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MICROREVIEW

Palladium Catalysis

J. Muzart* 3077–3089

Procedures for and Possible Mechanisms of Pd-Catalyzed Allylations of Primary and Secondary Amines with Allylic Alcohols

Keywords: Allylic alcohol / Allylic amine / Allylation / Palladium / Promoter / Reaction mechanisms

A wide structural variety of allylic alcohols are commercially available and are abundant in nature, while allylic amines are an important class of compounds and valuable synthetic intermediates. This Microreview provides an update on the different Pd-catalyzed methods that provide allylic amines from intermolecular reactions between allylic alcohols and amines and, with personal comments, the mechanisms that have been proposed.

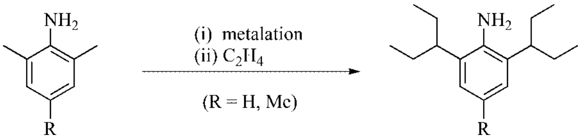
SHORT COMMUNICATION

Bulky Anilines

B. R. Steele,* S. Georgakopoulos,
M. Micha-Screttas,
C. G. Screttas 3091–3094

Synthesis of New Sterically Hindered Anilines

Keywords: Metalation / Alkylation / Amines / Steric Hindrance / Carbanions



Ring-alkylated primary, secondary and tertiary anilines are ethylated in a simple and inexpensive superbase-mediated one-pot procedure. Primary and secondary anilines are ethylated readily only at *ortho*-benzylic positions. Tertiary anilines are ethylated at all positions. Mono- or di-ethylation occurs depending on the steric constraints present.

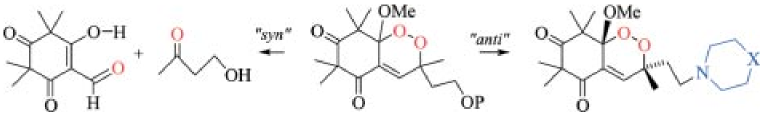
FULL PAPERS

Amino Endoperoxides

C. Givelet, V. Bernat, M. Danel,
C. André-Barrès,* H. Vial 3095–3101

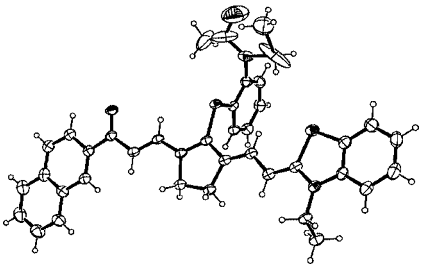
New Amino Endoperoxides Belonging to the Antimalarial G-Factor Series

Keywords: Endoperoxide / Malaria / Autoxidation / Hexacoordinate fluorosilicon complex / 1,2-Dioxetane



Differences in reactivity between two sets of diastereoisomers were observed. Amino endoperoxides were obtained in the "*anti*" series, while in the "*syn*" series an unexpected rearrangement occurred during the deprotection step. A transient 1,2-dioxetane was formed and then decomposed into an aldehyde and hydroxybutanone.

Rigidized Merocyanine Dyes



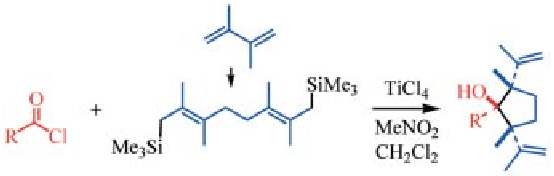
We have developed a simple and efficient method for the synthesis of rigidized mono- and bis-heptamethine merocyanines. The new dyes react easily with heterocyclic benzothiazolium compounds containing an activated methyl group to give access to new merocyanines with a lengthened polymethine chain and/or ramified by a second heterocyclic unit. X-ray crystallographic analysis reveals that the second heterocycle is incorporated via a sulfur bridge as a result of the opening of the benzothiazole ring.

