

























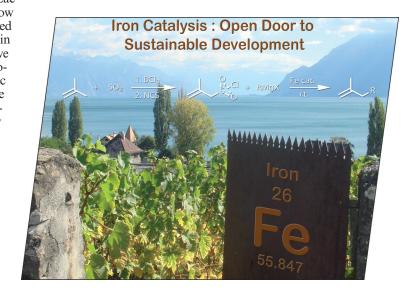




A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further members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

COVER PICTURE

The cover picture shows the iron door of the vineyard of Prof. Pierre Vogel in the Lavaux region, 12 km east of Lausanne along the Geneva Lake (Lac Léman) in Western Switzerland. This region is now part of the world heritage (UNESCO). The opened door symbolizes iron-catalyzed reactions and, in particular, a new allylation reaction of inexpensive Grignard reagents with alk-2-enesulfonyl chlorides obtained in a new way that is the endergonic H-ene reaction of sulfur dioxide with simple alkenes. The lake and the mountains in the background have been here for very long and will stay as such for much longer if civilization will concentrate on more sustainable development. Vineyards have existed in this area for more than 1200 years, and the grapes produced sometimes need a little sulfur dioxide to become a good wine (a practice that is ca. 8000 years old). The chemistry disclosed here uses sulfur dioxide for allylic C-H activation. The unstable alk-2enesulfinic acids so obtained are oxidized with NCS to alk-2-enesulfonyl chlorides. The latter are then coupled with Grignard reagents under desulfinylation conditions and iron catalysis. Sulfur dioxide can be recovered. Details are discussed in the article by P. Vogel et al. on p. 6281ff.



MICROREVIEW

Propargylic Substitution

R. J. Detz, H. Hiemstra, J. H. van Maarseveen* 6263–6276

Catalyzed Propargylic Substitution

Keywords: Alkynes / Copper / Enantioselectivity / Ruthenium

A critical overview of the quickly emerging field of propargylic substitutions is given. This Microreview focuses on experimental results that deal with catalyzed substitutions of propargylic alcohols and their derivatives.

SHORT COMMUNICATION

Organocatalysis

S. Číhalová, M. Remeš, I. Císařová, J. Veselý* 6277–6280

Highly Enantioselective Aza-Baylis—Hillman-Type Reaction of α , β -Unsaturated Aldehydes with In Situ Generated N-Bocand N-Cbz-Imines

Keywords: Aza-Baylis—Hillman reaction / Organocatalysis / Enantioselectivity / Diastereoselectivity / Sulfur

Chiral β -amino carbonyl compounds bearing an α -alkylidene group were easily synthesized under mild and simple conditions from α,β -unsaturated aldehydes and α -amido sulfones in good yields and diaster-eoselectivities and excellent enantioselectivities.

FULL PAPERS

Iron Catalysis

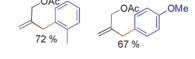
C. M. R. Volla, D. Marković, S. R. Dubbaka, P. Vogel* 6281-6288



Ligandless Iron-Catalyzed Desulfinylative C-C Allylation Reactions using Grignard Reagents and Alk-2-enesulfonyl Chlorides

Keywords: Iron / Grignard reaction / Sulfur / Homogeneous catalysis / Cross-coupling

We have developed an efficient and simple procedure for the cross-coupling of alk-2-enesulfonyl chlorides with Grignard reagents by using 5 mol-% of inexpensive and air stable Fe(acac)₃ as the catalyst in THF



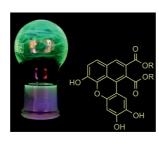
at room temperature. Iron-catalyzed reaction of Grignard reagents with functionalized alk-2-enesulfonyl chlorides provided the corresponding cross-coupling products in good yields.

Natural and Unnatural Lignans

C. Daquino, A. Rescifina, C. Spatafora, C. Tringali* 6289-6300

Biomimetic Synthesis of Natural and "Unnatural" Lignans by Oxidative Coupling of Caffeic Esters

Keywords: Oxidation / Lignans / Biomimetic synthesis / Reaction mechanisms / Manganese

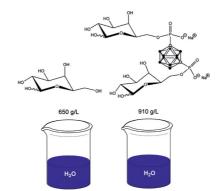


The metal-mediated oxidative coupling of caffeic acid esters has been employed in the biomimetic synthesis of dimeric lignans and neolignans. The manganese-mediated reactions afforded the unusual benzo[kl]-xanthene lignans 6 and 15. This route was employed to obtain rufescidride (9) and mongolicumin A (10). A mechanistic study was also carried out.



Water-Soluble Bis(glycophosphonates)

The synthesis and properties of highly water-soluble meta- and para-carbaboranecontaining bis(galactosyl phosphonates) are presented.



