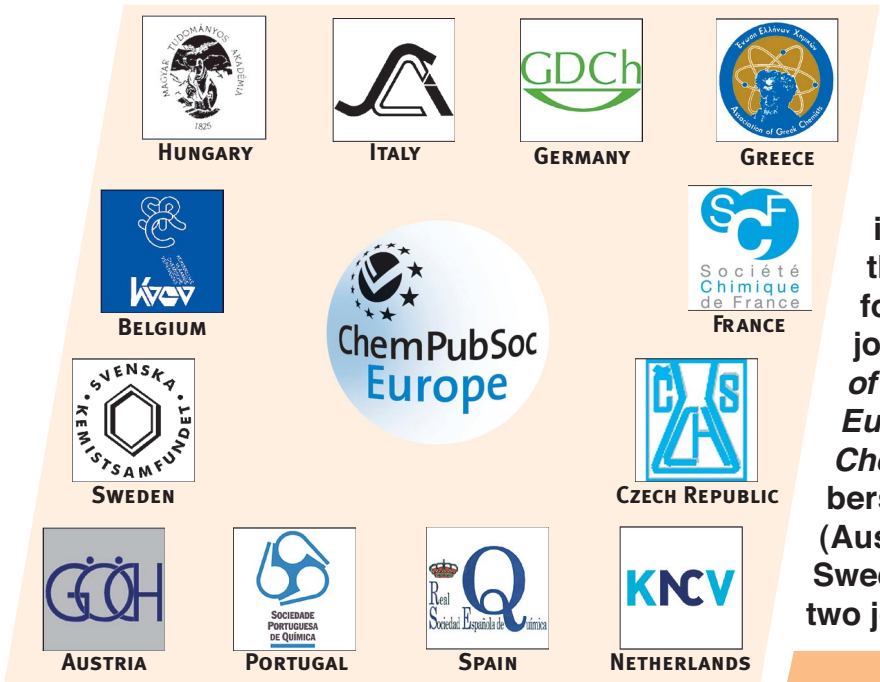
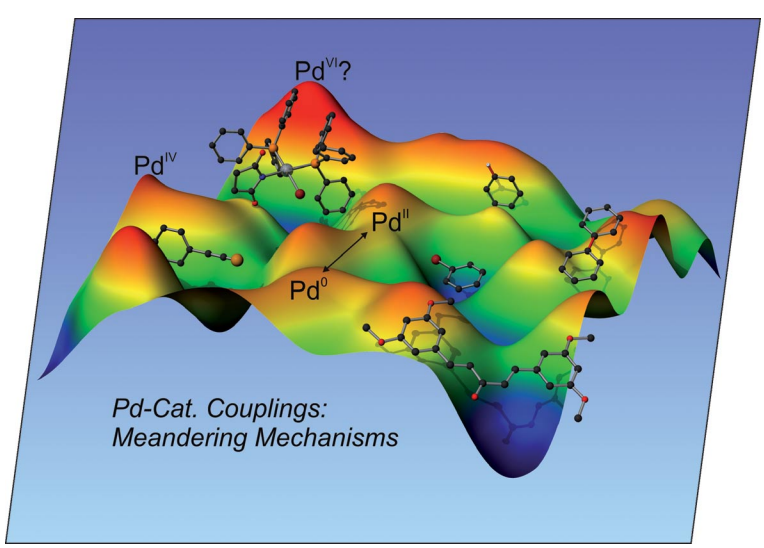


A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

The cover picture shows a hypothetical energy surface highlighting the multitude of reaction manifolds and pathways that are accessible in Pd-catalysed couplings. Acknowledgement: The image was produced by Dr. A. C. Whitwood (Computing Officer and X-ray Crystallographer, York, UK) using POV-Ray™ (ver. 3.6); structures of the Pd complex and dibenzylideneacetone derivative were based on crystal structures. Details are presented in the Microreview by G. P. McGlacken and I. J. S. Fairlamb on p. 4011ff.



