





























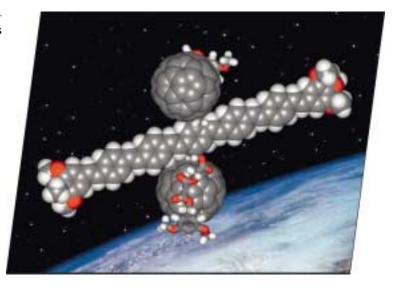




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic and Sweden) are Associates of the two journals.

## **COVER PICTURE**

The cover picture shows a satellite-shaped  $C_{60}-$  oligophenylenevinylene (OPV) conjugate. This compound has been prepared starting from a fullerene carboxylic acid derivative and an OPV heptamer bearing two alcohol functions. Electrochemical investigations revealed that the fist reduction of this hybrid compound is centered on the fullerene subunits, whereas the oxidation is centered on the OPV rod. Details are discussed in the article by J.-F. Nierengarten et al. on p. 3627ff.



## **MICROREVIEW**

#### **P-C Bond Formation**

#### L. Coudray, J.-L. Montchamp\* ... 3601-3613

Recent Developments in the Addition of Phosphinylidene-Containing Compounds to Unactivated Unsaturated Hydrocarbons: Phosphorus—Carbon Bond Formation by Hydrophosphinylation and Related Processes

**Keywords:** Hydrophosphinylation / Phosphaalkenes / Phosphanes / Phosphorus / Phosphonates / Phosphinates



Hydrophosphinylation and hydrophosphonylation reactions with R<sup>1</sup>R<sup>2</sup>P(O)H and alkenes or alkynes under free-radical or transition-metal catalysis are reviewed.

## **SHORT COMMUNICATIONS**

#### **Natural Products**

K. Krohn,\* S. F. Kouam, S. Cludius-Brandt, S. Draeger,

B. Schulz ...... 3615-3618

Bioactive Nitronaphthalenes from an Endophytic Fungus, *Coniothyrium* sp., and Their Chemical Synthesis

**Keywords:** Fungal metabolites / Nitronaphthalenes / *Coniothyrium* sp. / Bioactivity

For the first time, nitronaphthalenes have been isolated from a natural source, an endophytic fungus *Coniothyrium* sp. Two metabolites are members of the extremely rare naturally occurring family of dinitro

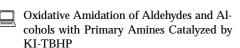
compounds. Their structures were confirmed by chemical synthesis. The nitronaphthols showed considerable antibacterial, antifungal, and antialgal properties.

#### **Oxidative Amidation**

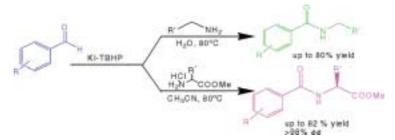
K. R. Reddy,\* C. U. Maheswari,

M. Venkateshwar,

M. L. Kantam ...... 3619-3622



**Keywords:** Oxidative amidation / Aldehydes / Alcohols / Primary amines / Potassium iodide



Oxidative amidation of aldehydes and alcohols with amines to give the corresponding amides in excellent yields and *ee* values over 98% is achieved by using a catalytic

amount of KI in combination with TBHP as the external oxidant. This method avoids the use of expensive and/or air-sensitive reagents.



### **Multicomponent Reactions**

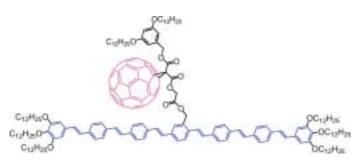
A novel by-product-catalyzed three-component synthesis of amine derivatives from readily available benzylic and allylic alcohols, acyl chlorides (chloroformates or sulfonyl chlorides), and hexamethyldisilaz-

ane (HMDS) has been developed. By-product TMSCl and its decomposition into HCl are responsible for promoting the three-component reaction.

Three-Component Synthesis of Amine Derivatives Using Benzylic and Allylic Alcohols as *N*-Alkylating Agents in the Absence of External Catalysts and Additives

**Keywords:** Multicomponent reactions / *N*-Alkylation / Alcohols / Amine derivatives / Catalyst-free reactions

## **FULL PAPERS**



Oligophenylenevinylene (OPV) derivatives substituted with one or two fullerene subunits have been prepared starting from a fullerene carboxylic acid derivative and OPV heptamers bearing one or two alcohol functions.

### $\pi$ -Conjugated Oligomer/C<sub>60</sub> Hybrids

Synthesis of Oligophenylenevinylene Heptamers Substituted with Fullerene Moieties

**Keywords:** Conjugated systems / Fullerene / Oligophenylenevinylene

Ketyl-Aryl Coupling

 $SmI_2$ -mediated cyclizations of a series of  $\gamma$ -aryl ketones with different substituents have been investigated. The ketyl—aryl cyclizations stereoselectively gave hexahydronaphthalines or in a few cases spiro com-

pounds. The influence of substituents and the mechanism involved are discussed. Regioselective trapping of the carbanionic intermediates with electrophiles led to products of synthetic interest.