L. Viteva, T. Gospodova, J. Rashkova, I. Abrahams, I. Timtcheva, S. Simova, M. R. Mazieres, J. G. Wolf* ... 3102−3114

Synthesis and Photophysical Properties of Some Rigidized Hepta- and Nonamethine Mono- and Bis(merocyanines): Ring-Opening of Quaternized 2-Methylbenzothiazole

Keywords: Merocyanine dyes / UV/Vis spectroscopy / Fluorescence spectroscopy / Structure elucidation / Benzothiazole ring cleavage

Double Allylation Reactions



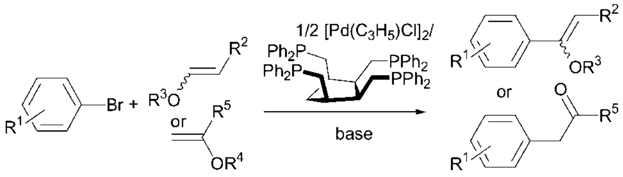
The preparation of (*E*,*E*)-2,3,6,7-tetramethyl-1,8-bis(trimethylsilyl)octa-2,6-diene and its titanium-mediated addition to aldehydes and acyl chlorides is described. Acyl chlorides afford highly substituted *meso* cyclopentanols whose structures allow a reaction mechanism for the double allylation of acyl chlorides to be described.

C. Aouf, D. El Abed, M. Ibrahim-Ouali, M. Giorgi, M. Santelli* .... 3115−3121

Stereoselective Reactions of (*E*,*E*)-2,3,6,7-Tetramethyl-1,8-Bis(trimethylsilyl)octa-2,6-diene with Aldehydes and Acyl Chlorides

Keywords: Acylation / Allylation / Carbocycles / Diastereoselectivity / Dimerisation

Palladium Catalysis



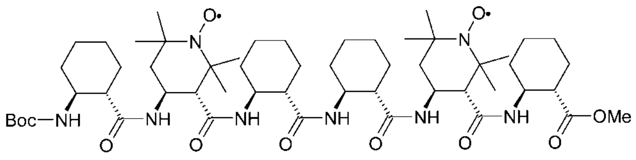
cis,*cis*,*cis*-1,2,3,4-Tetrakis(diphenylphosphanylmethyl)cyclopentane/[PdCl(C_3H_5)]$_2$ efficiently catalyses the Heck reaction of α- and β-substituted enol ethers with aryl bromides. The hydrolysis of these arylated enol esters gives very simple access to a wide variety of acetophenone or 1-arylpropanone derivatives.

A. Battace, M. Feuerstein, M. Lemhadri, T. Zair, H. Doucet,* M. Santelli* .... 3122−3132

Heck Reactions of α- or β-Substituted Enol Ethers with Aryl Bromides Catalysed by a Tetraphosphane/Palladium Complex − Direct Access to Acetophenone or 1-Arylpropanone Derivatives

Keywords: Palladium / Catalysis / Heck reaction / Disubstituted alkene / Enol ether / Aryl halide

Peptides and Nitroxides



Boc-[(1*S*,2*S*)-ACHC-(3*R*,4*S*)-β-TOAC-(1*S*,2*S*)-ACHC]$_2$-OMe

A model β-hexapeptide containing (3*R*,4*S*)-β-TOAC combined with (1*S*,2*S*)-ACHC was synthesised by solution methods and its preferred conformation (3_{14}-helix) was assessed by FTIR absorption, CD and EPR spectroscopy.

K. Wright,* M. Sarciaux, A. de Castries, M. Wakselman, J.-P. Mazaleyrat, A. Toffoletti, C. Corvaja, M. Crisma, C. Peggion, F. Formaggio, C. Toniolo* .... 3133−3144

Synthesis of Enantiomerically Pure *cis*- and *trans*-4-Amino-1-oxyl-2,2,6,6-tetramethylpiperidine-3-carboxylic Acid: A Spin-Labelled, Cyclic, Chiral β-Amino Acid, and 3D-Structural Analysis of a Doubly Spin-Labelled β-Hexapeptide

