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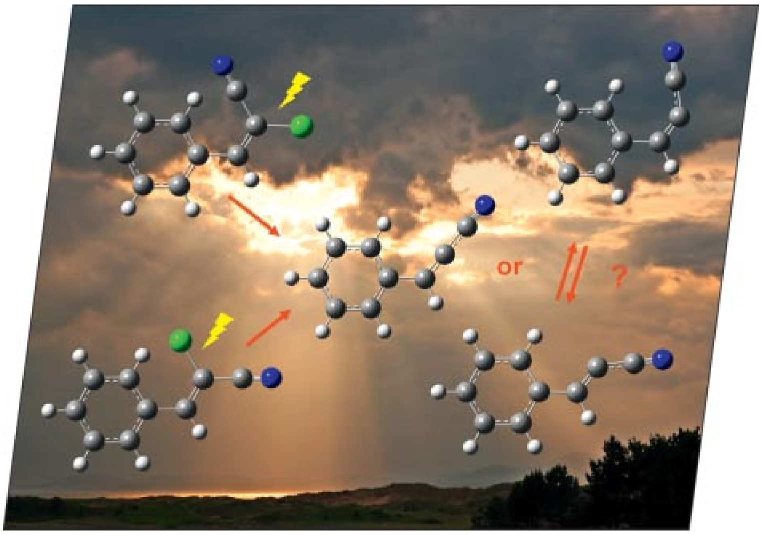
The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry.* Three further EUChemSoc Societies (Austria, Czech Republic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

COVER PICTURE

The cover picture shows how the structure of an α-CN vinyl radical is elucidated through the photolysis of stereoisomeric vinyl halide precursors. The vinyl radical intermediates react with the solvent to form stereoisomeric styrenes. Analysis of the yields of the styrenes as a function of temperature establishes the α-CN vinyl radical as a rapidly inverting bent, and not linear, species. The photolyses of α-Me, α-C(H)=O and α-F substituted bromostyrenes indicate that the α-Me vinyl radical is also rapidly inverting, while the α-C(H)=O and α-F vinyl radicals are stable bent species. The experimental results are supported by quantum chemical computations. Details are discussed in the article by G. Lodder et al. on p. 435ff. Patty Nieuwenburg is acknowledged for the background photo of the dunes of Harlech, Wales.



CONTENTS

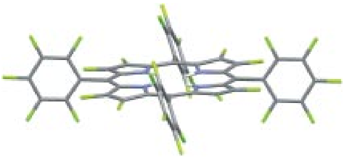
MICROREVIEW

Fluorinated Porphyrins

J. Leroy,* A. Bondon 417–433

β-Fluorinated Porphyrins and Related Compounds: An Overview

Keywords: Fluorinated ligands / Porphyrinoids / Nitrogen heterocycles / Synthetic methods



This microreview provides an update on the latest advances in the preparation and characterization of β-fluorinated and β-perfluoroalkylated porphyrins. In contrast to β-perfluoroalkylation, direct (poly)fluorination of a parent ligand must be circumvented by using fluorinated synthons.

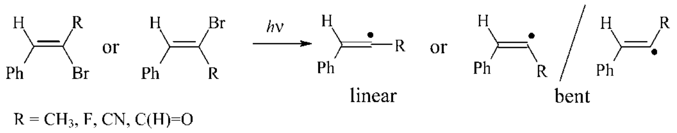
FULL PAPERS

Linear or Bent Vinyl Radicals

T. P. M. Goumans, K. van Alem, G. Lodder* 435–443

Photochemical Generation and Structure of Vinyl Radicals

Keywords: Photochemistry / Vinyl radicals / Structure elucidation / Stereoselectivity / Ab initio calculations



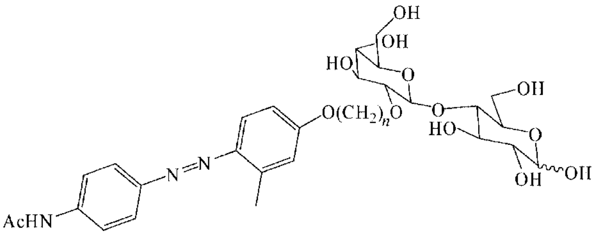
The structure of photogenerated vinyl radicals bearing various α-substituents has been investigated using product studies and quantum chemical calculations.

