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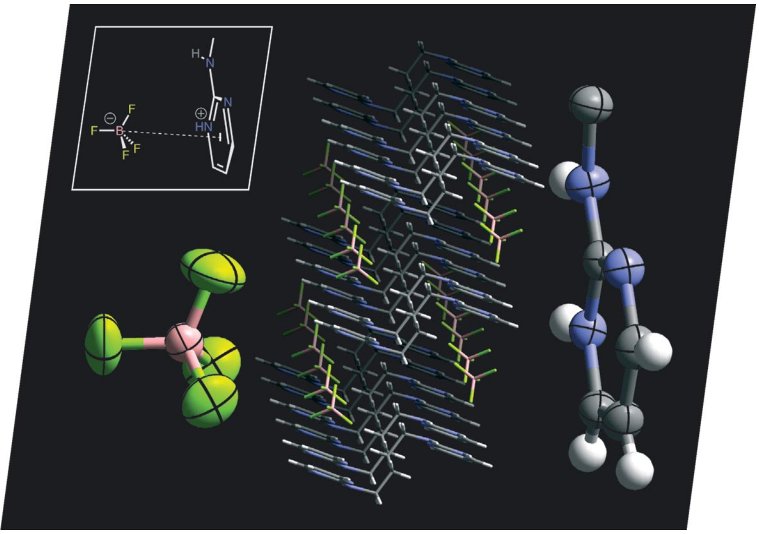
The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry.* Three further EUChemSoc Societies (Austria, Czech Republic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

COVER PICTURE

The cover picture shows the X-ray structure of the *N*,*N*′-tetramethylenebis(2-aminopyrimidinium) tetrafluoroborate salt, which exhibits interesting anion−π interactions that are responsible for the crystal packing. The anion forms a sandwich complex with two pyrimidine rings. A schematic representation of the interaction is depicted in the upper left-hand corner, which corresponds to the thermal ellipsoid plot. In the manuscript we include a theoretical study of the anion−π interaction involving charged pyrimidine rings, which is in good agreement with the findings of the experimental study. Details are discussed in the article by A. Garcia-Raso, A. Frontera, P. M. Deyà et al. on p. 5821 ff.



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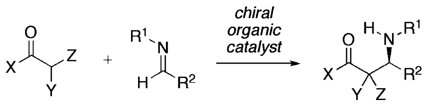
MICROREVIEW

Asymmetric Mannich Reaction

A. Ting, S. E. Schaus* 5797–5815

Organocatalytic Asymmetric Mannich Reactions: New Methodology, Catalyst Design, and Synthetic Applications

Keywords: Organocatalysis / Enantioselective synthesis / Asymmetric catalysis / Mannich reaction / Imines



Small organic molecules offer a catalytic route to the direct, asymmetric Mannich reaction. Stereocontrol may be achieved using organocatalysts such as proline, chiral pyrrolidines, chiral Brønsted acids, and *Cinchona* alkaloids. In this Microreview, recent contributions are discussed to present the methodology and synthetic advantages achieved so far in the asymmetric Mannich reaction.

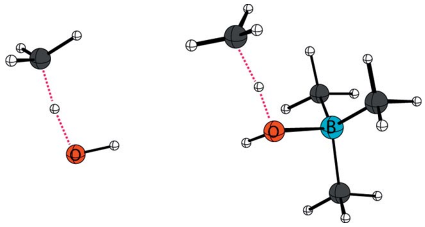
SHORT COMMUNICATION

Radical Reactions

W. Tantawy, H. Zipse* 5817–5820

Hydroxylic Solvents as Hydrogen Atom Donors in Radical Reactions

Keywords: Radical reaction / Hydrogen transfer / Water / Ab initio calculations



Coordination with BMe_3 transforms water and alcohols into highly reactive hydrogen-atom donors. This is due to the unique properties of trialkylboranes, acting as Lewis acids towards the closed-shell solvent, but as electron donors towards the evolving oxygen-centered radicals.

