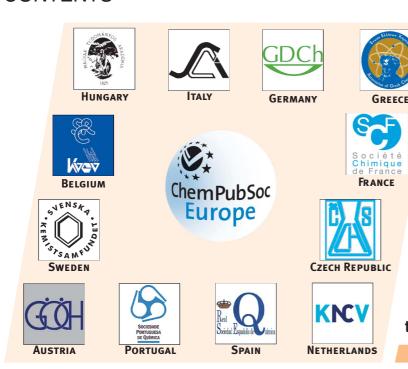
CONTENTS



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

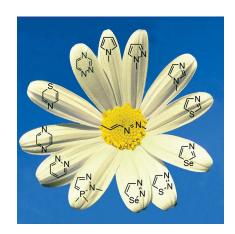
The cover picture shows the logo of the centenary year of the Società Chimica Italiana (SCI) superimposed on the view of the bay of Naples from Sorrento, where the SCI XXIII National Congress celebrating this anniversary will take place. The Società Chimica Italiana was one of the first to amalgamate its journal, Gazzetta Chimica Italiana, with those of other European Chemical Societies to form the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry with the far-sighted vision to create out of the national journals a high-quality international forum for the dissemination of research in chemistry in the broadest sense. The conglomerate of European Chemical Societies, now called Chem-PubSoc Europe, publishes a family of highquality journals based wherever possible on previously existing journals. Thus ChemPub-Soc Europe has turned two other journals previously owned by the Società Chimica Italiana into the highly successful ChemMedChem (formerly Il Farmaco) and ChemSusChem (Annali di Chimica).





MICROREVIEW

This microreview summarizes our progresses over the last years in the chemistry of 1,2-diaza-1,3-dienes and outlines some of the reactive peculiarities that make this class of compounds powerful tools in heterocyclic chemistry.



Heterocycles from Diazadienes

O. A. Attanasi,* L. De Crescentini, G. Favi, P. Filippone, F. Mantellini, F. R. Perrulli,

S. Santeusanio 3109-3127

Cultivating the Passion to Build Heterocycles from 1,2-Diaza-1,3-dienes: the Force of Imagination

Keywords: Diazadienes / Michael addition / Heterocycles / Domino reactions / Nucleophiles

SHORT COMMUNICATIONS

An effective way to produce six- and sevenmembered heterocycles from epoxy alkynes catalyzed by gold(I) or Yb(OTf)₃/gold(I) through selective carbon or oxygen nucleophilic addition to alkynes has been described.

Gold(I)-Catalyzed Cycloisomerization

L.-Z. Dai, M. Shi* 3129-3133

Gold(I) Catalysis: Selective Synthesis of Six- or Seven-Membered Heterocycles from Epoxy Alkynes

Keywords: Gold / Alkynes / Domino reactions / Heterocycles / Isomerization

Corey's Cyclopropanation

The total synthesis of (±)-cyclocolorenone (2) (an aromadendrane) was achieved in seven regio- and stereocontrolled steps via hydroazulenone 6 (a versatile intermediate), through efficient C-1 epimerization,

selective C-8,9 hydrogenation, and stereocontrolled construction of the aromadend-rane core. Reduction of **2** led to (\pm) - α -gurjunene.

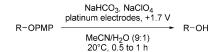
Short Access to the Aromadendrane Family: Highly Efficient Stereocontrolled Total Synthesis of (\pm) -Cyclocolorenone and (\pm) - α -Gurjunene

Keywords: Total synthesis / Sesquiterpenes / Isomerization / Hydrogenation / Cyclopropanation

CONTENTS

Cleavage of PMP Groups

C. Vaxelaire, F. Souquet, M.-I. Lannou, J. Ardisson,* J. Royer* 3138-3140



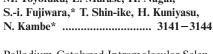
Anodic Oxidation: An Attractive Alternative to CAN-Mediated Cleavage of para-Methoxyphenyl Ethers

Keywords: Oxidation / Electrochemistry / Protecting groups / Cleavage reactions

Herein is reported the first anodic oxidation method for the cleavage of primary and secondary alkyl para-methoxyphenyl ethers. Under a controlled potential (1.7 V) and in the presence of NaHCO3, this reaction tolerates oxidation and acid-sensitive functions, thus constituting an efficient method for the orthogonal deprotection of para-methoxyphenyl ethers.

