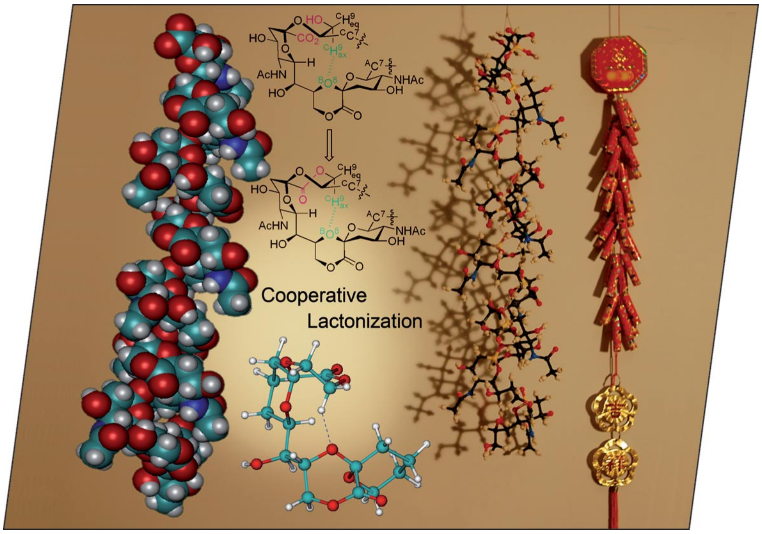
COVER PICTURE

The cover picture shows the simulated NMR spectroscopic structure of polysialic acid polylactone. The local turn conformation of this right-handed helix is held by an interresidual C–H···O hydrogen bond. The seams connected by C–H···O hydrogen bonds support the cooperative acid-catalyzed lactonization of oligosialic acid. The hydrogen bond can be seen as the detonator of a Chinese firecracker. Once the hydrogen bond is formed (just like the ignition of the detonator), the cooperative lactones are formed stepwise in the polysialic acid. The construction of the right-handed helix was described in a previous article (*Eur. J. Org. Chem.* **2007**, 3648). The observation of the C–H···O hydrogen bond is presented in the article by C.-S. Chen et al. on p. 3351ff. The authors thank Ms. Jui-Wen Sue for the photograph in the cover picture.



CONTENTS

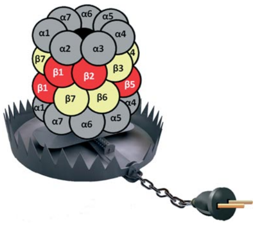
MICROREVIEW

Chemical Biology

M. Verdoes, B. I. Florea,
G. A. van der Marel,
H. S. Overkleeft* 3301–3313

Chemical Tools To Study the Proteasome

Keywords: Proteolysis / Proteasome / Electrophilic traps / Inhibitors / Natural inhibitors / Activity-based probes



Electrophilic traps, evolved in nature, have inspired the design and synthesis of chemical probes that greatly contributed to expanding our knowledge of proteasome activity and function. This microreview discusses the latest developments in this field, ranging from functional chemical biology probes to potential therapeutic candidates.

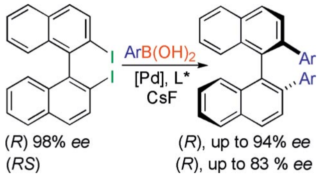
SHORT COMMUNICATIONS

Stereoselective Cross-Couplings

H. Brath, M. Mešková,
M. Putala* 3315–3318

Suzuki Cross-Coupling at the Chiral Groove of 1,1′-Binaphthyl: Stereoconservation versus Deracemization Pathway

Keywords: Asymmetric catalysis / Biaryls / C-C coupling / Palladium / P ligands



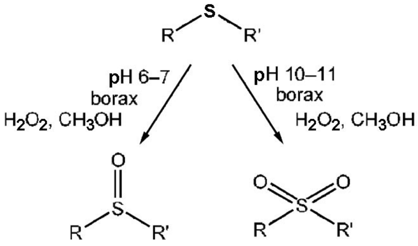
Depending on the ligand used, a stereoconservation or deracemization pathway can be achieved in the Suzuki diarylation of binaphthyl diiodide.

