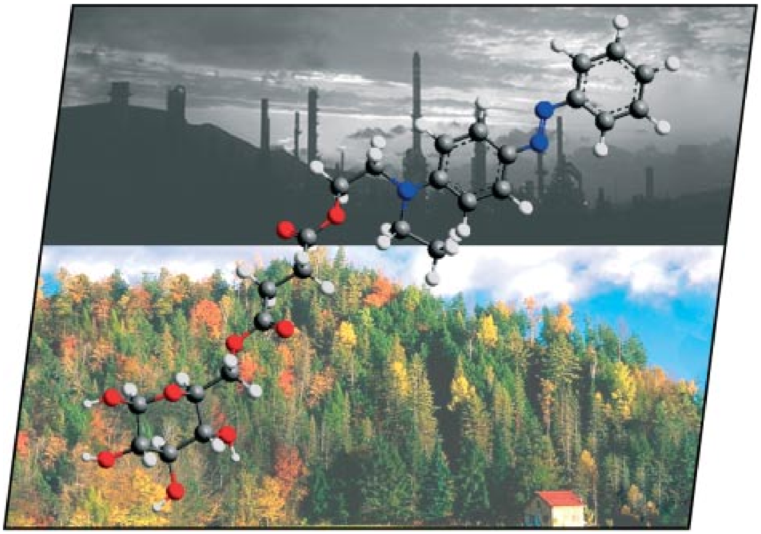
Hungary
Italy
Germany
Greece
Belgium
EUChemSoc
France
Sweden
Czech Republic
Austria
Portugal
Spain
Netherlands

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 a new class of dyes – glycoazodyes (GADs): "from textile industrial dyes to multipurpose naturalised dyes through glycoconjucation". Details are discussed in the article by R. Bianchini et al. on p. 588ff.



CONTENTS

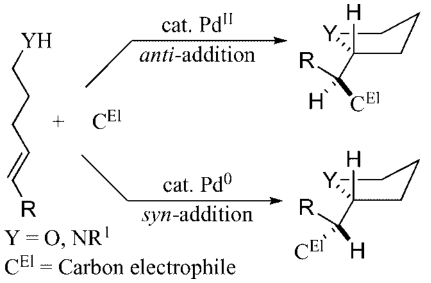
MICROREVIEW

Alkene Difunctionalization

J. P. Wolfe* 571–582

Palladium-Catalyzed Carboetherification and Carboamination Reactions of γ-Hydroxy- and γ-Aminoalkenes for the Synthesis of Tetrahydrofurans and Pyrrolidines

Keywords: Palladium / Heterocycles / Amines / Alcohols / Electrophilic addition



Palladium-catalyzed carboetherification and carboamination reactions provide a rapid and convergent means for the stereoselective construction of tetrahydrofurans and pyrrolidines.

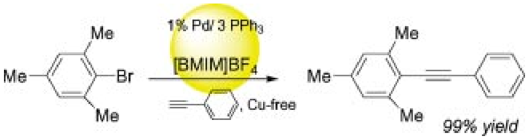
SHORT COMMUNICATION

Heck Alkynylations

J.-C. Hierso,* J. Boudon, M. Picquet,* P. Meunier 583–587

The First Catalytic Method for Heck Alkynylation of Unactivated Aryl Bromides (Copper-Free Sonogashira) in an Ionic Liquid: 1 mol-% Palladium/Triphenylphosphane/Pyrrolidine in [BMIM][BF$_4$] as a Simple, Inexpensive and Recyclable System

Keywords: Alkynylation / Aryl bromides / Ionic liquids / Heck reaction / Copper-free Sonogashira / Cross-coupling



The first catalytic method for Heck alkynylation of unactivated aryl bromides in an ionic liquid is presented. The system Pd/3·PPh$_3$ (1 mol-%) in [BMIM][BF$_4$] is efficient for the coupling of a variety of activated and deactivated aryl bromides: *para* and/or *ortho* mono- and disubstituted substrates, with aromatic (phenylacetylene) and aliphatic (long chain 1-decyne) terminal acetylenes.