α,β-Unsaturated Lactam Synthesis

M. Toyofuku, E. Murase, H. Nagai,



Palladium-Catalyzed Intramolecular Selenocarbamoylation of Allenes with Carbamoselenoates: A New Entry to α,β-Unsaturated Lactams

Keywords: Cycloaddition / Lactams / Allenes / Selenium / Allylic compounds

Carbamoselenoates having a buta-2,3-dienyl or penta-3,4-dienyl group on the nitrogen atom was found to undergo intramolecular selenocarbamoylation of an allene unit in the presence of a palladium catalyst to give rise to the corresponding α,β -unsaturated lactam having an allyl selenide unit.

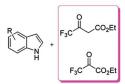
Asymmetric Arylation

J. Nie, G.-W. Zhang, L. Wang, D.-H. Zheng, Y. Zheng, J.-A. Ma* 3145-3149

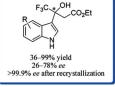


Chiral Brønsted-Acid-Catalyzed Enantioselective Arylation of Ethyl Trifluoroacetoacetate and Ethyl Trifluoropyruvate

Keywords: Chiral Brønsted acid / Enantioselective arylation / Asymmetric catalysis / Organocatalysis









Asymmetric arylation of ethyl 4,4,4-trifluoroacetoacetate catalyzed by a chiral Brønsted acid was developed to give tertiary alcohols in good yields with moderate enantiomeric excesses, which can be improved to 99.9% by single recrystallization. By extending this protocol to ethyl trifluoropyruvate, the direct arylation reactions proceeded well to afford the desired products in quantitative yields with 20−62% ee.

Heteroatomic Chemistry

Y. Macé, C. Urban, C. Pradet,

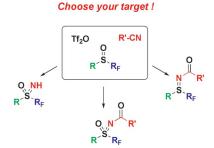
J. Marrot, J.-C. Blazejewski,

E. Magnier* 3150-3153



Sulfilimines and Sulfoximines by Reaction of Nitriles with Perfluoroalkyl Sulfoxides

Keywords: Synthetic methods / Fluorine / Sulfilimines / Sulfoximines / Nitriles



A perfect match of reagents (sulfoxides, nitriles and trifluoromethanesulfonic anhydride) allows a Ritter-like process for the preparation of fluorinated sulfilimines or sulfoximines. This versatile, solvent and metal free, reaction is an opening way through the synthesis of new ligands or electrophilic trifluoromethylating reagents.



FULL PAPERS

6-APA in Organocatalysis

$$O_2N \xrightarrow{+H_2N} O_2N \xrightarrow{+H_2N} O_2N \xrightarrow{OH} O O_2N \xrightarrow{OH} O O_2N \xrightarrow{anti} O$$

6-Aminopenicillanic acid (6-APA) and two of its derivatives have been evaluated as

catalysts for use in direct cross-aldol reactions for the first time.

Evaluation of 6-APA as a New Organocatalyst for a Direct Cross-Aldol Reaction

Keywords: Asymmetric catalysis / Aldol reactions / Penicillins / Organocatalysis

Multicomponent Reactions

Structurally different isoquinolin-3-ones could be selectively synthesised through a three-component, Pd-catalysed reaction starting from aryl iodides, chloroamides

and properly substituted olefins. An important beneficial effect of water on reaction selectivity was observed.