Water-Soluble Azodyes

R. Bianchini,* G. Catelani,* R. Cecconi, F. D'Andrea, L. Guazzelli, J. Isaad, M. Rolla 444–454

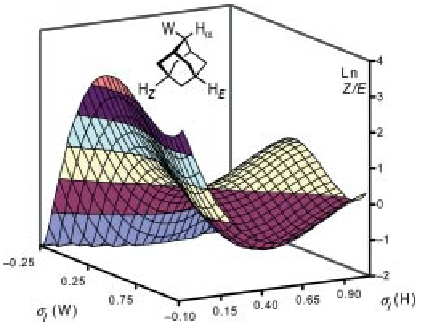
Ethereal Glycoconjugated Azodyes (GADs): A New Group of Water-Soluble, Naturalised Dyes

Keywords: Azodyes / Carbohydrates / Diethers / Conjugation / Textile dyeing



We report on a new generation of GADs (glycoazodyes) – that is, dyes glyconjugated through ethereal bonds with lactose, galactose or glucose in order to improve the stabilities of these new materials. These biethereal adducts has been shown to work very well in the tinctorial tests so far carried out, allowing different materials to be dyed with the same GAD (multipurposity) without any addition of surface agents or dangerous and expensive additives.

C(sp^3)−H σ-Bond Oxygenation



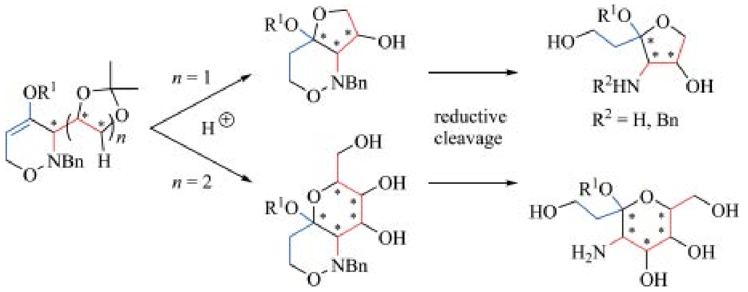
The reactivity of C(sp^3)−H σ-bonds distant from a Z substituent towards methyl(trifluoromethyl)dioxirane (**1**) allows to determine the electronic character of C$_\alpha$−H σ bonds adjacent to the substituent.

R. Mello, J. Royo, C. Andreu, M. Báguena-Añó, G. Asensio,* M. E. González-Núñez .... **455−466**

On the Reactivity of C(sp^3)−H σ-Bonds: Oxygenation with Methyl(trifluoromethyl)dioxirane

Keywords: Oxygenation / Dioxiranes / C−H activation / Hyperconjugation / Substituent effects

Dideoxyamino Carbohydrate Derivatives



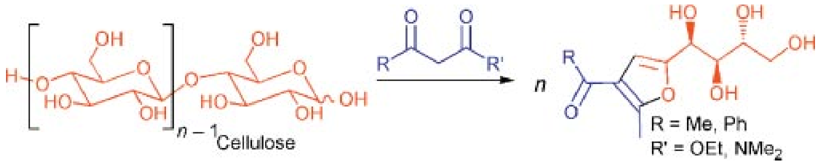
Dideoxyamino carbohydrate derivatives can easily be synthesized from 3,6-dihydro-2H-1,2-oxazines. Key steps are acid-induced rearrangements leading to furano- and pyrano-1,2-oxazines and subsequent reductive N−O bond cleavages.

