readily populated twisted conformations. The twisted and folded conformations interconvert rapidly. Details are discussed in the article by I. Agranat et al. on p. 5198 ff. The authors thank Dr. P. U. Biedermann (Max-Planck-Institut für Eisenforschung) for enlightening advice and suggestions.



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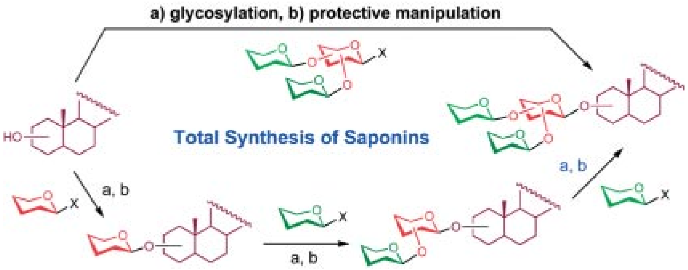
MICROREVIEWS

Synthesis of Saponins

B. Yu,* Y. Zhang, P. Tang 5145–5161

Carbohydrate Chemistry in the Total Synthesis of Saponins

Keywords: Saponins / Carbohydrates / Glycosylation / Protecting groups / Steroids / Triterpenes



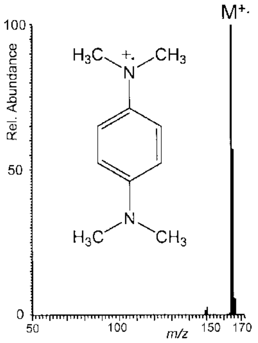
Significant examples relating to the total synthesis of natural saponins with potent biological activities are discussed, with major emphasis on the applicability of contemporary glycosylation and protecting group manipulation protocols to the sophisticated scaffolds of steroids/triterpenes.

Open-Shell Ions in ESI-MS

M. Schäfer,* M. Drayß, A. Springer, P. Zacharias, K. Meerholz 5162–5174

Radical Cations in Electrospray Mass Spectrometry: Formation of Open-Shell Species, Examination of the Fragmentation Behaviour in ESI-MS^n and Reaction Mechanism Studies by Detection of Transient Radical Cations

Keywords: Electrospray mass spectrometry / Radical molecular ions / Even electron rule / Reaction mechanism studies by ESI-MS/MS



Compounds with low oxidation potentials can form open-shell molecular ions in electrospray MS (ESI-MS). However, mechanistic studies of solution-phase reactions proceeding via open-shell intermediates require exclusive phase-transfer of the species formed in solution in the ESI-MS process. Correct assumptions therefore rely on suitable control experiments and cautious interpretation of ESI-MS and ESI-MS^n data sets.

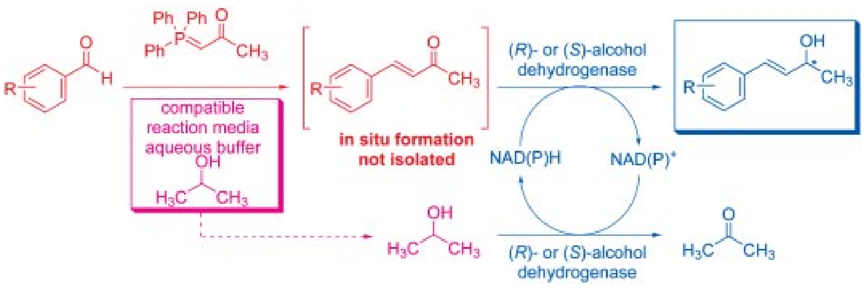
SHORT COMMUNICATIONS

Chemoenzymatic One-Pot Syntheses

M. Kraußer, W. Hummel, H. Gröger* 5175–5179

Enantioselective One-Pot Two-Step Synthesis of Hydrophobic Allylic Alcohols in Aqueous Medium through the Combination of a Wittig Reaction and an Enzymatic Ketone Reduction

Keywords: Alcohols / Chemoenzymatic synthesis / Enzyme catalysis / Reduction / Wittig reactions

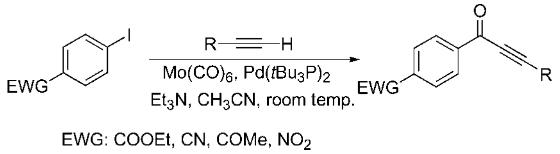


A one-pot two-step process for the enantioselective synthesis of hydrophobic allylic alcohols was developed, which comprises ketone formation by the Wittig reaction and their enzymatic in situ bioreduction into the desired products. The allylic alcohols were prepared with conversions of up to 90% and with *ee* values of >99%.

