

A union formed by chemical societies in Europe (ChemPubSoc Europe) has

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 mem-

bers of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the

two journals.



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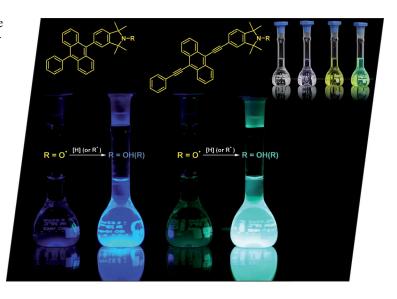






COVER PICTURE

The cover picture shows the minimal fluorescence emitted from a nitroxide-quenched diphenylanthracene fluorophore (left-hand side) and the contrasting strongly fluorescent result after the spin of the nitroxide radical has been removed by reduction or radical trapping (second from left). The same differential can be seen for the acetyleneextended system. The top right of the picture shows the same four flasks viewed in visible light. Details are discussed in the article by K.E. Fairfull-Smith and S. E. Bottle on p. 5391ff. Photo courtesy of Dr. Aaron Micallef, AIBN, University of Queensland, Australia.

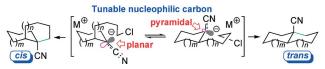


MICROREVIEW

Stereodivergent Cyclizations

Cyclic Metalated Nitriles: Stereoselective Cyclizations to *cis*- and *trans*-Hydrindanes, Decalins, and Bicyclo[4.3.0]undecanes

Keywords: Nitriles / Cyclizations / Stereoselectivity / Hydrindane / Decalin



Metalated nitriles are nucleophilic chameleons whose precise identity is determined by the nature of the metal, the solvent, the temperature, and the structure of the nitrile. The review surveys the different

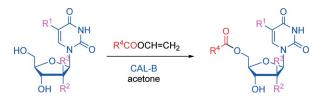
structural types and their cyclization trajectories to show how to selectively tune the metalated nitrile geometry for stereoselective cyclizations to a variety of cyclic hydrocarbons.

SHORT COMMUNICATIONS

Enzymatic Regioselective Acylation

Regioselective Acylation of Nucleosides Catalyzed by *Candida Antarctica* Lipase B: Enzyme Substrate Recognition

Keywords: Regioselective acylation / Candida antarctica lipase B / Substrate recognition / Enzyme catalysis / Nucleosides



The substrate recognition of Candida antarctica lipase B (CAL-B) in the acylation of nucleosides was revealed through rational substrate engineering for the first time.

Multicomponent/Domino Reactions

I. Reboul, T. Boddaert, Y. Coquerel,*
J. Rodriguez* 5379-5382



Synthetic Studies towards Guaianolide Sesquiterpene Lactones

Keywords: Chemoselectivity / Domino reaction / Guaianolides / Multicomponent reactions / Natural products



21% overall

Step-economical synthesis: The functionalized tricyclic core of guaianolides was stereoselectively prepared in a few chemical operations involving a multicomponent reaction and subsequent highly chemoselective and domino reactions.

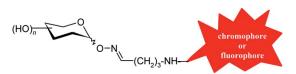
Carbohydrate Labelling

O. Renaudet,* P. Dumy* 5383-5386



Oxime-Based Synthesis of New Chromogenic and Fluorogenic Oligosaccharides

Keywords: Carbohydrate / Chemoselectivity / Fluororescent probes / Chromophores



An efficient and simple approach for the labelling of free carbohydrate recognition motifs with either a chromophore or a fluorophore is described. These new probes

provide a useful tool for recognition studies with carbohydrate-binding proteins in glycomics.



Zinc Selenolate

$$\begin{array}{c} \text{R-X} & \text{R-SePh} \\ \text{H}_2\text{O} & \text{R} = \text{aliphatic, aromatic, vinylic} \\ \\ \text{SeZnX} & \begin{array}{c} O \\ \\ \text{H}_2\text{O} \end{array} & \begin{array}{c} \text{Ph} \\ \\ \text{SePh} \end{array} \\ \\ \text{SePh} & \begin{array}{c} \text{EWG} \\ \\ \text{H}_2\text{O} \end{array} & \begin{array}{c} \text{SePh} \\ \\ \text{SePh} \end{array} \end{array}$$

Stable and reactive. Here we report that treatment of commercially available and inexpensive electrophilic selenium species with zinc causes umpolung on the selenium atom leading to a stable selenolate that shows an interesting and unexpected nucleophilic reactivity under "on water" conditions. The use of these new reagents in the ring opening of epoxides as well as in other nucleophilic substitution and addition reactions is described.

