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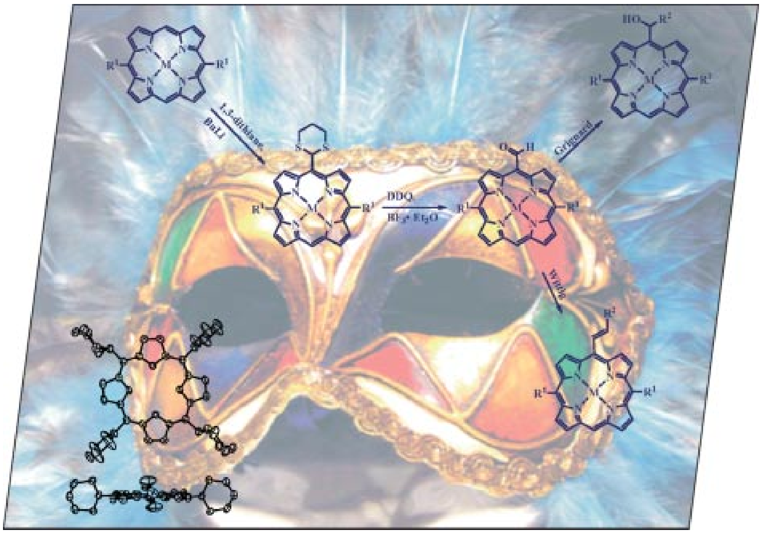
The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry.* Three further EUChemSoc Societies (Austria, Czech Republic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

COVER PICTURE

The cover picture shows the synthesis of formylporphyrins by Umpolung reactions that use 1,3-dithian-2-ylporphyrins as masked synthons. This method offers a new pathway for the preparation of free-base and metallo formylporphyrins under mild conditions. Grignard and Wittig reactions have been performed to demonstrate the wide range of applications for formylporphyrins. Details are discussed in the article by M. O. Senge et al. on p. 3833 ff.



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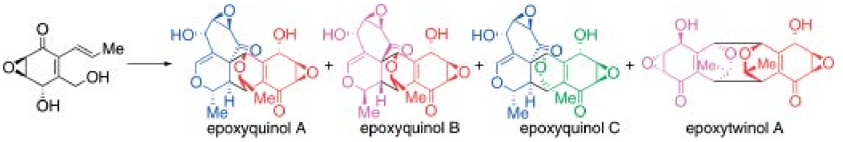
MICROREVIEWS

Natural Product Synthesis

M. Shoji, Y. Hayashi* **3783–3800**

Chemistry of Epoxyquinols A, B, and C and Epoxytwinol A

Keywords: Epoxyquinols A, B, C / Epoxytwinol A / Total synthesis / Electrocyclic reactions / Diels–Alder reactions / Density functional calculations



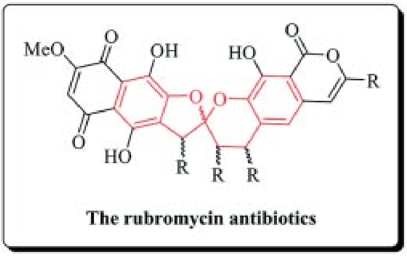
Epoxyquinols A, B, and C and epoxytwinol A have been synthesized by the postulated biosynthetic pathway which involves oxidation and 6π-electrocyclization followed by Diels–Alder or [4+4] cycloaddition reaction of the monomer. The mechanism for the oxidative dimerization reactions has also been elucidated by computational calculations which indicate that inter- and intramolecular hydrogen bonds play an important role in the formation of epoxyquinol B and epoxytwinol A.

Total Synthesis

M. Brasholz, S. Sörgel, C. Azap, H.-U. Reißig* **3801–3814**

Rubromycins: Structurally Intriguing, Biologically Valuable, Synthetically Challenging Antitumour Antibiotics

Keywords: Polyketides / Natural products / Spiroketals / Naphthoquinones / Total synthesis / Isocoumarins



The rubromycin antibiotics

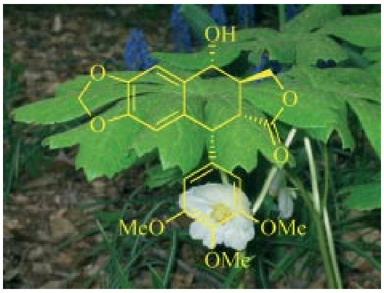
Although known for more than 50 years the rubromycin family still constitutes a fascinating class of antitumour antibiotics. While their impressive biological properties have been well recognized, some of the rubromycin structures remain partially unproven and efficient synthetic methodologies for the total synthesis of these natural products are still to be developed.

