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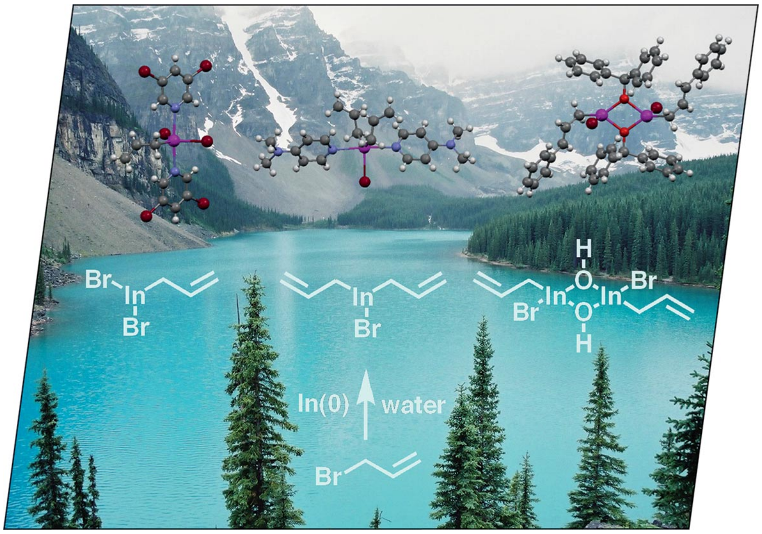
COVER PICTURE

The cover picture shows the species generated in the reductive system of allyl bromide with indium(0) in water. They include monoallylindium(III) dibromide, diallylindium(III) bromide, and allyl(μ-oxido)indium(III). These compounds were characterized on the basis of X-ray analysis. The allylindium compounds showed nucleophilicity towards carbonyl compounds with different reactivities. Details are discussed in the Short Communication by M. Yasuda, A. Baba et al. on p. 5359ff.



CONTENTS

MICROREVIEW

4-Hydroxy-2-cyclopentenones

S. P. Roche,* D. J. Aitken* 5339–5358

Chemistry of 4-Hydroxy-2-cyclopentenone Derivatives

Keywords: Natural products / Carbocycles / Enones / Stereoselective synthesis

Key players in the game for decades! The 4-hydroxy-2-cyclopentenone moiety is a highly valued building block, used in a large variety of complex molecule assemblies. This review highlights numerous convenient preparative methods in racemic and enantioselective fashion and illustrates access to complex frameworks from this core structure.

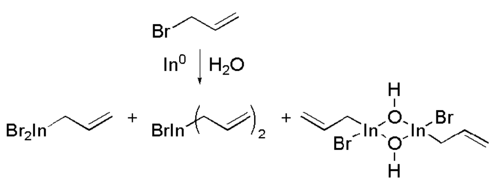
SHORT COMMUNICATIONS

Allylindium in Water

M. Yasuda,* M. Haga, Y. Nagaoka, A. Baba* 5359–5363

Characterization of the Nucleophilic Allylindium Species Generated from Allyl Bromide and Indium(0) in Aqueous Media

Keywords: Indium / Allylation / Aqueous media / X-ray analysis / Reduction



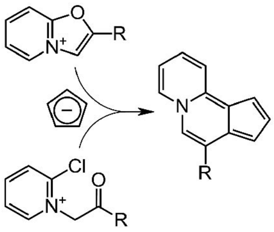
Allylindium species were generated from allylic halide/In^0 in aqueous media. Monoallylindium dibromide, diallylindium bromide, and indium alkoxide are real species in the reaction course. They were characterized by X-ray crystallography, and their structures and reactivities were revealed.

Unusual Pseudoazulenes

P. V. Gormay, V. B. Rybakov, E. V. Babaev* 5364–5368

Cyclopenta[*a*]quinolizine: A Novel Pseudoazulene with a Bridgehead Nitrogen Atom

Keywords: Nitrogen heterocycles / Fused-ring systems / Lithium / Aromaticity / Ring transformations



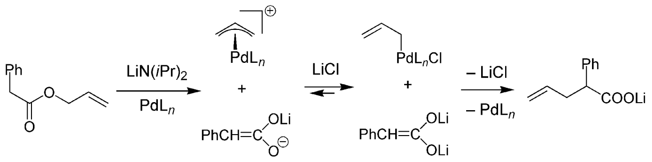
Cyclopenta[*a*]quinolizines, a new family of tricyclic pseudoazulenes, were prepared from cyclopentadienyllithium and oxazolo[3,2-*a*]pyridinium or 2-chloro-*N*-phenacyl pyridinium salts. X-ray data and spectroscopic analysis of the novel ring system were examined and discussed.