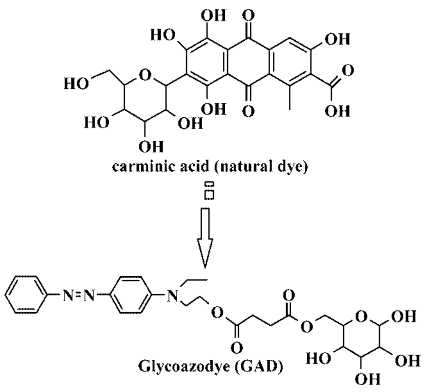
FULL PAPERS

Naturalised Dyes

G. Bartalucci, R. Bianchini,* G. Catelani, F. D'Andrea, L. Guazzelli 588–595

Naturalised Dyes: A Simple Straightforward Synthetic Route to a New Class of Dyes – Glycoazodyes (GADs)

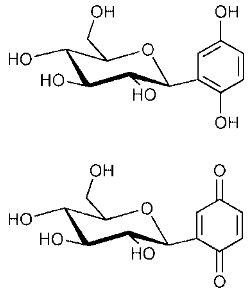
Keywords: Azodyes / Carbohydrates / Succinates / Conjugation / Textile dyes



We report a process to naturalise synthetic azodyes through their linkage with lactose, or its monosaccharide components, either galactose or glucose, to enhance their solubility, as many other natural dyes. This modification allows the dyeing process of textile materials to take place in water without the addition of surfactants or other additives. The synthesis of the first generation of glycoazodyes (GADs) is carried out with the use of a diester linker to bond the azodye and the sugar.

Inhibitors of Glycogenolysis

C-β-D-Glucopyranosylbenzo(hydro)quinones are moderate competitive inhibitors of glycogen phosphorylase found by crystallography to bind at the catalytic site.



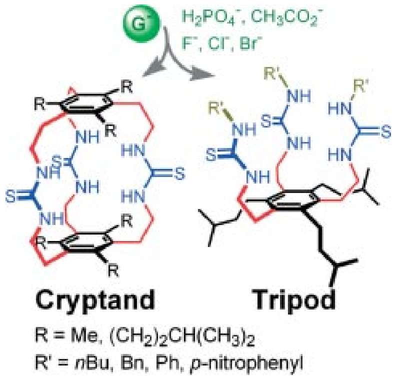
L. He, Y. Z. Zhang, M. Tanoh, G.-R. Chen, J.-P. Praly,* E. D. Chrysina, C. Tiraidis, M. Kosmopoulou, D. D. Leonidas, N. G. Oikonomakos **596–606**

In the Search of Glycogen Phosphorylase Inhibitors: Synthesis of C-D-Glycopyranosylbenzo(hydro)quinones – Inhibition of and Binding to Glycogen Phosphorylase in the Crystal

Keywords: C-Glycosides / Aromatic substitution / Inhibitors / X-ray diffraction / Glycogen phosphorylase

Homobenzylic Anion Receptors

Cryptand- and tripod-type thiourea derivatives, which have binding functionalities at the homobenzylic positions, were synthesized, and their anion binding abilities were evaluated by ^{1}H NMR and/or UV/Vis spectroscopic analysis.

