











FRANCE











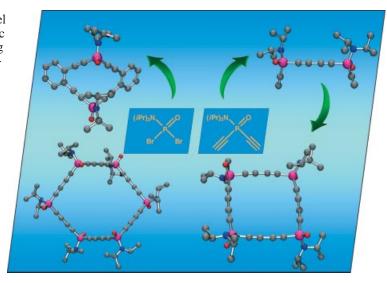




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic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

# COVER PICTURE

The cover picture shows the synthesis of three novel phosphorus-based macrocycles with acetylenic scaffolds from simple and accessible building blocks. The 14-membered macrocycle was obtained as cis and trans isomers from cyclization of disopropylphosphoramidic dibromide and 1,2-bis(ethynyl)benzene. The four- and six-edged macrocycles in which the iPr<sub>2</sub>NP(O) units are connected through 1,3-butadiyne rods were obtained after multiple acetylene coupling reactions under oxidative Hay conditions starting from the diethynylphosphinic amide building block. Further details are discussed in the article by K. Lammertsma et al. on p. 2405 ff.



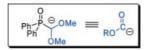
## **MICROREVIEW**

## **Synthetic Methods**

Small and Versatile – Formyl Anion and Dianion Equivalents

**Keywords:** Asymmetric synthesis / Carbanions / Formyl anions / Homologations / Umpolung

Formyl anion and hydroxycarbonyl anion equivalent



Formyl dianion equivalent

$$\mathbb{R}^{1}$$
S $\mathbb{S}^{\Theta}$ SR $^{1}$   $\cong$   $\mathbb{S}^{0}$ 

Lithiated (dimethoxymethyl)diphenylphosphane oxide is an ideal formyl anion equivalent for the asymmetric formylation of aldehydes, whereas the silyl-substituted carbanion may be looked upon as a latent dianion that can react either with two electrophiles or with bis-electrophiles, preferably with epoxides or epoxides carrying a remote leaving group.

## SHORT COMMUNICATION

## Pd/C-Catalyzed Cyanation

Y.-Z. Zhu, C. Cai\* ...... 2401-2404

Pd/C: A Recyclable Catalyst for Cyanation of Aryl Bromides

**Keywords:** Cyanation / Heterogeneous catalysis / Potassium hexacyanoferrate(II) / Palladium / Aryl cyanides

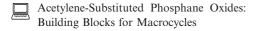
$$R \longrightarrow Br \xrightarrow{Pd/C, Na_2CO_3, Bu_3N} R \longrightarrow CN$$

Aryl cyanides have been prepared from the corresponding aryl bromides with potassium hexacyanoferrate(II) using Pd/C as a catalyst. The addition of  $Bu_3N$  is the key factor in obtaining the corresponding aryl

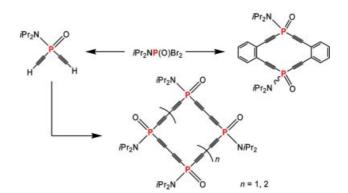
cyanides. The catalyst can be recycled by filtration and washing sequences, making the method attractive for industrial applications.

# **FULL PAPERS**

### **Phosphorus Acetylene Macrocycles**



**Keywords:** Phosphorus heterocycles / Alkynes / Macrocycles / Cross-coupling / Phosphanes



The synthesis of novel phosphorus- and acetylene-based macrocycles has been

explored through Grignard and acetylene coupling reactions.



### **Amavadin**

Secondary N-hydroxy amino acids have been synthesized through a strategy with nitrone reduction as its key step. The products are amavadin-related ligands, and their complexation with vanadium has been investigated.

Stabilizing Factors for Vanadium(IV) in Amavadin

**Keywords:** Amavadin / Vanadium / Reductive hydroxylamination / Hydroxylamines / Nitrones / Mass spectrometry

#### **Mesomeric Betaines**

A new example of the behaviour of *N*-aminides as 1,4-nucleophilic/electrophilic ylides is exemplified by reactions between 2-ethoxycarbonyl azinium salts and different types of reagents such as carbodimides, benzoyliso(thio)cyanates and heterocyclic imidoyl chlorides to afford new heterobetaines containing the [1,2,4]-triazinium system.

- J. Valenciano, E. Sánchez-Pavón, A. M. Cuadro,\* J. Alvarez-Builla, J. J. Vaquero\* ...... 2423–2429
- New Fused Triazinium Systems from Alkoxycarbonylazinium *N*-Aminides

**Keywords:** *N*-Aminides / 1,4-Dipole / Heterobetaines / Triazinium

### **Electrochemical Synthesis**

A versatile alternative approach to the synthesis of butenolides, quinolones and 3-pyrrolin-2-ones has been achieved by galvanostatic electrolysis of MeCN/TEATFB

solutions and subsequent addition of the cathodic solution to alkynes bearing proximate malonyl moieties.

