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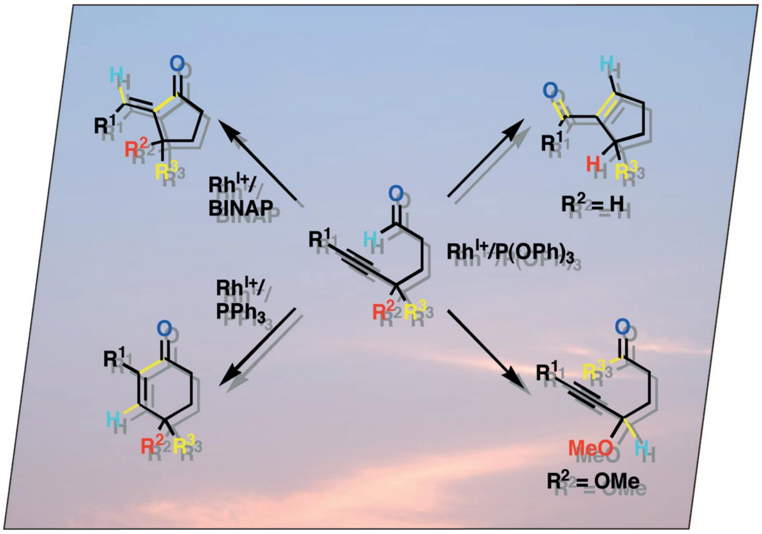
The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further EUChemSoc Societies (Austria, Czech Republic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

COVER PICTURE

The cover pocture shows the cationic rhodium(I) complex catalyzed isomerization of 5-alkynals to four different types of ketones. The catalytic isomerization of 5-alkynals to γ-alkynyl ketones and cyclopent-1-enyl ketones proceeds by using $\mathrm{Rh^{I+}}$/$\mathrm{P(OPh)_3}$, whereas the catalytic *endo*/*trans* and *exo*/*cis* hydroacylation of 5-alkynals to cyclohexenones and cyclopentanones proceeds by using $\mathrm{Rh^{I+}/PPh_3}$ and $\mathrm{Rh^{I+}}$/BINAP, respectively. The ligands of the Rh catalysts and the substituents at the 4-position of the 5-alkynals play an important role in determining which isomerization product results. Details are discussed in the article by K. Tanaka et al. on p. 5675ff.



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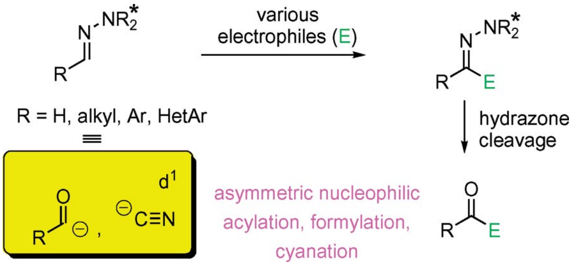
MICROREVIEW

Umpolung with Aza-Enamines

R. Brehme,* D. Enders,* R. Fernandez,* J. M. Lassaletta* 5629–5660

Aldehyde *N*,*N*-Dialkylhydrazones as Neutral Acyl Anion Equivalents: Umpolung of the Imine Reactivity

Keywords: Nucleophilic acylation / Umpolung / Hydrazones / Aza-enamines / Asymmetric synthesis



Aldehyde *N*,*N*-dialkylhydrazones react with various electrophiles at the imine carbon atom. Hydrolysis of the product hydrazones gives ketones and aldehydes or conversion into a nitrile; nucleophilic acylations, formylations, and cyanations are possible. High asymmetric inductions can be obtained and the first organocatalytic versions of this chemistry are presented.

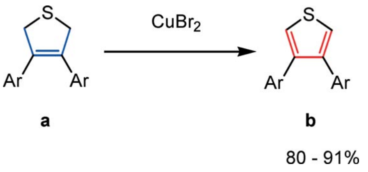
SHORT COMMUNICATIONS

Diarylthiophene Synthesis

Y. Dang, Y. Chen* 5661–5664

Oxidation of 3,4-Diaryl-2,5-dihydrothiophenes to 3,4-Diarylthiophenes Using $CuBr_2$: Simple and Efficient Preparation of 3,4-Diarylthiophenes

Keywords: Sulfur heterocycles / Copper / Oxidation



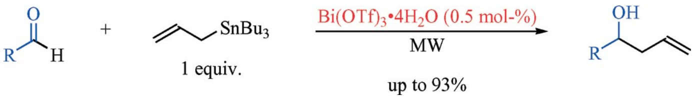
Facile and efficient preparation of 3,4-diarylthiophenes by the oxidation of 3,4-diaryl-2,5-dihydrothiophenes using $CuBr_2$.