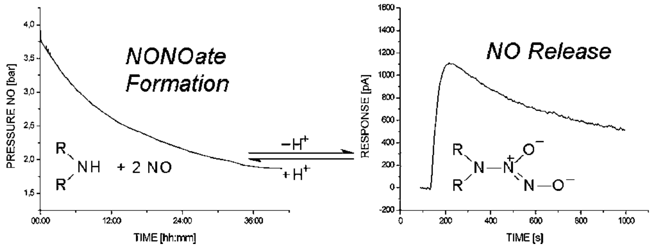


I. Hisaki, S.-i. Sasaki, K. Hirose, Y. Tobe* **607–615**

Synthesis and Anion-Selective Complexation of Homobenzylic Tripodal Thiourea Derivatives

Keywords: Anions / Cryptands / Host–guest systems / Hydrogen bonds / Receptors

Nitric Oxide Sources



A novel device (*NO*tizer) enables the monitoring of diazeniumdiolate (NONOate) formation and allows to characterize relations between the structures and the formation rates. Furthermore, correlations between formation and dissociation rates were identified by using a wide variety of diazeniumdiolates. Half-lives of novel diazeniumdiolates were also determined.

J. Konter, G. E.-D. A. A. Abuo-Rahma, A. El-Emam, J. Lehmann* **616–624**

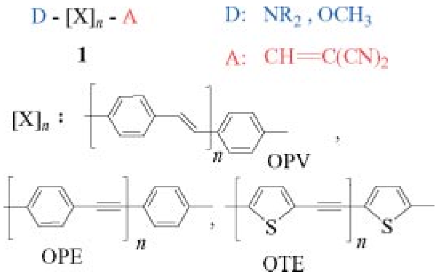
Synthesis of Diazen-1-ium-1,2-diolates Monitored by the “*NO*tizer” Apparatus: Relationship between Formation Rates, Molecular Structure and the Release of Nitric Oxide

Keywords: Diazeniumdiolate / NONOate / Nitric oxide / NO donors

Conjugated Oligomers

H. Meier,* B. Mühling, J. Gerold, D. Jacob, A. Oehlhof **625–631**

Push-Pull Oligomers with 2,2-Dicyanovinyl Groups as Electron Acceptors



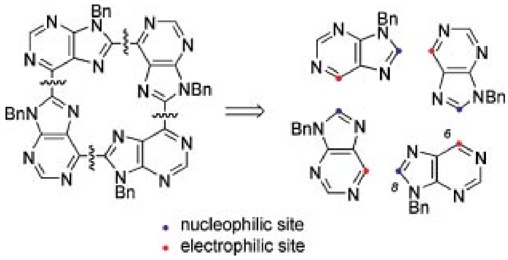
The depicted conjugated oligomers represent hypsochromic series, that means the extension of the chromophores from *n* to (*n* + 1) provokes a blue-shift o the long-wavelength absorption. The increasing distance D–A leads to adecreasing intramolecular charge transfer (ICT) which cannot be compensated by the extension of the conjugation.

Keywords: Chromophores / Conjugation / Oligomers / Push-pull effect

Quaterpurine

H. Guthmann, M. Könemann, T. Bach* **632–638**

Synthesis of a Cyclic Tetrameric Purine by Successive Cross-Coupling Reactions and Subsequent Pd-Catalyzed Cyclization



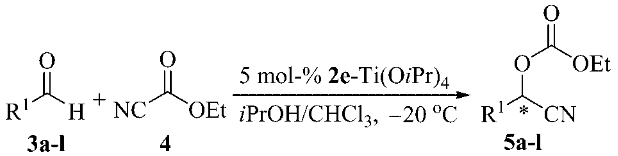
A tetrameric purine was obtained from known 9-benzyl-6-chloropurine in eight synthetic steps and in 17% overall yield as its palladium complex. Key steps of the synthetic route are the consecutive Negishi cross-coupling of the 8-zincated purine derived from 9-benzyl-6-chloro-8-iodopurine and the ring closure by a Pd-catalyzed reductive cyclization mediated by hexamethylditin.