A. Arcadi,\* A. Inesi, F. Marinelli, L. Rossi, M. Verdecchia ....... 2430–2437

An Electrochemical Alternative Approach to the Cyclization of Alkynes Bearing Proximate Malonyl Moieties

**Keywords:** Organic Electrosynthesis / Cyclization / Butenolides / Quinolones / 3-Pyrrolin-2-ones

## Flavylium-Derived Pigments

Common 3-deoxyanthocyanidins and novel dicationic flavylium-benzopyrylium derivatives are easily and efficiently synthesized through reactions between the corresponding phenols and aryl ethynyl ketones in the presence of aqueous hexafluorophosphoric acid. S. Chassaing,\* M. Kueny-Stotz, G. Isorez, R. Brouillard ....... 2438–2448

Rapid Preparation of 3-Deoxyanthocyanidins and Novel Dicationic Derivatives: New Insight into an Old Procedure

**Keywords:** Oxygen heterocycles / Ketones / Dyes / Pigments / Natural products / Synthetic method

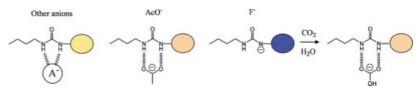
## CONTENTS

#### **Anion Chemosensors**

J. V. Ros-Lis, R. Martínez-Máñez,\* F. Sancenón, J. Soto, K. Rurack,\* H. Weißhoff ...... 2449-2458

Signalling Mechanisms in Anion-Responsive Push-Pull Chromophores: The Hydrogen-Bonding, Deprotonation and Anion-Exchange Chemistry of Functionalized Azo Dyes

**Keywords:** Chromophores / Dyes/Pigments / Chemosensors / Gas sensors / Carbon dioxide



A family of azo dyes containing amide, urea, thiourea, carbamate or amino hydrogen-bond donating groups were synthesized and their chromogenic response toward anions was studied. Two different effects were observed; (i) bathochromic shifts of

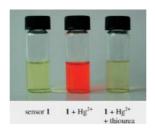
<40 nm due to anion coordination, and (ii) red shifts of ca. 200 nm due to deprotonation. This behaviour is associated with a balance between the deprotonation tendency of the binding sites and the proton affinities of the anions.

#### Sensors

Y. Fu, H. Li,\* W. Hu\* ...... 2459-2463

Small Molecular Chromogenic Sensors for Hg2+: A Strong "Push-Pull" System Exists after Binding

Keywords: Chemosensors / Mercury / Molecular recognition / Push-pull effects



Chromogenic mercury sensors based on structure-simple, electron-rich compounds and metal-induced charge-transfer effects are described.

## Lewis Acid Catalysis

M. Weïwer, X. Chaminade, J. C. Bayón, E. Duñach\* ...... 2464-2469

Indium Triflate-Catalysed Addition of Thio Compounds to Camphene: A Novel Route to 2,3,3-Trimethyl-2-thiobicyclo-[2.2.1]heptane Derivatives

Keywords: Indium triflate / Camphene / Thioacetylation / Hydrothiolation / Rearrangement

Efficient functionalisation of camphene by S-nucleophiles with the aid of indium(III) triflate catalysis, with suppression of the classical bicycle rearrangement to isobornane structures.

## **Deoxyglycoside Synthesis**

M. A. Rodríguez, O. Boutureira, M. I. Matheu, Y. Díaz,\*

S. Castillón\* ...... 2470-2476

Stereoselective Synthesis of 2-Deoxyglycosides from Sulfanyl Alkenes by Consecutive "One Pot" Cyclization and Glycosylation Reactions

Keywords: Glycosylation / Cyclization / Carbohydrates / Glycosides / Oligosaccharides



2-Deoxy-2-iodopyranosides were synthesized from sulfanyl alkenes using a "one pot" consecutive cyclization-glycosylation process. Sulfanyl alkenes of all configurations were used as starting materials.



Enedivnes

The synthesis of arenediynes from arene-1,2-dicarbaldehydes and bis(dibromomethyl) or bis(diazo) compounds is reported. Deuterium-labeling experiments established the predominance of alkylidenecarbenes in the case of tetrabromides. The scope of this novel method was extended to the synthesis of various heteroatom-based (S, Se, and P) enediynes by quenching the acetylides with suitable electrophiles.

$$CHO \longrightarrow CH=CX_2$$

$$CH=CX_2$$

$$\begin{bmatrix} CH=C: \\ CH=C: \end{bmatrix} \xrightarrow{1,2-shift}$$

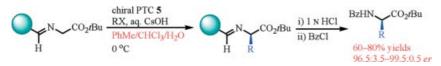
$$\bigcirc$$
 = aryl, heteroaryl; X = Br or N