C. Santi,* S. Santoro, B. Battistelli, L. Testaferri, M. Tiecco 5387-5390

Preparation of the First Bench-Stable Phenyl Selenolate: an Interesting "On Water" Nucleophilic Reagent

Keywords: Selenolate / Zinc / "On water" reactions / Epoxides / Nucleophiles

FULL PAPERS

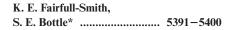
Profluorescent Nitroxides

·o_N

The synthesis and physical properties of mono- and di-isoindoline nitroxides are described. These nitroxide-fluorophore probes display strongly suppressed fluor-

·0 N O•

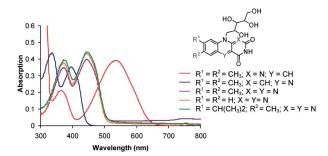
escence, even in the presence of only one nitroxide radical. Upon reduction or reaction with radicals, normal fluorophore emission is restored.



The Synthesis and Physical Properties of Novel Polyaromatic Profluorescent Isoindoline Nitroxide Probes

Keywords: Nitroxides / Fluorescence / Radicals / Profluorescent probes

Synthesis of Flavins



LOV domains (Light, Oxygen, and Voltage) are the light-absorbing units in phototropins. The chromophore in LOV domains is flavin-mononucleotide (FMN), which is derived from riboflavin. To investigate the

interaction of LOV with FMN and the structural changes occurring upon light activation, we designed a series of chromophore analogues.

Synthesis and Electrochemical Properties of Structurally Modified Flavin Compounds

Keywords: Flavins / Chromophores / Vitamin B₂

Bicyclooxacalix[4]arenes

A new family of isoxazolopyridobicyclooxacalix[4]arenes was obtained by reaction of dichloroisoxazolopyridines with phloroglucinol. They act as metal chelators and are of potential interest for host-guest interactions.

Synthesis of Isoxazolopyridobicyclooxacalix[4]arenes: A New Family of Heteracalixarene Systems

Keywords: Calixarenes / Cage compounds / Density functional calculations / X-ray diffraction

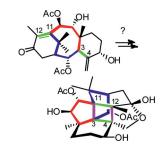
CONTENTS

Propeller Taxanes

M.-L. Zhang, M. Dong, C.-H. Huo, L.-G. Li, F. Sauriol, Q.-W. Shi,* Y.-C. Gu, H. Makabe, H. Kiyota* 5414-5417

Taxpropellane: A Novel Taxane with an Unprecedented Polycyclic Skeleton from the Needles of *Taxus canadensis*

Keywords: Propellanes / Structure elucidation / Terpenoids / Fused-ring systems



Taxpropellane, the first example of a taxane with an unprecedented 6/5/5/6/4/5-membered ring hexacyclic skeleton ([3.3.2]-propellane), was isolated from the needles of *Taxus canadensis*. This compound would be derived from a normal 6/8/6 taxane by a [2+2] cycloaddition reaction between the 3,4- and 11,12-double bonds.

One-Step Diketopiperazination

M. Jainta, M. Nieger, S. Bräse* 5418-5424

Microwave-Assisted Stereoselective One-Pot Synthesis of Symmetrical and Unsymmetrical 2,5-Diketopiperazines from Unprotected Amino Acids

Keywords: Amino acids / Diketopiperazines / Heterocycles / Natural products / One-pot reactions / Microwave-assisted organic synthesis (MAOS) / Ionic liquids

Unprotected natural and synthetic amino acids are used in a phosphite-promoted coupling to yield homo- and heterodiketo-piperazines. The combination of microwave irradiation and ionic liquids affords the op-

tically pure heterocycles with a unique stereoselectivity. A fast reaction with excellent yields accompanied by a simple workup complements this method.

OMe

Functionalization of Indoles

N. Schwarz, A. Pews-Davtyan,
D. Michalik, A. Tillack, K. Krüger,
A. Torrens, J. L. Diaz,
M. Beller* 5425-5435

Palladium-Catalyzed Amination and Sulfonylation of 5-Bromo-3-[2-(diethylamino)-ethoxy]indoles to Potential 5-HT₆ Receptor Ligands

Keywords: Indole / Sulfonylation / Amination / Palladium

 $R = CH_3$, CH_2Ph , Boc $R^1 = Aryl$, Alkyl $R^2 = Het$ -Aryl

A general and efficient palladium-catalyzed amination of 5-bromo-3-[2-(diethylamino)-ethoxylindoles has been developed. Sub-

sequent sulfonylation gave indoles that are of interest as potentially biological active 5-HT₆ receptor ligands.