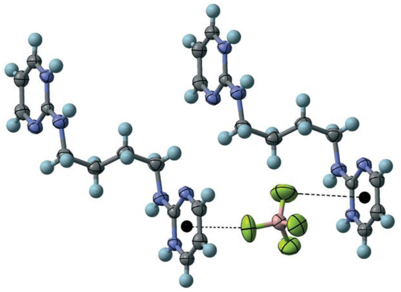
FULL PAPERS

Anion–π Interactions

A. Garcia-Raso,* F. M. Albertí, J. J. Fiol, A. Tasada, M. Barceló-Oliver, E. Molins, D. Escudero, A. Frontera,* D. Quiñonero, P. M. Deyà 5821–5825

A Combined Experimental and Theoretical Study of Anion–π Interactions in Bis(pyrimidine) Salts

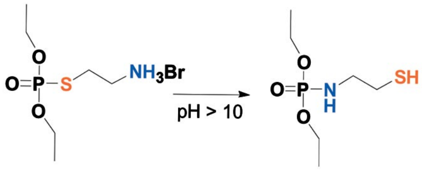
Keywords: Molecular recognition / Noncovalent interactions / Ab initio calculations / pi interactions



The synthesis and X-ray characterization of an N,N'-tetramethylenebis(2-aminopyrimidinium) tetrafluoroborate salt that exhibits anion–π interactions responsible for the crystal packing are reported. The anion forms a sandwich complex with two pyrimidine rings.

Novel Reaction at Phosphorus

It was discovered that *S*-(2-aminoethyl) thiophosphate rapidly rearranges to *N*-(2-mercaptoethyl)phosphoramidate under mild conditions. A reaction mechanism is proposed based on density functional theory calculations.



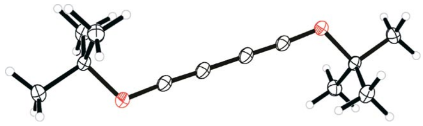
M. Chen, A. Maetzke, S. J. Knak Jensen, K. V. Gothelf* **5826–5833**

Rearrangement of *S*-(2-Aminoethyl) Thiophosphates to *N*-(2-Mercaptoethyl)phosphoramidates

Keywords: Rearrangement / Thiophosphate / Phosphoramidate / Density functional theory / Hydrolysis

Oxygen-Substituted Triple Bonds

The molecular and electronic structure of 1,4-bis(*tert*-butoxy)butadiyne was elucidated by X-ray crystallography and photoelectron spectroscopy. Reactions of this butadiyne and its ethyne congener with electrophilic cobalt complexes are reported.

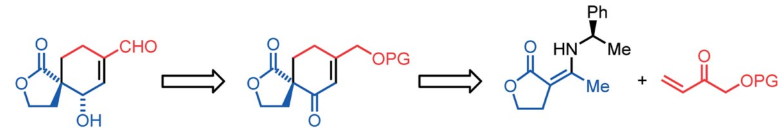


R. Gleiter, D. B. Werz, F. Rominger, E. Zhutov, N. S. Zefirov, M. V. Proskurnina **5834–5839**

Insights into the Molecular Structure and Reactivity of α,ω-Dialkoxy-Substituted Ethyne and Butadiyne

Keywords: Alkynes / Photoelectron spectroscopy / Cyclobutadiene cobalt complexes / Cyclopentadienone cobalt complexes

Optically Active Spirolactones



(+)-(*S*,*S*)-Canangone

The first synthesis of canangone and its 6-epimer is reported. The products are obtained in optically active form by an asymmetric Robinson annulation. The absolute and relative configuration of the natural product is established.

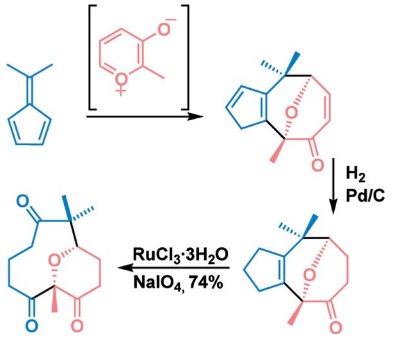
G. Koripelly, W. Saak, J. Christoffers* **5840–5846**

Synthesis of Optically Active (+)-Canangone, Its 6-Epimer, and Determination of Absolute Configuration

Keywords: Asymmetric synthesis / Lactones / Michael addition / Natural products / Spiro compounds

Fulvenes to Macrocycles

The [6+3] adduct of pentafulvenes with 3-oxidopyrylium betaine on selective reduction followed by ruthenium catalyzed oxidative cleavage afforded densely functionalized eleven-membered carbocyclic triketones. The methodology described here is noteworthy as it hardly requires an elaborated catalytic system and proceeds with high level of atom efficiency from cheap and easily available starting materials.