S. Stadlbauer, P. Lönnecke, P. Welzel, E. Hey-Hawkins* 6301-6310

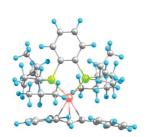
Water-Soluble Carbaborane-Bridged Bis(glycophosphonates)

Keywords: Boron / Antitumor agents / Medicinal chemistry / Phosphonates / Carbaboranes

(R,R)-DUPHOS-iPr was tested in the asymmetric allylic alkylation reaction using rac-1,3diphenylpropenyl acetate and a variety of Pd pre-catalysts. Excellent ee values could be obtained. There was a switch in the absolute configuration of the malonate product. DFT calculations were conducted on the active Pd-

allyl complexes to identify the most electro-

philic site for malonate attack.



Asymmetric Allylic Alkylation

V. R. Marinho, J. P. P. Ramalho, A. I. Rodrigues, A. J. Burke* 6311-6317

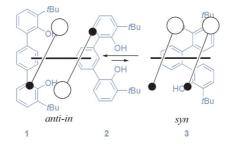
A Comparison of (R,R)-Me-DUPHOS and (R,R)-DUPHOS-iPr Ligands in the Pd⁰-Catalysed Asymmetric Allylic Alkylation Reaction:

Stereochemical and Kinetic Considerations

Keywords: Asymmetric catalysis / Alkylation / Palladium / P ligands / Fukui function / Kinetics

Atropisomerism

A series of isomeric "extended" biphenols based on the terphenyl backbone was synthesized by Suzuki cross-coupling. The ortho isomer (3) and its methylated precursor exist in the form of syn and anti atropisomers at low temperature, which were analyzed by DFT calculations and ¹H NMR spectroscopic studies.



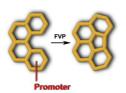
M. M. Gruza, J.-C. Chambron,* E. Espinosa,* E. Aubert 6318-6327

Synthesis and Stereochemical Properties of "Extended" Biphenols Bridged by ortho-, meta-, and para-Phenylene Spacers

Keywords: Cross-coupling / Biaryls / Atropisomerism / Density functional calculations

Flash Pyrolysis

The efficiency of various promoters in intramolecular C-C coupling reactions for the successful direct synthesis of fullerenes under flash pyrolysis conditions has been investigated with benzo[c]phenanthrene as a model system. Fluorine was found to be a promising candidate for efficient intramolecular condensation and seems to provide all the properties required for an "ideal promoter".



K. Y. Amsharov,* M. A. Kabdulov, M. Jansen 6328-6335

Highly Efficient Fluorine-Promoted Intramolecular Condensation of Benzo[c]phenanthrene: A New Prospective on Direct Fullerene Synthesis

Keywords: Flash pyrolysis / Cyclization / C-C coupling / Reaction mechanisms / Fullerenes

S-Arylation of Disulfides

J. Krouželka, I. Linhart* 6336-6340

Preparation of Arylmercapturic Acids by S-Arylation of N, N'-Diacetylcystine

Keywords: Arylation / Sulfides / Copper / Amino acids / Reaction mechanisms

N,N'-Diacetylcystine dimethyl ester has been arylated at both sulfur atoms with arylboronic acids in the presence of Cu^I or Cu^{II} complexes under modified Chan—Lam—Evans coupling conditions to yield arylmercapturic acids.

Electro-Optical Materials

Approaches to Fused Tetrathiafulvalene/ Tetracyanoquinodimethane Systems

Keywords: Quinones / Quinodimethanes / Sulfur heterocycles / Charge transfer / Donor-acceptor systems

Reactions between malononitrile and cyclopentadiene-protected fused 2-thioxo-1,3-dithiole-p-benzoquinones under different experimental conditions proceed either through the expected Knoevenagel condensation to afford the corresponding TCNQ analogues or through Michael additions with subsequent ring opening of the 1,3-dithiole moiety, leading to ketene imines.

Unsymmetrical Disulfides

Efficient Synthesis of Unsymmetrical Disulfides through Sulfenic Acids

Keywords: Sulfenic acids / Synthetic methods / Cross-coupling / Sulfur

This is a contribution in which a well-known reaction, that is, the coupling between sulfenic acids and thiols, can be regarded as a general methodology for the

synthesis of disulfides, where the S-S bridge links different residues with base-, acid- and temperature-sensitive functional groups. Compound 14 is an example.

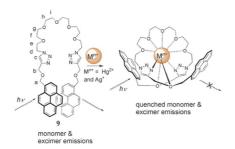
Host-Guest Chemistry

H.-C. Hung, C.-W. Cheng, Y.-Y. Wang, Y.-J. Chen, W.-S. Chung* 6360–6366



Highly Selective Fluorescent Sensors for Hg²⁺ and Ag⁺ Based on Bis-triazole-Coupled Polyoxyethylenes in MeOH Solution

Keywords: Sensors / Host-guest chemistry / Fluorescence / Fluorescent probes / Nitrogen heterocycles



Fluorescent chemosensors 6-9, bis-triazoles with a variable length polyoxyethylene chain, have been obtained by click chemistry. Of the 15 metal perchlorate salts screened, compounds 6-9 in MeOH showed selective fluorescence quenching towards only Ag^+ and Hg^{2+} . Under similar conditions, the control compound, a triazolylmethoxymethylpyrene, showed selective fluorescence quenching towards only Hg^{2+} .