Carbonyl Allylation

T. Ollevier,* Z. Li 5665–5668

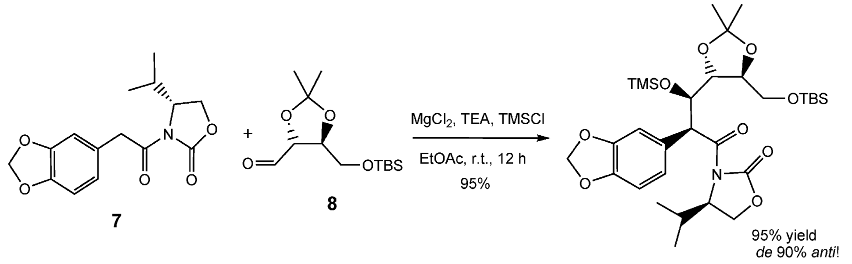
Bismuth Triflate Catalyzed Allylation of Aldehydes with Allylstannane under Microwave Assistance

Keywords: Allylation / Bismuth / Lewis acids / Microwaves / Allyltin



In the presence of a catalytic amount of $Bi(OTf)_3 \cdot 4H_2O$ and under microwave irradiation, mixtures of aldehyde and allylstannane afford smoothly the corresponding homoallylic alcohol. The reactions lead to the products in good to very good yields using catalytic amounts of $Bi(OTf)_3 \cdot 4H_2O$ (0.5 mol-%) and under microwave irradiation for a short time.

anti-Aldol Reactions



The magnesium chloride catalyzed *anti*-aldol reaction of phenyl acetate derived oxazolidinone **7** proceeds readily with enolizable L-threose derivative **8** to provide anti-aldol adducts in high yields and with very high diastereoselectivities.

J. McNulty,* J. J. Nair, M. Sliwinski,
L. E. Harrington, S. Pandey ... 5669–5673

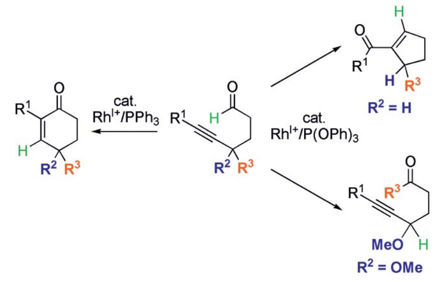
Unusual Magnesium Chloride Catalyzed Non-Evans *anti*-Aldol Reactions of an Enolizable L-Threose Derivative

Keywords: Aldol reactions / Synthetic methods / Diastereoselectivity / Natural products

FULL PAPERS

Catalytic Isomerizations of 5-Alkynals

We have developed catalytic isomerizations of 5-alkynals to λ-alkynyl ketones and cyclopent-1-enyl ketones using [Rh{P(OPh)$_3$}$_2$]BF$_4$ as a catalyst. The first catalytic *endo*/*trans* hydroacylation of acyclic 5-alkynals leading to cyclohexenones was also developed with [Rh(PPh$_3$)$_2$]BF$_4$ as a catalyst.



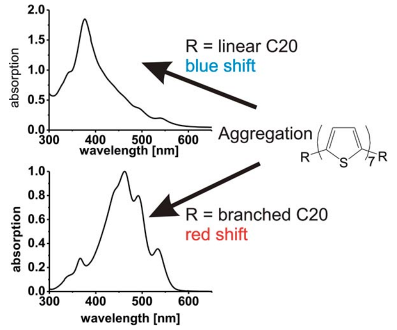
K. Tanaka,* K. Sasaki, K. Takeishi,
M. Hirano 5675–5685

Cationic P(OPh)$_3$- or PPh$_3$-Rhodium(I) Complex-Catalyzed Isomerizations of 5-Alkynals to δ-Alkynyl Ketones, Cyclopent-1-enyl Ketones, and Cyclohexenones

Keywords: Aldehydes / Ketones / Alkynes / Rhodium / Catalysis

Aggregation of Oligothiophenes

α- and α,ω-substituted oligothiophenes show a strong aggregation behaviour in solution depending on the geometry of the alkyl substituents which is reflected by a distinct blue or red shift, respectively, in the absorption spectra. A strong influence of the substituent is also found in the morphology of the aggregates and of thermal properties in the solid state.