Cytotoxic Imidazoles

F. Bellina,* S. Cauteruccio, A. Di Fiore, R. Rossi* 5436-5445



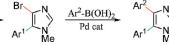
Regioselective Synthesis of 4,5-Diaryl-1-methyl-1*H*-imidazoles Including Highly Cytotoxic Derivatives by Pd-Catalyzed Direct C-5 Arylation of 1-Methyl-1*H*-imidazole with Aryl Bromides

Keywords: Direct arylation / Regioselectivity / Palladium / Imidazoles / Cytotoxicity

$$\begin{array}{c|c}
 & N \\
 & N \\
 & N \\
 & N \\
 & Me
\end{array}$$

$$\begin{array}{c|c}
 & N \\
 & NBS \\
 & NBS \\
 & NBS \\
 & Me$$

4,5-Diaryl-1-methyl-1*H*-imidazoles, including two highly cytotoxic compounds, have been regioselectively and efficiently synthesized by a three-step reaction sequence that involves the Pd-catalyzed direct arylation



of 1-methyl-1*H*-imidazole with aryl bromides and a PdCl₂(dppf)-catalyzed, Suzuki-type, cross-coupling between 5-aryl-4-bromo-1*H*-imidazoles and aryl-boronic acids as key steps.



Spiro-Fused Heterocycles

$$R = \begin{bmatrix} C \\ H \\ N \end{bmatrix} = \begin{bmatrix} C \\ R \end{bmatrix} = \begin{bmatrix} C \\ R$$

A facile stereoselective synthesis of spirofused (C-5)isoxazolino- or (C-3)pyrazolino-(C-3)quinolin-2-ones from the adducts obtained from the Baylis-Hillman reaction of 2-nitrobenzaldehydes and acrylates and their derivatives is described.

Straightforward Strategy for the Stereoselective Synthesis of Spiro-Fused (C-5)-Isoxazolino- or (C-3)Pyrazolino-(C-3)quinolin-2-ones from Baylis—Hillman Adducts by 1,3-Dipolar Cycloaddition and Reductive Cyclization

Keywords: Baylis—Hillman reactions / Cycloadditions / Reductive cyclizations / Spiro compounds / Quinolines

Electrophilic Addition

$$\begin{array}{c} \text{KOH, MeOH} \\ \\ \text{OH} \\ \\ R \\ \\ R \\ \\ \text{H} \\ \\ \\ \text{Et}_2\text{O}, -78 \, ^{\circ}\text{C} \sim \text{r.t.} \\ \\ \\ \text{O} \\ \\ \\ \text{R} \\ \\ \\ \\ \text{O} \\ \\ \\ \text{R} \\ \\ \\ \text{O} \\ \\ \\ \text{R} \\ \\ \\ \text{O} \\ \\ \\ \text{R} \\ \\ \\ \text{O} \\ \\ \text{O} \\ \\ \\ \text{O} \\ \\ \\ \text{O} \\ \\ \text{O} \\ \\ \text{O} \\ \\ \\ \text{O} \\ \\ \text{O} \\ \\ \\ \text{O} \\ \\ \text{O}$$

A novel synthetic method to prepare chalcones and chroman-4-ones by TMSOTfpromoted addition of alkynes to various aldehydes has been developed. The ratios of chalcones, chroman-4-ones and hydrated products vary depending upon the substituents on the alkynes. We also describe the transformation of the chalcones to the corresponding chroman-4-ones under basic conditions.

J. Y. Park, P. R. Ullapu, H. Choo, J. K. Lee, S.-J. Min, A. N. Pae, Y. Kim, D.-J. Baek, Y. S. Cho* 4561–5469

TMSOTf-Promoted Addition of Alkynes to Aldehydes: A Novel Synthesis of Chroman-4-ones

Keywords: Addition / Aldehydes / Alkynes / Chromanone

Samarium Chemistry

Intramolecular cyclization of 1,1-diaryl-2,2-dicyanoethenes promoted by samarium metal in DMF in the presence of TMSCl allowed direct construction of the indene core, whereas 1-alkyl-1-aryl-2,2-dicyanoethenes underwent intermolecular coupling cyclization and decyanation under the same conditions. Disilylation occurred at the amino moiety resulting from the reduction of the cyano group.

Y. Liu, F. Zhang, Y. Qi, Y. Zhang, S. Zhang* 4570-5476

Transformation of *gem*-Dicyanoethenes by Samarium: Direct Formation of Indenes or Direct Decyanation with in Situ Disilylation

Keywords: Samarium / Fused-ring systems / Dicyanoethenes / Cyanides / Disilylation

Supporting information on the WWW (see article for access details).

If not otherwise indicated in the article, papers in issue 31 were published online on October 16, 2008

^{*} Author to whom correspondence should be addressed.