Alkynylcarbonylation Reactions

M. Iizuka, Y. Kondo* 5180–5182

Palladium-Catalyzed Alkynylcarbonylation of Aryl Iodides with the Use of $Mo(CO)_6$ in the Presence of $t$$Bu_3P$ Ligand



Palladium-catalyzed alkynylcarbonylation of aryl iodides was accomplished by using $Mo(CO)_6$ as a CO source. The reaction was conducted at room temperature with the use of $t$$Bu_3P$ as a ligand, which was found to be essential for smooth carbonylation.

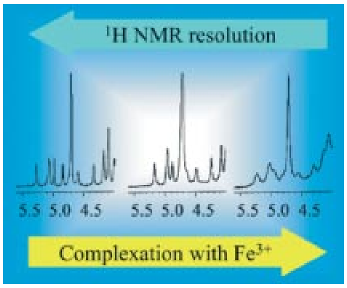
Keywords: Alkynylcarbonylation / Palladium / Molybdenum / Aryl Iodides / Phosphane ligands

FULL PAPERS

Exopolysaccharide Structure

S. Leone, C. De Castro,* M. Parrilli, F. Baldi, R. Lanzetta 5183–5189

Structure of the Iron-Binding Exopolysaccharide Produced Anaerobically by the Gram-Negative Bacterium *Klebsiella oxytoca* BAS-10



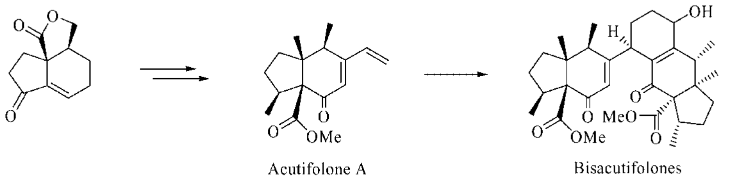
Klebsiella oxytoca BAS-10 is able to grow on high concentrations of heavy metals, responding to these conditions by producing large amounts of an exopolysaccharide with metal-chelating properties. Complex disruption was monitored by atomic absorption and by ^{1}H NMR, leading to the structure determination of the polysaccharide.

Keywords: Iron complexation / Exopolysaccharide / *Klebsiella oxytoca* / NMR spectroscopy

Liverwort Sesquiterpenoids

J. Shiina, M. Oikawa, K. Nakamura, R. Obata, S. Nishiyama* 5190–5197

Synthesis of Pinguisane-Type Sesquiterpenoids Acutifolone A, Pinguisenol, and Bisacutifolones by a Diels–Alder Dimerization Reaction



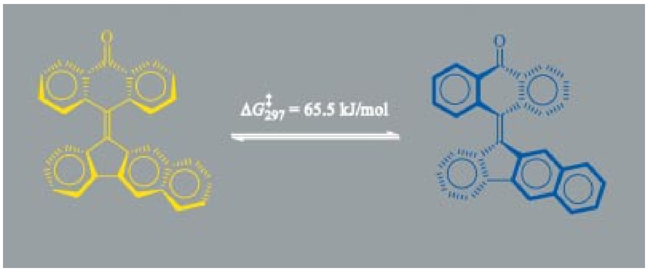
A practical approach to the synthesis of the liverwort sesquiterpenoids, including dimeric derivatives, from the common tricyclic intermediate is reported. The stereochemical nature of the Diels–Alder reaction has been calculated.

Keywords: Liverwort / Terpenoids / Total synthesis / Autoxidation / Biomimetic synthesis

Thermochromism of BAEs

A. Levy, S. Pogodin, S. Cohen, I. Agranat* 5198–5211

Thermochromism at Room Temperature in Overcrowded Bistricyclic Aromatic Enes: Closely Populated Twisted and Folded Conformations



The overcrowded fluorenylidene-anthrone and related bistricyclic aromatic enes (BAEs) exhibit thermochromic behavior at room temperature due to the equilibrium between the yellow *anti*-folded conformations and the intensive-colored twisted thermochromic conformations. Introducing nitrogens conformations into the *fjord* regions affects the balance between these conformations.