S. Ellinger, A. Kreyes, U. Ziener,*
C. Hoffmann-Richter, K. Landfester,
M. Möller 5686–5702

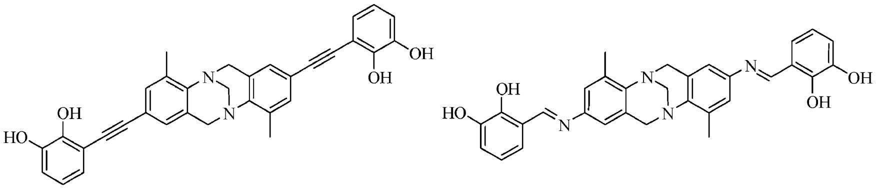
Aggregation Phenomena of Long α- and α,ω-Substituted Oligothiophenes – the Effect of Branched vs. Linear End-Groups

Keywords: Aggregation / Liquid crystals / Oligothiophenes / Self-assembly

Diastereomeric Helicates

U. Kiehne, A. Lützen* 5703–5711

Synthesis of Bis(catechol) Ligands Derived from Tröger's Base and Their Dinuclear Triple-Stranded Complexes with Titanium(IV) Ions



Dissymmetric bis(chelating) oxygen-donor ligands derived from 2,8-disubstituted Tröger's base and monofunctionalized catechols were synthesized, and their geometry is defined by the V-shaped structure of the core of Tröger's base. Self-assembly of the racemic ligands upon coordination to Ti^{IV} ions led to mixtures of six different diastereomeric helicates.

Keywords: Tröger's base / Self-assembly / Catechol / Titanium / Helicates

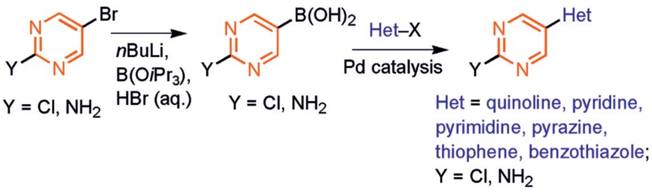
CONTENTS

Functionalized Heterocycles

K. M. Clapham, A. E. Smith,
A. S. Batsanov, L. McIntyre, A. Pountney,
M. R. Bryce,* B. Tarbit 5712–5716

New Pyrimidylboronic Acids and Functionalized Heteroarylpyrimidines by Suzuki Cross-Coupling Reactions

Keywords: Pyrimidine / Lithiation / Boronic acid / Cross-coupling



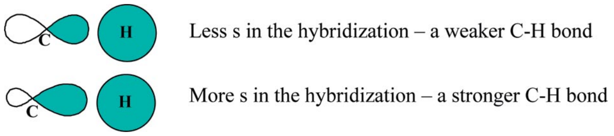
Heteroarylpyrimidines have been synthesized by the Suzuki methodology with 2-chloro-5-pyrimidylboronic acid and 2-amino-5-pyrimidylboronic acid as key reagents.

C–H Bond Dissociation Energies

A. Stanger* 5717–5725

A Simple and Intuitive Description of C–H Bond Energies

Keywords: DFT calculations / NBO analysis / C–H bond dissociation energies / Hybridization



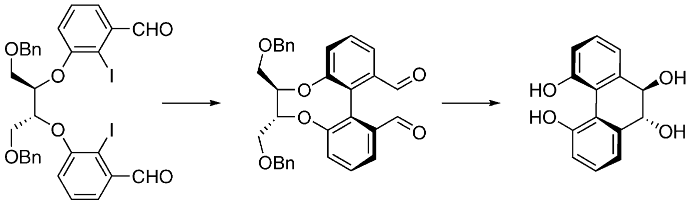
C–H bond dissociation energy (BDE) can be described as a second order polynomial function of hybridization and reorganization which is specific to group of compounds. Thirty five different C–H BDEs are analyzed and show the above-described dependence. The obtained correlations are used to predict C–H BDEs from a simple HF/3-21G calculation within less than 2 kcal mol^{-1} from the G3 results.

Atropselective Biaryl Synthesis

G. Stavrakov, M. Keller,
B. Breit* 5726–5733

From Central to Axial to Central Chirality: Enantioselective Construction of the *trans*-4,5,9,10-Tetrahydroxy-9,10-dihydrophenanthrene System

Keywords: Asymmetric synthesis / Biaryl coupling / Atropisomerism / Ullmann coupling



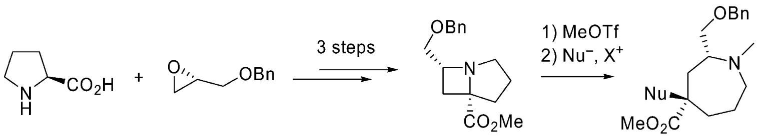
Atropselective synthesis of the core biaryl system of the antibiotics benanimicin, pradimicin and FD 594 is reported. Key to success was an imine-directed atropdiastereoselective Ullmann coupling under mild reaction conditions.

