























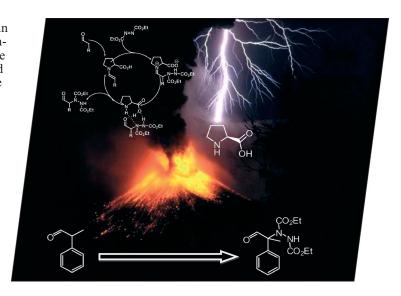




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic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

COVER PICTURE

The cover picture shows the use of L-proline as an organocatalyst for the construction of nitrogensubstituted quaternary carbon centres in the organocatalytic α -amination of α, α -disubstituted aldehydes. Since this reaction was found to be thermally accelerated, the use of microwave conditions resulted in a considerably reduced reaction time while both the yield and stereoselectivity were significantly increased. The beneficial effect of microwave irradiation may be associated with the quicker formation of intermediate dipolar adducts within the catalytic cycle. Details are presented in the article by S. Bräse et al. on p. 2207ff. This picture has been provided by M. Bächle, one of the members in the author's group.



MICROREVIEW

"New" Aromatics in Organic Materials

P. A. Peart, L. M. Repka, J. D. Tovar* 2193-2206

Emerging Prospects for Unusual Aromaticity in Organic Electronic Materials: The Case for Methano[10]annulene

Keywords: Conducting materials / Annulenes / Polymers / Cyclic voltammetry / UV / Vis spectroscopy

$$\pi = \frac{\pi}{\pi} \quad \text{and} \quad ??$$

Aromatics outside the 6π -electron motif offer promise as new electronic materials. This review examines the evolution and the current state-of-the-art for 10π -electron systems, emphasizing the [10]annulenes. These circuits can be viewed as viable components for new organic semiconductors alongside their role as landmark hydrocarbons.

FULL PAPERS

High-Temperature Organocatalysis

- T. Baumann, M. Bächle, C. Hartmann, S. Bräse* 2207–2212
- Thermal Effects in the Organocatalytic Asymmetric α-Amination of Disubstituted Aldehydes with Azodicarboxylates: A High-Temperature Organocatalysis

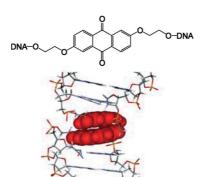
Keywords: Microwave / Organocatalysis / α-Amination / Amino aldehydes

A case of thermally accelerated organocatalytic α -amination of disubstituted aldehydes is presented. Compared to the results previously obtained at room temperature, both yield and enantioselectivity could be significantly increased. This improved protocol allows the fast and efficient synthesis of α,α -disubstituted amino aldehydes.

Anthraquinone-Modified DNA

- N. Bouquin, V. L. Malinovskii, R. Häner* 2213–2219
- Anthraquinones as Artificial DNA Building Blocks

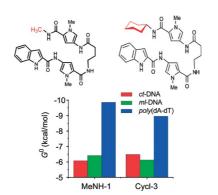
Keywords: DNA / Anthraquinone / Stacking interactions / Intercalations



Oligonucleotides containing different isomeric anthraquinone units are described. The site of linker attachment was found to be of critical importance for hybrid stability. Whereas the 2,6-isomer led to a significant stabilization, all other isomers had a negative effect on the stability of the duplex.



The distamycin-type γ -linked covalent dimer -Py- γ -Py-Ind has been shown, according to our fluorescence spectroscopy data, to be a neutral selective vector capable of transporting recognition elements to the minor groove of DNA for further structural studies.