Natural Product Synthesis

J. D. Sellars, P. G. Steel* **3815–3828**

Advances in the Synthesis of Aryltetralin Lignan Lactones

Keywords: Aryltetralin lignan / Podophyllotoxin / Synthesis design / Lactones / Stereochemistry



Providing both important biological activity and a stereochemical challenge, the synthesis of the aryltetralin lignan lactones, typified by podophyllotoxin, remains an attractive goal. This microreview will survey the various strategies used to assemble this class of natural product.

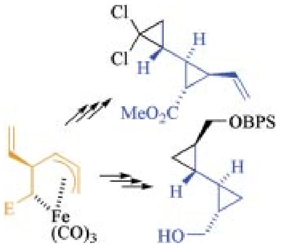
SHORT COMMUNICATION

Bi(cyclopropyl) Preparation

R. K. Pandey, S. Lindeman, W. A. Donaldson* **3829–3831**

Synthesis of Cyclopropanes via Organoiron Methodology: Stereoselective Preparation of Bi(cyclopropyl)s

Keywords: Pentenediyl ligands / Iron / Diastereoselectivity / Carbocycles



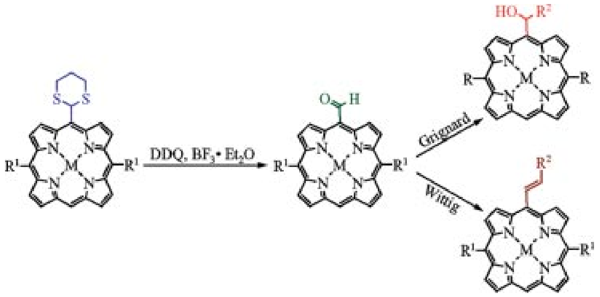
Cyclopropanation of [2-(alkenyl)pentenediyl]Fe(CO)$_3$ complexes occurs in a diastereoselective fashion to afford [2-(cyclopropyl)pentenediyl]Fe(CO)$_3$. The relative stereochemistry of the products was established by X-ray crystallography. The diastereoselectivity is rationalized on approach of the cyclopropanation reagent on the sterically more exposed face of the alkenylpentenediyl complex. Decomplexation gives stereodefined bi(cyclopropyl)s.

FULL PAPERS

Porphyrin Chemistry

K. Dahms, M. O. Senge,*
M. B. Bakar 3833–3848

Exploration of *meso*-Substituted Formylporphyrins and Their Grignard and Wittig Reactions



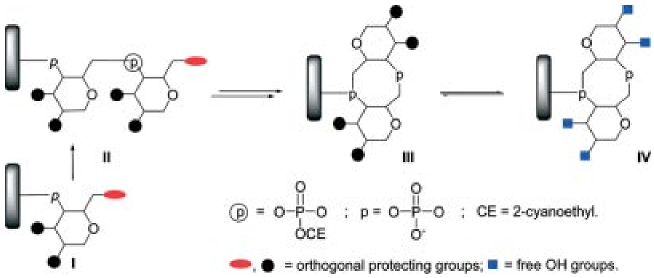
The 1,3-dithian-2-yl umpolung synthon for the formyl group was used to synthesise formylporphyrin free bases in moderate yields, and their metallated porphyrins were also prepared under mild conditions. To demonstrate the wide range of applications for the formyl group, studies of Grignard and Wittig reactions were performed.

Keywords: Porphyrinoids / Grignard reaction / Wittig reaction / Tetrapyrroles / Umpolung

Immobilized Oligosaccharides

J. D'Onofrio, C. Coppola,
G. Di Fabio, L. De Napoli,
D. Montesarchio* 3849–3858

Novel Cyclic Phosphate-Linked Oligosaccharides (CyPLOSs) Covalently Immobilized on Solid Supports for Potential Cation Scavenging



A synthetic procedure to functionalize a Tentagel solid support with novel cyclic phosphate-linked oligosaccharides (CyPLOS) is proposed, realized by a stepwise solid-phase synthesis of the linear dimer, by standard phosphoramidite protocols, followed by a synthesis of the cyclic molecule on the resin.