R. Ferraccioli,* A. Forni 3161-3166

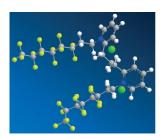
Selective Synthesis of Isoquinolin-3-one

Selective Synthesis of Isoquinolin-3-one Derivatives Combining Pd-Catalysed Aromatic Alkylation/Vinylation with Addition Reactions: The Beneficial Effect of Water

Keywords: Multicomponent reactions / Palladium / C-H activation / Water effect / Nitrogen heterocycles

Fluorinated Surfactants

A series of fluorinated gemini pyridinium amphiphiles have been prepared and fully characterized. The use of different characterization techniques, such as conductivity and surface tension measurements, shed light on the aggregation process. The title products showed interesting, unusual properties that are important for possible applications in gene therapy.

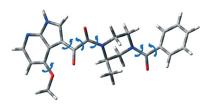


Synthesis and Characterization of Highly Fluorinated Gemini Pyridinium Surfactants

Keywords: Surfactants / Cationic surfactants / Fluorinated surfactants / Amphiphiles / Gemini pyridinium amphiphiles / Structure-activity relationships

Modeling HIV Inhibitors

A theoretical study of the HIV-1 inhibitor BMS-378806 was performed at the B3LYP/6-31G(d) level and the results were supported through high-field ¹H NMR at 248 K. Four conformational families were located by the calculations and four distinct series of signals were detected in the ¹H NMR spectrum.



An Exhaustive Conformational Evaluation of the HIV-1 Inhibitor BMS-378806 through Theoretical Calculations and Nuclear Magnetic Resonance Spectroscopy

Keywords: Molecular modeling / Density functional calculations / NMR spectroscopy / Antiviral agents / Nitrogen heterocycles

CONTENTS

3-Alkylindazoles

S. Campetella, A. Palmieri, M. Petrini* 3184–3188

Synthesis of 3-(Tosylalkyl)indazoles and their Desulfonylation Reactions – A New Entry to 3-Substituted Indazoles by an Unprecedented Friedel—Crafts Process

Keywords: Alkylation / Arenes / Electrophilic substitution / Nitrogen heterocycles / Fused-ring systems

The indazole ring is practically unreactive toward Friedel—Crafts reactions. However, under suitable conditions, it reacts with aliphatic aldehydes and *p*-toluenesulfinic acid to give the corresponding sulfonyl ind-

azoles. This unprecedented process provides easy access to 3-substituted indazoles that can be further desulfonylated under reductive conditions to give 3-alkylindazole derivatives.

C-H Activation

A. Biffis,* L. Gazzola, P. Gobbo, G. Buscemi, C. Tubaro,

M. Basato 3189-3198

Alkyne Hydroarylations with Chelating Dicarbene Palladium(II) Complex Catalysts: Improved and Unexpected Reactivity Patterns Disclosed Upon Additive Screening

Keywords: C-H activation / Palladium / Hydroarylation / Alkynes / Carbenes / Nheterocyclic carbenes

By choosing the right additives, the title compounds were found to efficiently catalyse the hydroarylation of alkynes at room temperature and with controllable selectivity

Lewis Acid Activation

Nickel-Catalyzed Asymmetric Hydrovinylation Using Lewis Acid Activation

Keywords: Enantioselective catalysis / Olefin dimerisation / Nickel / Indium / Anion effects / C-C coupling

ee up to 92%, TOF up to 410 h^{-1}

Lewis Acid = InI₃ InBr₃ BiBr₃ ZnCl₂ GaCl₃

Inexpensive, commercially available Lewis acids (LA) can efficiently activate metal halide precursors for asymmetric catalysis as demonstrated for the asymmetric Ni-catalysed hydrovinylation of styrene. In case

of InI₃ as LA, the performance of the easily generated catalytic system is equal or even better than that of the state-of-the-art Ni/BArF catalyst.