CONTENTS

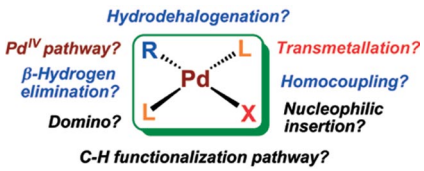
MICROREVIEW

Cross-Coupling Mechanisms

G. P. McGlacken,*
I. J. S. Fairlamb* 4011–4029

Palladium-Catalysed Cross-Coupling and Related Processes: Some Interesting Observations That Have Been Exploited in Synthetic Chemistry

Keywords: Palladium / Cross-coupling / Homogeneous catalysis / Reaction mechanisms / Side reactions



A subjective selection of Pd-catalysed cross-coupling processes are described. The primary objective of this Microreview is to highlight key observations made in this popular area of research, which have either been serendipitously discovered or identified through detailed mechanistic studies.

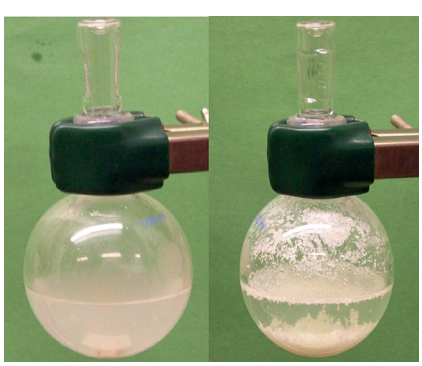
SHORT COMMUNICATIONS

Aqueous Wittig Chemistry

J. McNulty,* P. Das 4031–4035

Highly Stereoselective and General Synthesis of (*E*)-Stilbenes and Alkenes by Means of an Aqueous Wittig Reaction

Keywords: Alkenes / Chemoselectivity / Phosphorus / Water chemistry / Wittig reactions



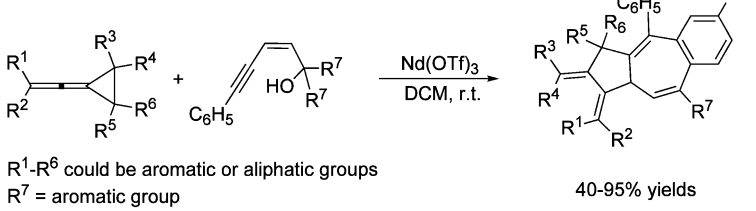
The chemoselective formation and Wittig reaction of semi-stabilized trialkylphosphane-derived ylides in water with aromatic, and enolizable aldehydes provides a new stereoselective, environmentally benign route to valuable (*E*)-stilbenes and alkenes.

Tricyclic Frameworks

L.-F. Yao, M. Shi* 4036–4040

$Nd(OTf)_3$-Catalyzed Cascade Reactions of Vinylidenecyclopropanes with Enynol: A New Method for the Construction of the 5–7–6 Tricyclic Framework and Its Scope and Limitations

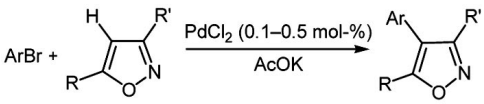
Keywords: Lewis acids / Small ring systems / Fused-ring systems / Enynes



Compounds containing a 5–7–6 tricyclic framework could be obtained in good yields from readily accessible starting materials vinylidenecyclopropanes **1** and enynols **2a–c** under mild conditions in the presence of $Nd(OTf)_3$.

FULL PAPERS

Catalysis



A wide variety of 4-arylisoxazole derivatives can be prepared very easily in good yields by the direct 4-arylation of 3,5-disubstituted isoxazole derivatives using aryl bromides. With most substrates, this reaction can be performed by using as little as 0.1−0.5 mol-% of ligand-free $PdCl_2$ as the catalyst.

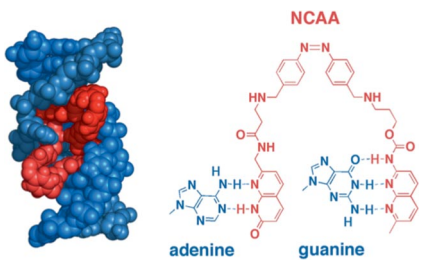
Y. Fall, C. Reynaud, H. Doucet,* M. Santelli* ..... 4041−4050

Ligand-Free-Palladium-Catalyzed Direct 4-Arylation of Isoxazoles Using Aryl Bromides

Keywords: Atom-economy / Homogeneous catalysis / C−H activation / Heteroaryl halides / Isoxazole / Palladium

Photoswichable DNA-Binding Ligand

We have established an efficient synthetic route for photoswitchable DNA-binding ligands incorporating two different base-recognition elements. A novel photoswitchable DNA-binding ligand, **NCAA** (naphthyridine-carbamate-azaquinolone-functionalized azobenzene), recognizes DNA duplexes containing a CAG/CAG sequence, and the binding is reversibly controlled by external light stimuli.