B. Bressel, B. Egart, A. Al-Harrasi, R. Pulz, H.-U. Reißig,* I. Brüdgam .... **467−474**

Acid-Induced and Reductive Transformations of Enantiopure 3,6-Dihydro-2H-1,2-oxazines − Synthesis of Dideoxyamino Carbohydrate Derivatives

Keywords: 1,2-Oxazines / Furans / Pyrans / Carbohydrates / Reductions / Samarium diiodide

Cellulose Chemistry



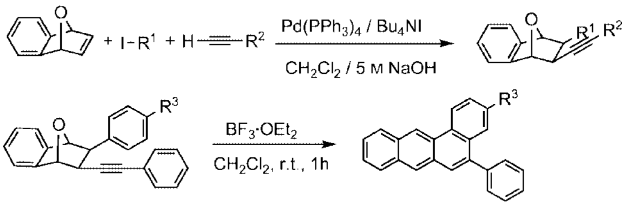
Proceeding from the reducing end of celluloses, the “furan endwise peeling” reaction causes the one-by-one loss of anhydroglucose units (AGUs) which are converted into trisubstituted furans by co-reacting with 1,3-dicarbonyl compounds. The key step of the reaction is the attack of the 2-OH group of the last-but-one AGU on the terminal furan and fragmentation of the resulting dioxepane intermediate by cleavage of the glycosidic bond, as demonstrated with differently substituted celluloses and also by extensive model compound studies.

Y. Yoneda, K. Krainz, F. Liebner, A. Potthast, T. Rosenau,* M. Karakawa, F. Nakatsubo .... **475−484**

“Furan Endwise Peeling” of Celluloses: Mechanistic Studies and Application Perspectives of a Novel Reaction

Keywords: Carbohydrates / Reaction mechanisms / Cleavage reactions / Heterocycles / Reactive intermediates / Cellulose

Disubstituted Oxabenzonorbornenes



A three-component coupling reaction of organic halides with oxabicyclic alkenes and terminal alkynes was catalyzed by a palladium complex to obtain a series of 5,6-disubstituted 7-oxabenzonorbornene derivatives. The disubstituted products from oxabenzonorbornadiene can be readily converted into polyaromatic hydrocarbons by a Lewis acid mediated deoxyaromatization reaction.

C.-J. Kuo, S.-J. Cheng, S.-T. Chang, C.-H. Liu* .... **485−491**

Palladium-Catalyzed 1,2-Addition of Organic Halides and Terminal Alkynes to 7-Oxabenzonorbornadiene: An Efficient Route to Polyaromatic Hydrocarbons

Keywords: Multicomponent reactions / Palladium / Oxabenzonorbornadiene / Alkynes

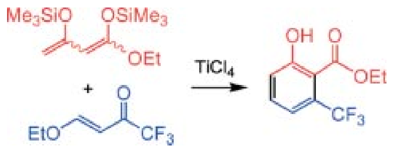
CONTENTS

[3+3] Cyclizations

C. Mamat, T. Pundt, T. H. T. Dang, R. Klassen, H. Reinke, M. Köckerling, P. Langer* 492–502

One-Pot Synthesis of Functionalized 3-(Trifluoromethyl)phenols by [3+3] Cyclization of 1,3-Bis(silyl enol ethers) with α,β-Unsaturated Trifluoromethyl Ketones

Keywords: Arenes / Cyclizations / Organic fluoro compounds / Silyl enol ethers / Regioselectivity



Functionalized 3-(trifluoromethyl)phenols were regioselectively prepared by formal [3+3] cyclizations of 1,3-bis(silyl enol ethers) with α,β-unsaturated trifluoromethyl ketones.

[3+3] Cyclizations

I. Hussain, M. A. Yawer, M. Lau, T. Pundt, C. Fischer, H. Görls, P. Langer* 503–518

Regioselective Synthesis of Fluorinated Phenols, Biaryls, 6*H*-Benzo[*c*]chromen-6-ones and Fluorenones Based on Formal [3+3] Cyclizations of 1,3-Bis(silyl enol ethers)

Keywords: Arenes / Cyclizations / Organic fluoro compounds / Silyl enol ethers / Regioselectivity

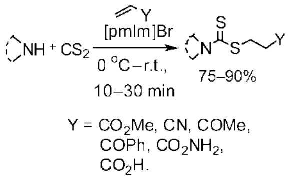
Fluorinated phenols, biaryls, biaryl lactones and fluorenones were regioselectively prepared based on formal [3+3] cyclizations of 1,3-bis(silyl enol ethers).

