# Chemical Science

# Organic Chemistry Organic Chemistry

#### INDEXED IN MEDLINE

#### Incorporating Acta Chemica Scandinavica



#### Cover

See Xin Li, Chris Abell, Miles S. Congreve, Brian H. Warrington and Mark Ladlow, pp. 989–998. The use of a bifunctional, phase-switching protecting group for the parallel solution phase synthesis of carboxamides.



Chemical biology articles published in this journal also appear in the Chemical Biology Virtual Journal: www.rsc.org/chembiol

# contents



### **Chemical Science**

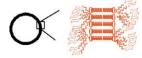
April 2004/Volume 1/Issue 4 www.rsc.org/chemicalscience

Drawing together the research highlights and news from all RSC publications, *Chemical Science* provides a 'snapshot' of the latest developments across the chemical sciences showcasing newsworthy articles, as well as the most significant scientific advances.





#### COMMUNICATIONS





## Multivalent binding of galactosylated cyclodextrin vesicles to lectin

Antonino Mazzaglia, Damien Forde, Domenico Garozzo, Paola Malvagna, Bart Jan Ravoo and Raphael Darcy

Novel amphiphilic cyclodextrins labelled with glycosyl groups form nanoparticles and vesicles for the recognition of carbohydratebinding cell receptors.



$$X = H, CH_3, CHO, CH=CH_2, CH_2NH_2$$
 $R = H, CH_2-CH=CH_2$ 
 $AcNH$ 
 $AcNH$ 

#### COMMUNICATIONS

### Formation of LacNAc mimetics employing novel donor substrates for enzymatic $\beta1\rightarrow4$ galactosylation

Saskia Weingarten and Joachim Thiem

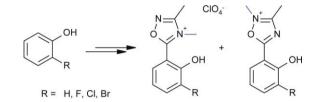
In examining C-6 modified 4-nitrophenyl  $\beta$ -D-galactopyranosides as donor structures the  $\beta$ -galactosidase (*Bacillus circulans*) revealed an unexpectedly broad substrate specificity which allowed successful syntheses of various disaccharide components.

# 963 964

## A short and efficient preparation of methyl-[1,2,4]-oxadiazolium derivatives with plant-inducing activity

Markus R. Dobler

We have developed an efficient synthetic method leading to a structurally diverse array of salicylic acid and oxadiazolium derivatives.



#### **□**



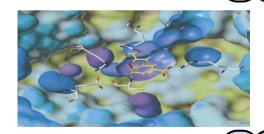
# Manganese(III) acetate mediated synthesis of oxygen heterocycles. Influence of copper(II) salts on product distribution

David G. Hulcoop, Helen M. Sheldrake and Jonathan W. Burton

Exposure of unsaturated malonates bearing pendant alcohols to manganese(III) acetate and a copper(II) salt gives rise to the formation of carbocycles linked to oxygen heterocycles. The use of copper(II) salts bearing poorly coordinating anions has a profound influence on the product distribution.

#### 968 980 A R

988

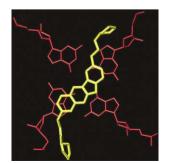


#### ARTICLES

Transition state stabilization and substrate strain in enzyme catalysis: *ab initio* QM/MM modelling of the chorismate mutase reaction

Kara E. Ranaghan, Lars Ridder, Borys Szefczyk, W. Andrzej Sokalski, Johannes C. Hermann and Adrian J. Mulholland

High-level modelling of Claisen rearrangement in *B. subtilis* chorismate mutase shows significant TS stabilization by the enzyme, compared to solution.



# Synthesis and evaluation of analogues of 10*H*-indolo-[3,2-*b*]quinoline as G-quadruplex stabilising ligands and potential inhibitors of the enzyme telomerase

Bérangère Guyen, Christoph M. Schultes, Pascale Hazel, John Mann and Stephen Neidle

A new class of quindoline analogues with substituents at the 2- and 7-positions have been synthesised and shown to stabilise an intramolecular G-quadruplex DNA against increases in temperature. The compounds shown exhibit modest inhibitory activity against telomerase.



#### A novel phase-switching protecting group for multi-step parallel solution phase synthesis

Xin Li, Chris Abell, Miles S. Congreve, Brian H. Warrington and Mark Ladlow

A novel protecting group that incorporates functionalities to facilitate compound purification by enabling solid-phase extraction in either an irreversible, or pH dependent reversible manner is presented, and its use in parallel synthesis is exemplified.