Towards a Carbohydrate-DNA Carrier

P. Peñalver, S. Abdelouahid, P. Bosch, C. A. Hunter, C. Vicent* 2220-2231

A Neutral DNA Sequence-Selective Vector for Interaction Studies: Fluorescence Binding Experiments Directed Towards a Carbohydrate-DNA Carrier



Keywords: Carbohydrates / DNA recognition / Fluorescence spectroscopy / Vectors

F-Amphiphilic 1,2,3-Triazoles

$$\begin{array}{c|c} F(CF_2)_n & COOR \\ \hline N & NH & F(CF_2)_n C = CHCOXR \\ \hline N & N_3 & N & COOMe \\ \hline \end{array}$$

a) acetone, H₂O, NaN₃, 10 equiv. b) MeOOC-C≡C-COOMe, 75 °C, without solvent

A series of fluoroalkylated 1,2,3-triazoles were synthesised in significant yields through unexpected intramolecular cyclisations of vinyl azides with neighbouring electron-withdrawing groups. The results

depend on the conditions. The proposed mechanism includes the participation of a catalytic amount of azide ions in the intramolecular cyclisation of the vinyl azides to triazoles. E. Mayot, P. Lemière, C. Gérardin-Charbonnier* 2232–2239

F-Amphiphilic 1,2,3-Triazoles by Unexpected Intramolecular Cyclisation of Vinyl Azides

Keywords: 1,2,3-Triazoles / Vinyl azides / Intramolecular cycloadditions / Fluorinated compounds

Phenonium Ion Chemistry

Phenyl cations generated by irradiation of electron-rich chloroaromatics (e.g., 4-chloroanisole) add to the C=C bond of alkenols. Ring closure or chloride addition compete along with rearrangements at the

cation stage (hydride shift, C-C bond rotation), as determined by the structure and the medium polarity (tight ion pair vs. free ions).

Photochemical Arylation of Alkenols: Role of Intermediates and Synthetic Significance

Keywords: Aromatic substitution / Cations / Oxygen heterocycles / Phenonium ion / Photochemistry

Hetero-Diels-Alder Reactions

Chiral magnesium complexes of enantiopure BINOL derivatives catalyze asymmetric hetero-Diels-Alder reactions of Danishefsky's diene with aldehydes, affording 2,3-dihydro-4*H*-pyran-4-ones in high yields and with excellent *ee* values.

H. Du, X. Zhang, Z. Wang, H. Bao, T. You, K. Ding* 2248-2254

BINOLate-Magnesium Catalysts for Enantioselective Hetero-Diels-Alder Reaction of Danishefsky's Diene with Aldehydes

of Danishefsky's Diene with Aldehydes

Keywords: Asymmetric catalysis / Hetero-

Neywords: Asymmetric catalysis / Hetero-Diels-Alder reactions / Nonlinear effect / Magnesium / Danishefsky's diene / Aldehydes

CONTENTS

Supported NHC-Cu^I Catalyst

M. Wang, P. Li, L. Wang* 2255-2261

Silica-Immobilized NHC-Cu^I Complex: An Efficient and Reusable Catalyst for A³-Coupling (Aldehyde-Alkyne-Amine) under Solventless Reaction Conditions

Keywords: Silica-immobilization / N-Heterocyclic carbenes / Copper / Coupling reactions / Heterogeneous catalysis / Solventless reactions

$$R = H + R^{1}CHO + NHR^{2}R^{3} \xrightarrow{SiO_{2}-NHC-Cu^{1} \text{ cat.}} R$$

$$R = \text{aromatic, aliphatic}$$

$$R^{1} = H, \text{ aromatic, aliphatic}$$

$$R^{2} \cdot R^{3} = \text{aromatic, aliphatic}$$

$$R^{3} = \text{aromatic, aliphatic}$$

A novel SiO₂-NHC-Cu^I complex was developed. It was used as a highly efficient and reusable catalyst in the three-component coupling reactions of aldehydes,

alkynes, and amines (A³-coupling) to generate the corresponding propargylamines in good yields at room temperature and in the absence of solvent.

