Hungary
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Austria
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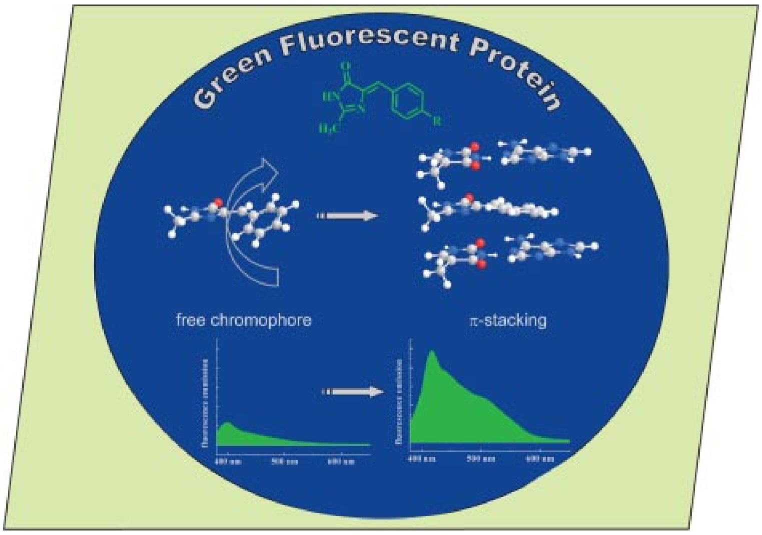
Netherlands

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 a chromophore of the Green Fluorescent Protein, which undergoes fast internal conversion by rotation causing the quenching of its fluorescence in solution. In contrast, the intact protein shows a high fluorescence quantum yield and there is still a need to understand the mechanism of this increase in fluorescence. The restriction of the chromophore's flexibility by simple π-stacking was achieved by incorporation of the chromophore into *N*-(2-aminoethyl)glycine-peptide nucleic acid and by pairing with complementary DNA. Interestingly, fluorescence appeared upon pairing with DNA, even though the fluorescence quantum yield is far below that of the natural counterpart. Details are discussed in the article by T. Stafforst and U. Diederichsen on p. 899 ff.



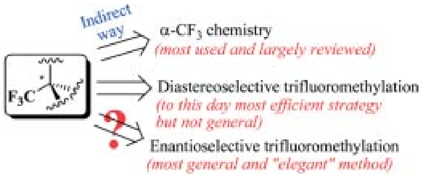
MICROREVIEW

Asymmetric Trifluoromethylation

T. Billard,* B. R. Langlois .... 891−897

How to Reach Stereogenic Trifluoromethylated Carbon? En Route to the "Grail" of the Asymmetric Trifluoromethylation Reaction

Keywords: Trifluoromethylation / Asymmetric synthesis / Enantioselectivity / Diastereoselectivity



Chiral trifluoromethylated compounds are emerging in various fields but their syntheses are still not easy. Asymmetric trifluoromethylation should become the best method in the future, but the enantioselective strategy is still not very powerful, despite numerous studies already performed, and to this day constitutes the new "Grail quest" of organofluorine chemistry.

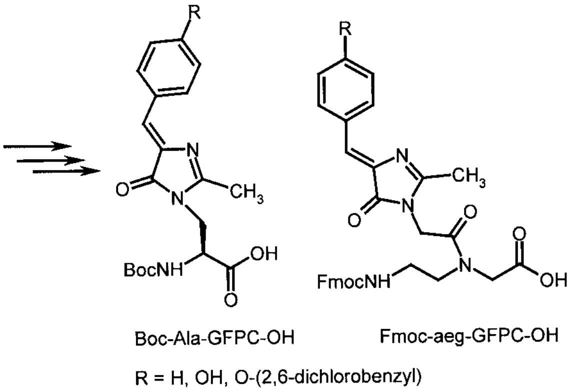
FULL PAPERS

Molecular Biology Diagnostics

T. Stafforst, U. Diederichsen* .... 899−911

Synthesis of Alaninyl and *N*-(2-Aminoethyl)glycinyl Amino Acid Derivatives Containing the Green Fluorescent Protein Chromophore in Their Side Chains for Incorporation into Peptides and Peptide Nucleic Acids

Keywords: Fluorescence / Chromophores / Peptide nucleic acid / Green Fluorescent Protein (GFP) / Solid-phase synthesis



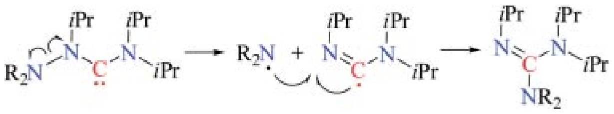
The synthesis of the chromophore of the Green Fluorescent Protein functionalized with alanine and *N*-(2-aminoethyl)glycine for solid-phase synthesis is reported. Its incorporation into aminoethylglycine-PNA and its properties are described.

