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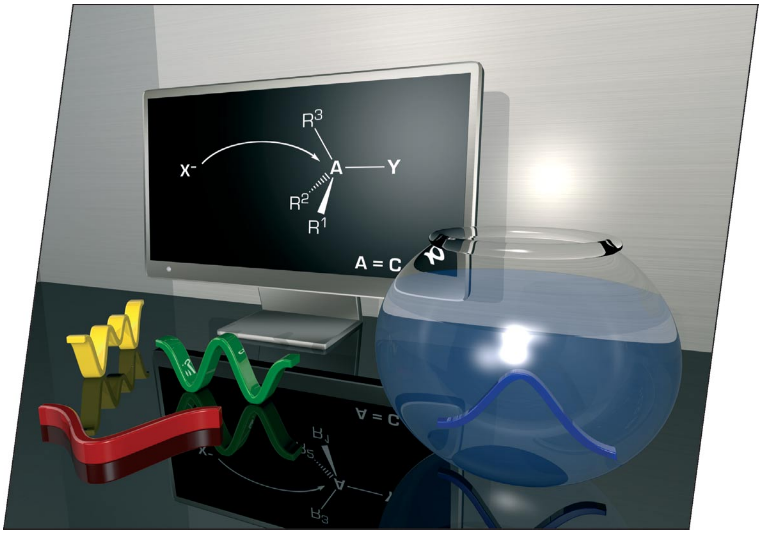
The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further EUChemSoc Societies (Austria, Czech Republic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

COVER PICTURE

The cover picture shows that solvation smoothes reaction profiles not only for S_N2 reactions at carbon but also for S_N2 reactions at silicon, tricoordinate phosphorus and tetracoordinate phosphorus. Thus, the characteristic double-well, single-well and triple-well structures on the gas-phase potential energy surfaces (PES) disappear, which results, in all cases, in a unimodal reaction profile in solution. Details are discussed in the article by M. A. van Bochove and F. M. Bickelhaupt on p. 649ff. We thank Dr. Marcello Luppi for the design of the cover picture.



CONTENTS

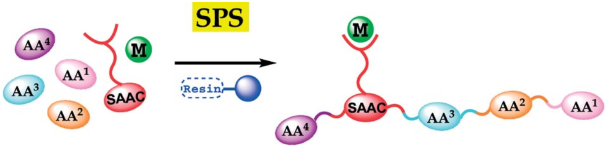
MICROREVIEW

Metal Complex Conjugates

G. Dirscherl, B. König* 597–634

The Use of Solid-Phase Synthesis Techniques for the Preparation of Peptide–Metal Complex Conjugates

Keywords: Solid-phase peptide synthesis / Metal complexes / Single amino acid chelates / Peptide receptors



Teaching old dogs new tricks may be an apt way to describe the recent application of the established method of solid-phase synthesis to the preparation of metal complex conjugates. The microreview summarizes recent reports from this field, focusing on the synthetic methodology.

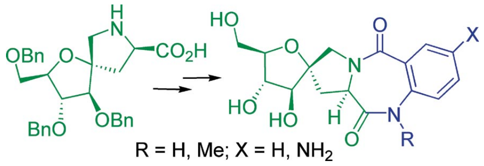
SHORT COMMUNICATIONS

Benzodiazepine Chimeric Scaffolds

A. C. Araújo, F. Nicotra, C. Airoldi, B. Costa, G. Giagnoni, P. Fumagalli, L. Cipolla* 635–639

Synthesis and Biological Evaluation of Novel Rigid 1,4-Benzodiazepine-2,5-dione Chimeric Scaffolds

Keywords: Benzodiazepine / Carbohydrates / GABA$_A$ receptor / Lead generation / Biological activity studies



R = H, Me; X = H, NH$_2$

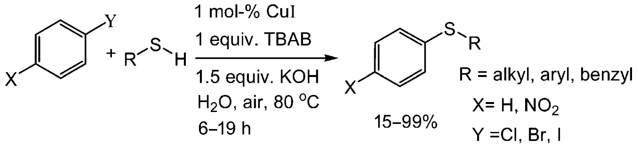
Hybrid fructose-proline-benzodiazepines adopting a rigid conformation have been synthesised and preliminary biological evaluation as GABA$_A$ receptor ligands has been performed.