Keywords: Thermochromism / Strained molecules / Conformation analysis / Density functional calculations

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Alkaloids

S. Aubry, S. Pellet-Rostaing,*
M. Lemaire* 5212–5225

Oxidative Nucleophilic Substitution (S_NOx) of the Benzylic Position as a Tunable Synthesis of Tetrahydroisoquinoline Natural Alkaloid Analogues

Keywords: Alkaloids / Oxidation / Donor–acceptor systems / Nucleophilic substitution

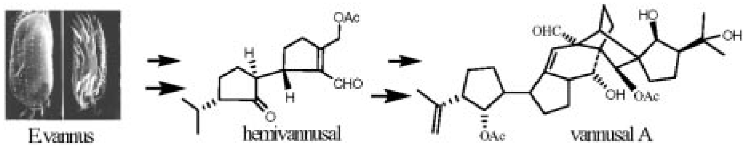
Synthetic investigations of 1,3-dichloro-5,6-dicyanobenzoquinone-mediated benzylic oxidation is reported for the synthesis of natural alkaloid analogues. Extensive explorations of the oxidative nucleophilic substitution of the benzylic position of β-phenylethylamine derivatives and the synthesis of functionalized tetrahydroisoquinolines of ecteinascidin 743 precursors have been carried out.

Sesquiterpenoid Chemistry

G. Guella,* E. Callone, G. Di Giuseppe,
R. Frassanito, F. P. Frontini, I. Mancini,
F. Dini 5226–5234

Hemivannusal and Prevannusadials – New Sesquiterpenoids from the Marine Ciliate Protist *Euplotes vannus*: The Putative Biogenetic Precursors of Dimeric Terpenoid Vannusals

Keywords: Terpenoids / Marine ciliates / Structure elucidation / Ab initio calculations / Endosymbionts



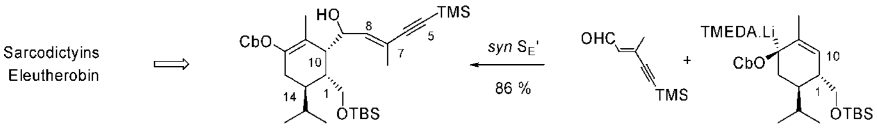
Hemivannusal, isolated from a cell culture of the marine ciliate *Euplotes vannus*, is thought to be a biogenetic precursor of vannusal A. The chemodiversity observed in secondary metabolites isolated from *E. vannus* is thought to derive from the divergence in the cyclization processes from common biogenetic precursors.

syn S_E' Processes

S. Dhulut, A. Bourin, M.-I. Lannou,
E. Fleury, N. Lensen,* E. Chelain,*
A. Pancrazi, J. Ardisson,
J. Fahy* 5235–5243

Cyclic Allyl Carbamates in Stereoselective *syn* S_E' Processes: Synthetic Approach to Sarcodictyins and Eleutherobin

Keywords: Cytotoxic agents / Synthesis / *syn* S_E' / Carbamates / Terpenoids



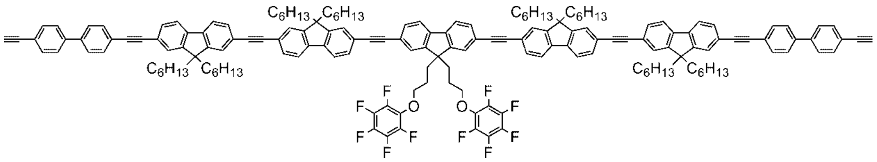
Our synthetic approach to marine diterpenoids sarcodictyins A and B and eleutherobin relies on the one-step attachment of a C5–C9 side chain at the C10 position. The C1,C10 *cis*-disubstituted cyclohexene derivative is obtained in 86 % yield with total stereoselectivity. The reaction is based on a *syn* S_E' process involving a cyclic (*Z*)-allyl diisopropylcarbamate.