B. Sahu, R. Muruganantham, I. N. N. Namboothiri\* ....... 2477-2489

Synthetic and Mechanistic Investigations on the Rearrangement of 2,3-Unsaturated 1,4-Bis(alkylidene)carbenes to Enediynes

**Keywords:** Vinylidenecarbene / Enediyne / Corey—Fuchs reaction / Bestmann—Ohira reagent / Enynes / Rearrangement

#### **Solid-Phase PTC**



Solvent effects in the enantioselective catalytic-phase-transfer alkylation of polymer-supported glycine—imine *tert*-butyl esters to afford (R)- $\alpha$ -amino acid derivatives are

described. The chemical yields and enantioselectivities were found to be dramatically dependent upon the ratio of water to organic solvent.

Solvent Effects in the Enantioselective Catalytic-Phase-Transfer Alkylation of Polymer-Supported Glycine–Imine *tert*-Butyl Ester: Asymmetric Solid-Phase Synthesis of (*R*)-α-Amino Acid Derivatives

Keywords: Phase-transfer catalysis / Solidphase synthesis / Solvent effects /  $\alpha$ -Amino acids

## Homogeneous Catalysis

$$CDG = OPPB$$

$$(CDG)O CO/H_2 CHO + R^{X-1} R^{X-1}$$

$$R^{X-1} R^{X-1} R$$

Branched-regioselective and positionselective hydroformylation of allylic alcohol systems can be accomplished with mono-, di-, and trisubstituted alkene functions by employing the catalyst-directing o-DPPB group (CDG = catalyst-directing group).

Directed Branched-Regioselective Hydroformylation of 2-Substituted Allylic o-DPPB Esters

**Keywords:** Homogeneous catalysis / Hydroformylation / C-C coupling / Catalyst-directing group

#### **Geranylated Flavonoids**

Two new cyclized *C*-geranylated flavonoids were isolated as minor compounds from the aerial parts of *Bonannia graeca* (Umbelliferae). The structures were elucidated by a combined approach of spectroscopic and quantum mechanical methods.

S. Rosselli, M. Bruno,\* A. Maggio, G. Bellone, C. Formisano, C. A. Mattia, S. Di Micco, G. Bifulco\* ...... 2504–2510

Two New Flavonoids from *Bonannia* graeca: a DFT-NMR Combined Approach in Solving Structures

**Keywords:** Umbelliferae / *Bonannia* graeca / Geranylated flavonoids / DFT

## **CONTENTS**

## **Peptidomimetics**



Succinimidyl Carbamate Derivatives from *N*-Protected α-Amino Acids and Dipeptides—Synthesis of Ureidopeptides and Oligourea/Peptide Hybrids

**Keywords:** Peptidomimetics / Peptides / Solid-phase synthesis / Urea / Oligomers

$$R^{1}$$
 $R^{3}$ 
 $R^{3$ 

A series of succinimidyl carbamate derivatives has been prepared starting from diversely substituted N-protected  $\alpha$ -amino acids and dipeptides, and their reactivity with external amines has been studied. The synthesis of ureidopeptides and oligourea/peptide hybrids, together with their propensity to promote local folded conformations, are reported.

### **β-Lactam Chemistry**

G. Cainelli, P. Galletti,\* D. Giacomini,S. Licciulli, A. Quintavalla ..... 2526-2533

Vinylic Halogenation in 4-Alkylidenazetidin-2-ones

**Keywords:** Halogenation / 4-Alkylidenazetidin-2-ones / Vinylic substitution / Lactams / Azetidinones

The synthesis of a new family of halogenated  $\beta$ -lactams by oxidative substitution of vinylic hydrogen in conjugated double

bonds of 4-alkylidenazetidinones is reported. Optimised procedures give chloro, bromo, iodo and nitro derivatives.

#### **Diastereoselective Transformations**

P. Chochrek, J. Wicha\* ...... 2534-2542

1,3-Chirality Transfer by Fragmentation of Allylsulfinic Acids: A Diastereoselective Approach to Vinyl Bromides Related to trans-Hydrindane or trans-Decalin

**Keywords:** Synthetic methods / Diastereoselectivity / *trans*-Decalin / *trans*-Hydrindane / Allylic thiols / Allylsulfinic acids

Bromoallylic alcohols were transformed diastereoselectively into the respective vinyl bromides in a sequence of reactions involving the following key steps: (1) the Mitsunobu inversion using 1,3-benzothiazol-2-yl sulfide, (2) cleavage of 1,3-benzothiazol-2-yl sulfides (or the respective sulfones) and (3) fragmentation of allylsulfinic acids.

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