HUNGARY ITALY GERMANY GREECE

BELGIUM FRANCE

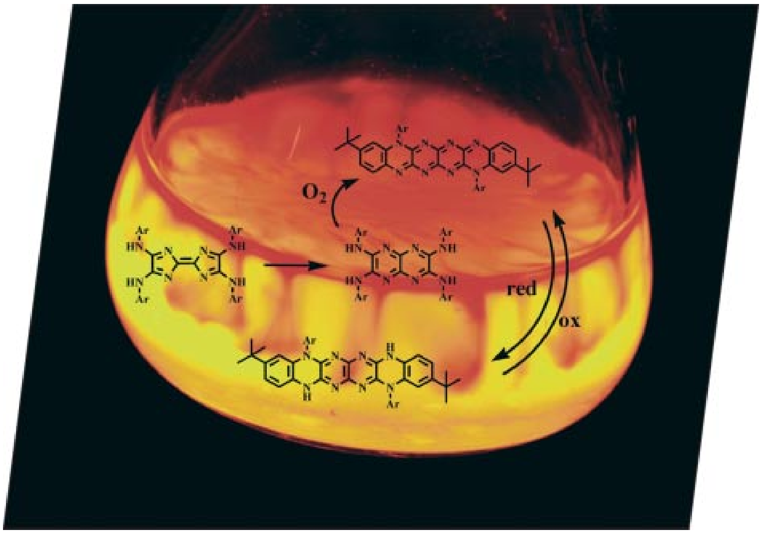
SWEDEN EUChemSoc CZECH REPUBLIC

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 the dyotropic rearrangement of 1,4,5,8-tetraazafulvalenes into pyrazino[2,3-*b*]pyrazines. In the case of Ar = 4-*tert*-butylphenyl, the products were immediately transformed, in the presence of oxygen, into derivatives of octaazahexacene through a cascade reaction. These highly ring-fused compounds display a strong red fluorescence in solution and, in addition, can easily be reduced reversibly. In contact with air, the yellow fluorescent leuco compound formed quickly reoxidized, which is visible by red fluorescent streaks. Details are discussed in the article by R. Beckert et al. on p. 1237ff.



CONTENTS

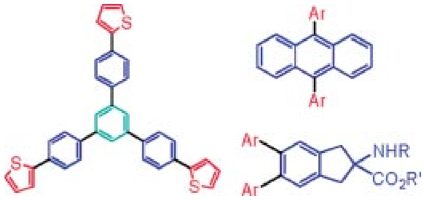
MICROREVIEW

Suzuki–Miyaura Cross-Coupling

S. Kotha,* K. Lahiri 1221–1236

Expanding the Diversity of Polycyclic Aromatics Through a Suzuki–Miyaura Cross-Coupling Strategy

Keywords: C–C Coupling / Polycycles / Amino acids / Palladium / Boron



This Microreview describes the application of the Suzuki–Miyaura (SM) cross-coupling reaction with several complex molecular structures (ca. 16) of particular relevance to scientists working at the interfaces of chemistry, biology and material sciences. In this regard, the diversity of various polycyclic molecules through SM cross-coupling reaction has been expanded.

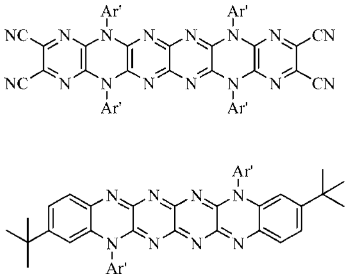
FULL PAPERS

Ring Fusion Reactions

F. Stöckner, R. Beckert,* D. Gleich, E. Birckner, W. Günther, H. Görls, G. Vaughan 1237–1243

Polyazaacenes – On the Way to Stable, Fluorescent and Redox-Active Derivatives

Keywords: Fused ring systems / Polycycles / Nitrogen heterocycles / Rearrangement / Redox chemistry