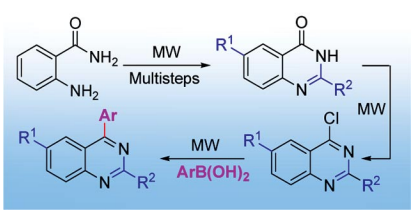
C. Dohno, T. Yamamoto, K. Nakatani* ..... 4051−4058

Photoswitchable Unsymmetrical Ligand for DNA Hetero-Mismatches

Keywords: DNA / Mismatch / Azobenzenes / Photoswitch / Nanostructures / Ligand design

Microwave-Assisted Cross-Coupling

The synthesis of new quinazolines substituted at the 4-position by a Suzuki−Miyaura coupling reaction is reported. This synthesis was optimized under microwave irradiation conditions.



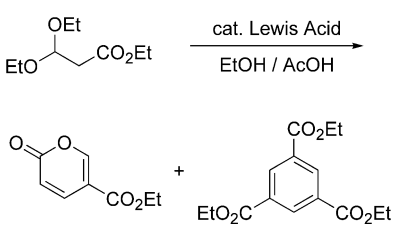
Y. Kabri, A. Gellis, P. Vanelle* ..... 4059−4066

Synthesis of Original 2-Substituted 4-Arylquinazolines by Microwave-Irradiated Suzuki−Miyaura Cross-Coupling Reactions

Keywords: Boron / Microwave chemistry / Cross-coupling / Nitrogen heterocycles

Coumalate Synthesis

Acetals like 3,3-diethoxypropionate bearing electron-withdrawing groups were found to undergo cyclodimerization and cyclotrimerization in the presence of Lewis acids to give coumalates and 1,3,5-trisubstituted benzenes. The selectivity of these products depended on the Lewis acids employed.



S. Maeda, Y. Obora, Y. Ishii* ..... 4067−4072

Selective Cyclodimerization and Cyclotrimerization of Acetals Bearing Electron-Withdrawing Groups Catalyzed by Lewis Acids

Keywords: Cyclodimerization / Cyclotrimerization / Acetals / Lewis acids / Annulation

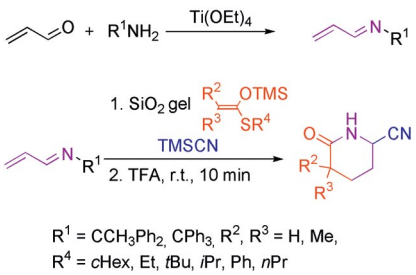
CONTENTS

N-Allylideneamines

I. Mizota, Y. Matsuda, I. Hachiya, M. Shimizu* 4073–4084

N-Allylideneamines Derived from Acrolein: Synthesis and Use as Acceptors of Two Nucleophiles

Keywords: Amines / Allylic compounds / Nucleophilic addition / Regioselectivity / Amino acids



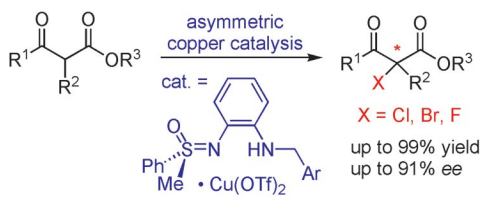
N-Allylideneamines have been synthesized from acrolein and bulky primary amines in the presence of $Ti(OEt)_4$. 1,4- and 1,2-Double nucleophilic addition of ketene silyl (thio)acetals and trimethylsilyl cyanide to *N*-allylideneamines gave amino acids and/or valerolactams.