Keywords: Cross-coupling / Dyes / Pigments / Halogenation / Metalation / Nitrogen heterocycles

Asymmetric Catalysis

S.-K. Chen, D. Peng, H. Zhou, L.-W. Wang, F.-X. Chen, X.-M. Feng* **639–644**

Highly Enantioselective Cyanoformylation of Aldehydes Catalyzed by a Mononuclear Salen-Ti(O*i*Pr)$_4$ Complex Produced In Situ



An efficient enantioselective cyanoformylation of aldehydes with ethyl cyanoformate, catalyzed by a salen-Ti(O*i*Pr)$_4$ complex generated in situ, has been developed. Studies of nonlinear effects indicated that the mononuclear salen-titanium complex, and not a heterochiral complex, played a key role in the stereodiscriminating step of the reaction. In the presence of 5 mol-% of catalyst, the reaction can be carried out in excellent yields (up to 99%) with high enantioselectivities (up to 91% *ee*).

Keywords: Asymmetric catalysis / Cyanohydrin / In situ preparation / Solvent effects / Titanium

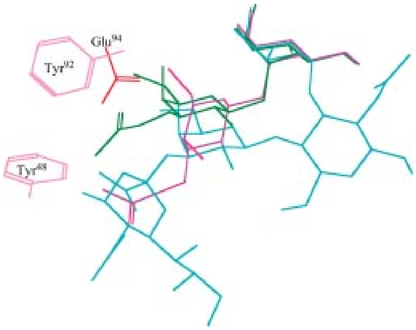
Carbohydrate Recognition

R. W. Denton, X. Cheng, K. A. Tony, A. Dilhas, J. J. Hernández, A. Canales, J. Jiménez-Barbero, D. R. Mootoo* 645–654

C-Disaccharides as Probes for Carbohydrate Recognition – Investigation of the Conformational Requirements for Binding of Disaccharide Mimetics of Sialyl Lewis X

Keywords: Carbohydrates / Glycomimetics / Selectin / C-Glycoside / Oxocarbenium ion / Conformation

Disaccharide mimetics of sialyl Lewis X were synthesized and their conformational behavior and inhibition of P-selectin binding were evaluated. Analogs with very different conformational properties around their intersaccharide torsions showed similar inhibitory activity.

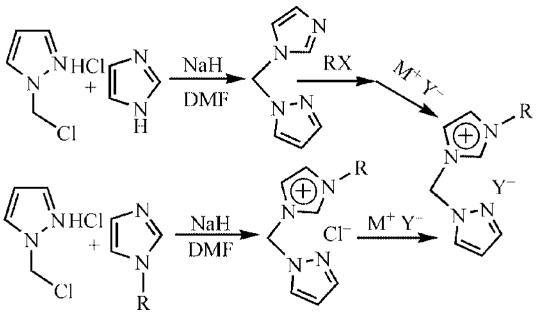


Heck Reaction in Ionic Liquids

R. Wang, Z. Zeng, B. Twamley, M. M. Piekarski, J. M. Shreeve* 655–661

Synthesis and Characterization of Pyrazolyl-Functionalized Imidazolium-Based Ionic Liquids and Hemilabile (Carbene)palladium(II) Complex Catalyzed Heck Reaction

Keywords: Fluorine / Ionic liquids / Heck reaction / Carbene complex / Palladium



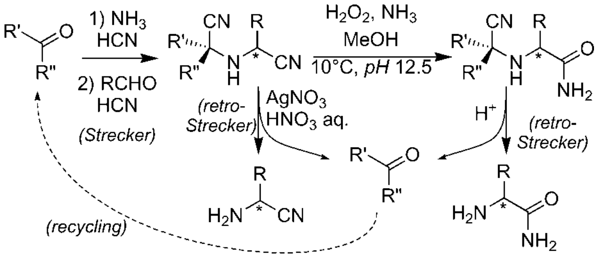
A series of pyrazolyl-functionalized imidazolium-based ionic liquids bearing alkyl and polyfluoroalkyl substituents were synthesized. Heck cross-coupling reactions were preliminarily evaluated using an (N-heterocyclic carbene)palladium complex in the corresponding ionic liquid.