Transient Amino-Hydrazino-Carbenes

X. Cattoën, H. Gornitzka,
F. S. Tham, K. Miqueu, D. Bourissou,*
G. Bertrand* .... 912−917

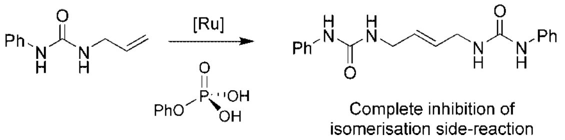
Transient Amino-Hydrazino-Carbenes: A Radical Pathway for Intramolecular 1,2-Migration Reactions

Keywords: Carbenes / 1,2-Migration / Radical process / DFT calculations



The substitution pattern of the hydrazino group dramatically influences the lifetime of amino-hydrazino-carbenes, which are prone to undergo intramolecular 1,2-migration reactions through a radical pathway according to DFT calculations.

Inhibition of Olefin Isomerisation



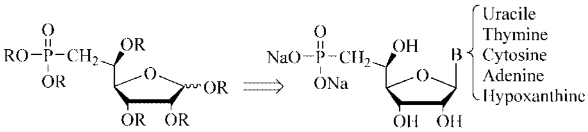
Alkene isomerisation is often an unwanted side reaction in ruthenium-catalysed alkene metathesis. Herein, a systematic study of the ruthenium-catalysed metathesis of alkenes containing hydrogen-bonding groups is presented. Under standard conditions, these substrates undergo alkene isomerisation instead of the targeted metathesis. However, this unwanted isomerisation process can be suppressed by addition of phenylphosphoric acid to the reaction mixture.

N. Gimeno, P. Formentín, J. H. G. Steinke,* R. Vilar* ..... **918−924**

Phenylphosphoric Acid as a New Additive to Inhibit Olefin Isomerisation in Ruthenium-Catalysed Metathesis Reactions

Keywords: Homogenous catalysis / Metathesis / Ruthenium / Alkenes / Ureas

Hydroxyphosphonate Nucleosides



A new series of mononucleotide analogues bearing a nonhydrolysable P−C bond instead of the P−O phosphate linkage is reported. A stereoselective approach was set up to reach β-hydroxyphosphonate nucleoside analogues as a single diastereoisomer. It involved the synthesis of a key "sugar-phosphonate" intermediate which was obtained through an Arbusov reaction.

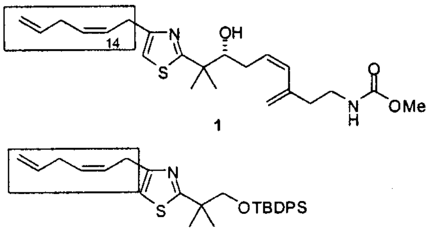
F. Gallier, S. Peyrottes,* C. Périgaud .... **925−933**

Ex-Chiral-Pool Synthesis of β-Hydroxyphosphonate Nucleoside Analogues

Keywords: Nucleotides / Phosphorus / Carbohydrates / Glycosylation

Structure Elucidation

The synthesis of the C8−C18 fragment with (Z)-Δ^{14} double bond configuration is performed for the first time in order to verify the configuration of the C14−C15 double bond.



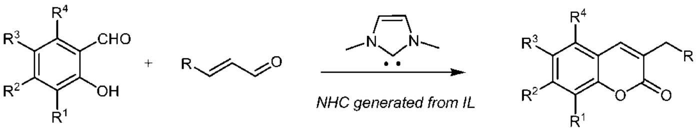
1

M. Rega, P. Candal, C. Jiménez, J. Rodríguez* .... **934−942**

Mycothiazole: Synthesis of the C8−C18 Subunit and Further Evidence of the (Z)-Δ^{14} Double Bond Configuration

Keywords: Sulfur heterocycles / Cross metathesis / Configuration determination

Heterocycles through Umpolung



Starting from salicylaldehydes and α,β-unsaturated aldehydes, a new coumarin synthesis in ionic liquids is presented. The key feature is the generation of N-heterocyclic carbenes (NHC) and an Umpolung reaction.