Rate Acceleration by Ionic Liquids

B. C. Ranu,* A. Saha, S. Banerjee 519–523

Catalysis by Ionic Liquids: Significant Rate Acceleration with the Use of [pmIm]Br in the Three-Component Synthesis of Dithiocarbamates

Keywords: Ionic liquids / Dithiocarbamates / Multicomponent reactions / Catalysis / Rate acceleration



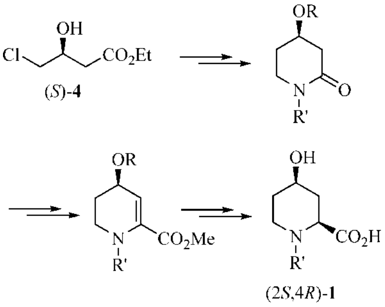
An easily accessible ionic liquid, 1-methyl-3-pentylimidazolium bromide, offers significant improvements with regard to reaction time and yield in the three-component condensation of an amine, carbon disulfide, and an activated alkene to produce substituted dithiocarbamates.

Synthesis of 4-Hydroxypipecolic Acid

E. G. Occhiato,* D. Scarpi, A. Guarna 524–531

Stereoselective Synthesis of (2*S*,4*R*)-4-Hydroxypipecolic Acid

Keywords: Amino acids / Natural products / Lactams / Carbonylation / Hydrogenation



A new synthetic route to enantiopure (2*S*,4*R*)-4-hydroxypipecolic acid (20% yield over 10 steps) from commercial ethyl (3*S*)-4-chloro-3-hydroxybutanoate is reported. The synthesis is based on the Pd-catalyzed methoxycarbonylation of a 4-alkoxy-substituted valerolactam-derived vinyl triflate followed by the stereocontrolled hydrogenation of the enamine double bond.

Asymmetric Catalysis

I. Reboule, R. Gil,*
J. Collin* 532–539

Enantioselective Conjugate Addition of Aromatic Amines to *N*-Alkenoyloxazolidinones Catalyzed by Iodido(binaphtholato)samarium

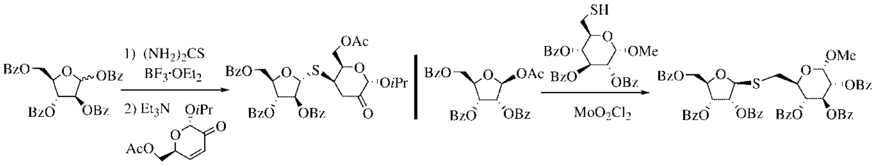
Iodido(binaphtholato)samarium is an efficient enantioselective catalyst for aza-Michael reactions. By varying the temperature an isoinversion of the asymmetric induction was observed.

Keywords: Asymmetric catalysis / Michael addition / Conjugate addition / Samarium / Lanthanides / Amines

Furanose Thiodisaccharides

E. Repetto, C. Marino, M. L. Uhrig,
O. Varela* 540–547

Two Straightforward Strategies for the Synthesis of Thiodisaccharides with a Furanose Unit as the Nonreducing End



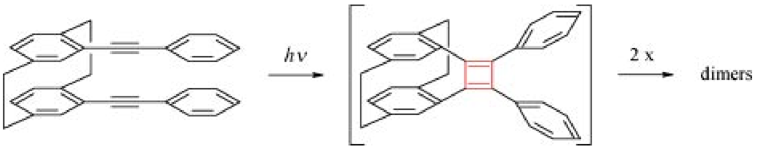
Per-*O*-acylpentofuranoses were used as glycosyl donors in the synthesis of thiodisaccharides having a thiopentofuranose as a nonreducing end. The per-*O*-acylfuranoses were converted into 1-thiofuranose derivatives and coupled, by Michael addition, to a sugar enone. The acylfuranose derivatives were also employed as glycosylating agents.