Quinone Methides

D. Richter, N. Hampel, T. Singer, A. R. Ofial, H. Mayr* 3203-3211



Synthesis and Characterization of Novel Quinone Methides: Reference Electrophiles for the Construction of Nucleophilicity Scales

Keywords: Electrophilicity / Nucleophilicity / Kinetics / Linear free-energy relationships / Quinone methides

From the second-order rate constants of the reactions of the aryl-substituted para quinone methides (Ar-QM) with stabilized carbanions, electrophilicity parameters E as defined by $\log k = s(N + E)$ have been determined.

Ar-QM



Conjugated Bis(phthalocyanines)

New ethynyl- and butadyinyl-bridged bis(phthalocyaninates), peripherally functionalized with strong donor moieties, have been synthesized. The attachment of six butoxy groups to each phthalocyanine core increases the solubility and electron richness for optical properties, further the formation of regiosomers is precluded. Preliminary Z-scan experiments have been also performed on binuclear Pb^{II} complexes to evaluate their optical limiting capabilities.

Synthesis and Optical Properties of Regioisomerically Pure Alkynyl-Bridged Bis(phthalocyanines)



Keywords: Phthalocyanines / Lead complexes / Optical limiting / Stille reaction

Rapid Strategy Assembly

overall yield: 40-87 %

 $R^1 = Ar$, *N*-het, alkenyl $R^2 = Alkyl$, Ar, *N*-het, alkenyl

A modular approach to the synthesis of unsaturated carbonyl motifs is reported with the design and use of a bifunctional olefinic template. A small olefin unit, (E)-1,2-disilylethene 5, was activated selectively and

sequentially by transition-metal catalysis to give a series of diverse and conjugated α,β -unsaturated ketones through a coupling/acylation sequence.

Sequential Hiyama Coupling/Narasaka Acylation Reaction of (E)-1,2-Disilylethene: Rapid Assembly of α,β -Unsaturated Carbonyl Motifs

Keywords: Acylation / Cross-coupling / Rhodium / Palladium / Ketones

Cross-Coupling

The application of the halogen dance reaction for the synthesis of starting materials for cross-coupling reactions is reported. The obtained compounds were then suc-

cessfully applied in sequential Stille and Suzuki-Miyaura cross-coupling reactions to obtain novel thiazole derivatives.

Polyarylated Thiazoles via a Combined Halogen Dance – Cross-Coupling Strategy

Keywords: Protein kinase inhibitor analogues / Halogen dance / Cross-coupling / Palladium / Polyarylated thiazoles

Novel Merocyanine-Type Dyes

A number of new specific merocyaninetype dyes have been obtained by incorporating polymethine substituents into the *meso* position of BODIPY. The prepared dyes show intense long-wavelength absorption and weak fluorescence.

Boradipyrromethenecyanines

Keywords: BODIPY compounds / Boron dipyrromethene dye / Merocyanine / Polymethine dye / Long-wavelength dye / Heterocycles

Chiral Supramolecular Fluorophore

Y. Imai,* K. Murata, Y. Nakano, T. Harada, T. Sato, N. Tajima, M. Fujiki, R. Kuroda, Y. Matsubara* 3244-3248

Solid-State Optical Properties of a Chiral Supramolecular Organic Fluorophore Consisting of Fluorescent 1-Pyrenesulfonic Acid and Amine Molecules

Keywords: Chirality / Circularly polarized luminescence / Crystal engineering / Fluorescence / Supramolecular chemistry

$$\lambda_{em} = 467 \text{ nm}, \ \Phi_F = 0.11, \ g_{em} = -1.0 \times 10^{-3}$$

By using (*R*)-1-phenylethylamine as a chiral molecule and 1-pyrenesulfonic acid as a fluorescent molecule, a chiral supramolecular organic fluorophore composed of a 2D

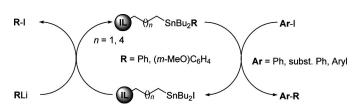
layered structure was successfully developed. This chiral supramolecular fluorophore possesses circularly polarized luminescence properties (CPL) in the solid state.