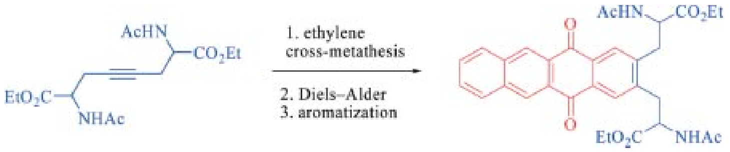
Synthesis and characterization of novel polyazaacenes starting from oxalic amidines/pyrazino[2,3-b]pyrazines by a condensation reaction with dichlorodicyanopyrazine. Highly fluorescent octaazahexacenes were synthesized by way of a cascade reaction which involves a dyotropic rearrangement, an intramolecular Diels-Alder reaction and a multistep redox process.

Quinone–Amino Acid Hybrids

S. Kotha,* K. Mandal, S. Banerjee, S. M. Mobin 1244–1255

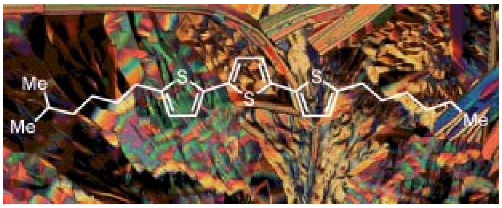
Synthesis of Novel Quinone–Amino Acid Hybrids via Cross-Enyne Metathesis and Diels–Alder Reaction as Key Steps

Keywords: Quinone–amino acid hybrids / Cross-enyne metathesis / Cycloaddition / Fullerenes



A “Building Block Approach” has been envisaged for the construction of novel quinone–amino acid hybrids using highly atom economical reactions such as ethylene cross–enyne metathesis and the Diels–Alder reaction.

Liquid Crystalline Oligothiophenes



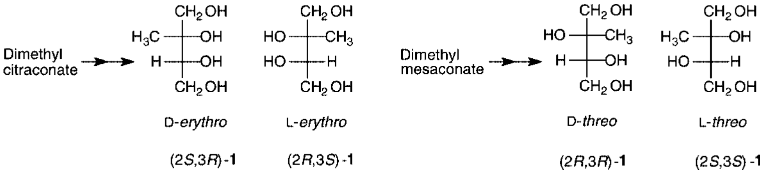
A well-adjusted balance between the π-π stacking of the aromatic core and the disorder caused by the peripheral alkyl chains is demonstrated to be important for the control of the thermotropic behavior of oligothiophene mesogens.

J. Leroy, N. Boucher, S. Sergeyev,
M. Sferrazza, Y. H. Geerts* .. 1256−1261

Symmetrical and Nonsymmetrical Liquid Crystalline Oligothiophenes: Convenient Synthesis and Transition-Temperature Engineering

Keywords: Oligothiophenes / Semiconductors / Liquid crystals / Transition-temperature engineering / Cross-coupling

Chemo-Enzymatic Synthesis



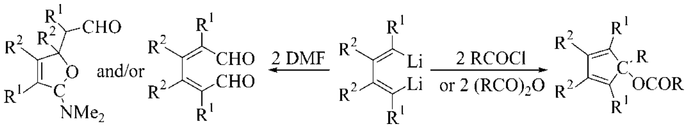
Oxidation of dimethyl citraconate followed by lipase-catalysed enantioselective resolution of the formed dimethyl (2R*,3S*)-2,3-dihydroxy-2-methylbutanedioate and subsequent reduction yields (2*R*,3*S*)- and (2*S*,3*R*)-2-methylbutane-1,2,3,4-tetraol. Similar reactions starting with dimethyl mesaconate gave the (2*R*,3*R*)- and (2*S*,3*S*)-isomers.