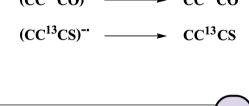
## 999 1006

1012

## Do the interstellar molecules CCCO and CCCS rearrange when energised?

Khoa Minh Tran, Andrew M. McAnoy and John H. Bowie

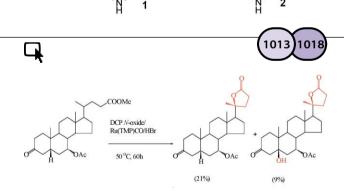
The neutrals CCCO and CCCS can be made by one-electron vertical oxidation of the anion precursors (CCCO)<sup>-\*</sup> and (CCCS)<sup>-\*</sup>. The majority are stable for at least a microsecond.



# Conformation inversion of an inositol derivative by use of silyl ethers: a modified route to 3,6-di-*O*-substituted-L-*ido*-tetra-hydroxyazepane derivatives

Gavin F. Painter, Andrew Falshaw and Herbert Wong

Silyl substitution on an inositol ring causes ring inversion, allowing an otherwise unreactive *trans*-diaxial diol to react with periodate.



# The remote-oxyfunctionalization of unactivated carbons in (5β)-3-oxobile acids by 2,6-dichloropyridine *N*-oxide catalyzed by ruthenium–porphyrin and HBr: a direct lactonization at C-20

Shoujiro Ogawa, Takashi Iida, Takaaki Goto, Nariyasu Mano, Junichi Goto and Toshio Nambara

A direct, one-step lactonization of the unactivated carbon at C-20 in 3-oxobile acid methyl ester-acetylates was attained by the title oxidant system.



## Efficient conversion of 6-cyanopurines into 6-alkoxyformimidoylpurines

M. Alice Carvalho, Teresa M. Esteves, M. Fernanda Proença and Brian L. Booth

6-Cyanopurines were selectively converted into 6-alkoxy or 6-alkoxyformimidoylpurines. The reaction of 6-alkoxyformimidoylpurines with methylamine led to 6-amidinopurines in excellent yield.



#### ARTICLES

### Synthesis of the tetraethyl substituted pH-sensitive nitroxides of imidazole series with enhanced stability towards reduction

Igor A. Kirilyuk, Andrey A. Bobko, Igor A. Grigor'ev and Valery V. Khramtsov

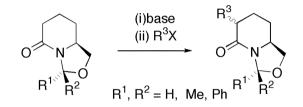
The pH-sensitive spin probes of a 2,2,5,5-tetraethylimidazole series are much more stable in blood and in ascorbate solutions than their 2,2,5,5-tetramethyl analogs.

# 1031 1043

## **Enantiopure bicyclic piperidinones: stereoselectivity in lactam enolate alkylations**

Andrew G. Brewster, Simon Broady, Catherine E. Davies (née Mills), Thomas D. Heightman, Stephen A. Hermitage, Mark Hughes, Mark G. Moloney and Gordon Woods

The synthesis and alkylation of [4.3.0]-bicyclic lactams, derived from 6-oxopipecolic acid, have been investigated.

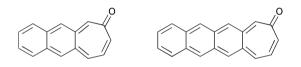


## 1044 1050

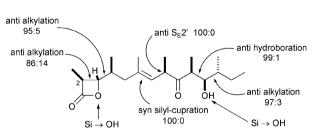
# $\pi$ -Extended o-quinoidal tropone derivatives: experimental and theoretical studies of naphtho[2,3-c]tropone and anthro[2,3-c]-tropone

Masakazu Ohkita, Kieko Sano, Takanori Suzuki, Takashi Tsuji, Tadatake Sato and Hiroyuki Niino

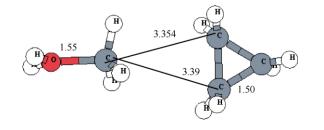
 $\pi$ -Extended o-quinoidal naphtho[2,3-c]tropone has been generated photochemically under matrix isolation conditions and characterized.



# 1051 1064







# Stereocontrol in organic synthesis using silicon-containing compounds. Studies directed towards the synthesis of ebelactone A

Sarah C. Archibald, David J. Barden, Jérôme F. Y. Bazin, Ian Fleming, Colin F. Foster, Ajay K. Mandal, Amit K. Mandal, David Parker, Ken Takaki, Anne C. Ware, Anne R. B. Williams and Anna B. Zwicky

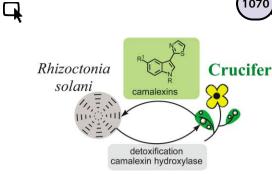
A silyl group controlled all the relative stereochemistry in the assembly of three components designed for a synthesis of ebelactone A, but the configuration at C-2 was inadvertently inverted at a later stage.

### Relative reactivity of three and four membered rings – the absence of charge effect

Joel L. Wolk, Milon Sprecher, Harold Basch and Shmaryahu Hoz

Breaking one bond alleviates strain from half of the carbons in cyclobutane but two thirds of the carbons in cyclopropane.

