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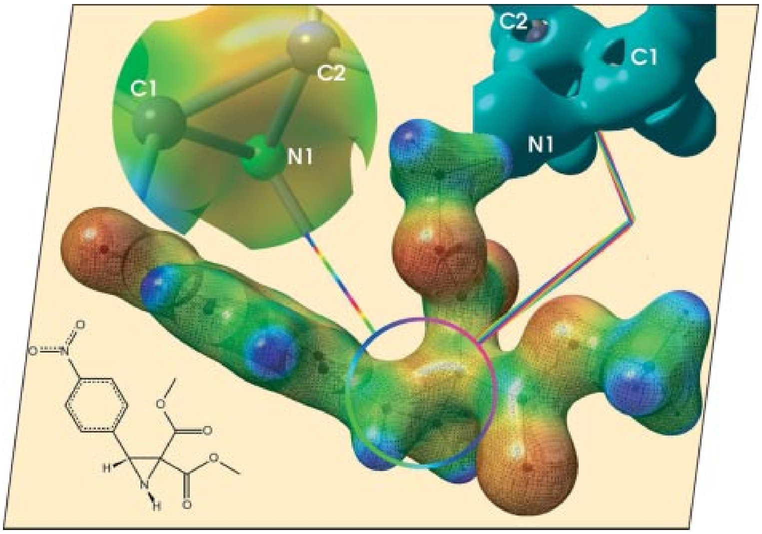
The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry.* Three further EUChemSoc Societies (Austria, Czech Republic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

COVER PICTURE

The cover picture shows iso-surfaces of a protease inhibitor model compound that provides information on its reactivity. The electrostatic potential mapped on the electron density of the complete molecule and on the biologically active aziridine region shows that a nucleophilic attack must take place at carbon atom C1 of the aziridine ring. The Zero Laplacian iso-surface shows possible sites of the attack by means of holes in this surface. The results were obtained from ultra-high resolution synchrotron X-ray experiments at 9 K. Details are discussed in the article by T. Schirmeister et al. on p. 2759 ff. C. B. Hübschle is acknowledged for preparing the artwork for the cover picture.



CONTENTS

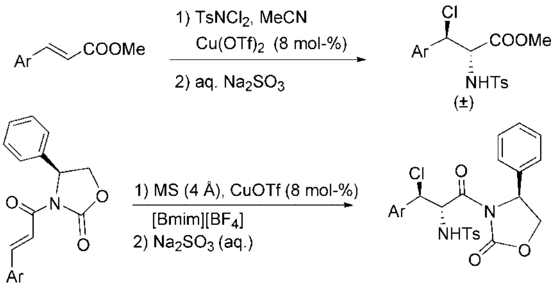
MICROREVIEW

Aminohalogenation of Olefins

G. Li,* S. R. S. S. Kotti,
C. Timmons 2745–2758

Recent Development of Regio- and Stereoselective Aminohalogenation Reaction of Alkenes

Keywords: Aminohalogenation / Haloamidation / Cinnamate / Aziridinium ion / Ionic liquid



The catalytic aminohalogenation of α,β-unsaturated esters, α,β-unsaturated ketones and α,β-unsaturated nitriles has been described. The first asymmetric aminohalogenation was achieved by the use of Evans chiral auxiliaries. The aziridinium intermediate is believed to exist during aminohalogenation process.

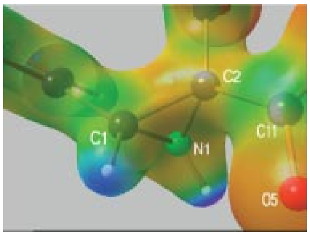
FULL PAPERS

Electron-Density Determination

S. Grabowsky, T. Pfeuffer, L. Chęcińska,
M. Weber, W. Morgenroth, P. Luger,
T. Schirmeister* 2759–2768

Electron-Density Determination of Electrophilic Building Blocks as Model Compounds for Protease Inhibitors

Keywords: Aziridine / Charge density / Electron density / Nucleophile / Protease



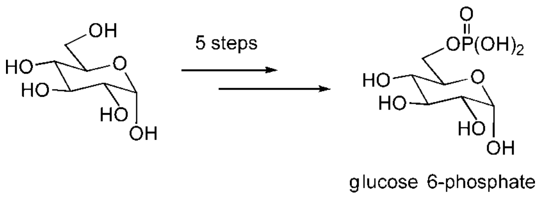
Experimental electron-density determination by means of ultra-high resolution X-ray diffraction at low temperature was used to characterise the detailed geometrical properties, bonding situations, hydrogen bonding properties, topological properties, atomic charges, and the electrostatic potential of dimethyl 3-(4-nitrophenyl)aziridine-2,2-dicarboxylate.