Cross-Coupling Reactions

L. Rout, P. Saha, S. Jammi, T. Punniyamurthy* 640–643

Efficient Copper(I)-Catalyzed C–S Cross Coupling of Thiols with Aryl Halides in Water

Keywords: C–S Cross-coupling reactions / Copper catalyst / Thiols / Aryl halides



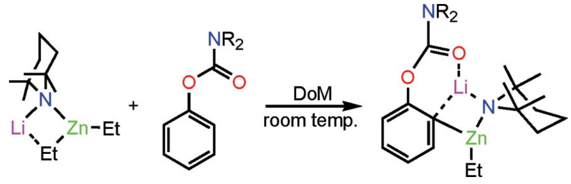
CuI efficiently catalyzes the C–S cross coupling of thiols with aryl halides in the presence of tetrabutylammonium bromide (TBAB) in water under air.

ortho-Deprotonated Carbamates

F. García, M. McPartlin, J. V. Morey, D. Nobuto, Y. Kondo, H. Naka, M. Uchiyama,* A. E. H. Wheatley* 644–647

Suppressing the Anionic Fries Rearrangement of Aryl Dialkylcarbamates; the Isolation of a Crystalline *ortho*-Deprotonated Carbamate

Keywords: Carbamates / Directed *ortho*-metalation / Lithium / Zincates

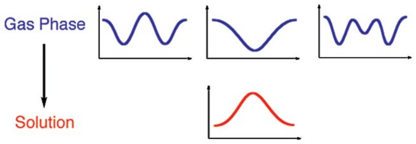


Amidozincate bases effect directed *ortho*-metallation (DoM) of aromatic substrates under exceptionally mild conditions and promise greater directing-group tolerance. We report here on the clean DoM of phenyl dialkylcarbamates. While *ortho*-lithiation leads to anionic Fries rearrangement to the corresponding salicylamides, rearrangement is supressed in the more stable *ortho*-zincates – even at room temperature.

FULL PAPERS

Reaction Mechanisms

Solvent "irons" reaction profiles: We show, among others, that solvation smoothes reaction profiles not only for S_N2 at carbon but also for S_N2 at silicon, tri-coordinate phosphorus and tetra-coordinate phosphorus. Thus, the characteristic double-well, single-well and triple-well structures on the gas-phase PESs disappear, resulting in all cases in a unimodal reaction profile in solution.

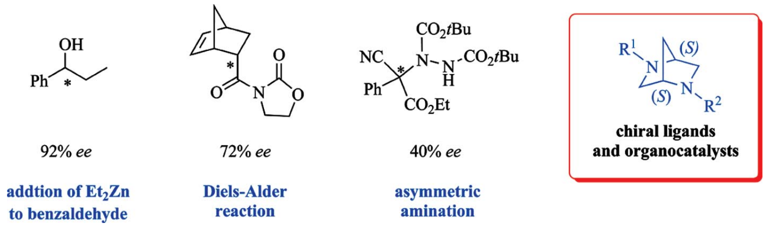


M. A. van Bochove,
F. M. Bickelhaupt* 649–654

Nucleophilic Substitution at C, Si and P: How Solvation Affects the Shape of Reaction Profiles

Keywords: Density functional calculations / Nucleophilic substitution / Phosphorus / Reaction mechanisms / Silicon / Solvent effects

Ligand Design



The title bicyclic heterocycles are interesting chiral molecules with potential in a variety of asymmetric transformations, such as the addition of dialkylzinc organometallics to benzaldehyde, the Diels–Alder reaction, and enantioselective amination en route to α- and β-amino acids.

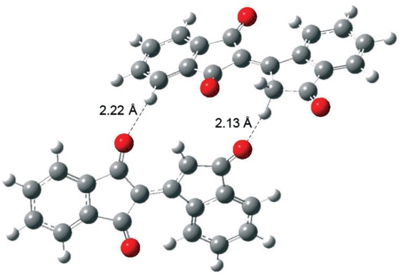
R. Melgar-Fernández, R. González-Olvera,
J. L. Olivares-Romero, V. González-López,
L. Romero-Ponce,
M. del Refugio Ramírez-Zárate,
P. Demare, I. Regla,*
E. Juaristi* 655–672

Synthesis of Novel Derivatives of (1*S*,4*S*)-2,5-Diazabicyclo[2.2.1]heptane and Their Evaluation as Potential Ligands in Asymmetric Catalysis

Keywords: Chiral ligands / Chiral diamines / Chiral Lewis acids / Asymmetric catalysis / Organocatalysis

Ionic Hydrogen Bonds

The products of 1,3-indandione self-condensation, in particular, bindone, readily form anionic hydrogen bonded complexes owing to partial ionization in polar solvents such as DMSO. Formation of the complex is proved by the presence of proton exchange between the neutral and anionic moieties. The anionic species also possess intramolecular aromatic C–H···O hydrogen bonds.