Molecular Wires

X. Zeng, C. Wang, M. R. Bryce,*
A. S. Batsanov, S. Sirichantaropass,
V. M. García-Suárez, C. J. Lambert,
I. Sage 5244–5249

Functionalized 8 nm Long Aryleneethynylene Molecular Wire with Alkyne Termini

Keywords: Molecular wires / Conjugation / Fluorene / Sonogashira reaction / Aryleneethynylene

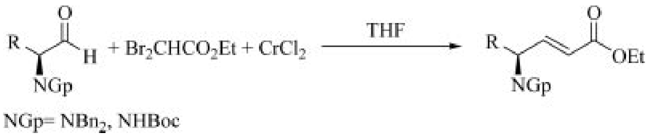


An aryleneethynylene derivative of ca. 8 nm molecular length with terminal alkyne substituents and 9,9-dihexylfluorene units in the backbone has been synthesized.

Enantiopure γ-Amino Acids

J. M. Concellón*
C. Méjica **5250–5255**

Highly Selective Synthesis of Enantiopure (*S*,*E*)-α,β-Unsaturated γ-Amino Esters Through a Sequential Reaction of Ethyl Dibromoacetate with α-Amino Aldehydes Promoted by Chromium Dichloride



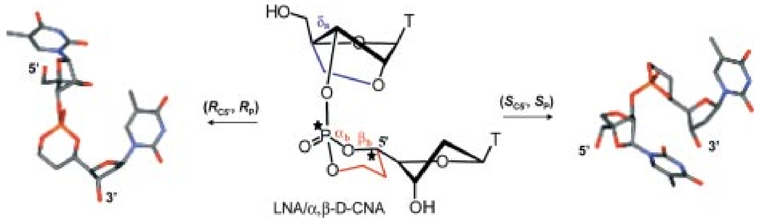
Enantiopure *N*,*N*-dibenzyl- or *N*-Boc-protected (*S*,*E*)-α,β-unsaturated γ-amino esters have been readily prepared by $CrCl_2$-mediated sequential reaction of ethyl dibromoacetate with various *N*,*N*-dibenzyl- or *N*-Boc-α-amino aldehydes. The C=C bond was generated with total or very high *E* selectivity and the (*S*,*E*)-α,β-unsaturated γ-amino esters were obtained with complete enantiomeric purity, except from *N*-Boc-phenylalaninal (chiral HPLC).

Keywords: Diastereoselectivity / Chromium / Asymmetric synthesis / Amino esters / Sequential reactions

Constrained Nucleotides

C. Dupouy, P. Lavedan,
J.-M. Escudier* **5256–5264**

Synthesis and Structure of Dinucleotides Featuring Canonical and Non-canonical A-Type Duplex α, β and δ Torsion Angle Combinations (LNA/α,β-D-CNA)



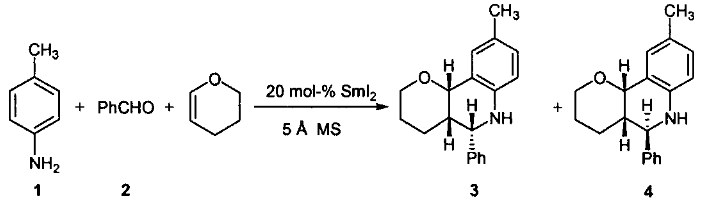
The synthesis of diastereoisomers of LNA/α,β-D-CNA dinucleotide building units of nucleic acids, in which one δ torsional angle is constrained by an LNA structure and the α and β torsional angles are stereocontrolled by a dioxaphosphorinane ring structure is described. NMR structural analysis showed that δ_a, α_b and β_b torsional angles of the $(R_{C5'},R_P)$-configured LNA/α,β-D-CNA TT dimer are restricted to the canonical {*gauche*(+)/*anticlinal*(+), *gauche*(−), *trans*} conformation typically observed in A-type duplexes

Keywords: Strained molecules / Conformational analysis / Nucleotides / DNA structures / Phosphorus heterocycles