Peptidic Antitumor Agents

Pretubulysin, a biosynthetic precursor of the tubulysins, shows potent biological activity in the subnanomolar range towards various tumor cell lines and is therefore an ideal lead structure for the development of tubulysin-based anticancer drugs.

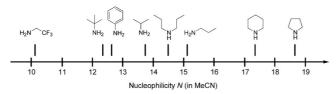
A. Ullrich, J. Herrmann, R. Müller, U. Kazmaier* 6367-6378

Synthesis and Biological Evaluation of Pretubulysin and Derivatives



Keywords: Total synthesis / Antitumor agents / Myxobacteria / Natural products / Tubulysins / Pretubulysin

Kinetics



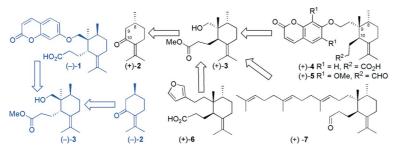
The kinetics of the reactions of primary and secondary amines with benzhydrylium ions and quinone methides have been studied spectrophotometrically in acetonitrile at 20 °C. From the linear free energy relationship $\log k_2$ (20 °C) = s(N + E), the N and s parameters of these amines were determined.

T. Kanzian, T. A. Nigst, A. Maier, S. Pichl, H. Mayr* 6379-6385

Nucleophilic Reactivities of Primary and Secondary Amines in Acetonitrile

Keywords: Kinetics / Linear free energy relationships / Solvent effects / Nucleophilicity / Amines

A-seco Terpenes



From readily available pulegone 2 (Mentha pulegium, Pennyroyal), galbanic acid (Ferula asafetida), iridals (Iris germanica), and various analogues have been synthesized via a common intermediate 3 by using the appropriate antipodes.

A. Corbu, M. Aquino, M. Perez, Z. Gandara, S. Arseniyadis* ... 6386-6392

Natural and Unnatural A-seco Terpenes from Pulegone: Synthesis of Galbanic Acid and Marneral Revisited



Keywords: Terpenoids / Natural products / Chiral pool / Mitsunobu etherification / Microwave chemistry

Asymmetric Catalysis

The asymmetric synthesis of a novel tetradentate 1,10-phenanthroline from two starting pyridine subunits with subsequent coupling reactions has been accomplished.

The new chiral ligand has been successfully employed in metal-catalyzed epoxide-opening reactions and in enantioselective aminations of \beta-keto esters.

M. V. Nandakumar, S. Ghosh, C. Schneider* 6393-6398

Enantioselective Synthesis of a Novel Chiral 2,9-Disubstituted 1,10-Phenanthroline and First Applications in Asymmetric Catalysis

Keywords: Amination / Asymmetric catalysis / Desymmetrization / Phenanthrolines / Scandium

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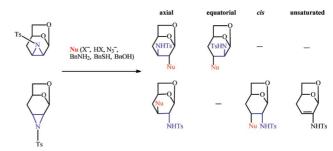
Aziridine Cleavage

J. Karban,* J. Kroutil, M. Buděšínský, J. Sýkora, I. Císařová 6399–6406



Ring-Opening Reactions of Aziridines Fused to a Conformationally Locked Tetrahydropyran Ring

Keywords: Aziridines / Regioselectivity / Carbohydrates / Nitrogen heterocycles / Cleavage reactions



The ring-opening reactions of aziridine derivatives of 1,6-anhydro-2,3,4-trideoxy-2,3-(tosylepimino)-β-D-hexopyranoses with nucleophiles [azide, halides, haloacids, benzylamine, benzyl alcohol and benzyl mer-

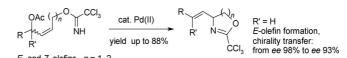
captan (BnSH)] were studied, and the regioselectivity and stereoselectivity of the cleavage with respect to the Fürst-Plattner rule were examined.

Olefin Aminopalladation



Cyclization of Trichloroacetimidates by Olefin Aminopalladation β-Heteroatom Elimination

Keywords: Amination / Palladium / Chirality / Heterocycles / Elimination



 Pd^{II} -catalysed cyclization of O-allylic and O-homoallylic trichloroacetimidates provides 4-vinyloxazolines and a 4-vinyldihydrooxazine, respectively. (Z)-Allylic imidates with a secondary δ -acetoxy group

give (*E*)-4-vinyloxazolines selectively and with high chirality transfer. The mechanism of the reaction is discussed based on the observed stereoselectivity.

CORRECTION

V. S. Sudhir, N. B. R. Baig, S. Chandrasekaran* 6413 Convenient Synthesis of Ferrocene Conjugates Mediated by Benzyltriethylammonium Tetrathiomolybdate in a Multi-Step Tandem Process

Keywords: Sandwich complexes / Ferrocene conjugates / Cyclic voltammetry / Amino acids / Carbohydrates



The editorial staff and the publishers thank all readers, authors, referees, and advertisers for their interest and support over the past year and wish them all a happy new year.

If not otherwise indicated in the article, papers in issue 35 were published online on November 20, 2009