Sulfoxidation

S. Hussain, S. K. Bharadwaj, R. Pandey,
M. K. Chaudhuri* 3319–3322

Borax-Catalyzed and pH-Controlled Selective Oxidation of Organic Sulfides by H_2O_2: An Environmentally Clean Protocol

Keywords: Sustainable chemistry / Acidity / Chemoselectivity / Oxidation / Sulfur



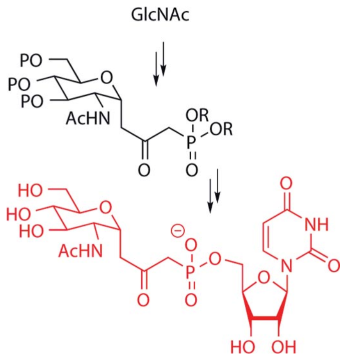
The selective oxidation of sulfides to sulfoxides and sulfones was achieved in high yields at room temperature with borax as a recyclable catalyst and H_2O_2 as the terminal oxidant by varying the pH of the reaction medium. The borax/H_2O_2 system can chemoselectively oxidize alkyl and aryl sulfides in the presence of oxidation-prone functional groups such as C=C, –CN, and –OH.

Sugar Nucleotides

N. Auberger, C. Gravier-Pelletier,*
Y. Le Merrer* 3323–3326

Synthesis of a β-Ketophosphonate Bioisostere of UDP-*N*-acetylglucosamine

Keywords: Antibiotics / C-glycosides / Nucleotides / Drug design / Inhibitors

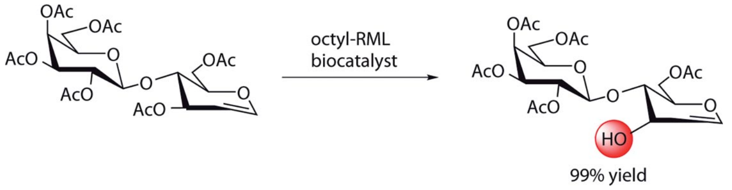


A concise and straightforward route to a new β-ketophosphonate bioisostere of UDP-*N*Ac-glucosamine is described. It is a key intermediate of enzyme substrates involved in peptidoglycan biosynthesis and identified as a target for the development of new antibiotics.

Regioselective Hydrolysis

M. Filice, R. Vanna, M. Terreni, J. M. Guisan,* J. M. Palomo* 3327–3329

Lipase-Catalyzed Regioselective One-Step Synthesis of Penta-*O*-acetyl-3-hydroxylactal



Acetylated 3-hydroxylactal has been synthesized in >95% overall yield in one step by a regioselective hydrolysis catalyzed by immobilized *R. miehei* lipase.

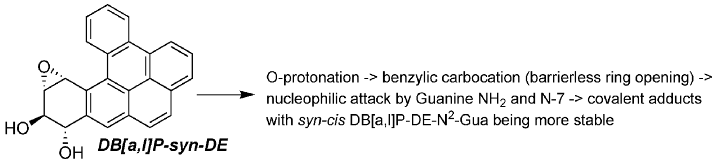
Keywords: Hydrolysis / Regioselectivity / Carbohydrates / Supported catalysts / Enzyme catalysis

FULL PAPERS

PAH Carbocations

G. L. Borosky,* K. K. Laali* 3331–3339

A DFT Model Study of the Carbocations Formed via the Fjord- and Bay-Region Diol Epoxide Metabolites of Isomeric Dibenzopyrenes and Naphthopyrene



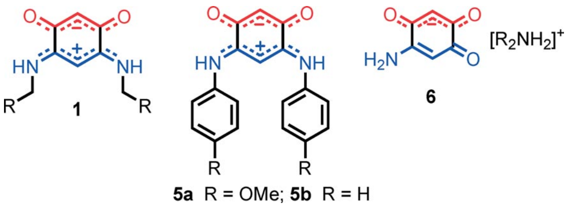
The biological activity of this family of compounds was found to correlate with the degree of deviation from planarity of the aromatic system, in accordance with the higher bioactivity of the fjord- and methylated bay-region PAHs. Relative formation of the possible carbocations derived from each structure was explained by their relative carbocation stabilities.

Keywords: Hydrocarbons / Polycycles / Carbocations / Density functional calculations / Structure–activity relationships / Polycyclic aromatic hydrocarbons (PAH) / DNA

Quinonoid Molecules

F. B. Tamboura, C. S. J. Cazin, R. Pattacini, P. Braunstein* 3340–3350

Reactions of Amines with Zwitterionic Quinoneimines: Synthesis of New Anionic and Zwitterionic Quinonoids



Transamination on a quinonoid molecule of the type $[C_6H_2(\overset{\cdots}{=}NHCH_2R)_2(\overset{\cdots}{=}O)_2]$ (**1**) was extended to primary arylamines (see **5a**,**b**). In contrast, secondary amines led to partial hydrolysis products **6**. Crystal structures reveal the bonding situation within these molecules, which includes a number of packing effects and H-bonding interactions in the solid state.