Keywords: Thiodisaccharides / Furanose / Glycosylation / Catalysis / Molybdenum / Michael addition

Cyclobutadiene Intermediates

J. Kubitschke, H. Hopf,* P. G. Jones,
I. Dix, L. Ernst 548–554

A Cyclobutadiene Intermediate in the Intramolecular Cycloaddition of 4,15-Bis(phenylethynyl)[2.2]paracyclophane



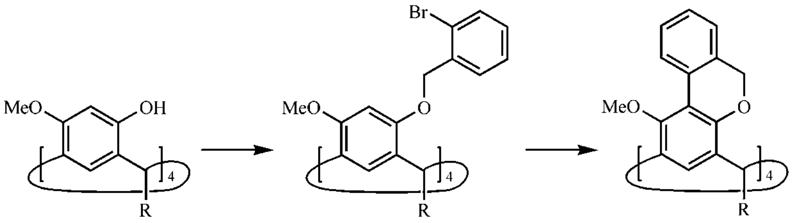
Two triple bonds can be held in parallel by a [2.2]paracyclophane spacer, which positions the units appropriately to generate a cyclobutadiene intermediate. This was shown by the formation of dimerization products and a tricarbonyliron complex of a cyclopentadienone formed by carbonyl insertion into the cyclobutadiene intermediate.

Keywords: Cyclophanes / Cycloadditions / Cylobutadiene / Proximity effects

Chiral Resorcin[4]arenes

M. Paletta, M. Klaes, B. Neumann,
H.-G. Stammler, S. Grimme,
J. Mattay* 555–562

Cavity-Extended Inherently Chiral Resorcin[4]arenes: Synthesis and Chiroptical Properties of the Cycloenantiomers



The cavities of inherently chiral resorcin[4]arenes were enlarged by a quadruple intramolecular cross-coupling reaction, which generated four atropisomeric biaryl units. The cycloenantiomers were characterised by CD spectroscopy.

Keywords: Atropisomerism / Calixarenes / Chirality / Circular dichroism / Cross-coupling

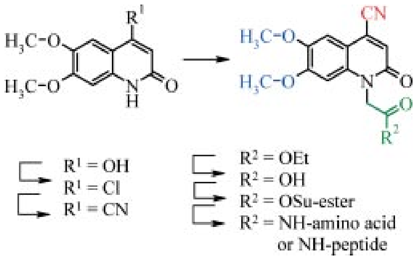
CONTENTS

Fluorescent 4-Cyanocarbostyrils

A. B. Ahvale, H. Prokopcová, J. Šefčovičová, W. Steinschifter, A. E. Täubl, G. Uray, W. Stadlbauer* .... 563−571

4-Cyano-6,7-dimethoxycarbostyrils with Solvent- and pH-Independent High Fluorescence Quantum Yields and Emission Maxima

Keywords: Quinolones / Carbostyrils / Fluorescent probes / Fluorescence labeling / Amino acids / Peptides



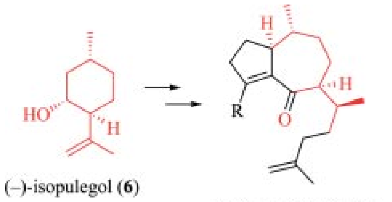
The synthesis of highly fluorescent and stable 4-cyano-6,7-dimethoxycarbostyrils is reported; these compounds fluoresce in different solvents with almost constant quantum yields over the pH range 1−11. These properties could lead to a broadly usable fluorescence standard, and these cyanoquinolones can be used as a fluorescence label for amino acids or peptides.

Hydroazulene Synthesis

T. Kreuzer, P. Metz* .... 572−579

Enantioselective Synthesis of the Hydroazulene Core of 3α-Hydroxy-15-rippertene

Keywords: Hydroazulenes / Hydroboration / Ring expansion / Organocopper compounds / Aldol reactions



(−)-isopulegol (**6**)

4a: R = H; **4b**: R = Me

As part of a project directed toward the total synthesis of the tetracyclic diterpene 3α-hydroxy-15-rippertene, a constituent of the defense secretion of higher termites, a fast access to two advanced hydroazulene key intermediates has been achieved by starting from (−)-isopulegol.