Chemoenzymatic Synthesis of G-6-P

T. Rodríguez-Pérez, I. Lavandera,
S. Fernández, Y. S. Sanghvi, M. Ferrero,*
V. Gotor* 2769–2778

Novel and Efficient Chemoenzymatic Synthesis of D-Glucose 6-Phosphate and Molecular Modeling Studies on the Selective Biocatalysis

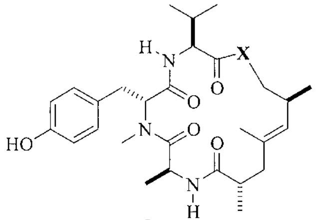
Keywords: Carbohydrates / Enzyme catalysis / Molecular modeling



A concise chemoenzymatic synthesis of glucose 6-phosphate is described. *Candida rugosa* lipase was found to be an efficient catalyst for both regio- and stereoselective deacetylation of the primary hydroxy group in the peracetylated D-glucose. The high overall yield and the easy scalability makes this chemoenzymatic strategy attractive for industrial application. Furthermore, molecular modeling of phosphonate transition-state analog for the enzymatic step supports the substrate selectivity observed.

Cyclodepsipeptide Conformation

The preparation and conformational studies of the two 17-membered macrocycles **32** and **35** is described. Compared to the cyclodepsipeptide geodiamolide, which features an 18-membered ring, the conformation of these truncated analogs is significantly different.



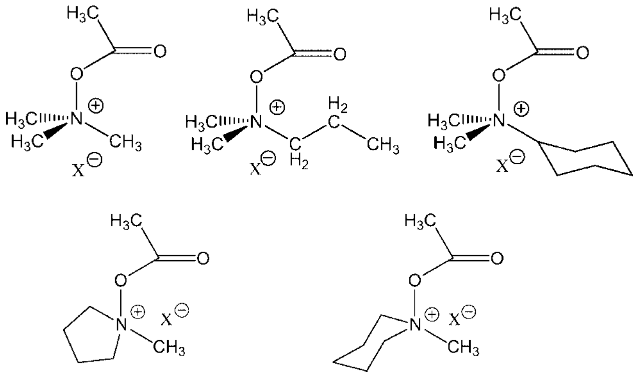
32 X = O
35 X = NH

S. Marimganti, R. Wieneke, A. Geyer, M. E. Maier* **2779–2790**

Synthesis and Conformational Analysis of Geodiamolide Analogues

Keywords: Depsipeptides / Peptidomimetics / Amino acids / Hydroxy acids / Conformation

Reactive Intermediates



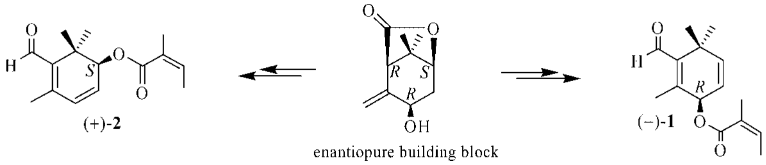
N-Acetoxyammonium salts were postulated by Huisgen in 1962 to be the initially formed reactive intermediates in the Polonovski reaction. In this article the preparation of *N*-acetoxyammonium salts under various conditions and characterization by chemical and spectroscopic methods is described. The geometries and energies of the *N*-acetoxyammonium ions were determined by DFT calculations. The calculated chemical shifts of the *N*-acetoxyammonium ions are in good agreement with the experimental values and offer a good proof for the reliability of the DFT calculations.

H. Volz,* H. Gartner **2791–2801**

N-Acetoxyammonium Ions – Reactive Intermediates in the Polonovski Reaction

Keywords: *N*-Acetoxyammonium salts / Polonovski reaction / Density functional calculations / Elimination reactions

Natural Product Synthesis



(+)-**2**

enantiopure building block

(−)-**1**

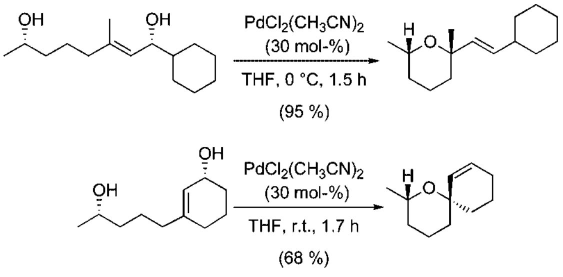
The first enantioselective synthesis of two new monoterpene aldehyde-esters (−)-**1** and (+)-**2** from *Bupleurum gibraltaricum*, starting from an enantiopure building block, is described. The previously unknown absolute stereochemistries of these natural products have been established.