Enantioselective Halogenation

M. Frings, C. Bolm* 4085–4090

Enantioselective Halogenation of β-Oxo Esters Catalyzed by a Chiral Sulfoximine–Copper Complex

Keywords: Asymmetric catalysis / Copper / Halogenation / Sulfoximines / Enantioselectivity



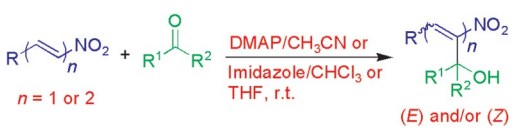
Enantioselective halogenation reactions catalyzed by chiral sulfoximine–copper complexes provided products with up to 91% *ee*. The influence of the catalyst structure, reaction conditions, and halogen source has been studied.

α-Hydroxyalkyl Nitroalkenes

I. Deb, P. Shanbhag, S. M. Mobin, I. N. N. Namboothiri* 4091–4101

Morita–Baylis–Hillman Reactions Between Conjugated Nitroalkenes or Nitrodienes and Carbonyl Compounds

Keywords: Alkenes / α-Hydroxyalkylation / C–C coupling / Nitroalkenes / Morita–Baylis–Hillman (MBH) reaction / Synthetic methods



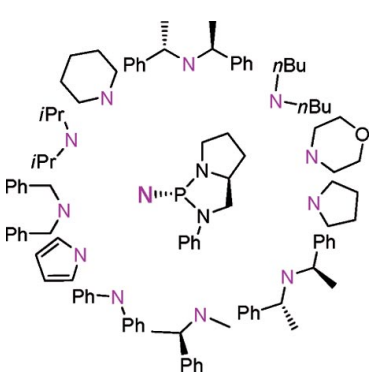
α-Hydroxyalkylation of nitroalkenes or nitrodienes with various carbonyl compounds under mild nucleophilic Lewis base conditions has been performed. The superior catalytic roles played by DMAP and imidazole, the selectivities observed in these reactions, and the formation of certain unusual products have been explained.

P-Chiral Ligands

K. Barta, M. Hölscher, G. Franciò,* W. Leitner* 4102–4116

Modular Synthesis of Novel Chiral Phosphorous Triamides Based on (*S*)-*N*-(Pyrrolidin-2-ylmethyl)aniline and Their Application in Asymmetric Catalysis

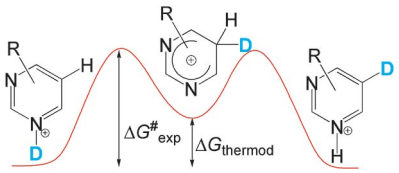
Keywords: P ligands / Aminophosphanes / Hydrovinylation / Michael addition / Asymmetric catalysis



New P-chiral phosphorous triamides based on (*S*)-*N*-(pyrrolidin-2-ylmethyl)aniline were prepared in high diastereomeric purity by modular synthetic procedures. These ligands were evaluated in the Cu-catalysed Michael addition reaction of Et_2Zn to cyclohex-2-enone and in the asymmetric Ni-catalysed hydrovinylation of styrene. Conversions and chemoselectivities were good, enantioselectivities up to 60%.

Pyrimidine *C*-Protonation

The proton-to-deuterium exchange reaction of the hydrogen atom at the 5-position of pyrimidine derivatives has been studied. Under acidic conditions, the mechanism involves protonation at the 5-position (forming an σ complex), whereas under alkaline conditions, tautomers with an sp^3-hybridised carbon atom at the 5-position may be present.

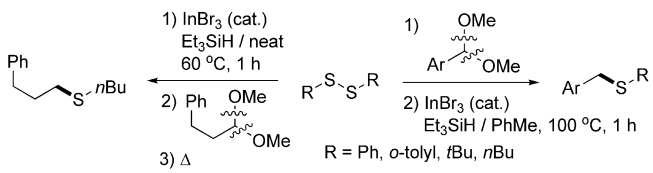


M. Dračínský, A. Holý, P. Jansa, S. Kovačková, M. Buděšínský* 4117–4122

Isotopic Exchange of Hydrogen at C-5 in Pyrimidine Derivatives: Tautomers with an sp^3-Hybridised C-5 Carbon Atom

Keywords: Density functional calculations / Protonation / Nitrogen heterocycles / NMR spectroscopy / Isotopes

Sulfide Synthesis



A facile and direct synthesis of sulfide derivatives using acetals and ketals with disulfides and an $InBr_3$–Et_3SiH reducing system is described herein.