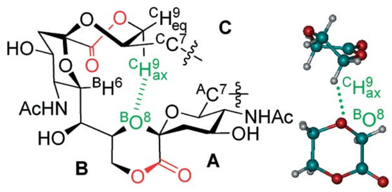
Keywords: C–N activation / Hydrogen bonds / Quinones / Amination / Zwitterions

C–H···O Hydrogen Bonding

C.-S. Chen,* Y.-P. Yu, B.-C. Lin, J. Gervay-Hague, J.-M. Fang, C.-P. Hsu, S.-H. Wu* 3351–3356

The Observation of the C–H···O$^{sp^3}$ Hydrogen Bond in Trisialic Acid Lactone and Its Implications for Cooperative Lactonization

The C–H···O hydrogen bond of trisialic acid lactone has been directly observed by analysis of LRCOSY spectra. ^{3h}J correlations confirmed the existence of C–H···O hydrogen-bond connections in trisialic acid lactone, and the theoretical binding energy of this hydrogen bond was estimated to be 1.0–1.6 kcal/mol by ab initio calculations.



Keywords: Sialic acids / Lactones / Hydrogen bonds / Ab initio calculations / NMR spectroscopy

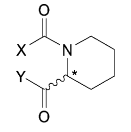
CONTENTS

Organocatalysis

J. F. Collados,* M. L. Quiroga-Feijóo,
C. Alvarez-Ibarra* 3357–3367

New Chiral Lewis Bases Derived from L-Pipecolinic Acid Showing Stereocontrol Highly Dependent on the Catalyst Design in the Hydrosilylation of *N*-Phenyl Ketimines

Keywords: Asymmetric catalysis / Schiff bases / Lewis bases / Organocatalysis / Reduction



4a–h (*R*): *ee* up to 87%
5a–e (*S*): *ee* up to 67%

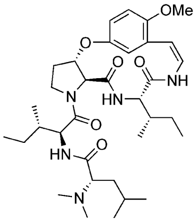
Diamides, diamide dipeptides, and amide urea derivatives of L-pipecolinic acid have been evaluated as catalysts in the benchmark reduction of *N*-phenyl methyl (4-trifluoromethylphenyl) ketimine with trichlorosilane. A significant inversion to unlike stereoinduction was observed for **5c** (X = Y = 3,5-$\mathrm{Me_2C_6H_3NH}$) [up to 67% (*S*)].

Natural Product Synthesis

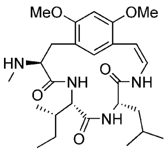
M. Toumi, V. Rincheval, A. Young,
D. Gergeres, E. Turos, F. Couty,
B. Mignotte, G. Evano* 3368–3386

A General Route to Cyclopeptide Alkaloids: Total Syntheses and Biological Evaluation of Paliurines E and F, Ziziphines N and Q, Abyssenine A, Mucronine E, and Analogues

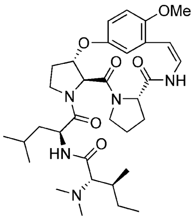
Keywords: Alkaloids / Biological activity / Copper catalysis / Cyclopeptide alkaloids / Macrocycles / Total synthesis



Paliurine F



Mucronine E



Ziziphine N

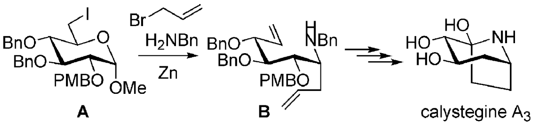
Total syntheses of the cyclopeptide alkaloids paliurine E and F, ziziphine N and Q, abyssenine A, and mucronine E are reported. A key feature is an intramolecular amidation of a vinyl iodide, allowing us simultaneously to address two challenges: formation of the enamide and macrocyclization. We also report antibacterial and cytotoxic properties of the natural products and analogues.