Reaction Mechanism

M. Braun,* P. Meletis, W. Schrader 5369–5372

Evidence for a Non-Concerted, Dissoziative Mechanism of the Palladium-Catalyzed "Enolate Claisen Rearrangement" of Allylic Esters

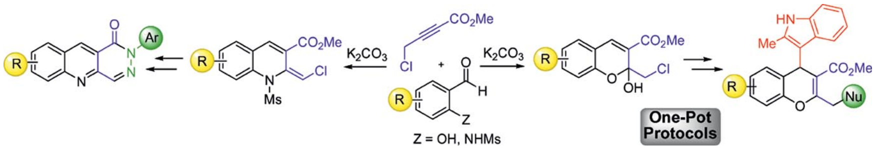
Keywords: Allylation / Enantioselectivity / Ion pairs / Lithium / Homogeneous catalysis



Dissociation into carboxylic-acid dianions and palladium complexes rather than a concerted [3,3]-sigmatropic rearrangement occurs upon exposure of the lithium enolate derived from allyl phenylacetate to catalytic Pd^0. Only after the fragments escaped from the solvent cage, they combine under carbon-carbon-bond formation and give the allylated carboxylic acid.

FULL PAPERS

Heterocyclic Synthesis



Methyl 4-chloro-2-butynoate was used in a modified Morita–Baylis–Hillman reaction with salicylic aldehydes. The chlorine atom in the alkynoate moiety remains in the adduct as a reactive site. Further one-pot derivatization leads to a variety of substituted chromenes and quinolines.

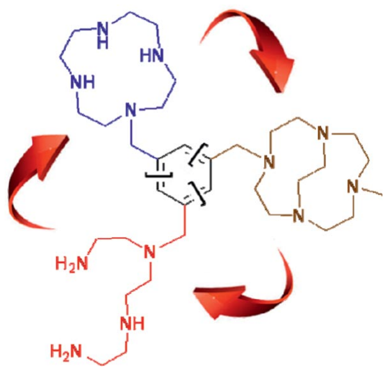
D. Bello, J. Ruiz-Rodríguez, F. Albericio,* R. Ramón, R. Lavilla* **5373–5379**

Streamlined Access to Functionalized Chromenes and Quinolines using Domino Reactions of Salicylic Aldehydes and Methyl 4-Chloro-2-butynoate

Keywords: Synthetic methods / Cyclization / Domino reactions / Nitrogen heterocycles / Isomerization

Tritopic Ligands

The bisaminal route leads easily to three tetraamine-based trimeric ligands, involved afterward in host–guest investigations with triphosphate and nucleotides anions. Potentiometric and NMR spectroscopic investigations clearly show different acid–base properties leading to variable complexation processes in aqueous solution especially with ATP and triphosphate.

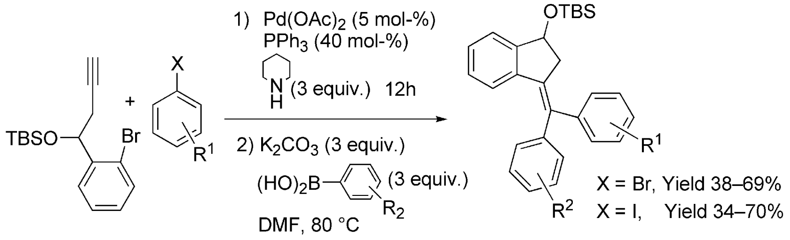


A.-S. Delépine, R. Tripier,* M. Le Baccon, H. Handel **5380–5390**

From Flexible to Constrained Tris(tetraamine) Ligands: Synthesis, Acid–Base Properties, and Structural Effect on the Coordination Process with Nucleotides

Keywords: Amines / Macrocycles / Proton sponges / Anions / Nucleotides / N ligands

Tandem Reaction



A novel Sonogashira/carbopalladation cyclization/Suzuki coupling cascade combination for the synthesis of various indene derivatives in the presence of a single palladium source by using protected homopropargyl alcohol is described.