A. R. Moen, K. Ruud,
T. Anthonsen* .... 1262−1266

Chemo-Enzymatic Synthesis of All Isomers of 2-Methylbutane-1,2,3,4-tetraol − Important Contributors to Atmospheric Aerosols

Keywords: Chemo-enzymatic synthesis / Tetraols / Isoprenoids / Carbohydrates

Organodilithio Reagents



1,4-Dilithio-1,3-dienes reacted with acyl chlorides or anhydrides to afford multiply substituted cyclopentadienes in excellent isolated yields. When instead treated with DMF, multiply substituted 2,4-diene-1,6-dials and/or 2,5-dihydrofuran derivatives were obtained, depending on the substitution patterns of the butadienyl skeletons.

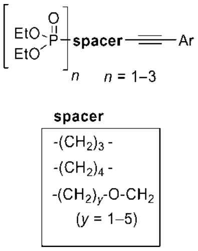
C. Wang, G.-L. Mao, Z.-H. Wang,
Z.-F. Xi* .... 1267−1273

Facile Synthesis of Multiply Substituted Cyclopentadienes and Conjugated Dienals through Reactions between 1,4-Dilithio-1,3-dienes and Carboxylic Acid Derivatives Including Acyl Chlorides, Anhydrides, and DMF

Keywords: Cyclopentadienes / Dienals / 2,5-Dihydrofurans / 1,4-Dilithio-1,3-dienes / Organo-bimetallic reagents

Immobilisation of Ligands

The synthesis of ω-alkyne-phosphonates is reported. These precursors are used for the Sonogashira cross-coupling with aryl iodides and bromides including 3-bromo-1,10-phenanthroline. The resulting molecules are ready to be immobilised on inorganic surfaces.



L. Delain-Bioton, D. Villemin,*
P.-A. Jaffrès* .... 1274−1286

ω-Alkyne-Mono- and Diphosphonates − Synthesis and Sonogashira Cross-Coupling Reaction with Aryl Halides

Keywords: Alkynes / Cross-coupling / N ligands / Phosphonates

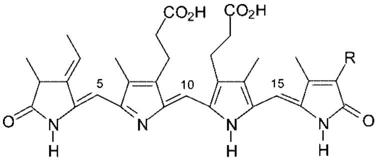
CONTENTS

Phytochrome Chromophore

Y. Makhynya, Z. Hussain,
T. Bauschlicher, P. Schwinte, F. Siebert,
W. Gärtner* 1287–1293

Synthesis of Selectively ^{13}C-Labelled Bilin Compounds

Keywords: Isotope labelling / Bilin / Phytochrome / Infra-red spectroscopy / Tetrapyrrole chromophore / Phycocyanobilin



1: R = C_2H_5; 5-^{13}C-PCB
2: R = C_2H_5; 10-^{13}C-PCB
3: R = C_2H_5; 15-^{13}C-PCB
4: R = C_2H_5; 10,15-^{13}C-PCB
5: R = C_2H_3; 10-^{13}C-PΦB

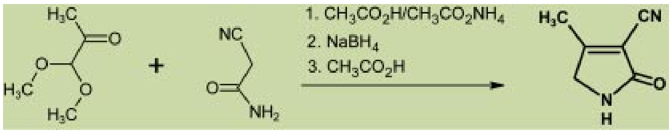
Open-chain tetrapyrroles bearing ^{13}C isotopes at selected positions were synthesized de novo. Such compounds, which serve as chromophores in the plant photoreceptor phytochrome, have been employed for structural analysis of the protein-bound chromophore by NMR and vibrational spectroscopy.

Extended Knoevenagel Condensation

P. B. Shrestha-Dawadi,*
J. Lugtenburg 1294–1300

Efficient Preparation of [2-^{13}C]- and [3-^{13}C]-3-Cyano-4-methyl-3-pyrrolin-2-one

Keywords: Phytochrome / Pyrrolinone / Isotopic labeling / Extended Knoevenagel condensation



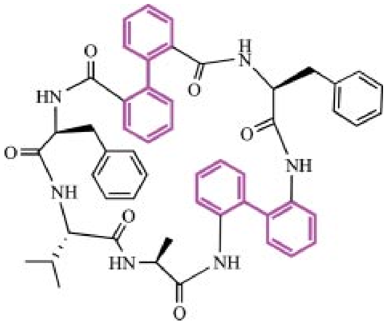
1,1-Dimethoxyacetone and 2-cyanoacetamide react under Knoevenagel conditions. The resulting substituted acrylamide can be reduced by $NaBH_4$. This product under acid catalysis forms 3-cyano-4-methyl-3-pyrrolin-2-one in a few steps and in high yield.