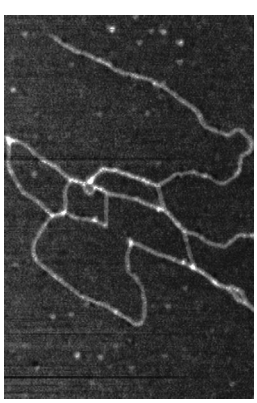
N. Sakai,* K. Moritaka, T. Konakahara 4123–4127

A Novel Approach to the Practical Synthesis of Sulfides: An $InBr_3$–Et_3SiH Catalytic System Promoted the Direct Reductive Sulfidation of Acetals with Disulfides

Keywords: Sulfides / Reduction / Acetals / Indium / Silanes

Supramolecular Self-Assembly

Cofacial reversible self-assembly of a *meso*-substituted octaphosphonate porphyrin with cyclam yields micrometer-long nanowires with heights of about 1–1.5 nm; the resulting wires were characterized by UV/Vis absorption, emission and atomic force microscopy and transmission electron microscopy.

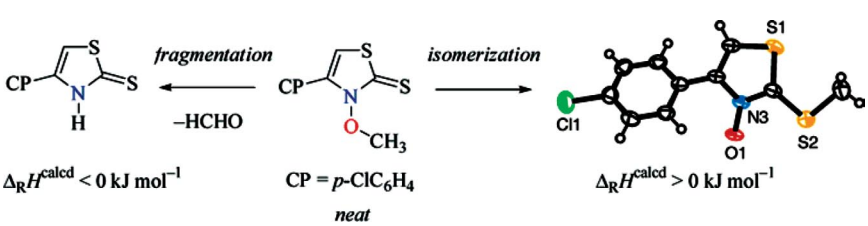


Shesh. V. Bhosale,* M. B. Kalyankar, S. J. Langford, Sid. V. Bhosale,* R. F. Oliver 4128–4134

Synthesis and Supramolecular Properties of a Novel Octaphosphonate Porphyrin

Keywords: Porphyrinods / Self-assembly / Supramolecular chemistry / Nitrogen heterocycles / Nanostructures / Electron microscopy

Reactivity of Thiazolethiones



Distinguished neat 3-alkoxy-4-(*p*-chlorophenyl)-1,3-thiazole-2(3*H*)-thiones showed unexpected background reactivity via (i) isomerization (ii) rearrangement, or (iii) fragmentation. Selectivity was guided by the nature of the 3-alkoxy substituent.

J. Hartung,* K. Daniel, U. Bergsträßer, I. Kempter, N. Schneiders, S. Danner, P. Schmidt, I. Svoboda, H. Fuess 4135–4142

Lessons of 3-Alkoxy-4-(*p*-chlorophenyl)-1,3-thiazole-2(3*H*)-thione Chemistry Learned from Structural Investigations

Keywords: Radicals / Heterocycles / Isomerization / Molecular modeling / Rearrangement / Sulfur

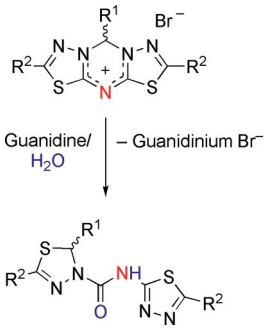
CONTENTS

Novel Heterocyclic Ureas

M. Schulz, M. Michnacs, H. Görls, E. Anders* 4143–4148

Synthesis of Unusually Substituted Ureas Starting from Bis(1,3,4-thiadiazolo)-1,3,5-triazinium Halides via Oxo-imidothioate Zwitterions

Keywords: Rearrangement / Nitrogen heterocycles / Sulfur heterocycles / Nucleophilic addition



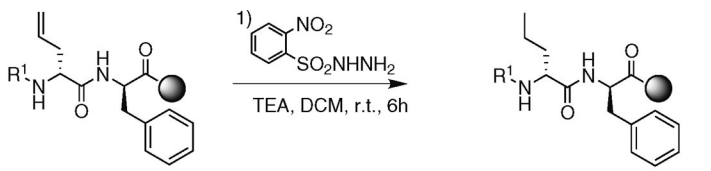
Bis(1,3,4-thiadiazolo)-1,3,5-triazinium halides form novel heterocyclic-substituted carboxamide derivatives in aqueous solution. The reaction proceeds by the nucleophilic attack of hydroxide ions generated by guanidines. The use of the carboxamides as ligands is shown by the formation of a dinuclear copper complex.