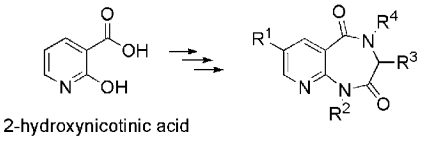
X. Wang, L. Liu,* W. Chang, J. Li* **5391–5396**

Sequential Sonogashira/Carbopalladative Cyclization/Suzuki Reactions Catalyzed by a Single Palladium Source by Using Protected Homopropargyl Alcohol

Keywords: Alkynes / Palladium / Cross-coupling / Cyclization / Domino reactions

Pyridodiazepinediones

3,4-Dihydro-1*H*-pyrido[2,3-*e*][1,4]diazepine-2,5-dione compounds were prepared by using an Ugi strategy starting from easily accessible materials (see scheme). 2-Isocyanophenylbenzoate was used as the convertible isocyanide in this multicomponent reaction.



A. M. Van den Bogaert, J. Nelissen, M. Ovaere, L. Van Meervelt, F. Compernolle, W. M. De Borggraeve* **5397–5401**

Synthesis of Pyridodiazepinediones by Using the Ugi Multicomponent Reaction

Keywords: Ugi reaction / Pyridodiazepinediones / NMR spectroscopy / Multicomponent reactions

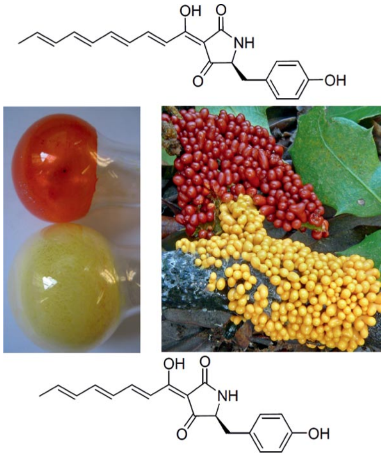
CONTENTS

Natural Product Synthesis

N. Riache, C. Bailly, A. Deville,
L. Dubost, B. Nay* ....,,,,,,,...... 5402−5408

Total Synthesis of Tyrosine-Derived Tetramic Acid Pigments from a Slime Mould

Keywords: Dyes/pigments / Total synthesis / Wittig reactions / Multicomponent reactions / Antibiotics



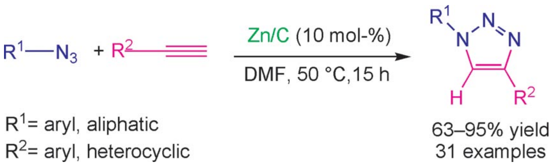
The picture on the right shows the slime mould *Leocarpus fragilis* at two maturation stages characterized by different pigmentation. The left picture shows the red (top structure) and yellow (bottom structure) synthetic pigments in flasks. These pigments are polyenoyl tetramic acids, the synthesis of which was undertaken using a one-pot process.

Heterogeneous Catalysis

X. Meng, X. Xu, T. Gao,
B. Chen* .... 5409−5414

Zn/C-Catalyzed Cycloaddition of Azides and Aryl Alkynes

Keywords: Zinc / Cycloaddition / Heterogeneous catalysis / Azides / Click chemistry



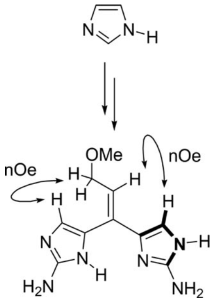
1,4-Disubstituted 1,2,3-triazoles and 1,4,5-trisubstituted 1,2,3-triazoles were easily obtained by a novel Zn/C-catalyzed [3+2] cycloaddition between organic azides and alkynes.