Strained Bicyclic Azetidines

M. Sivaprakasam, F. Couty,* O. David,
J. Marrot, R. Sridhar, B. Srinivas,
K. Rama Rao 5734–5739

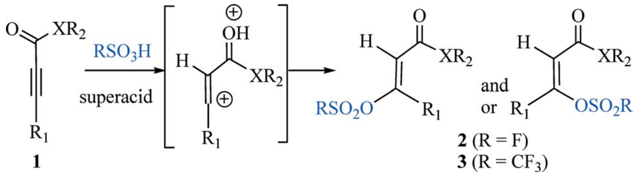
A Straightforward Synthesis of Enantiopure Bicyclic Azetidines

Keywords: Nitrogen heterocycles / Bicyclic compounds / Fused-ring systems / Strained molecules



Understudied enantiomerically pure 1-azabicyclo[3.2.0]heptane derivatives were synthesized in a three-step sequence starting from *O*-substituted glycidols and L-proline. These strained bicyclic nitrogen heterocycles could be efficiently transformed into azepanes by ring cleavage.

Fluorosulfonate Synthesis



Triflic or fluorosulfonic acids rapidly added to acetylenic acids and esters and to acetylenic ketones to yield the corresponding vinyl triflates or fluorosulfonates with high stereoselectivity. Depending on the reaction conditions either the *E* or the *Z* isomer can be obtained. This method offers *a one step* synthesis of vinyl triflates.

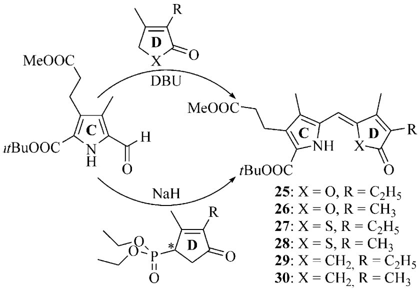
A. V. Vasilyev, S. Walspurger, S. Chassaing, P. Pale,* J. Sommer* **5740–5748**

One-Step Addition of Sulfonic Acids to Acetylene Derivatives: An Alternative and Stereoselective Approach to Vinyl Triflates and Fluorosulfonates

Keywords: Superacidic systems / Alkynes / Vinyl triflates / Sulfones / Carbocations

Bilin Building Blocks

Six heteroaromatic compounds were synthesized and condensed with a methyl propionate-substituted pyrrole to yield the "right" moiety of open-chain tetrapyrroles. X-ray crystal structure analysis of the 10-oxapyrromethen-1-one **25** reveals a planar conformation. All pyrrole-substituted heteroaromatic derivatives **25–30** show absorbances in the UV/Vis spectra with high molar extinction coefficients.



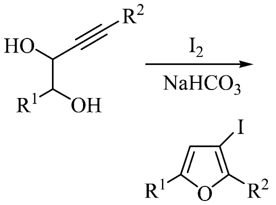
C. Bongards, W. Gärtner* **5749–5758**

Synthesis of Hetero Atom Modified Pyrromethenones

Keywords: Tetrapyrrole chromophore / Phytochrome / Bilin / Phycocyanobilin

Iodofurans

5-*endo-dig* cyclisations of 3-alkyne-1,2-diols using iodine as the electrophile proceed smoothly to deliver excellent yields of the corresponding β-iodofurans. The necessary precursors are available from regioselective bis-hydroxylation of conjugated enynes and the addition of acetylides to α-hydroxy carbonyls.

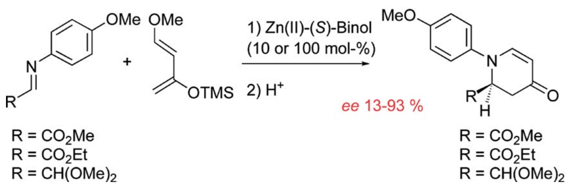


S. P. Bew, G. M. M. El-Taeb, S. Jones, D. W. Knight,* W.-F. Tan **5759–5770**

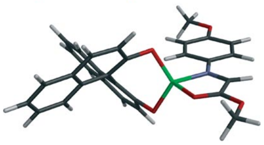
Expedient Syntheses of β-Iodofurans by 5-*endo-dig* Cyclisations

Keywords: Cyclisation / Iodocyclisation / Furans

Asymmetric Imino Cycloaddition



Intermediate zinc(II)-(*S*)-binol-imine complex for methyl ester



A series of *N*-aryl imines were treated with Danishefsky's diene in the presence of zinc(II)–binol under catalytic and stoichiometric conditions. CD was used to determine the absolute stereochemistry of a new cycloadduct to compare with other examples, and semi-empirical calculations were used to explain the origin of asymmetric induction.

L. Di Bari, S. Guillarme, J. Hanan, A. P. Henderson, J. A. K. Howard, G. Pescitelli, M. R. Probert, P. Salvadori, A. Whiting* **5771–5779**

Application of Zinc(II)–Binol for the Formal Aza-Diels–Alder Reaction of *N*-Arylimines with Danishefsky's Diene: CD-Based Absolute Stereochemistry Determination, Origin of Asymmetric Induction and Mechanistic Considerations

Keywords: Cycloaddition / Asymmetric catalysis / Configuration analysis / Nitrogen heterocycle / Lewis acid / Reaction mechanism