P. Brémond, G. Audran,* T. Juspin, H. Monti **2802–2807**

First Enantioselective Synthesis and Absolute Stereochemistry Assignment of New Monoterpene Aldehyde-Esters from *Bupleurum gibraltaricum*

Keywords: Natural products / Terpene / Enantioselective synthesis / Absolute configuration determination

Palladium(II) Catalysis



The construction of tetrasubstituted chiral carbon units in tetrahydropyrans through stereospecific Pd^{II}-catalyzed cyclizations of chiral allylic alcohols has been developed.

N. Kawai,* J.-M. Lagrange, J. Uenishi* **2808–2814**

Stereochemistry and Construction of Tetrasubstituted Chiral Carbon Centers in Intramolecular Pd-Catalyzed 1,3-Chirality Transfer Reactions

Keywords: Tetrasubstituted chiral carbon / 1,3-Chirality transfer / Pd^{II}-catalyzed cyclization / Tetrahydropyran / Spiro compounds

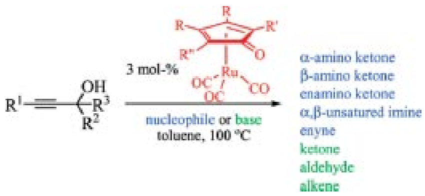
CONTENTS

Homogeneous Catalysis

E. Haak* **2815–2824**

Ruthenium Complexes of Electronically Coupled Cyclopentadienone Ligands – Catalysts for Transformations of Propargyl Alcohols

Keywords: Homogeneous catalysis / Propargyl alcohols / Ruthenium / Vinylidene complexes / Synthetic methods



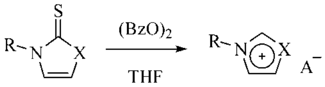
Ruthenium complexes of electronically coupled donor- and acceptor-substituted cyclopentadienone ligands exhibit promising catalytic activities towards propargyl alcohols. The dependence of the reaction mode on the ligands substitution pattern is investigated.

Ionic Liquid Preparation

D. M. Wolfe,
P. R. Schreiner* **2825–2838**

Oxidative Desulfurization of Azole-2-thiones with Benzoyl Peroxide: Syntheses of Ionic Liquids and Other Azolium Salts

Keywords: Anion exchange / Heterocycles / Ionic liquids / Oxidation / Sulfur



R = Bu; X = NMe; A = OBz, BF_4, CF_3CO_2
R = Me; X = NMe; A = OBz, CF_3CO_2
R = Ph; X = NPh; A = OBz, CF_3CO_2
R = Bu, X = S; A = CF_3CO_2, BF_4, PF_6

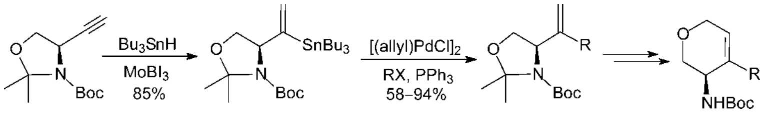
Imidazole- and thiazole-2-thiones, the preparations of which are also reported, were oxidatively desulfurized with benzoyl peroxide and, after anionic exchange, azolium salts were obtained with high concentrations of the desired cations.

Hydrostannation

H. Lin, U. Kazmaier* **2839–2843**

Regioselective Mo-Catalyzed Hydrostannations as Key Steps in the Synthesis of Functionalized Amino Alcohols and Heterocycles

Keywords: Cross coupling / Hydrostannation / Metathesis / Molybdenum / Stannanes



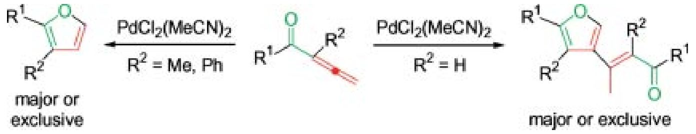
Molybdenum-catalyzed hydrostannation of suitable protected propargylic amino alcohols provides the corresponding functionalized vinyl stannanes, which are useful synthetic intermediates for the combinatorial synthesis of amino alcohols and heterocycles.

Substituents Effects

B. Alcaide,* P. Almendros,*
T. Martínez del Campo **2844–2849**

Allene Substitution-Controlled Switching of Dimerization to Cycloisomerization in the Pd^{II}-Catalyzed Reaction of Terminal α-Allenones

Keywords: Allenes / Cyclization / Heterocycles / Palladium / Substituent effects



Control of cycloisomerization vs. dimerization in the Pd^{II}-catalyzed reaction of terminal α-allenones can be achieved just by a subtle variation in the substitution at the allene component, being for the first time the mode of reaction of α-allenones substrate-directable.

Anion Recognition

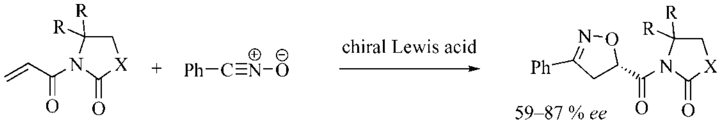
A series of urea/amide-substituted quinoline derivatives were prepared and investigated as anion receptors in chloroform. The derivative with R = Ph and R′ = C_6H_{13} binds fluoride with high selectivity and high affinity (K_a = 150000 M^{-1}). The experimental findings are supported by computational considerations.