K. S. Krishnan, J. M. Kuthanapillil, R. Rajan, E. Suresh, K. V. Radhakrishnan* **5847–5851**

A Simple and Efficient Strategy Towards Eleven-Membered Carbocycles via Novel Synthetic Transformations of Pentafulvenes

Keywords: Pentafulvenes / Pyrylium betaines / Oxidative cleavage / Eleven-membered carbocycles

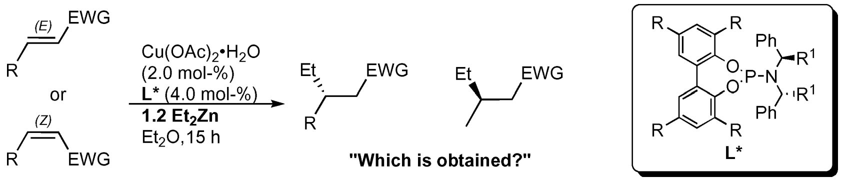
CONTENTS

Asymmetric Catalysis

M. Vuagnoux-d'Augustin,
A. Alexakis* 5852–5860

Influence of the Double-Bond Geometry of the Michael Acceptor on Copper-Catalyzed Asymmetric Conjugate Addition

Keywords: Michael addition / Asymmetric catalysis / Diethylzinc / Copper / Double-bond geometry



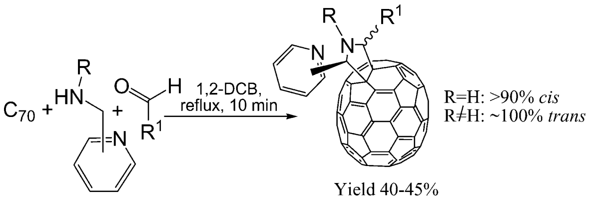
Focusing on the mechanistic aspects, a study of the influence of the double-bond geometry of the Michael acceptor on the enantioselectivity of the copper-catalyzed asymmetric conjugate addition of diethylzinc to various (*E*) and (*Z*) substrates has been realized.

Derivatisation of [70]Fullerene

P. A. Troshin,* A. S. Peregudov,
S. M. Peregudova,
R. N. Lyubovskaya 5861–5866

Highly Regio- and Stereoselective [2+3] Cycloadditions of Azomethine Ylides to [70]Fullerene

Keywords: Fullerenes / Cycloaddition / Ylides / Nitrogen heterocycles / Diastereoselectivity



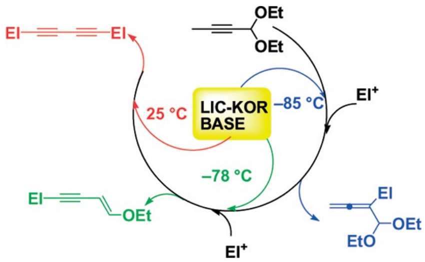
The use of pycolylamines as reagents for the generation of azomethine ylides in [2+3] cycloaddition reactions with [70]fullerene results in the highly selective formation of 8,25-addition products with controlled *cis* or *trans* addend arrangement patterns with respect to the pyrrolidine ring.

Diynes from Propargylic Acetals

M. Blangetti, A. Deagostino,
H. Rosso, C. Prandi,* C. Zavattaro,
P. Venturello 5867–5874

Rapid and Easy Access to (*E*)-1,3-Enynes, 1,3-Diynes and Allenes Starting from Propargylic Acetals, Exploiting the Different Reactivity of Lithium and Mixed Lithium–Potassium Organometallic Reagents

Keywords: Acetals / Superbases / Metalation / Enynes / Diynes



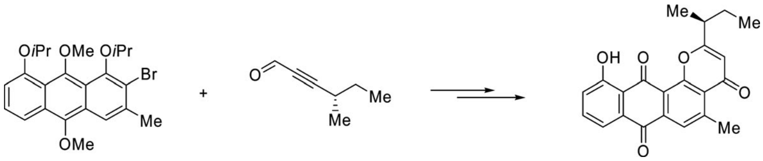
The treatment of propargylic acetals with various lithium and mixed lithium–potassium Schlosser's reagents allows a one-pot synthesis of (*E*)-1,3-enynes, 1,3-diynes and allenes, depending on the reaction conditions and the selected base. The metallation–elimination sequence in the presence of a suitable electrophile provides a linear route to functionalized (*E*)-conjugated enynes, diynes and allenes.