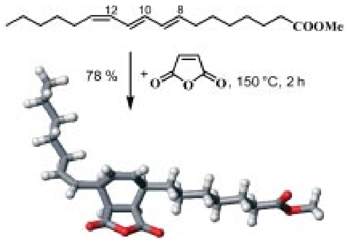
Keywords: Carbohydrates / Cyclic oligosaccharide analogues / Solid-phase synthesis / Protecting groups / Lipophilicity / ^{31}P NMR spectroscopy

Renewable Feedstock

U. Biermann, W. Butte, T. Eren, D. Haase,
J. O. Metzger* 3859–3862

Regio- and Stereoselective Diels–Alder Additions of Maleic Anhydride to Conjugated Triene Fatty Acid Methyl Esters

Thermal, solvent-free addition of maleic anhydride to methyl calendulate occurs with very high regio- and stereoselectivity at C-8 and C-11 of the fatty compound giving the *endo*-Diels–Alder adduct with retention of the *cis*-configured double bond.

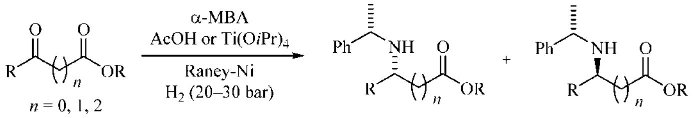


Keywords: Diels–Alder reaction / Cyclization / Methyl calendulate / Methyl α-eleostearate / Maleic anhydride / Renewable feedstock

Reductive Amination of Keto Esters

T. C. Nugent,* A. K. Ghosh ... 3863–3869

Selective Synthesis of Unnatural α-, β- and γ-Amino Esters



Unnatural α-, β- and γ-amino esters are synthesized by reductive amination of keto esters with α-methylbenzylamine, hydrogen and Raney-Ni. This strategy obviates the need for the isolation of enamine or imine intermediates.

Keywords: Asymmetric reductive amination / Amino esters / Heterogeneous hydrogenation

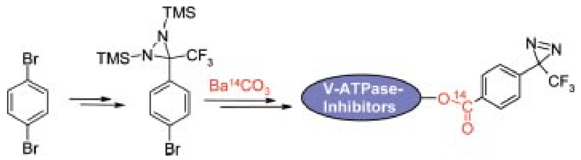
CONTENTS

Photoaffinity Labeling

**T. Bender, M. Huss,
H. Wieczorek, S. Grond,*
P. von Zezschwitz* 3870–3878**

Convenient Synthesis of a [1-^{14}C]Diazirinylbenzoic Acid as a Photoaffinity Label for Binding Studies of V-ATPase Inhibitors

Keywords: Photoaffinity labeling / V-ATPase inhibitors / Carboxylation / ^{14}C-Label / Diazirines / Natural products



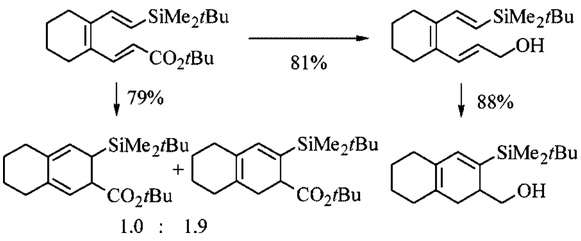
A convenient synthesis of a radioactive, ^{14}C-containing diazirinylbenzoic acid suitable for photoaffinity labeling is described. This label was connected to the known, highly potent and specific V-ATPase inhibitors bafilomycin and a concanamycin-derived concanolide. Preliminary results of inhibition assays with these derivatives are presented.