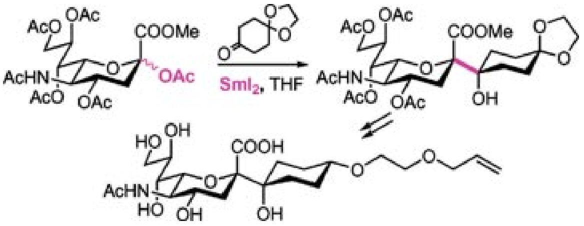
Keywords: Circular dichroism / Conformation analysis / EPR spectroscopy / β-Peptides / Nitroxide radicals

C-Sialoside Mimics

A. Malapelle, A. Coslovi, G. Doisneau, J.-M. Beau* 3145–3157

An Expeditious Synthesis of *N*-Acetylneuraminic Acid α-*C*-Glycosyl Derivatives ("α-*C*-Glycosides") from the Anomeric Acetates

Keywords: Carbohydrates / *C*-Glycosides / Reductive metallation / Samarium / Sialic acid



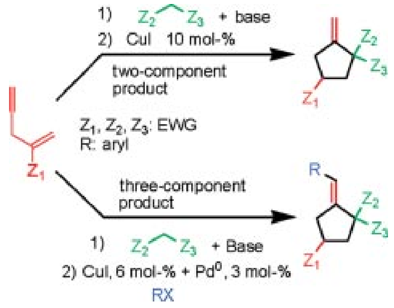
The readily available peracetylated derivatives of methyl *N*-acetylneuraminate are useful precursors of *C*-ketosides through reductive samariation at room temperature in the presence of carbonyl compounds. This procedure provides a fast route to α-*C*-ketosides of sialic acid and is remarkably efficient for coupling with cyclic ketones.

Palladium and Copper Catalysis

N. Coia, D. Bouyssi, G. Balme* 3158–3165

Efficient, Transition Metal Mediated, Sequential, Two- and Three-Component Coupling Reactions for the Synthesis of Highly Substituted Five-Membered Ring Carbocycles

Keywords: Synthetic design / Multicomponent reactions / Methylenecyclopentanes / Arylidenecyclopentanes / Copper iodide / Palladium



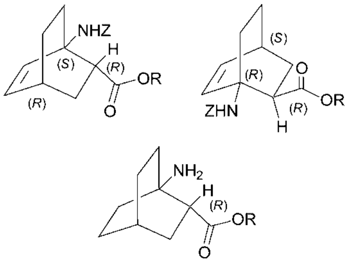
Two transition metal mediated approaches for the one-pot synthesis of a variety of highly functionalised methylenecyclopentanes and arylidenecyclopentanes from readily or commercially starting materials are reported.

β-Amino Acids

O. Songis, C. Didierjean, C. Laurent, J. Martinez, M. Calmès* 3166–3172

Asymmetric Diels–Alder Cycloaddition of 1-Aminocyclohexadiene to Chiral Acrylate: Synthesis of Enantiopure Bridgehead-Aminobicyclo[2.2.2]octane-2-carboxylic Acid Derivatives

Keywords: Asymmetric synthesis / Diels–Alder reactions / Chiral auxiliaries / Bicyclic β-amino acids / Microwave activation



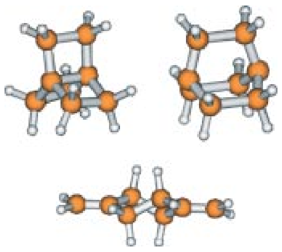
The acrylate derivative of the (*R*)-4-(3-hydroxy-4,4-dimethyl-2-oxopyrrolidin-1-yl)benzoic acid benzyl ester reacts with 1-(benzyloxycarbonylamino)cyclohexadiene under microwave irradiation in solvent-free conditions to yield [4+2] cycloadducts in good yields (91 %). The reaction proceeded with moderate *endo* selectivity (67 %) and good facial selectivity (90 %). The major cycloadducts were isolated and transformed to afford three enantiopure bicyclic β-amino acids.

