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Cover

#### Incorporating Acta Chemica Scandinavica

See Barry K. Carpenter, pp. 103–109. *Ab initio* electronic-structure calculations have shown that the stereoselectivities of two seemingly unrelated reactions – the Cope rearrangement of 1,5-hexadiene and the ring opening of bicyclo[2.1.0]pentane – are controlled by very similar orbital interactions in their transition states. Molecular structures and orbitals were created with MacMoIPIt: B. M. Bode and M. S. Gordon, *J. Mol. Graphics Mod.*, 1998, **16**, 133.



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Chemical Science



Pd(PtBu<sub>3</sub>)<sub>2</sub>

KF or CsF

DMF

60 °C

5 min

Q

CH<sub>3</sub>I

CH<sub>3</sub>I/Sn/Pd/F<sup>-</sup> = 1/40/1/2

#### PERSPECTIVE

23

27

CH-

74-96% for

CH<sub>3</sub>I consumption

#### Ru complexes bearing bidentate carbenes: from innocent curiosity to uniquely effective catalysts for olefin metathesis

Amir H. Hoveyda, Dennis G. Gillingham, Joshua J. Van Veldhuizen, Osamu Kataoka, Steven B. Garber, Jason S. Kingsbury and Joseph P. A. Harrity

New class of Ru catalysts promote olefin metathesis reactions and provide reactivity and selectivity levels not available by other complexes.

#### COMMUNICATIONS

#### Rapid methylation of terminal acetylenes by the Stille coupling of methyl iodide with alkynyltributylstannanes: a general protocol potentially useful for the synthesis of shortlived <sup>11</sup>CH<sub>3</sub>-labeled PET tracers with a 1-propynyl group

Takamitsu Hosoya, Masahiro Wakao, Yurie Kondo, Hisashi Doi and Masaaki Suzuki

The Pd(0)-mediated rapid coupling (trapping) reaction of methyl iodide with an excess amount of alkynyltributylstannane has been developed with the aim to incorporate a short-lived <sup>11</sup>C-labeled methyl group into biologically active organic compounds with a 1-propynyl structural unit.

### A novel and facile synthesis of dienals and substituted 2H-pyrans *via* the Vilsmeier reaction of $\alpha$ -oxo-ketenedithioacetals

Yingchun Liu, Dewen Dong, Qun Liu, Yimei Qi and Zuo Wang

A novel and facile synthesis of dienals and substituted 2H-pyrans from a series of  $\alpha$ -oxo ketenedithioacetals containing a methyl group adjacent to the carbonyl group *via* the Vilsmeier reaction has been developed.

#### Synthesis of an S-linked glycopeptide analog derived from human Tamm–Horsfall glycoprotein

Xiangming Zhu, Tobias Haag and Richard R. Schmidt

S-Linked glycopeptide 1, which mimics the peptide sequence Ala484–Ala490 in Tamm–Horsfall protein, was synthesized in solution phase.

#### ARTICLES

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## Diamagnetic and paramagnetic ring currents in expanded porphyrins

Erich Steiner and Patrick W. Fowler

Computed global ring currents in expanded porphyrins are diatropic or paratropic and dominated by 4 or 2 electrons, according to the nature of the HOMO–LUMO transition.



SnBu<sub>3</sub>



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#### ARTICLES

## Total synthesis of (-)-microcarpalide, a novel microfilament disrupting metabolite

Paolo Davoli, Alberto Spaggiari, Luca Castagnetti and Fabio Prati

The total synthesis of (-)-microcarpalide was accomplished through stereoselective homologation of boronic esters and RCM as the key steps.

#### Absolute stereochemistry of dihydrofuroangelicins bearing C-8 substituted double bonds: a combined chemical/exciton chirality protocol

Katsunori Tanaka, Gennaro Pescitelli, Lorenzo Di Bari, Tom L. Xiao, Koji Nakanishi, Daniel W. Armstrong and Nina Berova

A variety of the substituted C=C double bonds of synthetic dihydrofuroangelicins were converted into a styrenoid chromophore and their absolute configurations were assigned by non-empirical CD analysis.

## New isocysteine building blocks and chemoselective peptide ligation

Christian Dose and Oliver Seitz

Novel isocysteine building blocks enabled the solid-phase synthesis of isocysteinyl peptides suitable for fragment ligations in water.

The use of new isocysteine building blocks provided access to isocysteinyl peptides that enable chemoselective ligation of unprotected peptide fragments in water.

### Stabilisation of the transition state of phosphodiester bond cleavage within linear single-stranded oligoribonucleotides

Ulla Kaukinen, Harri Lönnberg and Mikael Peräkylä

Within linear single-stranded oligoribonucleotides, the TS of phosphodiester bond cleavage is stabilised by the enhanced stacking of bases.