Natural Products

R. N. Monrad, C. B. Pipper,
R. Madsen* 3387–3395

Synthesis of Calystegine A_3 from Glucose by the Use of Ring-Closing Metathesis

Keywords: Allylation / Carbohydrates / Metathesis / Natural products / Total synthesis



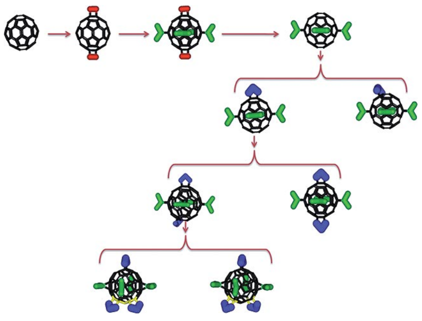
Calystegine A_3 is prepared in 13 steps from glucose. The key step is a zinc-mediated tandem reaction where iodo glucoside **A** is converted into diene **B**. Subsequent ring-closing metathesis yields the corresponding cycloheptene, which is then converted into the natural product.

Fullerenes

A. L. Ortiz, D. M. Rivera, A. J. Athans,
L. Echegoyen* 3396–3403

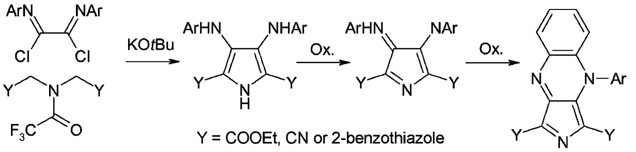
Regioselective Addition of *N*-(4-Thiocyanatophenyl)pyrrolidine Addends to Fullerenes

Keywords: Fullerenes / Nitrogen heterocycles / Cycloaddition / Bingel–Hirsch reaction / Orthogonal transposition / Regioselectivity / Isomers



A protection/deprotection scheme based on the orthogonal transposition approach has been developed to synthesize pentakis-, hexakis- and heptakis-adducts of C_{60}-fullerene regioselectively.

Heterocyclic Chemistry



A new synthesis of push-pull pyrroles was developed starting from bis(imidoyl chlorides) and various iminodiacetic acid derivatives. A step-wise oxidation reaction leads to 3*H*-pyrroles and finally to 3*H*-pyrrolo[3,4-*b*]quinoxalines via intramolecular ring anellation. The fluorescence properties of the pyrroles are reported.

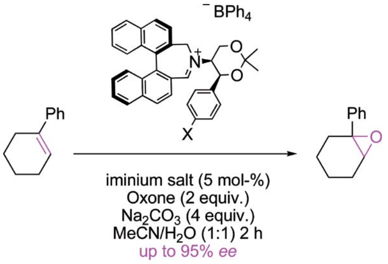
G. Buehrdel, R. Beckert,* P. Herzigova, E. Petrlikova, D. Schuch, E. Birckner, H. Goerls **3404–3412**

A New Synthesis of Push-Pull Pyrroles, Their Oxidation to Stable 3*H*-Pyrroles and an Unexpected Anellation Reaction

Keywords: Pyrrole / Cyclization / Acylation / Fused-ring systems / Fluorescence

Organocatalysis

Catalysts possessing chiral binaphthalene and chiral substituted dioxane moieties were designed and tested in the asymmetric epoxidation of unfunctionalized alkenes. The iminium salt organocatalysts were found to be highly selective and provided the epoxide products with *ee* values up to 95%.

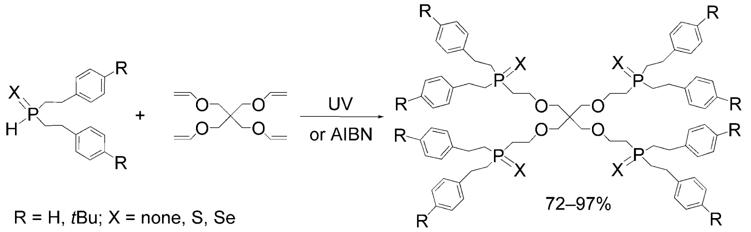


P. C. B. Page,* B. R. Buckley, M. M. Farah, A. J. Blacker **3413–3426**

Binaphthalene-Derived Iminium Salt Catalysts for Highly Enantioselective Asymmetric Epoxidation

Keywords: Organocatalysis / Epoxidation / Enantioselectivity / Asymmetric catalysis

Tetrapodal P Ligands



The exhaustive addition of secondary phosphanes and phosphane chalcogenides to the tetravinyl ether of pentaerythritol is readily effected under free-radical conditions to afford cleanly and regiospecifically the anti-Markovnikov tetraadducts, new families of hyper-branched tertiary tetraphosphanes and tetraphosphane chalcogenides, in good to excellent yields.