Coupling Reactions

Phuoc Dien Pham, Jürgen Vitz,* Cécile Chamignon, Arnaud Martel, Stéphanie Legoupy* 3249-3257

Stille Cross-Coupling Reactions with Tin Reagents Supported on Ionic Liquids

Keywords: C-C coupling / Ionic liquids / Tin / Homogeneous catalysis



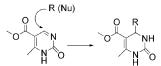
A novel organotin reagent supported on an ionic liquid is applied to a number of Stille cross-coupling reactions to afford biaryl compounds. The products, which are obtained in high yields at low temperature un-

der solvent- and ligand-free conditions, may be easily purified. The catalyst retains its activity for up to five reactions. A catalytic cycle is proposed, which also explains the formation of side products.

Heterocyclic Chemistry

An Efficacious Protocol for 4-Substituted 3,4-Dihydropyrimidinones: Synthesis and Calcium Channel Binding Studies

Keywords: Multicomponent reactions / Lithiation / Regioselectivity / Chiral auxiliaries / Medicinal chemistry / Vascular smooth muscles



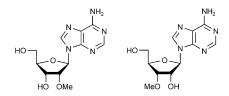
4-Subsituted dihydropyrimidinones were synthesized through highly regio- and chemoselective addition reactions of carbon nucleophiles in a synthetically useful manner.

Enzymatic Regioisomer Separation

S. Martínez-Montero, S. Fernández, T. Rodríguez-Pérez, Y. S. Sanghvi, K. Wen, V. Gotor,* M. Ferrero* 3265–3271

Improved Synthesis and Isolation of 2'-O-Methyladenosine: Effective and Scalable Enzymatic Separation of 2'/3'-O-Methyladenosine Regioisomers

Keywords: Nucleosides / Enzymes / Isomers / Separation of isomers / Acylation / Green chemistry



2'-O-methyladenosine

3'-O-methyladenosine

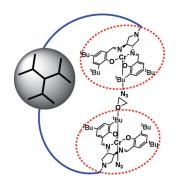
Enzymatic Separation

Direct alkylation of adenosine with methyl *p*-toluenesulfonate furnishes a mixture 2'/3'-O-methyladenosine regioisomers which upon enzymatic acylation with *Pseudomonas cepacia* lipase selectively yields acylated 2'-O-methyladenosine. Chromatographic separation and hydrolysis of the latter offers easy access to 2'-O-methyladenosine.



Cooperative Bimetallic Catalysis

To support the cooperative bimetallic mechanism of the ring-opening of *meso*-epoxides with TMSN₃, symmetrical salen-Cr^{III} complexes were immobilized on hyperbranched polyglycerol. Further investigations were performed to understand the influence of the length of the linker between polymer and catalyst. Higher *ee* values were obtained with longer linkers.



J. Keilitz, R. Haag* 3272-3278

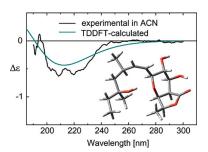
Intramolecular Acceleration of Asymmetric Epoxide Ring-Opening by Dendritic Polyglycerol Salen—Cr^{III} Complexes



Keywords: Supported catalysts / Ring opening / Dendrimers / Epoxides / Enantioselectivity / Chromium

Natural Products

Two new bicyclic fusidilactones D and E have been isolated, along with the known fusidilactone B, from the fungal endophyte *Fusidium* sp. The relative configuration of the latter was established by X-ray diffraction and the absolute configurations by TDDFT calculations of CD spectra using the solid-state CD/TDDFT approach. The metabolites showed antifungal, antibacterial, and antialgal activities.



S. Qin, K. Krohn,* U. Flörke, B. Schulz, S. Draeger, G. Pescitelli, P. Salvadori, S. Antus, T. Kurtán 3279–3284

Two New Fusidilactones from the Fungal Endophyte *Fusidium* sp.

Keywords: Natural products / Endophytic fungi / Fusidilactones / Configuration determination / Density functional calculations / Biological activity

^{*} Author to whom correspondence should be addressed.

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