Marine Natural Products

N. Jacobi, T. Lindel* .... 5415−5425

Assembly of the Bis(imidazolyl)propene Core of Nagelamides C and S by Double Grignard Reaction

Keywords: Natural products / Alkaloids / Nitrogen heterocycles / Nagelamides



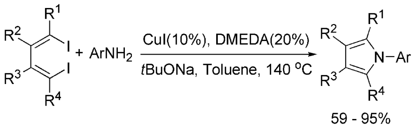
Bis(2-aminoimidazolyl)propenes can be synthesized via double Grignard reaction starting from 4-iodoimidazoles, followed by introduction of the amino groups.

Double Vinylation of Amines

Q. Liao, L. Zhang, F. Wang, S. Li,
C. Xi* .... 5426−5431

Copper-Catalyzed Double *N*-Vinylation of Aromatic Amines: An Efficient Synthesis of Various Substituted *N*-Arylpyrroles

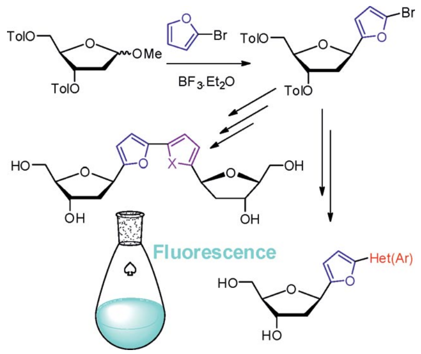
Keywords: Nitrogen heterocycles / Amines / Copper iodide / Vinylation



Efficient synthetic copper-catalyzed reactions leading to various substituted *N*-arylpyrroles have been developed. This approach makes use of 1,4-diiodo-1,3-dienes and aromatic amines and proceed via inter- and intramolecular *N*-vinylations of amines.

C-Nucleosides

Fluorescent 5-(hetero)arylfuran *C*-2′-deoxyribonucleosides were prepared by Friedel–Crafts C-glycosidation of 2-bromofuran followed by cross-coupling reactions. Novel covalent nucleoside pairs were prepared by borylation and cross-coupling.



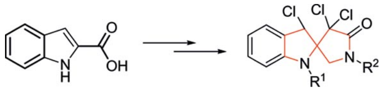
J. Bárta, L. Slavětínská, B. Klepetářová, M. Hocek* 5432–5443

Modular Synthesis of 5-Substituted Furan-2-yl *C*-2′-Deoxyribonucleosides and Biaryl Covalent Base-Pair Analogues

Keywords: Alkylation / Cross-coupling / C-glycosides / DNA structures / Nucleosides

Nitrogen Heterocycles

Spiro[2-oxoindole-pyrrolidines] can be synthesized in a straightforward manner from indole-2-carboxylic acid. The key reaction is a Kharasch radical cyclization reaction of trichloroacetylated precursors.

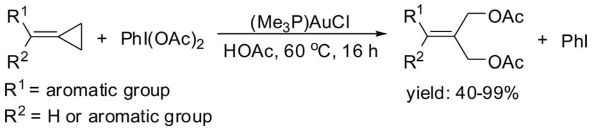


S. Van der Jeught, N. De Vos, K. Masschelein, I. Ghiviriga, C. V. Stevens* 5444–5453

Kharasch-Type Cyclizations of 2-Substituted Indole Derivatives Surprisingly Lead to Spiroindoles

Keywords: Nitrogen heterocycles / Spiro compounds / Cyclization / Radicals

Gold-Catalyzed Diacetoxylation



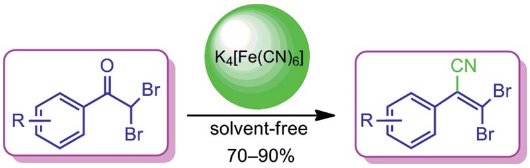
A gold-catalyzed diacetoxylation of methylenecyclopropanes under mild conditions involving a Au^{I}/Au^{III} catalytic cycle is described.

D.-H. Zhang, L.-Z. Dai, M. Shi* 5454–5459

C(sp^3)–C(sp^3) Bond Breaking in Methylenecyclopropanes Involving a Au^{I}/Au^{III} Catalytic Cycle

Keywords: Gold / C–C bond activation / Methylenecyclopropanes

Eco-Friendly Cyanide Source



A chemoselective route for the synthesis of 2-aryl-3,3-dibromoacrylonitriles by solvent-free cyanation of α,α-dibromoacetophenones by using potassium hexacyanoferrate(II) as an eco-friendly cyanide source is developed. The merits of this procedure include avoiding the use of a strong toxic cyanide source, a catalyst, and volatile organic solvents and the high yields of the products.