1,3,5-Hexatrienes

**H. W. Sünnemann, M. G. Banwell,
A. de Meijere* 3879–3893**

Synthesis and Use of New Substituted 1,3,5-Hexatrienes in Studying Thermally Induced 6π-Electrocyclizations

Keywords: Pericyclic Reactions / Regioselectivity / Palladium catalysis / Cross coupling / Oligocyclic systems



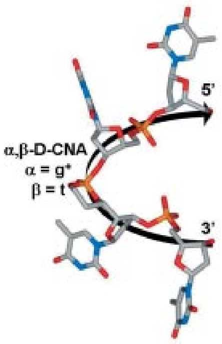
The thermal 6π-electrocyclizations of unsymmetrically 1,6-disubstituted (*E*,*Z*,*E*)-1,3,5-hexatrienes, which are easily assembled by a sequence of Stille and Heck cross-coupling reactions, are often followed by a 1,5-hydrogen shift, leading to a mixture of regioisomeric cyclohexa-1,3-dienes. By appropriate modification of the functional groups at the termini, e.g. reduction of an acrylate to an allylic alcohol moiety, the 1,5-hydrogen shift can apparently be accelerated so that a single product is formed.

Constrained Nucleotides

**I. Le Clézio, C. Dupouy, P. Lavedan,
J.-M. Escudier* 3894–3900**

Synthesis and Structure of an α,β-D-CNA Featuring a Noncanonical α/β Torsion Angle Combination within a Tetranucleotide

Keywords: Strained molecules / Nucleotides / DNA structures / Phosphorus heterocycles / Conformation analysis



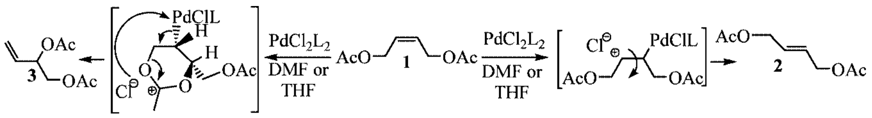
Synthesis and structural analysis of an α,β-D-CNA with α and β torsional angles constrained to noncanonical values [*gauche*(+), *trans*] within a tetranucleotide showed that the solution structure determined at the dinucleotide level was unchanged. A sharp turn was therefore induced to the single stranded tetranucleotide providing a hairpin loop shape.

Isomerization Reactions

**A. M. Zawisza, S. Bouquillon,
J. Muzart* 3901–3904**

Palladium(II)-Catalyzed Isomerization of (*Z*)-1,4-Diacetoxy-2-Butene: Solvent Effects

Keywords: Palladium / Catalysis / Allylic diacetate / Isomerization / Solvent effects

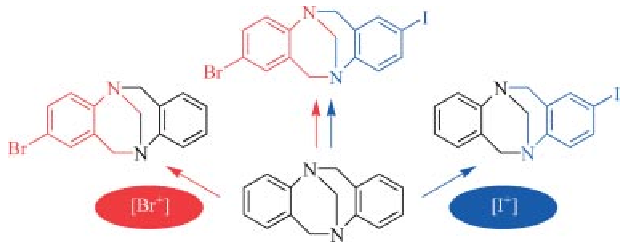


The PdCl$_2$(MeCN)$_2$-catalyzed isomerization of **1** occurs more rapidly in THF than in DMF. The formation of **2** is more favored in DMF than in THF. Interpretations are provided for the crucial role of the nature of both solvent and intermediates on the course of the reactions.

Analogs of Tröger's Base

D. Didier, S. Sergeyev* 3905–3910

Bromination and Iodination of 6*H*,12*H*-5,11-Methanodibenzo[*b*,*f*][1,5]diazocine: A Convenient Entry to Unsymmetrical Analogs of Tröger's Base



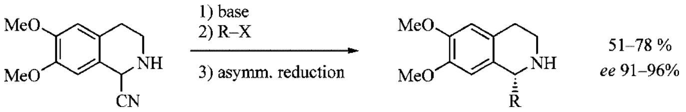
Convenient methods for the synthesis of (±)-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*]-[1,5]diazocine from aniline and its transformation into 2-bromo, 2-iodo, or 8-bromo-2-iodo derivatives by electrophilic substitutions are described.