Stereoselective Diels–Alder Reactions

Z. Zhou, F. Xu,* X. Han, J. Zhou,
Q. Shen* **5265–5269**

Stereoselective Synthesis of Pyrano[3,2-*c*]- and Furano[3,2-*c*]quinolines: Samarium Diiodide-Catalyzed One-Pot Aza-Diels–Alder Reactions



50 °C, 5 h, THF, yield: 93%, **3**/**4** = 4:96
0 °C, 24 h, solvent-free, yield: 70%, **3**/**4** = 82:18

Three-component aza-Diels–Alder reactions involving aromatic aldehydes, aromatic amines, and dihydropyran or dihydrofuran are effectively catalyzed by samarium diiodide to afford pyrano[3,2-*c*]- or furano[3,2-*c*]quinolines in good yields and with high stereoselectivities. Either the *cis* or the *trans* isomers can be obtained as the major products by conveniently controlling the reaction conditions.

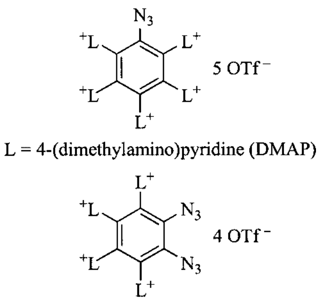
Keywords: Catalysis / Diastereoselectivity / Cycloaddition / Samarium / Quinoline

Electrostatic Effects

R. Weiss,* F. G. Pühlhofer,
S. M. Huber **5270–5276**

Syntheses and Reactions of Polycationically Substituted Azido- and Diazidobenzenes

The syntheses of a pentacationically substituted azidobenzene and the tetracationically substituted *o*-diazidobenzene are reported. Their corresponding triphenylphosphazides are stable at room temperature. Application of the Staudinger reaction yielded the corresponding polyoniosubstituted aniline and *o*-phenylenediamine, respectively.



L = 4-(dimethylamino)pyridine (DMAP)

Keywords: Azides / Electrostatic interactions / Ion cluster / Solvolysis / Staudinger reaction

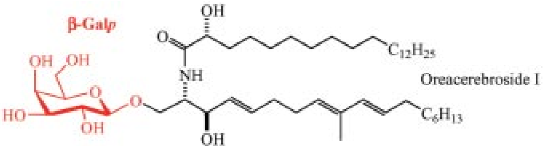
CONTENTS

Sea Star Glycosphingolipids

V. Costantino, C. de Rosa, E. Fattorusso, C. Imperatore, A. Mangoni,* C. Irace, C. Maffettone, D. Capasso, L. Malorni, R. Palumbo, C. Pedone .... 5277−5283

Oreacerebrosides: Bioactive Cerebrosides with a Triunsaturated Sphingoid Base from the Sea Star *Oreaster reticulatus*

Keywords: Angiogenesis / Cerebrosides / Glycolipids / Sphingolipids / Structure elucidation



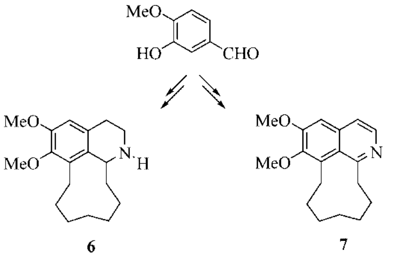
The sea star *Oreaster reticulatus* contains oreacerebrosides A−I, which are glycosphingolipids with a triunsaturated sphingoid base. Oreacerebrosides A−C have a β-glucopyranoside as the sugar residue, and oreacerebrosides D−I are β-galactosylceramides. The proangiogenic and cytotoxic activity of oreacerebrosides was shown to be affected by the nature of the sugar.

Alkaloid Synthesis

A. B. J. Bracca, T. S. Kaufman* .... 5284−5293

Synthesis of the Carbon Framework of the Stephaoxocanes Employing a Sequential RCM/Pomeranz−Fritsch Approach

Keywords: Synthesis design / Cyclization / Stephaoxocanes / Carbon framework / Isoquinolines / Alkaloids



The syntheses of cyclodeca[*ij*]isoquinoline derivatives **6** and **7**, which embody the carbon framework of stephaoxocanidine, excentricine and the recently isolated stephalonganines A, B and C, are reported. These were accomplished employing ring-closing metathesis and variations of the Pomeranz−Fritsch cyclization, as key steps.