Z. Zhao, Z. Li* 5460–5463

Solvent-Free Chemoselective Cyanation of α,α-Dibromoacetophenones Using Potassium Hexacyanoferrate(II) as an Eco-Friendly Cyanide Source

Keywords: Cyanides / Nucleophilic addition / Iron / Sustainable chemistry

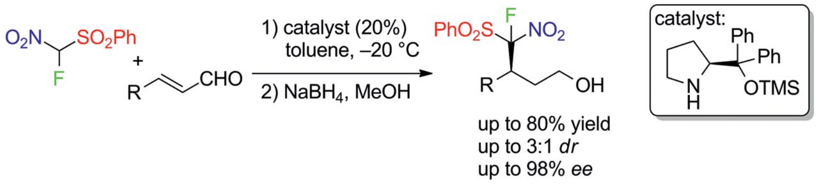
CONTENTS

Asymmetric Organocatalysis

M. Kamlar, N. Bravo, A.-N. R. Alba,
S. Hybelbauerová, I. Císařová, J. Veselý,*
A. Moyano,* R. Rios* 5464–5470

Highly Enantioselective Addition of 1-Fluoro-1-nitro(phenylsulfonyl)methane to α,β-Unsaturated Aldehydes

Keywords: Fluorine / Organocatalysis / Aldehydes / Enantioselectivity / Diastereoselectivity / Michael addition



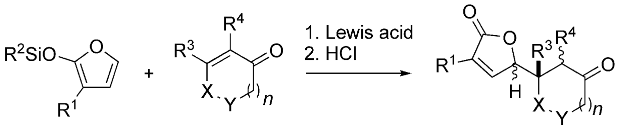
An asymmetric organocatalytic Michael addition of 1-fluoro-1-nitro(phenylsulfonyl)methane to aromatic or aliphatic α,β-unsaturated aldehydes is reported. The reaction is efficiently catalyzed by commercially available chiral pyrrolidine derivatives and gives the corresponding adducts in moderate to good yields, with moderate diastereoselectivities and excellent enantioselectivities (up to 99:1 *er*).

Mukaiyama–Michael Reaction

L. Chabaud,* T. Jousseaume, P. Retailleau,
C. Guillou* 5471–5481

Vinylogous Mukaiyama–Michael Reactions between 2-Silyloxyfurans and Cyclic Enones or Unsaturated Oxo Esters

Keywords: Homogeneous catalysis / Michael addition / Mukaiyama reaction / Diastereoselectivity / Cyclic enones



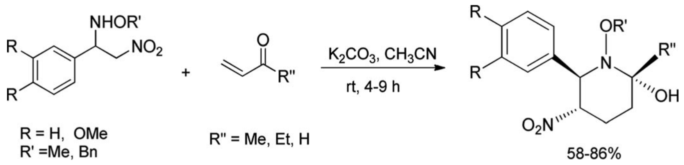
Lewis acids were shown to catalyze vinylogous Mukaiyama–Michael reactions between 2-(trialkysilyloxy)furans and a range of cyclic enones and α,β-unsaturated oxo esters. The reactions usually proceed in high yields and with modest to good levels of diastereocontrol.

Multicomponent Synthesis

M. Á. López-García, I. Maya,
J. G. Fernández-Bolaños,* G. Bosica,
R. Ballini* 5482–5488

1-Alkoxyamino-2-nitroalkanes as Key Building Blocks for a Chemo- and Diastereoselective Synthesis of a New Type of Polyfunctionalized *N*-Alkoxypiperidine

Keywords: Michael addition / Nitrogen heterocycles / Diastereoselectivity / Nitroalkanes / Alkoxyamines



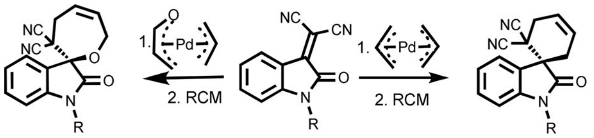
An unprecedented conversion of β-nitrostyrenes into a new class of functionalized *N*-alkoxy-2-hydroxypiperidines by a base-catalyzed, two-step procedure involving 1-alkoxyamino-2-nitroalkanes intermediates, is described. Although three stereogenic centers are formed, only one diastereoisomer is detected.