Samarium Diiodide Mediated Ketyl—Aryl Coupling Reactions — Influence of Substituents and Trapping Experiments

**Keywords:** Samarium diiodide / Ketyl coupling / Cyclizations / Radical reactions / Substituent effects

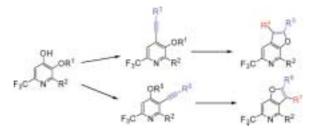
## **CONTENTS**

#### **Modular Furo-pyridine Synthesis**

T. Lechel, J. Dash, I. Brüdgam, H.-U. Reißig\* ...... 3647–3655

Novel Furo-pyridine Derivatives via Sonogashira Reactions of Functionalized Pyridines

**Keywords:** Pyridines / Allenes / Palladium catalysis / Furo-pyridines / Fluorescence



A series of 4-pyridyl nonaflates was coupled with alkynes to efficiently provide new 4-alkynyl-substituted pyridines. Apt conditions were developed for their conversion into furo[2,3-c]pyridines. 3-Pyridyl nonaflates offer access to regioisomeric furo[3,2-c]-

pyridines. An alternative cyclization method employing iodine monochloride furnishes iodinated furo-pyridines which can undergo a second Pd-catalyzed step. Some of the newly prepared compounds are fluorescent and show strong Stokes shifts.

### 2H-Pyrroles

N. Ghavtadze, R. Fröhlich, E.-U. Würthwein\* ...... 3656–3667

2*H*-Pyrrole Derivatives from an Aza-Nazarov Reaction Cascade Involving Indole as the Neutral Leaving Group

**Keywords:** Aza compounds / Cyclization / Pyrroles / Quantum chemical calculations / Cations / Nazarov reactions

The formation of indoles as very unusual leaving groups facilitates the aza-Nazarov reactions of 1-azapenta-1,4-dien-3-ones **4**. Upon treatment with polyphosphoric acid/anhydride mixtures, novel trifluoromethyl-

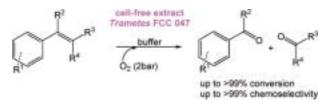
substituted 2*H*-pyrrole derivatives **8** were formed and isolated from compounds **4**, which extends the scope of the classical Nazarov cyclization reaction considerably.

#### **Biocatalytic Alkene Cleavage**

M. Lara, F. G. Mutti, S. M. Glueck, W. Kroutil\* ...... 3668–3672

Biocatalytic Cleavage of Alkenes with O<sub>2</sub> and *Trametes hirsuta* G FCC 047

**Keywords:** *Trametes hirsuta /* Alkenes / "Green" chemistry / Oxidation / Biocatalysis



A cell-free extract of the wood-degrading fungus *Trametes hirsuta* FCC 047 has been applied for the oxidative alkene cleavage of substrates possessing a C=C bond adjacent to an aromatic ring. O<sub>2</sub> was employed oxi-

dant in aqueous buffer. Up to 96 reactions could be performed in parallel at 2 bar  $\rm O_2$  in special laboratory equipment. A broad spectrum of aryl-alkenes was converted with up to >99% chemoselectivity.

#### **Solvent Effect in Sialylation**

C. De Meo,\* M. Farris, N. Ginder, B. Gulley, U. Priyadarshani,

M. Woods ...... 3673-3677

Solvent Effect in the Synthesis of Sialosyl  $\alpha(2-6)$  Galactosides: Is Acetonitrile the only Choice?

**Keywords:** Sialylation / Solvent effect / Oxazolidinone / Glycoconjugates



Due to their biological activity, sialic acid bearing glycoconjugates are very attractive synthetic targets. The chemical synthesis of sialosides is often plagued by low yields (due to competitive elimination reactions) and relatively poor stereoselectivities (due to competitive formation of the unnatural  $\beta$ -anomer). In spite of an outstanding pro-

gress achieved in the past decades, sialylation reactions still require low temperatures (-40 to -78 °C) and the presence of nitrile solvents. Herein we report that it is possible to obtain high yields and stereoselectivities for the synthesis of  $\alpha(2-6)$  galactosides using tetrahydrofuran solvent systems even at ambient temperature.



### Stereoselectivity in Ugi-3CR

D-*lyxo*-Pyrroline is an intermediate in the tandem Staudinger/aza-Wittig/Ugi three-component reaction. In this study we explored the effect of Lewis acids on the 2,3-cis/trans diastereoselectivity of the final

Ugi-3CR step with this cyclic imine. A diverse set of Lewis acids was evaluated in combination with varying reaction parameters and Ugi-3CR carboxylic acid/isocyanide components.