α-Amino Acid Chemistry

J.-C. Rossi,* M. Marull, L. Boiteau, J. Taillades 662–668

Regioselective Hydration and Deprotection of Chiral, Dissymmetric Iminodinitriles in the Scope of an Asymmetric Strecker Strategy

Keywords: Iminodinitriles / Chiral α-aminonitriles / α-Amino acids / Regioselective hydration / Asymmetric Strecker synthesis



Controlled hydration/decomposition of the title compounds, affording non-racemised, free α-amino amides (or nitriles), was achieved by treatment with aqueous H_2O_2/NH_3 followed by mild acidic conditions (or aq. $AgNO_3$/HNO_3) with good recovery of the chiral auxiliary. This opens up perspectives to a cheap asymmetric Strecker synthesis.

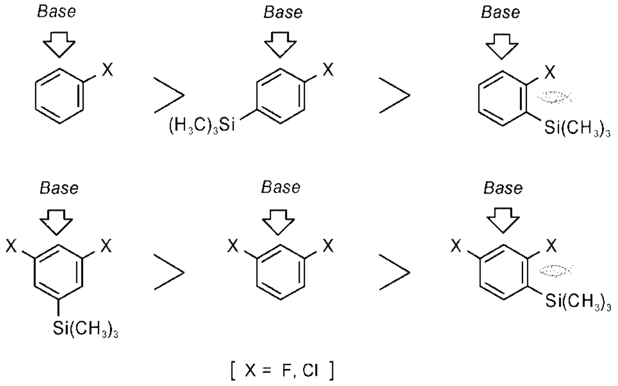
CONTENTS

Substituent Effects

C. Heiss, E. Marzi, F. Mongin, M. Schlosser* **669–675**

Remote Trimethylsilyl Groups Interfering with the *ortho* Deprotonation of Fluoroarenes and Chloroarenes

Keywords: Acidity / Buttressing effect / Competition kinetics / (Haloaryl)silanes / *ortho*- and *meta*-Metalation



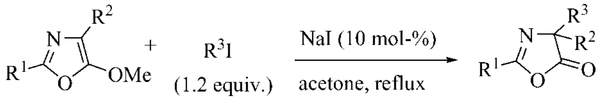
The *ortho* deprotonation (accomplished with *sec*-butyllithium or lithium 2,2,6,6-tetramethylpiperidide) of fluoroarenes and chloroarenes is little affected by trialkylsilyl groups if occupying *meta'* or *para* positions but, due to buttressing effects, considerably retarded if attached to the *ortho'* position.

Heterocycles by Inorganic Catalysis

L. Lu, P. Lu, S. Ma* **676–680**

I^--Catalyzed Reaction of 5-Methoxyoxazoles with Organic Iodides – An Efficient Synthesis of Azalactones

Keywords: Oxazoles / Organic iodides / Azalactones / Cleavage reactions / Heterocycles



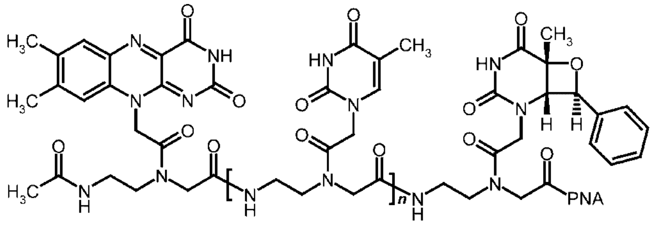
An I^--catalyzed methoxy carbon–oxygen bond cleavage in 5-methoxyoxazoles leading to the synthesis of azalactones, precursors of quaternary amino acids, has been developed. A series of 4-substituted azalactones were obtained through the variation of the alkyl iodides and differently substituted 5-methoxyoxazoles. Further study indicated that in one case the azalactone may be easily converted to the benzoyl-protected quaternary amino acid.