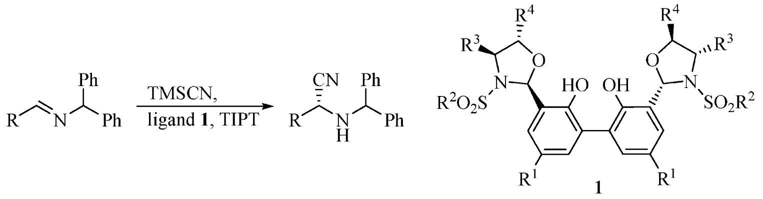


M. Sigalov,* P. Krief, L. Shapiro,
V. Khodorkovsky* 673–683

Inter- and Intramolecular C–H···O Bonding in the Anions of 1,3-Indandione Derivatives

Keywords: Indandiones / Ionization / Hydrogen bonds

Intramolecular Asymmetric Activation



A library of novel tropos biphenyldiols is applied in an asymmetric titanium-catalysed Strecker reaction. A correlation between the *ee* values in the product and the diastereomeric ratio concerning the chiral axis in the ligand is made: strong preference for one conformer gives higher enantioselectivity.

S. Wünnemann, R. Fröhlich,
D. Hoppe* 684–692

Asymmetric Strecker Reaction of *N*-Benzhydrylimines Utilising New Tropos Biphenyldiol-Based Ligands

Keywords: Oxazolidines / Atropisomerism / Ligand design / Hydrocyanation / Titanium

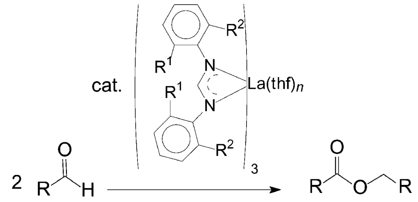
CONTENTS

Catalysis

A. Zuyls, P. W. Roesky,* G. B. Deacon, K. Konstas, P. C. Junk* 693–697

Lanthanide Formamidinates as Improved Catalysts for the Tishchenko Reaction

Keywords: Aldehydes / Homogeneous catalysis / Lanthanum / N ligands / Rare-earth formamidinates



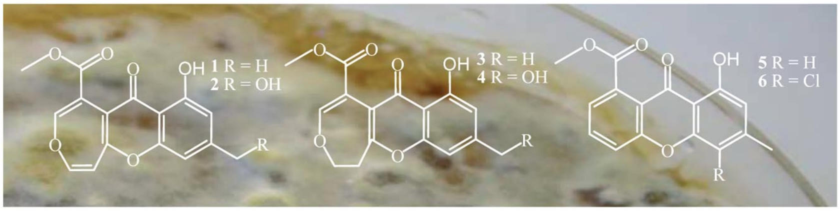
Tris(formamidinato)lanthanum(III) complexes represent a new and very active class of precatalysts for the Tishchenko reaction.

Natural Product Chemistry

S. Lösgen, J. Magull, B. Schulz, S. Draeger, A. Zeeck* 698–703

Isofusidienols: Novel Chromone-3-oxepines Produced by the Endophytic Fungus *Chalara* sp.

Keywords: Fungal metabolites / Fused-ring systems / Antibacterial agents / Oxygen heterocycles / *Chalara* sp.



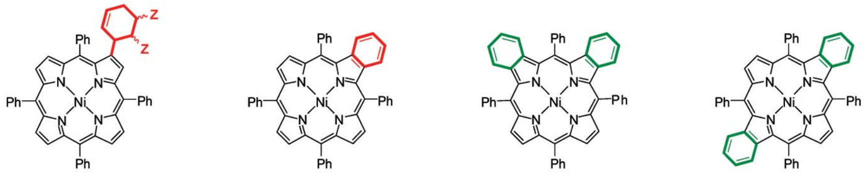
Isofusidienol A, B, C, and D (**1**–**4**) were produced by cultures of *Chalara* sp., and they exhibit antifungal activity against *Candida albicans* and antibacterial activity against gram-positive and gram-negative bacteria. The unprecedented chromone-3-oxepine structure of the compounds was established by detailed spectroscopic analysis. Xanthones **5** and **6** were also isolated.

Benzoporphyrins

A. M. G. Silva, K. T. de Oliveira, M. A. F. Faustino, M. G. P. M. S. Neves, A. C. Tomé, A. M. S. Silva, J. A. S. Cavaleiro,* P. Brandão, V. Felix 704–712

Chemical Transformations of Mono- and Bis(buta-1,3-dien-1-yl)porphyrins: A New Synthetic Approach to Mono- and Dibenzoporphyrins

Keywords: Porphyrinoids / Wittig reactions / Diels–Alder reactions / Electrocyclic reactions / Cycloaddition



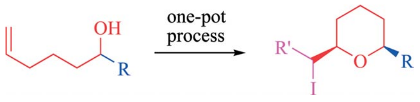
β-Butadienyl- and β,β′-dibutadienylporphyrins were prepared. Reaction of the β-porphyrin with dienophiles afforded the corresponding Diels–Alder adducts. In the absence of dienophiles, the β-porphyrin was converted into monobenzoporphyrin by electrocyclization, followed by oxidation. Adjacent and opposite dibenzoporphyrins were synthesized from the β,β′-porphyrins.