Solid-Phase Hydrogenation

M. I. García-Aranda, R. González-Muñiz, M. T. García-López, M. J. Pérez de Vega* 4149–4157

Diimine Reduction of C=C Double Bonds: Scope and Limitations of the Application to Solid-Phase Peptide Synthesis

Keywords: Solid-phase synthesis / Hydrogenation / Alkenes / Peptides / Reduction



R^1 = $COCH_3$, Boc, $COC(CH_3)_2$-N_3, $COCH_2Cl$, Fmoc-Xaa
Xaa = Lys(Boc), Lys(Alloc), Asp(O*t*Bu), Asp(OAll), Asp(OBz), Ser(*t*Bu), Ser(Bz), Trp, Met

Experiments were performed to prove that 2-nitrobenzenesulfonohydrazide is a very useful tool for the on-resin reduction of olefins embedded in peptide derivatives, being compatible with common protecting groups and different resin types.

Synthetic Methodology

G. Kumaraswamy,* D. Rambabu, N. Jayaprakash, G. V. Rao, B. Sridhar 4158–4164

Cu- and Mo-Catalysed Expedient Synthesis of Alkynyl-Substituted Derivatives of 1,2-Dihydropyridines, -quinolines and -isoquinolines

Keywords: Nitrogen heterocycles / Alkynes / Copper / Molybdenum

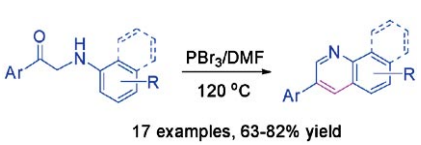
1,2-Dihydroisoquinolines, -quinolines and -pyridines have been prepared by highly efficient Cu- and Mo-catalysed regioselective addition of metallo-alkynyl reagents to activated isoquinolines, quinolines and pyridines.

Quinoline Synthesis

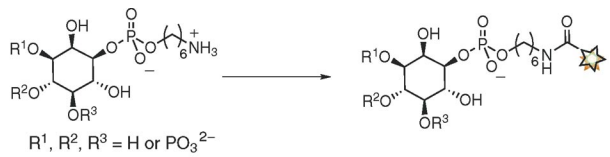
Y. Wang, X. Xin, Y. Liang, Y. Lin,* R. Zhang, D. Dong* 4165–4169

A Facile and Efficient One-Pot Synthesis of Substituted Quinolines from α-Arylamino Ketones Under Vilsmeier Conditions

Keywords: Heterocycles / Cyclization / Aromatization / Amino ketones / Formylation / Vilsmeier–Haack reaction



A one-pot synthesis of substituted quinolines has been developed from α-arylamino ketones by sequential Vilsmeier–Haack reaction, intramolecular cyclization and aromatization reactions.



D. Gong, H. E. Bostic, M. D. Smith, M. D. Best* 4170–4179

Synthesis of Modular Headgroup Conjugates Corresponding to All Seven Phosphatidylinositol Polyphosphate Isomers for Convenient Probe Generation

Keywords: Phosphoinositides / Lipid signaling / Probes / Phospholipids / Membranes / Bioorganic chemistry

Phosphoinositide lipids play key roles in biological pathways, and derivatized analogs of these structures are beneficial as chemical tools for elucidating signaling and binding activities. Herein, we present an efficient probe generation by the synthesis of amino conjugates of all seven isomers as convenient modular precursors for rapid access to functionalized analogues.

CORRECTION

Keywords: Cyclopropanation / Organocatalysis / Enantioselectivity / Diastereoselectivity / Quaternary centers

Asymmetric Organocatalytic Cyclopropanation – Highly Stereocontrolled Synthesis of Chiral Cyclopropanes with Quaternary Stereocenters

X. Companyó, A.-N. Alba, F. Cárdenas, A. Moyano, R. Rios* 4180

* Author to whom correspondence should be addressed.

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

If not otherwise indicated in the article, papers in issue 23 were published online on July 27, 2009