#### 1 (1070)1076)



#### ARTICLES

### Designer phytoalexins: probing camalexin detoxification pathways in the phytopathogen *Rhizoctonia solani*

M. Soledade C. Pedras and Jun Liu

Detoxification *via* oxidation of the indole moiety of camalexins is predominant in the transformation of camalexin and 5-methylcamalexin, whereas detoxification of 1-methylcamalexin and 5-fluorocamalexin involves reaction at the thiazole ring. From a plant's perspective, 1-methylcamalexin appears to be a more effective antifungal defence than camalexin.

# EtO<sub>2</sub>C R<sup>1</sup> + EtO<sub>2</sub>C R<sup>2</sup> Chiral catalyst good yield high enantioselectivity

Isotetronic acids

### Direct catalytic asymmetric aldol reactions of pyruvates: scope and mechanism

Nicholas Gathergood, Karsten Juhl, Thomas B. Poulsen, Karl Thordrup and Karl Anker Jørgensen

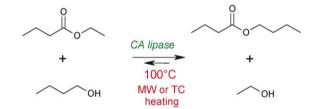
The direct aldol reaction of 2-ketoesters catalyzed by chiral bisoxazoline copper(II) complexes has been investigated.

## 1086 1089

### Stability improvement of immobilized *Candida antarctica* lipase B in an organic medium under microwave radiation

Barbara Réjasse, Sylvain Lamare, Marie-Dominique Legoy and Thierry Besson

Enhancement of enzymatic stability has been observed when microwave heating (MW) was used rather than thermal classical heating (TC), especially in a more polar solvent.



# 1090 1092

## Alkylation of guanosine and 2'-deoxyguanosine by o-quinone $\alpha$ -(p-anisyl)methide in aqueous solution

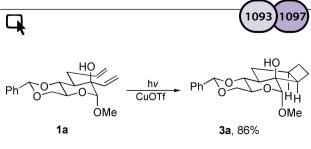
Yvonne Chiang and A. Jerry Kresge

o-Quinone  $\alpha$ -(p-anisyl)methide is a potent guanosine and 2'-deoxyguanosine alkylator.

$$BH_{2} \xrightarrow{K_{1}} BH^{-} + H^{+} \xrightarrow{K_{2}} B^{=} + 2H$$

$$QM \downarrow k_{1} \qquad QM \downarrow k_{2} \qquad QM \downarrow k_{3}$$

QM = o-quinone  $\alpha$ -(p-anisyl)methide BH<sub>2</sub> = guanosine or 2'-deoxyguanosine



 $CuOTf = [(CuSO_3CF_3)_2.C_6H_6]$ 

The synthesis of fused and spiro annulated carbohydrate structures using copper(I) catalysed intramolecular photoannulation of glucose derivatives

David J. Holt, William D. Barker, Subrata Ghosh and Paul R. Jenkins

Intramolecular [2 + 2] photoannulation catalysed by copper(I) triflate has been applied to a series of carbohydrate derivatives obtained from glucose.



#### ARTICLES

Thorpe–Ingold effects in cyclizations to five-membered and six-membered rings containing planar segments. The rearrangement of N(1)-alkyl-substituted dihydroorotic acids to hydantoinacetic acids in base

Jose Kaneti, Anthony J. Kirby, Asen H. Koedjikov and Ivan G. Pojarlieff

When  $R \ge Me \ 2^{2^-}$  cyclizes to  $3^{2^-}$  the driving force is the smaller angles enforced in the 5-membered ring with planar segments.



#### CONFERENCE DIARY

Dates, venues and contact details of forthcoming events.

#### COPIES OF CITED ARTICLES

The Library and Information Centre (LIC) of the RSC offers a first class Document Delivery Service for items in Chemistry and related subjects. Contact the LIC, The Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN, UK;

Tel: +44 (0) 20 7437 8656; Fax: +44 (0) 20 7287 9798; E-mail: library@rsc.org

This service is only available from the LIC in London and not the RSC in Cambridge.

#### FREE E-MAIL ALERTS

Contents lists in advance of publication are available on the web via www.rsc.org/obc – or take advantage of our free e-mail alerting service (www.rsc.org/ej\_alert) to receive notification each time a new list becomes available.

#### ADVANCE ARTICLES AND ELECTRONIC JOURNAL

Free site-wide access to Advance Articles and the electronic form of this journal is provided with a full-rate institutional subscription. See www.rsc.org/ejs for more information.

\* Indicates the author for correspondence: see article for details.

**□** 

Electronic supplementary information is available on http://www.rsc.org/esi: see article for further information.