Peptide Hybrid

A. Montero, F. Albericio,* M. Royo,*
B. Herradón* 1301–1308

Synthesis of a 24-Membered Cyclic Peptide-Biphenyl Hybrid

Keywords: Biaryls / Calpain inhibitors / Macrocycles / Peptide-biphenyl hybrids / Solid-phase synthesis



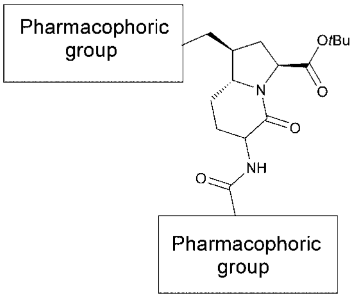
The synthesis of a 24-membered macrocyclic peptide-biphenyl hybrid with four amino acid residues and two biphenyl fragments has been performed by a combination of solid-phase and solution methodologies.

Nonpeptide Integrin Antagonists

L. Manzoni,* M. Bassanini, L. Belvisi,
I. Motto, C. Scolastico, M. Castorina,
C. Pisano 1309–1317

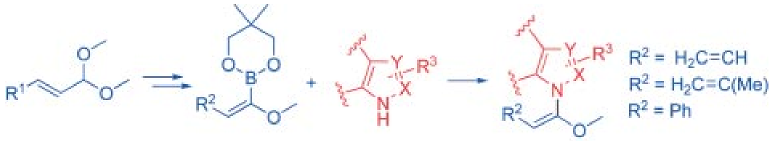
Nonpeptide Integrin Antagonists: RGD Mimetics Incorporating Substituted Azabicycloalkanes as Amino Acid Replacements

Keywords: Angiogenesis / Antitumor agent / Lactams / Azabicycloalkanes / RGD mimetics



Azabicyclo[4.3.0]alkanes appropriately substituted on both cycles can serve as scaffold mimics of the RGD signaling motif of integrin.

C–N Cross-Coupling



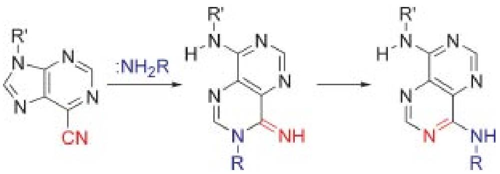
Alkoxydienyl and alkoxystyryl boronates have been used in various copper-mediated cross-coupling reactions with azoles. The process utilizes $Cu(OAc)_2$ in the presence of CsF in CH_2Cl_2 at room temperature. The good yields and the mild conditions of this methodology make it a promising method for *N*-functionalization of heterocycles.

A. Deagostino, C. Prandi,* C. Zavattaro, P. Venturello 1318–1323

N-Functionalization of Azoles through Coupling Reactions with Alkoxydienyl and Alkoxystyryl Boronic Esters

Keywords: Azoles / Vinyl boronates / Cross-coupling / C–N bond formation / Copper catalysis

Biologically Active Pyrimido-Pyrimidines



A short and efficient synthesis of pyrimido[5,4-*d*]pyrimidines and 7,8-dihydropyrimido[5,4-*d*]pyrimidines, based on reactions between 9-aryl-6-cyanopurines and primary amines, is described.