Anthrapyran Antibiotics

L. F. Tietze* R. R. Singidi, K. M. Gericke,
H. Böckemeier, H. Laatsch 5875–5878

Isolation, Enantioselective Total Synthesis and Structure Determination of the Anthrapyran Metabolite SS 43405-e

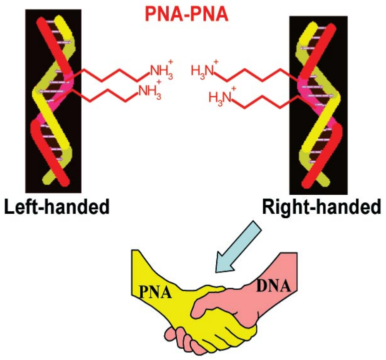
Keywords: Anthraquinones / Anthrapyrans / Antibiotics / Diels–Alder reaction / Pluramycins / Streptomycetes



The first enantioselective total synthesis of the enantiomer of the anthrapyran metabolite SS 43405-e has been achieved, which allowed the determination of the so far unknown absolute (*R*) configuration of the natural product.

DNA Recognition

Chiral PNAs with two lysine-based stereogenic centres in the same monomer induce different preferential helix handednesses, which emerge from the "converging" or "conflicting" induction of the two individual stereocentres. The helical preferences in turn tune the PNA affinities for the complementary DNA.

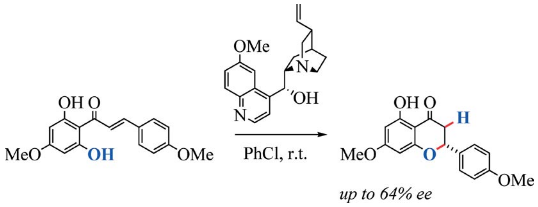


S. Sforza, T. Tedeschi, R. Corradini, R. Marchelli* **5879–5885**

Induction of Helical Handedness and DNA Binding Properties of Peptide Nucleic Acids (PNAs) with Two Stereogenic Centres

Keywords: Peptide nucleic acids / DNA / Chiral recognition / Supramolecular chirality / Induced handedness

Asymmetric Brønsted Acid/Base Catalysis



Enzymes mediate the asymmetric cyclizations of 2′-hydroxychalcones to flavanones with ease, but a corresponding small-molecule catalyst has remained elusive. An early claim of asymmetric Brønsted acid catalysis has now been disproved. Now the first case of asymmetric cyclization with chiral Brønsted bases (cinchona alkaloids) is presented.

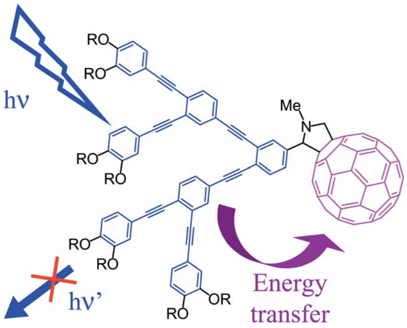
C. Dittmer, G. Raabe, L. Hintermann* **5886–5898**

Asymmetric Cyclization of 2′-Hydroxychalcones to Flavanones: Catalysis by Chiral Brønsted Acids and Bases

Keywords: Asymmetric catalysis / Chiral Brønsted acid / Cyclization / Flavanones / Oxygen heterocycles

Light-Harvesting Devices

The wider spectral profile of fullerene dyads with 1,2,4-triethynylbenzene branching units when compared to their 1,3,5-triethynylbenzene analogues clearly points out improved light-harvesting capabilities.



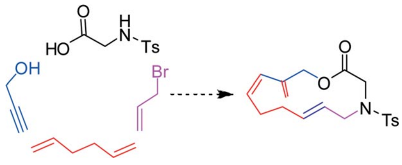
J. N. Clifford, A. Gégout, S. Zhang, R. Pereira de Freitas, M. Urbani, M. Holler, P. Ceroni,* J.-F. Nierengarten,* N. Armaroli* **5899–5908**

Fullerene Derivatives Substituted with Differently Branched Phenyleneethynylene Dendrons: Synthesis, Electronic and Excited State Properties

Keywords: Conjugated systems / Dendrimers / Electrochemistry / Energy transfer / Fullerene / Photophysical properties

Diversity-Oriented Synthesis

Suitably functionalized glycine derivatives undergo a cross-enyne and ring-closing metathesis cascade to generate macroheterocyclic ring systems in good yield. These macroheterocycles, prepared on the basis of a building block approach, consist of 13–16-membered rings.