Acid-Sensitive PNA Building Blocks

T. Stafforst, U. Diederichsen* **681–688**

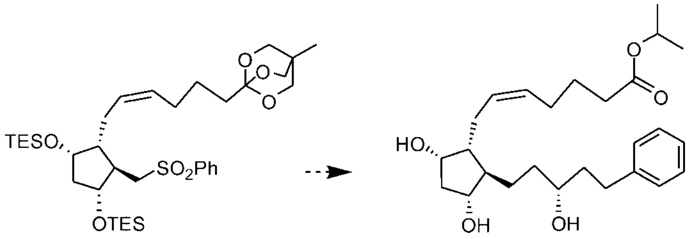
Solid-Phase Synthesis of Acid-Sensitive *N*-(2-Aminoethyl)glycine-PNA Oligomers by the Fmoc/Bhoc Strategy

Keywords: Peptide nucleic acids / Solid-phase synthesis / Flavin / Oxetane / Electron transfer



The solid-phase synthesis of highly acid-sensitive bis-functionalized *N*-(2-aminoethyl)-glycine-PNA by an adapted Fmoc/Bhoc strategy on Sieberamide resin has been achieved.

Novel Latanoprost Synthesis



A novel C(13)-sulfone prostaglandin intermediate was prepared from the (−)-“Corey lactone” by the attachment of a highly enantiomerically pure latanoprost “ω chain” synthon and desulfonylation through an alkylation/reduction protocol. This approach ensures high enantiomeric purity of the thus synthesized prostaglandin F analogs.

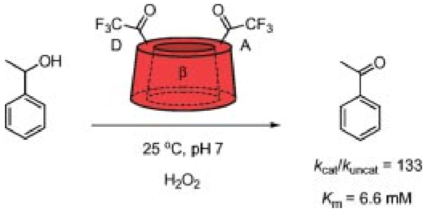
J. G. Martynow,* J. Jóźwik, W. Szelejewski,
O. Achmatowicz,* A. Kutner,
K. Wiśniewski, J. Winiarski,
O. Zegrocka-Stendel,
P. Gołębiewski .... **689−703**

A New Synthetic Approach to High-Purity (15*R*)-Latanoprost

Keywords: Prostaglandins / Chiral pool / Alkylation / Nucleophilic substitution / Reductive desulfonylation

Artificial Enzymes

Trifluoromethyl ketone containing cyclodextrins can catalyse the oxidation of amines or alcohols by hydrogen peroxide as coenzyme.

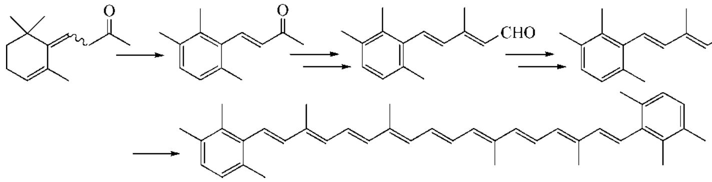


J. Bjerre, T. Hauch Fenger,
L. G. Marinescu, M. Bols* .... **704−710**

Synthesis of Some Trifluoromethylated Cyclodextrin Derivatives and Analysis of Their Properties as Artificial Glycosidases and Oxidases

Keywords: Enzyme catalysis / Enzyme models / Supramolecular chemistry / Oxidation / Hydrolysis

Aromatization of Terpenoids



A new chemical reaction which mimics biological syntheses of the end groups of aromatic carotenoids that occur in the sponge *Reniera japonica* and some anoxygenic phototrophic bacteria or nonphotosynthetic actinomycetes is reported, examplified for the synthesis of isorenieratene.

A. Valla,* Z. Andriamialisoa, B. Valla,
R. Labia, R. L. Guillou, L. Dufossé,
D. Cartier .... **711−715**

A New Biomimetic-Like Aromatization of the Cyclic End Groups of Terpenoids with Stereospecific Migration of One of the Methyl Groups: A Convenient Route to Isorenieratene (ϕ,ϕ-Carotene)

Keywords: Isorenieratenes / Carotenoids / Aromaticity