#### Cyclic PNA-based compound directed against HIV-1 TAR RNA: modelling, liquid-phase synthesis and TAR binding

Geoffrey Depecker, Nadia Patino, Christophe Di Giorgio, Raphael Terreux, Daniel Cabrol-Bass, Christian Bailly, Anne-Marie Aubertin and Roger Condom

A cyclic molecule including a hexameric PNA sequence has been designed and synthesized in order to target the TAR RNA loop of HIV-1 through the formation of a "kissing complex".



#### ARTICLES

#### Oligodeoxynucleotides containing a-L-ribo configured LNA-type C-aryl nucleotides

Raunak, B. Ravindra Babu, Mads D. Sørensen, Virinder S. Parmar, Niels H. Harrit and Jesper Wengel

Synthesis of phenyl and pyrenyl derivatives of  $\alpha$ -L-LNA-type C-aryl nucleosides has been accomplished as has their efficient incorporation into 9-mer DNA and α-L-LNA strands. Fluorescence measurements indicated intercalation of the pyrenyl moiety into the nucleobase stack of the duplexes.

#### Atom-efficient electrophilic aromatic nitration by dinitrogen pentoxide catalysed by zirconium(IV) 2,4-pentanedionate

Adrian J. Hill, Ross W. Millar and John P. B. Sandall

A 5000 fold increase in rate constant is observed on addition of 1 mol% of catalyst.

#### The fluorine-containing $\pi$ -allylmetal complex. The transition metal-catalyzed allylic substitution reaction of fluorinated allyl mesylates with various carbon nucleophiles

Tsutomu Konno, Tsuyoshi Takehana, Takashi Ishihara and Hiroki Yamanaka

The reaction proceeded with high regioselectivity to give the  $\gamma$ -fluoroalkylated products in excellent yields.

#### Esterase-assisted accumulation of 3-carboxy-2,2,5,5tetramethyl-1-pyrrolidinyloxyl into lymphocytes

Joseph P. Y. Kao and Gerald M. Rosen

The results presented here indicate that it should be feasible to use the labile ester approach to load spin traps into living cells to detect intracellularly generated HO'.

#### Understanding the puzzling chemistry of bicyclo[2.1.0]pentane

Barry K. Carpenter

CASPT2 calculations are used to investigate unimolecular and bimolecular reactions of bicyclo[2.1.0]pentane.

# 110 113



no protection!

South

85%, based on organozinc

North





 $\mathbf{X} = NH_2$ , CI, OCH<sub>3</sub>;  $\mathbf{Y} = H$ , NH<sub>2</sub>





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### ARTICLES

Direct synthesis of unprotected phenols using palladiumcatalysed cross coupling reactions of functionalised organozinc reagents

Richard F. W. Jackson, Ian Rilatt and P. John Murray

Coupling of functionalised organozinc reagents with unprotected iodophenols proceeds in moderate to excellent yields.

#### NMR and UV studies of 3'-S-phosphorothiolate modified DNA in a DNA : RNA hybrid dodecamer duplex; implications for antisense drug design

Andrew P. G. Beevers, Kevin J. Fettes, Ghalia Sabbagh, Fatima K. Murad, John R. P. Arnold, Richard Cosstick and Julie Fisher

NMR and UV melting studies of 3'-S-phosphorothiolate-modified nucleic acids provide insight into the cause of transmission of the north/south equilibrium shift.

#### Synthesis and cytotoxicity of 9-(2-deoxy-2-alkyldithio-β-Darabinofuranosyl)purine nucleosides which are stable precursors to potential mechanistic probes of ribonucleotide reductases

Stanislaw F. Wnuk, Elzbieta Lewandowska, Dania R. Companioni, Pedro I. Garcia Jr and John A. Secrist III

A series of 2'-thionucleosides, as potential inhibitors of ribonucleotide reductases, has been synthesized.

#### Conformation-activity relationships in polyketide natural products. Towards the biologically active conformation of epothilone

Richard E. Taylor, Yue Chen, Gabriel M. Galvin and Praveen K. Pabba

The conformation–activity relationships for the biologically active polyketide, epothilone, have been determined, and are shown to be an important complement to structure–activity data.

#### Application of Fmoc-amino acid carrying an unmasked carbohydrate to the synthesis of the epidermal growth factor-like domain of bovine blood coagulation factor IX

Toshio Takemura, Hironobu Hojo, Yoshiaki Nakahara, Takeshi Ishimizu and Sumihiro Hase

The EGF-like domain of the bovine factor IX carrying glucose was synthesized by the Fmoc solid-phase method. The introduction was accomplished by Fmoc-Ser carrying an unmasked glucose by the DCC–HOBt method.



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