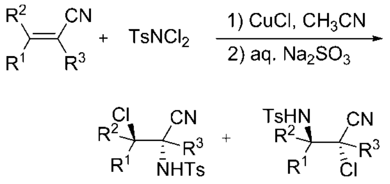
M. A. Carvalho, S. Esperança, T. Esteves, M. F. Proença* 1324–1331

An Efficient Synthesis of 7,8-Dihydropyrimido[5,4-*d*]pyrimidines

Keywords: Cyanopurines / Amines / Rearrangement / Pyrimido[5,4-*d*]pyrimidines

Aminohalogenation

The regio- and stereoselective aminochlorination of α,β-unsaturated nitriles by use of *N,N*-dichloro-*p*-toluenesulfonamide (4-$TsNCl_2$) as the nitrogen/halogen sources and CuCl as the catalyst (10 mol-%) in the presence of molecular sieves (4 Å) has been developed. The new method provides an easy route to vicinal haloamine nitriles and the reaction is very convenient to carry out at room temperature without the protection of inert gases. The stereochemistry has been unambiguously confirmed by X-ray structural analysis.



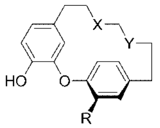
J.-L. Han, S.-J. Zhi, L.-Y. Wang, Y. Pan,* G. Li* 1332–1337

CuCl-Catalyzed Regio- and Stereoselective Aminohalogenation of α,β-Unsaturated Nitriles

Keywords: Aminohalogenation / α,β-Unsaturated nitriles / Copper chloride

Cyclic Diarylheptanoid

A versatile method for the total synthesis of cyclic diphenyl ether-type diarylheptanoids, acerogenin C, acerogenin L, (±)-galeon, and (±)-pterocarine was described. The Ullmann reaction of suitably substituted linear diphenylheptanoids was employed for the intramolecular formation of the key ether intermediates as the final step.



1a X = CH_2, Y = CH(OH), R = H (acerogenin A)
b X = CH(OH), Y = CH_2, R = H (acerogenin B)
c X = CH_2, Y = C=O, R = H (acerogenin C)
d X = C=O, Y = CH_2, R = H (acerogenin L)
e X = C=O, Y = CH_2, R = OCH_3 (galeon)
f X = C=O, Y = CH_2, R = OH (pterocarine)

B.-S. Jeong, Q. Wang, J.-K. Son, Y. Jahng* 1338–1344

A Versatile Synthesis of Cyclic Diphenyl Ether-Type Diarylheptanoids: Acerogenins, (±)-Galeon, and (±)-Pterocarine

Keywords: Heptanoids / Macrocycles / Ethers / Aldol reactions / Natural products

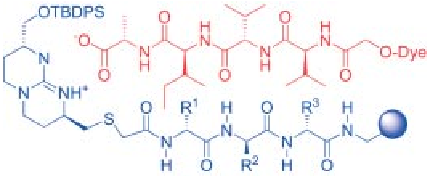
CONTENTS

Combinatorial Supramolecular Chemistry

J. Shepherd, G. J. Langley, J. M. Herniman, J. D. Kilburn* .... **1345−1356**

Rapid Sequencing of Split-and-Mix Peptide Receptor Libraries − Identification of Binding Partners for Val-Val-Ile-Ala in Aqueous Solution

Keywords: Peptides / Coding / Sequencing / Combinatorial chemistry / Receptors / Screening



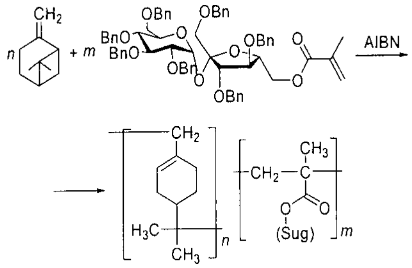
Split-and-mix peptide libraries have been encoded by capping cleavable, laddered sequences with *p*-bromobenzoic acid. The encoding methodology has been used to prepare a library of tripeptides, functionalised with a bicyclic guanidinium unit, which was screened to identify binding partners for the C-terminal tetrapeptide sequence of the amyloid-β protein, Aβ(1-42).