Allylindium Addition to 1,6-Diols

S. Kim, P. H. Lee* 2262-2266

Regioselective Addition of Allylindium Reagents to Allenes in Functionalized 1,6-Diols Bearing Allenynes

Keywords: Electrophilic addition / Allenes / Allylation / Indium

We have demonstrated that addition of allylindium reagents to functionalized allenyne 1,6-diols proceeds regioselectively

R² = H, Me X = Br, I through anti-Markovnikov addition to produce exclusively dienyne 1,6-diols in good

3-HOC₆H₄, 4-MeO₂CC₆H₄

= nPropyl, Cyclohexyl, Ph, 4-ClC₆H₄, 3-MeOC₆H₄ 4-MeOC₆H₄, 4-MeC₆H₄, 2,4,6-Me₃C₆H₂

Trifluorovinylation

Insight into the Reactions of Trifluorovinylsilanes with Aromatic Aldehydes

Keywords: Trifluoroallylic alcohols / Aldehydes / Elimination / Nucleophilic addition / Stereoselectivity

$$\begin{array}{c} O \\ Ar \end{array} + \begin{array}{c} C \\ Et_3SiCF = CF_2 \end{array} + \begin{array}{c} CSF \\ -60 \\ C \end{array} \\ \begin{array}{c} O \\ C \end{array} \\ \begin{array}{c} O \\ C \end{array} \\ \begin{array}{c} F \\ \end{array} \\ \begin{array}{c} OSiE \\ \end{array} \\ \begin{array}{c} F \\ \end{array} \\ \begin{array}{c} OSiE \\ \end{array} \\$$

yields.

The selective addition of trialkyl(trifluorovinyl)silanes to the C=O bond of aromatic aldehydes in the presence of cesium fluoride to give the corresponding "silylated" alcohols in high yields was performed. The reactivity of the "silylated" alcohols in the presence of nucleophilic reagents and Brönsted acids was studied.

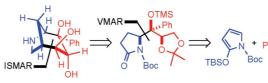
Vinylogous Aldol Addition

F. Zanardi,* C. Curti, A. Sartori,

G. Rassu, A. Roggio, L. Battistini,

P. Burreddu, L. Pinna, G. Pelosi,

G. Casiraghi* 2273-2287



Further Uses of Pyrrole-Based Dienoxysilane Synthons: A Full Aldol Approach to Azabicyclo[x.2.1]alkane Systems

Keywords: Asymmetric synthesis / Aldol reactions / Diastereoselectivity / N-heterocycles / Ketones

A highly productive strategy involving a crossed vinylogous Mukaiyama aldol reaction (VMAR) and an intramolecular silylative Mukaiyama aldol reaction (ISMAR) has been developed by using 1-(tert-butoxy-carbonyl)-2-(tert-butyldimethylsilyloxy)pyrrole and suitable ketones as the donor and

acceptor species, respectively. Densely functionalized 2-azabicyclo[2.2.1]heptanes and 6-azabicyclo[3.2.1]octanes have been accessed in useful overall yields and with good-to-excellent margins of regio- and diastereoselectivity.



Wittig-Type Pyrrole Synthesis

3-[(Diphenylmethylene)amino]propionitrile (5) and [3-¹⁵N]-[(diphenylmethylene)amino]propionitrile (5a) react with diethyl chlorophosphate in the presence of LDA and subsequently with 1,1-dimethoxyacetone to

form a new Wittig adduct, which under acid catalysis forms 3-cyano-4-methyl-1*H*-pyrrole (1) and [1-¹⁵N]-3-cyano-4-methyl-1*H*-pyrrole (1a), respectively.

Efficient Preparation of [1-¹⁵N]-3-Cyano-4-methyl-1*H*-pyrrole by a Wittig-Based Strategy

Keywords: Nitrogen heterocycles / Mass spectrometry / NMR spectroscopy

Cyclotrimerisation

The regioselectivity of the cyclotrimerisation of phenylacetylene can be altered dramatically with a disulfide ligand in a cobalt-catalysed process. The strong solvent dependency of the regioselectivity of the

reaction allows an extremely simple alteration of the reaction outcome and generates the desired products in quantitative yields with good to excellent regioselectivities.