Propellane Rearrangement

I. Antol, M. Eckert-Maksić,* H. Lischka, Z. B. Maksić 3173–3178

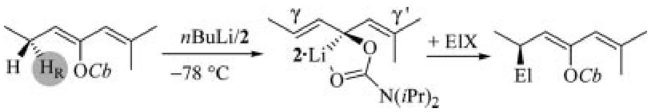
[2.2.2]Propellane Isomerization by Grob Rearrangement: An Ab Initio MR-AQCC Study

Keywords: Ab initio calculations / Grob rearrangement / Isomerization / [2.2.2]Propellane / Strained molecules



The MR-AQCC method has been employed to explore bond-stretch isomerism as well as Grob-type fragmentation in the [2.2.2]propellane system. It is shown that the open form of propellane is not a stable species and undergoes almost barrierless cage-opening to the most stable 1,4-dimethylenecyclohexane. Therefore bond-stretch isomerism does not occur in this system.

Asymmetric Synthesis



Highly stereoselective asymmetric deprotonation 1,3-dien-2-yl carbamates with the chiral base pair *n*-butyllithium/(−)-sparteine (**2**) and substitution reactions allow the flexible synthesis of substituted stereohomogeneous 1,3-dienes. Diastereo- and enantioselective homoaldol reactions with aldehydes are possible after transmetallation of the lithium species with $ClTi(NEt_2)_3$. The regioselectivity is mainly determined by steric effects.

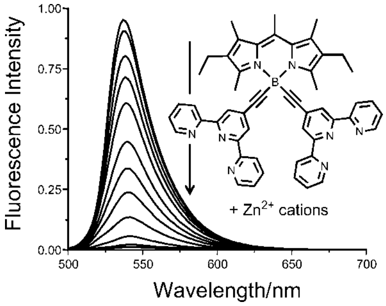
R. Bou Chedid, R. Fröhlich, B. Wibbeling, D. Hoppe* .... **3179−3190**

Enantioselective γ-Deprotonation of Alkyl-Substituted *O*-1,3-Butadien-2-yl Carbamates and Regioselective Asymmetric Homoaldol Reaction

Keywords: (−)-Sparteine / Asymmetric synthesis / Carbanions / Homoaldol reaction / Cross-coupling

Dye Photochemistry

Equipping bodipy dyes with terpyridine (terpy) units leads to two distinct types of self-assembled structures: In the presence of zinc(II) cations, the terpy units facilitate formation of the corresponding dinuclear complexes. In certain solvents, those dyes bearing B-ethynylpyrene residues assemble into π-stacked structures that fluoresce at longer wavelength.

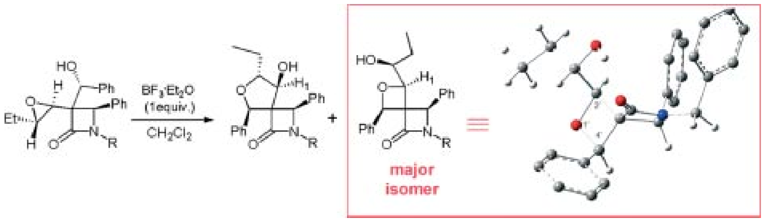


A. Harriman,* L. J. Mallon, B. Stewart, G. Ulrich, R. Ziessel* .... **3191−3198**

Boron Dipyrromethene Dyes Bearing Ancillary 2,2′:6′,2′′-Terpyridine Coordination Sites

Keywords: Dyes / Fluorescence / Photochemistry / Electron transfer / Complexation / Self assembly

Spiro-β-lactams



The intramolecular ring-opening of well-defined hydroxy epoxides allowed unprecedented classes of spiro-lactams to be obtained. The effect of the hydroxy group configuration and of the reaction temperature on the regioselective formation of five- or four-membered ring spiro derivatives was explored.