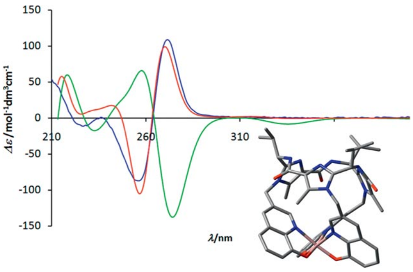
B. A. Trofimov,* S. F. Malysheva, N. A. Belogorlova, V. A. Kuimov, A. I. Albanov, N. K. Gusarova **3427–3431**

Facile Synthesis of Hyper-Branched Tetraphosphanes and Tetraphosphane Chalcogenides

Keywords: Ligand design / Phosphorylation / Radical reactions / Phosphanes

Chirality Transfer

The synthesis of a chiral hydroxyquinoline ligand based on a macrocyclic peptide scaffold is reported along with the investigation of the formation of its hexadentate metal complexes. The highly diastereoselective formation of the complexes was observed by CD measurements and was confirmed by ab initio calculations.



E. Ziegler, G. Haberhauer* ... **3432–3438**

Controlling the Helicity of Hydroxyquinoline Metal Complexes Based on a Macrocyclic Peptide Scaffold

Keywords: Peptides / Circular dichroism / Nitrogen heterocycles / Macrocycles / Molecular modeling

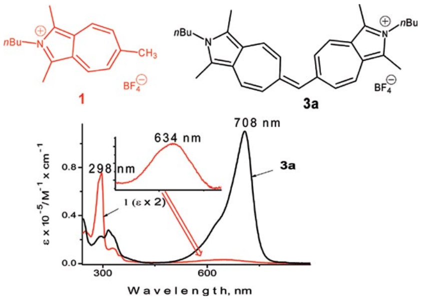
CONTENTS

2-Azaazulenium Cyanine Dyes

J. Bricks,* A. Ryabitskii,
A. Kachkovskii 3439–3449

Studies of 2-Azaazulenium Derivatives: The Natures of Electron Transitions in the 2-Azaazulenium Cation and in Monomethine Cyanine Dyes Bearing 2-Azaazulenium Moieties as Terminal Groups

Keywords: Cyanines / Azaazulenes / Quantum chemistry / Absorption / Electron transfer



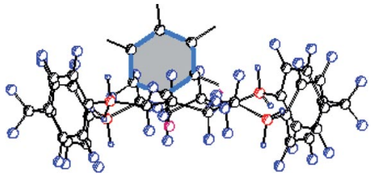
The synthesis of new monomethine cyanines containing 2-azaazulenium terminal group(s) and a comparative analysis of the spectral properties and the natures of electron transitions in chromophores of these dyes and of the reference salt 2-butyl-1,3,6-trimethylcyclohepta[*c*]pyrrolium tetrafluoroborate are reported.

Cyclophane Complexes

P. Wald, H.-J. Schneider* 3450–3453

Reinvestigation of Supramolecular Complexes with Cyclophanes of the Stetter and Koga Type: Agreement and Disagreement with Solid-State Structures

Keywords: Cyclophanes / Supramolecular chemistry / NMR spectroscopy



Some of the oldest reports on complexations of cyclophanes were leading to partially conflicting results. NMR spectroscopy shows that in contrast to the crystal structure Stetter's cyclophane exhibits intracavity inclusion of benzene. A new cyclophane combines features of the well-known Koga- and Stetter-type cyclophanes.

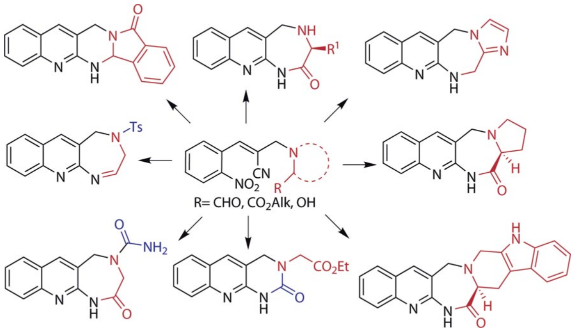
Polycyclic Quinolines

V. Singh, S. Hutait,
S. Batra* 3454–3466

💻

Reductive-Cyclization-Mediated Synthesis of Fused Polycyclic Quinolines from Baylis–Hillman Adducts of Acrylonitrile: Scope and Limitations

Keywords: Cyclization / Nitrogen heterocycles / Annulation / Polycycles



The Baylis–Hillman derivatives generated from adducts of 2-nitrobenzaldehydes and acrylonitrile serve as versatile precursors for the synthesis of a variety of polycyclic quinolines. The strategy involves two successive intramolecular cyclization reactions triggered by the catalytic reduction of the aromatic nitro group.

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* Author to whom correspondence should be addressed.

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