M. Albrecht,* Triyanti, S. Schiffers, O. Osetska, G. Raabe, T. Wieland, L. Russo, K. Rissanen **2850–2858**

Anion Receptors Based on a Quinoline Backbone

Keywords: Anions / Quinoline / Receptors / Ab initio calculations / Fluorescence

1,3-Dipolar Cycloadditions



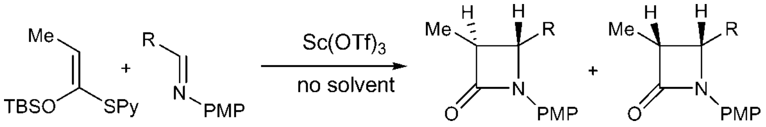
Enantioselective 1,3-dipolar cycloaddition of benzonitrile oxide to three acrylamides bearing an oxazoline or imidazoline auxiliary proceeded in the presence of a Lewis acid with a pybox chiral ligand to afford isoxazolines with moderate-to-high *ee* values.

H. Yamamoto,* S. Hayashi, M. Kubo, M. Harada, M. Hasegawa, M. Noguchi, M. Sumimoto, K. Hori **2859–2864**

Asymmetric 1,3-Dipolar Cycloaddition Reactions of Benzonitrile Oxide Mediated by a Chiral Lewis Acid

Keywords: Asymmetric synthesis / Chirality / Cycloaddition / Enantioselectivity / Heterocycles

β-Lactam Synthesis



The $Sc(OTf)_3$-catalyzed reaction of silyl ketene thioacetals with imines in the absence of any solvent affords β-lactams in a convenient one-pot, solvent-free procedure.

M. Benaglia, F. Cozzi, A. Puglisi* **2865–2869**

Solvent-Free, One-Pot Synthesis of β-Lactams by the $Sc(OTf)_3$-Catalyzed Reaction of Silyl Ketene Thiocetals with Imines

Keywords: Synthetic methods / Lactams / Scandium triflate / Solvent-free conditions / Catalysis

Substituent Effects

Effects of larger alkyl groups can be qualitative described as polarizability since they make acids more acidic and bases more basic (in the gas phase). However, this description fails in the quantitative sense since the effect on the bases is much stronger than in structurally similar acids. This was shown for several model reactions from their DFT-calculated reaction energies.

$$\mathrm{ROH} \rightleftharpoons \mathrm{RO}^- + \mathrm{H}^+$$

$$\mathrm{ROH} + \mathrm{H}^+ \rightleftharpoons \mathrm{ROH_2}^+$$

O. Exner, S. Böhm* **2870–2876**

Substituent Effects of the Alkyl Groups: Polarity vs. Polarizability

Keywords: Density functional calculations / Hyperconjugation / Inductive effect / Polarizability

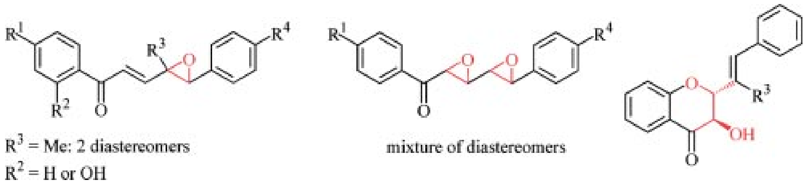
CONTENTS

Salen-Mn^{III}-Catalysed Epoxidation

C. M. M. Santos, A. M. S. Silva,*
J. A. S. Cavaleiro, A. Lévai,
T. Patonay 2877–2887

Epoxidation of (*E*,*E*)-Cinnamylideneacetophenones with Hydrogen Peroxide and Iodosylbenzene with Salen-Mn^{III} as the Catalyst

Keywords: Cinnamylideneacetophenones / Epoxidation / Jacobsen's catalyst / Hydrogen peroxide / Iodosylbenzene



γ,δ-Monoepoxides and a diastereomeric mixture of α,β,γ,δ-diepoxides were obtained by the epoxidation of cinnamylideneacetophenones. γ-Methylcinnamylideneacetophenones afforded two γ,δ-monoepoxide diastereomers, while 2′-hydroxy derivatives yielded γ,δ-monoepoxides and (*E*)-2,3-*trans*-3-hydroxy-2-styryl-4-chromanones.

AMENDMENT

D.-M. Shen, C. Liu,
Q.-Y. Chen* 2888

Synthesis and Versatile Reactions of β-Azidotetraarylporphyrins

Keywords: Porphyrinoids / Azido / Thermal reactions / Cycloaddition