J. Toräng, S. Vanderheiden, M. Nieger, S. Bräse* .... **943−952**

Synthesis of 3-Alkylcoumarins from Salicylaldehydes and α,β-Unsaturated Aldehydes Utilizing Nucleophilic Carbenes: A New Umpoled Domino Reaction

Keywords: Coumarins / Ionic liquids / N-heterocyclic carbene (NHC) / Domino reaction / Umpolung

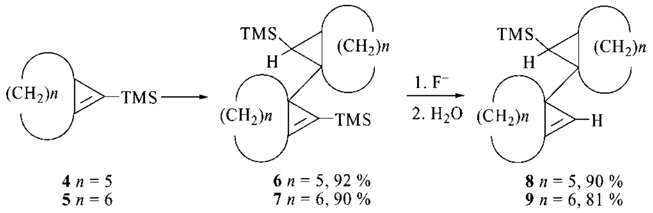
CONTENTS

Ene Reactions of Cyclopropenes

K. C. Chen, W. C. Wang, M.-Y. Chen, W.-C. Chen, M.-C. Her, G.-A. Lee* 953–958

Regio- and Stereoselectivity of Ene Reactions: The Dimerization of Bicyclic 1,3-Fused 2-(Trimethylsilyl)cycloprop-1-enes

Keywords: Cyclopropene / Regioselectivity / Stereoselectivity / Ene reaction / Dimerization



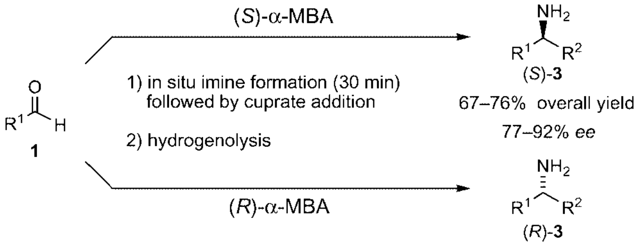
Both 8-(trimethylsilyl)bicyclo[5.1.0]oct-1(8)-ene (**4**) and 9-(trimethylsilyl)bicyclo-[6.1.0]non-1(9)-ene (**5**) undergo ene dimerization via the same steric isomer and an *endo* transition state to generate the stable adducts **6** and **7** as the sole isomers. Both of the ene dimers, (trimethylsilyl)cyclopropenes **6** and **7**, can be converted into cyclopropenes **8** and **9** by treatment with a fluoride salt followed by protonation.

Chiral Amines

V. N. Wakchaure, R. R. Mohanty, A. J. Shaikh, T. C. Nugent* 959–964

A One-Pot Asymmetric Sequential Amination-Alkylation of Aldehydes: Expedient Synthesis of Aliphatic Chiral Amines

Keywords: Amines / Enantioenriched amines / In situ aldimine formation / Cuprates / (*R*)- or (*S*)-α-(methylbenzyl)-amine



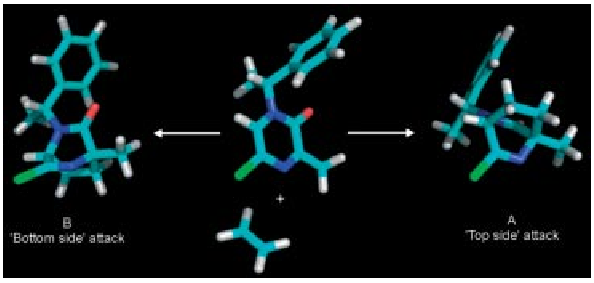
Aliphatic chiral amines are historically challenging to synthesize in a concise manner and in high *ee*. Starting from commercially available aldehydes, a two-step procedure is presented for the synthesis of a diverse set of primary aliphatic amines in good to high overall yield and *ee*.