Heterocyclic Chemistry

S. C. George, J. John, S. Anas, J. John,
Y. Yamamoto, E. Suresh,
K. V. Radhakrishnan* 5489–5497

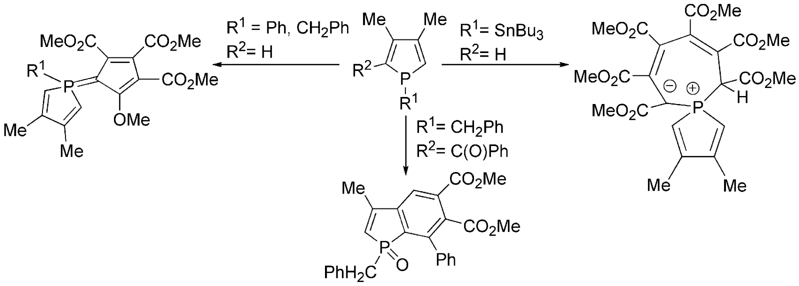
Palladium-Catalyzed Bis-Functionalization of Isatylidenes: A Facile Route towards Spiro-Indol-2-ones

Keywords: Nitrogen heterocycles / Spiro compounds / Palladium / Allylation / Ring closing metathesis



Quaternizing and twisting: Amphiphilic bis-π-allylpalladium and related intermediates were effectively utilized for the quaternization of C-3 position of oxindole towards disubstituted functionalized indol-2-ones. These products were subjected to ring-closing metathesis towards the synthesis of spiro[cyclohexene-1,3′-indol]-2′-ones and spiro[oxep-5-ene-2,3′-indol]-2′-ones.

Phosphorus Heterocycles



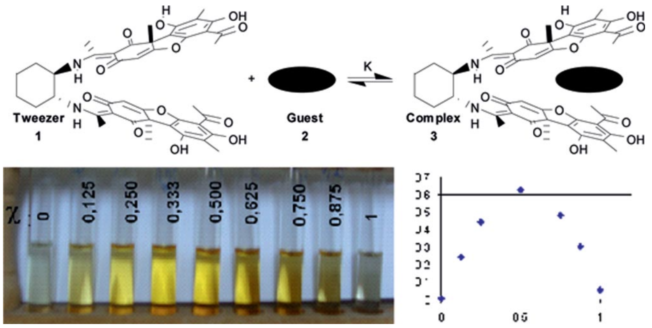
C. Huang, H. Liu, J. Zhang, Z. Duan,*
F. Mathey* **5498–5502**

Dimethyl Acetylenedicarboxylate and Phospholes: A Variety of Reaction Pathways

Keywords: Phosphorus heterocycles / Cycloaddition / Ylides / Structure elucidation

The reaction of phospholes with DMAD heavily depends on the substitution pattern of the ring. With 1-phenyl- or 1-benzyl-3,4-dimethylphosphole, a cyclopentadienylidenephosphorane is obtained. With 1-stannylphosphole, a seven-membered ring is produced. With 1-phenyl-2-benzoylphosphole, a [4+2] cycloaddition takes place on the dienol tautomer of the unsaturated ketone and a phosphindole is the result.

Molecular Tweezers



B. Legouin, M. Gayral, P. Uriac,
J.-F. Cupif, N. Levoin, L. Toupet,
P. van de Weghe* **5503–5508**

Molecular Tweezers: Synthesis and Formation of Host–Guest Complexes 💻

Keywords: Supramolecular chemistry / Host-guest systems / Pi interactions / Molecular recognition

New chiral molecular tweezers were synthesized. The formation of host–guest complexes with electron-poor aromatic derivatives and determination of the association constants with the help of ^{1}H NMR titrations is discussed.

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* Author to whom correspondence should be addressed.

💻 Supporting information on the WWW (see article for access details).