S. Kotha,* K. Singh **5909–5916**

Cross-Enyne and Ring-Closing Metathesis Cascade: A Building-Block Approach Suitable for Diversity-Oriented Synthesis of Densely Functionalized Macroheterocycles with Amino Acid Scaffolds

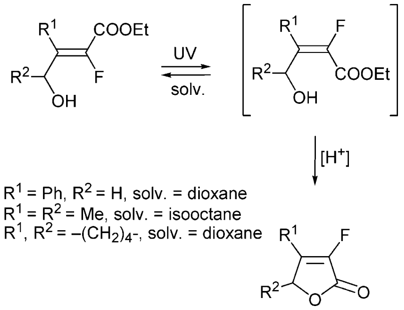
Keywords: Amino acids / Tandem reactions / Metathesis / Heterocycles / Macrocycles / Ring-closing metathesis

Z/*E* Photoisomerisation

K. Pomeisl,* J. Čejka, J. Kvíčala, O. Paleta **5917–5925**

Synthesis of 3-Fluorofuran-2(5*H*)-ones Based on *Z*/*E* Photoisomerisation and Cyclisation of 2-Fluoro-4-hydroxybut-2-enoates

Keywords: Horner–Wadsworth–Emmons reaction / Phosphonates / Photolysis / Isomerization / Fluorofuranones



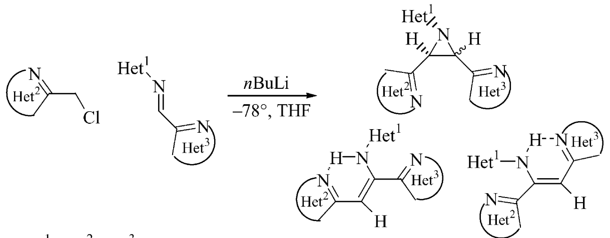
The *Z*/*E* photoisomerisation of some 2-fluoroalkenoates as Horner–Wadsworth–Emmons intermediates can be considered as a significant alternative tool for the preparation of alkyl- and phenyl-substituted 2-fluorobut-2-enolides owing to its simplicity and efficiency.

Aziridine Rearrangement

E. Pindinelli, T. Pilati, L. Troisi* **5926–5933**

Synthesis and Rearrangement of 1,2,3-Triheteroaryl(aryl)-Substituted Aziridines

Keywords: Aziridines / Enamines / Rearrangement / Carbanions / Nitrogen heterocycles



Het^1, Het^2, Het^3 = phenyl, pyridinyl, thiazolyl, benzothiazolyl

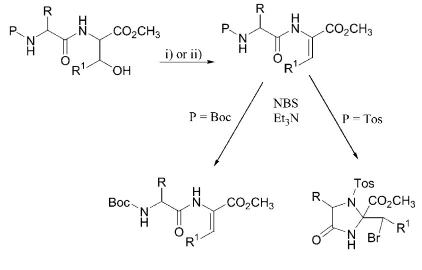
Aziridines with electron-withdrawing heteroaryl groups were synthesised with sufficient diastereoselectivity. The *cis* aziridines are susceptible to ring opening and rearrangement when the formation of secondary enamines in stable hexacyclic structures with a N–H···N hydrogen bond is possible.

Bromination of Dehydroamino Acids

P. M. T. Ferreira,* L. S. Monteiro,* G. Pereira, L. Ribeiro, J. Sacramento, L. Silva **5934–5949**

Reactivity of Dehydroamino Acids and Dehydrodipeptides Towards *N*-Bromosuccinimide: Synthesis of β-Bromo- and β,β-Dibromodehydroamino Acid Derivatives and of Substituted 4-Imidazolidinones

Keywords: Amino acids / Peptides / Bromination reactions / Imidazolidinones



i) Boc$_2$O (3.3 equiv.)/DMAP-TFA; ii) Boc$_2$O (1 equiv.)/DMAP-TMG

Several methyl esters of dehydroamino acid derivatives have been synthesized by using a modification of a previously developed method. The products were converted into β,β-dibromodehydroalanines, β-bromo β-substituted dehydroamino acids and imidazolidin-4-ones.