G. Hilt,* C. Hengst, W. Hess 2293-2297

Solvent-Dependent Regiochemical Cyclotrimerisation of Phenylacetylene with Cobalt Catalysts Containing Disulfide Ligands: A Case Study

Keywords: Cobalt / Disulfide ligands / Cyclotrimerisation / Regioselectivity / Heterogeneous catalysis

Asymmetric Hydroformylation

Asymmetric hydroformylation of three *meso*-bicyclic hydrazines followed by the reduction of the formyl product yielded the

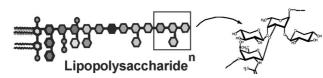
corresponding desymmetrized optically enriched hydroxymethyl hydrazines (up to 77.5%ee).

C. Bournaud, T. Lecourt, L. Micouin,* C. Méliet, F. Agbossou-Niedercorn* 2298-2302

Desymmetrization of *meso*-Bicyclic Hydrazines by Rhodium-Catalyzed Enantioselective Hydroformylation

Keywords: Asymmetric catalysis / Hydroformylation / Rhodium / N heterocycles

Lipopolysaccharides



Burkholderia phytofirmans PsJN is a gramnegative bacterium capable of endophytic colonization of potato, grapevine, tomato, and other plants. It is able to promote plant growth and health. A key role in these interactions is played by lipopolysaccharides (LPSs). In this paper we studied the chemical structure of the O-chain polysaccharide from its LPS.

The Structure of the O-Chain Polysaccharide from the Gram-Negative Endophytic Bacterium *Burkholderia phytofirmans* Strain PsJN

Keywords: Lipopolysaccharides / NMR spectroscopy / Carbohydrates

CONTENTS

Carbon Dioxide Fixation

Reusable Polymer-Supported Amine-Copper Catalyst for the Formation of α -Alkylidene Cyclic Carbonates in Supercritical Carbon Dioxide

Keywords: Polymer-supported catalysts / Carbon dioxide fixation / Cyclic carbonates / Supercritical carbon dioxide / Cyclization / Copper

$$= \begin{matrix} OH \\ R^2 \end{matrix} R^1 \begin{matrix} CuI \\ scCO_2 \end{matrix} \begin{matrix} R^1 \end{matrix} \begin{matrix} O \\ R^2 \end{matrix}$$

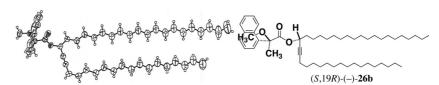
A polymer-supported catalyst containing cuprous iodide and amine functions efficiently catalyzes the cyclization of propargyl alcohols in supercritical carbon dioxide (scCO $_2$) to give α -alkylidene cyclic carbonates. The catalyst can be recovered easily by simple filtration and reused several times after minimal treatment.

Enantiopure Acetylene Alcohols



Synthesis of Enantiopure Aliphatic Acetylene Alcohols and Determination of Their Absolute Configurations by ¹H NMR Anisotropy and/or X-ray Crystallography

Keywords: Acetylene alcohols / Configuration determination / Absolute configuration / $M\alpha NP$ esters / NMR anisotropy / X-ray diffraction



Enantiopure aliphatic acetylene alcohols have been synthesized by the $M\alpha NP$ acid method and their absolute configurations

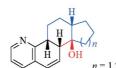
unambiguously determined by ¹H NMR anisotropy and/or by X-ray crystallography.

Azasteroids

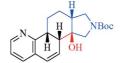


Nitrogen-Containing Tricyclic and Tetracyclic Compounds by Stereoselective Samarium Diiodide Promoted Cyclizations of Quinolyl-Substituted Ketones – A New Access to Azasteroids

Keywords: Samarium / Electron transfer / Quinolines / Steroids / C-C coupling



The stereoselective synthesis of azasteroid analogues by samarium diiodide promoted cyclizations of quinolyl-substituted ketones is reported. The precursors were prepared



by Heck-type couplings of hetaryl nonaflates with the corresponding olefins followed by appropriate (de)functionalization

If not otherwise indicated in the article, papers in issue 12 were published online on April 2, 2008