K. M. Bonger, T. Wennekes, D. V. Filippov, G. Lodder, G. A. van der Marel, H. S. Overkleeft\* ....... 3678–3688

The Effect of Lewis Acids on the Stereochemistry in the Ugi Three-Component Reaction with D-*lyxo*-Pyrroline

**Keywords:** Multicomponent reactions / Diastereoselectivity / Indium(III) chloride / Imines / Nitrogen heterocycles

**Hydrogen Bonding** 

NMR spectroscopy can reliably detect  $C-H\cdots O$  hydrogen bonding in solution through tracking of the solvent-induced shifts of the  $^1H$  chemical shifts and the one-bond C-H coupling constants. Quantum mechanical calculations on a series of model compounds gave hydrogen bond energy estimations of about  $4 \text{ kcal mol}^{-1}$  in the gas phase and  $2.5 \text{ kcal mol}^{-1}$  in DMSO solution.

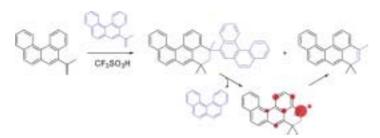


C. Niebel, V. Lokshin, M. Sigalov, P. Krief, V. Khodorkovsky\* .... 3689–3699

Intra- and Intermolecular  $C(sp^2)-H\cdots O$  Hydrogen Bonds in a Series of Isobenzofuranone Derivatives: Manifestation and Energetics

**Keywords:** Hydrogen bonds / NMR spectroscopy / Density functional calculations

# Polycyclic Aromatic Hydrocarbons



Novel PAH dimers and/or phenalenes were synthesized via the isopropenyl derivatives in simple one-pot reactions using triflic acid. Mechanistic aspects were probed via direct NMR study of the carbocation intermediates.

Superacid-Catalyzed Dimerization/Cyclization of Isopropenyl-PAHs — Novel Pathways to PAH Dimers, Phenalenes and Their Stable Carbocations

**Keywords:** Polycyclic aromatic hydrocarbons / Wittig olefination / Superacids / Carbocations / Phenalenes

4-Spirocyclopropanated methyl oxazoline-carboxylates, which are easily obtained from methyl 2-chloro-2-cyclopropylidene-acetate and arenecarboxamides under basic conditions, can further be modified at the carboxylate group and at the appropriately substituted aryl moiety to provide a library of such heterocyclic compounds for biological testing.

CI
$$CO_{2}Me$$

$$R^{2} = aryl, aminoaryl, biaryl$$

$$R^{2} = CO_{2}H, benzoxazolyl$$

$$32 examples$$

Spiro[cyclopropane-1,4'-oxazoline]s

S. Dalai, M. Es-Sayed, M. Nötzel, A. de Meijere\* ...... 3709-3713

A Convenient Access to Variously Substituted Spiro[cyclopropane-1,4 $^{\prime}$ -oxazoline]s

**Keywords:** Amides / Nitrogen heterocycles / Michael addition / Buchwald—Hartwig amination / Suzuki coupling / Cyclopropanes / Spiro compounds

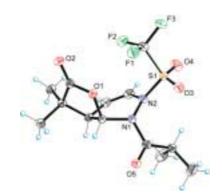
## **CONTENTS**

#### **Polycyclic Lactones**

A. Garduno-Alva, Y. Xu, N. Gualo-Soberanes, J. Lopez-Cortes, H. Rudler,\* A. Parlier, M. C. Ortega-Alfaro, C. Alvarez-Toledano,

Synthesis of New Polycyclic  $\gamma$ - and  $\delta$ -Lactones upon Activation of, and Nucleophilic Additions to, Diazines: Influence of the Activating Agents

**Keywords:** Lactones / Azo compounds / Cyclization / Silyl enol ethers / Polycycles



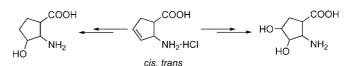
Whereas pyridine, pyrazine, quinoxaline and pyrimidine react with bis(trimethylsilyl)-ketene acetals in the presence of both methyl chloroformate and triflic anhydride to give the same type of lactonization reactions, pyridazine appears to be peculiar, giving  $\delta$ -lactones with the first activating agent and  $\gamma$ -lactones with the second one.

### **Hydroxy-Substituted Cispentacin**

G. Benedek, M. Palkó, E. Wéber, T. A. Martinek, E. Forró, F. Fülöp\* ...... 3724–3730

Efficient Synthesis of Hydroxy-Substituted Cispentacin Derivatives

**Keywords:** Amino acids / Hydroxycispentacin / Hydroxylation / Diastereoselectivity / Regioselectivity



New mono- and dihydroxy-substituted cispentacin derivatives have been prepared with functionalization of the olefinic bond of the *cis*-2-aminocyclopent-3-enecarboxylic acid. The enantiomers of these mole-

cules were also prepared by the same pathway. The structures, stereochemistry and relative configurations of the synthesized compounds were proved by NMR spectroscopy.

### IN MEMORIAM

G. Häfelinger\* ...... 3731-3746

□ Eugen Müller (1905−1976)

**Keywords:** Reminiscences



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

If not otherwise indicated in the article, papers in issue 20 were published online on June 23, 2008

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