Diastereoselective Diels–Alder Additions

J. Alen, W. J. Smets, L. Dobrzańska, W. M. De Borggraeve,* F. Compernolle, G. J. Hoornaert 965–971

Diastereoselective Diels–Alder Additions of Ethene to Substituted Homochiral 2(1*H*)-Pyrazinones

Keywords: Cycloaddition / Diastereoselectivity / Chiral auxiliaries / Pyrazinone / Ethene



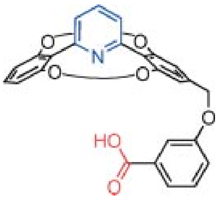
A new and useful method to prepare diastereomeric Diels–Alder adducts of 2(1*H*)-pyrazinones through introduction of a homochiral α-methylbenzyl group has been developed. The diastereisomers can be separated by column chromatography. To the best of the authors' knowledge, this Diels–Alder reaction with ethene is the first one showing diastereoselectivity.

Acid–Base Catalysis

T. Liebig, M. Abbass, U. Lüning* 972–980

Concave Pyridines for Bifunctional Acid–Base Catalysis

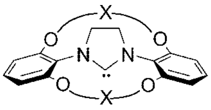
Keywords: Acid catalysis / Base catalysis / Bifunctional catalysis / Heterocycles / Macrocycles / Supramolecular chemistry



A benzoic acid was attached to concave pyridines to give bifunctional acid–base catalysts. The design ensures that no intramolecular hydrogen bond can be formed between the carboxylic acid and the pyridine nitrogen atom.

N-Heterocyclic Carbenes

An imidazolinium unit as a precursor to an N-heterocyclic carbene (NHC) has been embedded into a bimacrocyclic concave environment. By deprotonation, an NHC was generated and scavenged by CS_2.

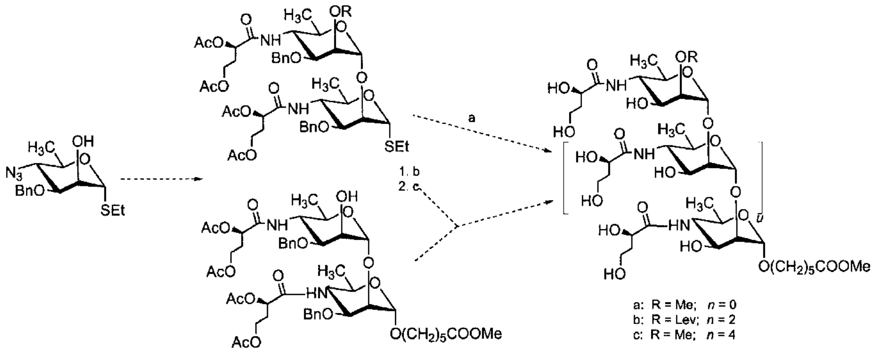


O. Winkelmann, C. Näther,
U. Lüning* 981–987

Concave Imidazolinium Salts as Precursors to Concave N-Heterocyclic Carbenes

Keywords: Betaines / Carbenes / Heterocycles / Macrocycles / Supramolecular chemistry

Stereoselective Mannosylation



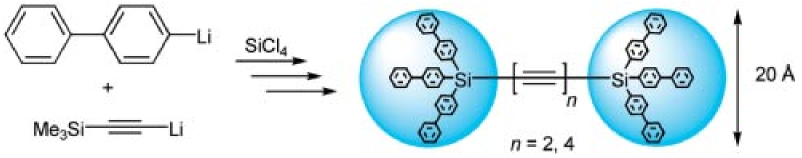
Stereoselectivity of α-mannosylation could be markedly improved by conducting the glycosylation at high temperature.

R. Adamo, P. Kováč* 988–1000

Glycosylation under Thermodynamic Control: Synthesis of the Di- and the Hexasaccharide Fragments of the O-SP of *Vibrio Cholerae* O:1 Serotype Ogawa from Fully Functionalized Building Blocks

Keywords: Carbohydrates / Oligosaccharides / Synthetic methods / Thioglycosides / Cholera vaccine

Polyyne Synthesis



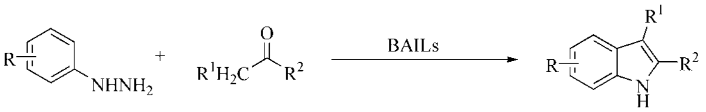
Bigger is better: Introduction of a new, sterically more demanding silyl-protecting group for polyynes can influence the packing distance between molecules, helping to increase stability.