Sugar-Based Copolymers

M. T. Barros,* K. T. Petrova,* A. M. Ramos .... **1357−1363**

Potentially Biodegradable Polymers Based on α- or β-Pinene and Sugar Derivatives or Styrene, Obtained under Normal Conditions and on Microwave Irradiation

Keywords: Green chemistry / Pinene / Sucrose / Biodegradable copolymers / Radical copolymerisation / Microwave irradiation



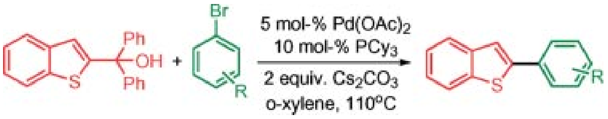
The homopolymerisation of α-and β-pinene, and their copolymerisation with styrene and hepta-*O*-benzyl-6′-*O*-methacryloyl-sucrose (BMS) have been examined in the presence of AIBN as free-radical initiator in toluene or without solvent at 80 °C at normal pressure and in a synthetic microwave oven.

Directed Cross-Coupling

A. B. Bíró, A. Kotschy* .... **1364−1368**

Selective Palladium-Catalysed *ipso* Arylation of α,α-Disubstituted Benzo[*b*]thien-2-ylmethanols with Aryl Bromides using PCy_3 as Ligand

Keywords: Benzothiophenes / Cross-coupling / Palladium / *ipso* Coupling



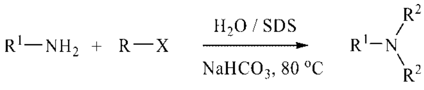
α,α-Diphenylbenzo[*b*]thien-2-yl-methanol and α,α-diphenylbenzo[*b*]thien-3-ylmethanol undergo *ipso* coupling with aryl bromides to give the appropriate 2-, and 3-arylbenzo[*b*]thiophenes in good to excellent yield with concomitant formation of benzophenone. In the latter case, the reaction is biased by concurrent *ortho* arylation.

Aqueous *N*-Alkylation

C. B. Singh, V. Kavala, A. K. Samal, B. K. Patel* .... **1369−1377**

Aqueous-Mediated *N*-Alkylation of Amines

Keywords: Amines / Alkylation / Tertiary amines / Aqueous media / Surfactants



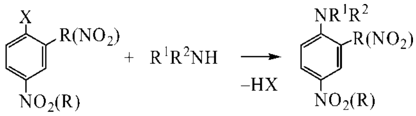
$$R^1{-}NH_2 + R{-}X \xrightarrow[NaHCO_3,\ 80\ ^\circ C]{H_2O\ /\ SDS} R^1{-}N(R^2)R^2$$

R = aliphatic, aromatic, X = H, NO_2

Direct *N*-alkylation of primary amines to secondary/tertiary amines and of secondary amines to tertiary amines has been achieved in excellent yields by employing alkyl, benzylic and allylic halides in the presence of $NaHCO_3$ in an aqueous medium.

Kinetics of S_NAr Reactions

Comparison with previous results for more strongly activated compounds shows that values of both k_1 for nucleophilic attack and, when base catalysis is observed, values of k_{Am}/k_{-1} are lowered. The latter reflects increases for the more weakly activated compounds in values of k_{-1} and decreases in value of k_{Am} as the proton transfer from zwitterionic intermediates to catalysing amine becomes less thermodynamically favourable.



X = Cl, F, OPh; R = CN, CF_3, ring N;
R^1R^2 = *n*-butyl, H; $-(CH_2)_4-$; $-(CH_2)_5-$.

M. R. Crampton,* T. A. Emokpae, C. Isanbor* **1378–1383**

The Effects of Ring Substituents and Leaving Groups on the Kinetics of S_NAr Reactions of 1-Halogeno- and 1-Phenoxy-nitrobenzenes with Aliphatic Amines in Acetonitrile

Keywords: Nucleophilic aromatic substitution / Reactivity–substituent effects / Amines