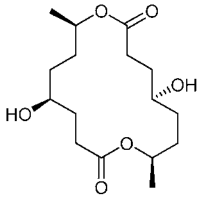
F. Benfatti, G. Cardillo,* L. Gentilucci, A. Tolomelli* .... **3199−3205**

Synthesis of Four-Membered Ring Spiro-β-lactams by Epoxide Ring-Opening

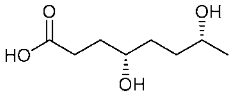
Keywords: Lactams / Oxygen heterocycles / Spiro compounds / Ring-opening / Regioselectivity

Metabolites from Fungi

Among other metabolites, tetrahydropyrenophorol and 2,3-dihydropyrenophorolic acid were isolated from the culture broth of an endophytic *Phoma* sp. The relative configuration of tetrahydropyrenophorol was confirmed by X-ray single crystal analysis and its absolute configuration determined by the solid-state TDDFT/CD methodology. Bioactivity tests were performed.



tetrahydropyrenophorol



2,3-dihydropyrenophorolic acid

K. Krohn,* U. Farooq, U. Flörke, B. Schulz, S. Draeger, G. Pescitelli, P. Salvadori, S. Antus, T. Kurtán .... **3206−3211**

Secondary Metabolites Isolated from an Endophytic *Phoma* sp. − Absolute Configuration of Tetrahydropyrenophorol Using the Solid-State TDDFT CD Methodology

Keywords: Fungal metabolites / Pyrenophorol / Tetrahydropyrenophorol / Pyrenophorolic acid / Antifungal activity / Algicidal activity / Absolute configuration / Solid-state TDDFT CD methodology / CD sector rules

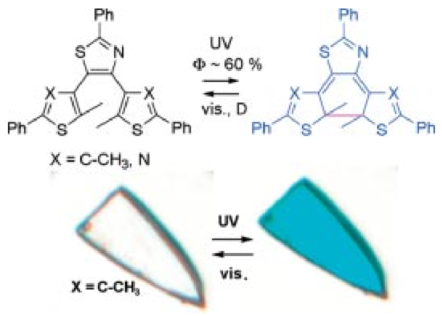
CONTENTS

Photochromic Triangle-Terarylenes

T. Nakashima, K. Atsumi, S. Kawai, T. Nakagawa, Y. Hasegawa, T. Kawai* 3212–3218

Photochromism of Thiazole-Containing Triangle Terarylenes

Keywords: Photochromism / Photochemistry / Dyes / Heterocycles



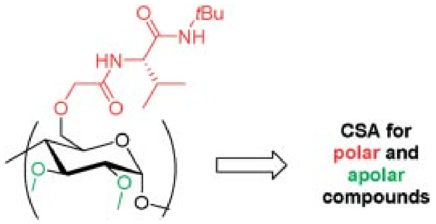
Photochromic triangle-terarylenes containing thiazolyl groups have been developed. Monothiazolyl-substituted terarylene (X = C–CH$_3$) shows photochromic reactivity in the single-crystal state. The low steric hindrance and the aromaticity of the thiazole group are responsible for the high photocoloration reactivity and the enhanced thermal stability, respectively, of the closed-ring isomers.

CSA for NMR

G. Uccello-Barretta, S. Nazzi, F. Balzano, P. A. Levkin, V. Schurig, P. Salvadori* 3219–3226

Heptakis[2,3-di-*O*-methyl-6-*O*-(L-valine-*tert*-butylamide-N^{α}-ylcarbonylmethyl)]-*β*-cyclodextrin: a New Multifunctional Cyclodextrin CSA for the NMR Enantiodiscrimination of Polar and Apolar Substrates

Keywords: Cyclodextrins / Chiral auxiliaries / NMR spectroscopy / Enantiodiscrimination / Polar and apolar chiral compounds



A new exhaustively derivatized cyclodextrin can be employed for the efficient enantiodiscrimination of chiral polar and apolar substrates by NMR spectroscopy.

Eight-Membered Ring Lactams

R. Pflantz, P. Tielmann, M. Rössle, C. Hoenke, J. Christoffers* 3227–3238

Eight-Membered-Ring Lactams – New Scaffolds for Combinatorial Chemistry Prepared by Ring-Expansion of 1,4-Diketones with Primary Amines

Keywords: Ketones / Lactams / Ring expansion / Heterocycles / Combinatorial chemistry

Eight-membered-ring lactams are prepared from 1,4-diketones and primary amines. The scope and limitations of this Bi-catalyzed reaction have been investigated. Furthermore, we explored these heterocycles as scaffolds for combinatorial libraries in a drug discovery context by synthesizing a small model amide library and testing its stability and solubility.