W. A. Chalifoux, M. J. Ferguson,
R. R. Tykwinski* 1001–1006

Tris(biphenyl-4-yl)silyl-Endcapped Polyynes

Keywords: Polyynes / Alkynes / Hay coupling / Cadiot-Chodkiewicz coupling / Ethynylsilanes / Alkyne protecting groups

Green Chemistry



We describe a new method for a one-pot synthesis of the Fischer indole scaffold with the use of ecofriendly Brønsted acidic ionic liquids (BAILs) which act as catalysts as well. The BAILs could be readily reused without efficiency loss after simple treatment involving the use of only 1 equiv. of HCl for neutralization followed by filtration.

D.-Q. Xu, W.-L. Yang,
S.-P. Luo, B.-T. Wang, J. Wu,
Z.-Y. Xu* 1007–1012

Fischer Indole Synthesis in Brønsted Acidic Ionic Liquids: A Green, Mild, and Regiospecific Reaction System

Keywords: Ionic liquids / Indoles / Regiospecificity / Recycling

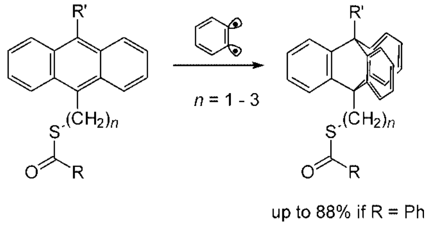
CONTENTS

Protecting Groups against Benzynes

C. Fowelin, B. Schüpbach, A. Terfort* 1013–1017

Aromatic Thioesters as Protecting Groups for Thiols Against 1,2-Didehydrobenzenes

Keywords: Didehydrobenzene / Benzyne / Protecting groups / Thiols / Triptycenes / Cycloaddition



up to 88% if R = Ph

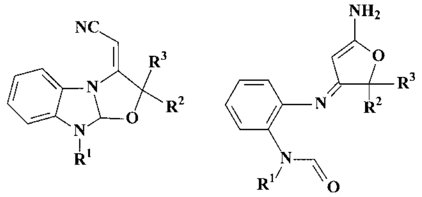
Aromatic acyl groups were identified as suitable protective groups for thiols under the reaction conditions typically used for the synthesis of triptycenes, that is, 1,2-didehydrobenzene generated in situ from 2-diazoniobenzenecarboxylate at elevated temperature. These protective groups even permit the conversion of electron-poor anthracene derivatives into the respective triptycenes.

Hydrolytic Rearrangement

B. A. Trofimov,* L. V. Andriyankova, A. G. Mal'kina, K. V. Belyaeva, L. P. Nikitina, O. A. Dyachenko, O. N. Kazheva, A. N. Chekhlov, G. V. Shilov, A. V. Afonin, I. A. Ushakov, L. V. Baikalova 1018–1025

Annelation of Benzimidazoles with α,β-Acetylenic γ-Hydroxyacid Nitriles and Hydrolytic Rearrangement of the Cycloadducts on Alumina

Keywords: Annelation / Benzimidazoles / Nitriles / Rearrangement / Formamides



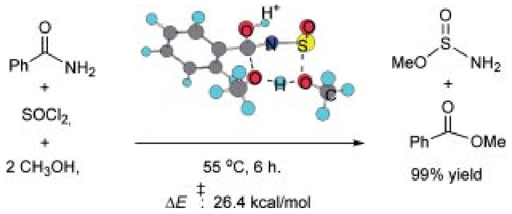
An unexpected facile hydrolytic rearrangement (Al_2O_3, room temperature) of oxazolobenzimidazoles, the cycloadducts of benzimidazole with available α,β-acetylenic γ-hydroxyacid nitriles, has been discovered. The rearrangement proceeds by the ring opening of the imidazoline and 1,3-oxazolidine cycles to assemble an iminodihydrofuran cycle attached to an arylaminoformamide moiety, which provides novel heteroatomic long-range heteroconjugated push–pull systems that may serve as building blocks in the design of drugs and optoelectronic materials.

Functional Group Interconversion

L.-C. Li, J. Ren, T.-G. Liao, J.-X. Jiang, H.-J. Zhu* 1026–1030

A Novel Direct Conversion of Primary Amides to Their Corresponding Methyl Esters

Keywords: Amides / Esters / Reaction Mechanisms / Density functional calculations



Experimental and theoretical studies on a novel direct conversion of primary amides to the corresponding methyl esters were performed. The reaction conditions are mild.