Keywords: Heterocycles / Electrophilic substitution / Tröger's base / Bromination / Iodination

Chiral α-Branched Amines

F. Werner, N. Blank,
T. Opatz* 3911–3915

Synthesis of (−)-(*S*)-Norlaudanosine, (+)-(*R*)-*O*,*O*-Dimethylcoclaurine, and (+)-(*R*)-Salsolidine by Alkylation of an α-Aminonitrile



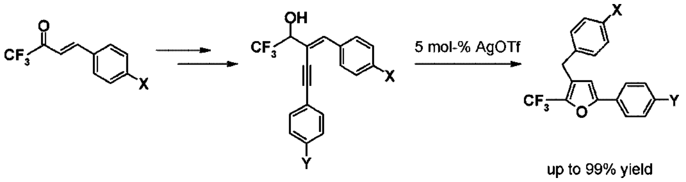
The α-alkylation of unprotected α-aminonitriles and subsequent elimination of HCN furnishes ketimines, which can be subjected to asymmetric hydrogenation. Three tetrahydroisoquinoline alkaloids have been prepared in high enantiomeric excess from a common precursor by this strategy for the reversible umpolung of the C=N bond.

Keywords: Alkaloids / Heterocycles / Umpolung / Asymmetric catalysis / Aminonitriles

Fluorinated Heterocycles

D. H. Zhang, C. Y. Yuan* 3916–3924

Reaction of 1,2-Unsaturated Trifluoromethyl Ketones and Their Conversion to 1-(Trifluoromethyl)furan Derivatives



A novel synthetic protocol for the preparation of α-(trifluoromethyl)furan derivatives is reported. It is based on an intramolecular cyclization of (*E*)-3-phenyl-2-(2-phenylethynyl)-1-(trifluoromethyl)allyl alcohols catalyzed by AgOTf in fair yield.

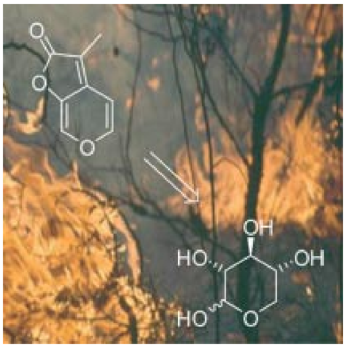
Keywords: Fluorinated substituents / Furans / Intramolecular cyclization / Ag catalysis / Synthetic methods

Germination Stimulants

E. D. Goddard-Borger,* E. L. Ghisalberti, R. V. Stick 3925–3934

Synthesis of the Germination Stimulant 3-Methyl-2*H*-furo[2,3-*c*]pyran-2-one and Analogous Compounds from Carbohydrates

The potent germination stimulant (pictured) has been prepared on an unprecedented multi-gram scale in high overall yield using a new synthetic strategy beginning with D-xylose. This approach has proven to be superior to the only other synthesis published to date. Extension of the strategy permitted the syntheses of a suite of analogues using both D-xylose and D-glucuronic acid γ-lactone as starting materials.



Keywords: Carbohydrates / Total synthesis / Germination stimulant / Heterocycles

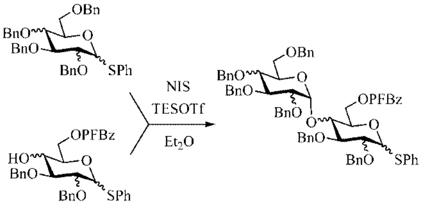
CONTENTS

Selective Glycosylations

T. H. Schmidt,
R. Madsen* 3935–3941

Glycosylations Directed by the Armed-Disarmed Effect with Acceptors Containing a Single Ester Group

Keywords: Carbohydrates / Glycosylation / Protecting groups / Tandem reactions / Armed-disarmed effect



PFBz = pentafluorobenzoyl

A selective glycosylation takes place with phenyl thioglycosides when the donor is fully protected with benzyl ethers and the acceptor is protected with benzyl ethers at the position 2 and 3, and an electron-withdrawing pentafluorobenzoate at position 6. The product disaccharide can participate in an additional glycosylation in the same pot if another acceptor is added.

CORRECTIONS

A. Singh, B. Ganguly* 3943

DFT Studies toward the Design and Discovery of a Versatile Cage-Functionalized Proton Sponge

Keywords: Basicity / Cage compounds / DFT calculations / Design

L. Fischer, V. Semetey, J.-M. Lozano,
A.-P. Schaffner, J.-P. Briand, C. Didierjean,
G. Guichard* 3944

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