Tandem Reactions

M.-A. Hiebel, B. Pelotier, P. Goekjian, O. Piva* 713–720

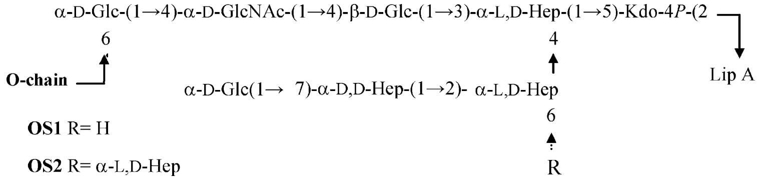
2,6-Disubstituted Tetrahydropyrans by Tandem Cross-Metathesis/Iodocyclisation

Keywords: Metathesis / Cyclization / Tandem reactions / Tetrahydropyrans



Cross-metathesis and iodoetherification reactions can be combined to rapidly access a diverse range of substituted oxygenated heterocycles.

Lipopolysaccharides



The core structure of the lipopolysaccharide obtained from *Halomonas pantelleriensis* was characterized. The LPS was hydrolyzed under both mild acid and strong alkaline conditions. The core oligosaccharide structure and its linkage to the O-chain repeating unit were determined, and this is the first core structure described for a lipopolysaccharide of an extremophile bacterium.

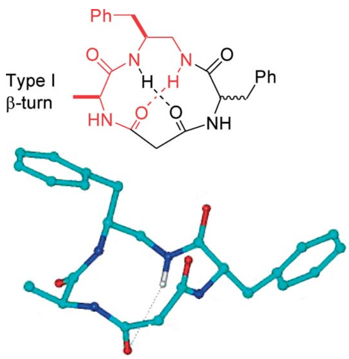
G. Pieretti, M. M. Corsaro,* R. Lanzetta, M. Parrilli, B. Nicolaus, A. Gambacorta, B. Lindner, O. Holst 721–728

Structural Characterization of the Core Region of the Lipopolysaccharide from the Haloalkaliphilic *Halomonas pantelleriensis*: Identification of the Biological O-Antigen Repeating Unit

Keywords: Core oligosaccharide / *Halomonas* / Structure elucidation

13-Membered Cyclotetrapeptides

Easily available 13-membered cyclotetrapeptides containing a retro-inverso modification can be regarded as minimalistic, structurally defined β-turn mimics. These lipophilic, low-weight peptidomimetics can be utilized as scaffolds for the spatial screening of alternative bioactive conformations. A preliminary application to the synthesis of RGD-mimics as integrin inhibitors is shown.



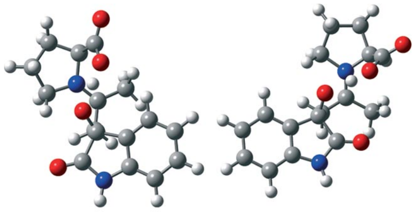
L. Gentilucci,* G. Cardillo, A. Tolomelli, S. Spampinato, A. Sparta, F. Squassabia 729–735

8Cyclotetrapeptide Mimics Based on a 13-Membered, Partially Modified Retro-Inverso Structure

Keywords: Medicinal chemistry / Inhibitors / Peptidomimetics / Conformation analysis / Cell adhesion

Organocatalysis

The steric and stereoelectronic effects that control the enantioselectivity in the cross-aldol addition of acetone to isatins catalyzed by L-proline have been studied by means of DFT and AIM calculations. The reaction of isatin results in a reversal of enantioselectivity compared with the corresponding cross-aldol addition to 4,6-dibromoisatin and aldehydes.



anti-S-cis
($\Delta G = 0.0$)

anti-R-trans
($\Delta\Delta G = 1.0$ kcal/mol)

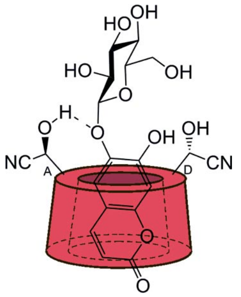
R. J. Corrêa, S. J. Garden,* G. Angelici, C. Tomasini* 736–744

A DFT and AIM Study of the Proline-Catalyzed Asymmetric Cross-Aldol Addition of Acetone to Isatins: A Rationalization for the Reversal of Chirality

Keywords: Asymmetric catalysis / Organocatalysis / Proline / Isatin / Density functional calculations / Atoms in molecules

Artificial Enzymes

An artificial enzyme was shown to be able to hydrolyse toxic coumarin glycosides.



J. Bjerre, E. H. Nielsen, M. Bols* 745–752

Hydrolysis of Toxic Natural Glucosides Catalyzed by Cyclodextrin Dicyanohydrins

Keywords: Artificial enzyme / Supramolecular chemistry / Glycosidase