Hungary Italy Germany Greece

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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 members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

The cover picture shows new members of the subphthalocyanine family that were obtained by peripheral derivatization of this C_3-symmetrical macrocycle. The incorporation of novel functionalities onto these dyes provides wider versatility that could be exploited in artificial photosynthetic systems and other applied fields. Details are discussed in the article by D. González-Rodríguez and T. Torres on p. 1871ff.

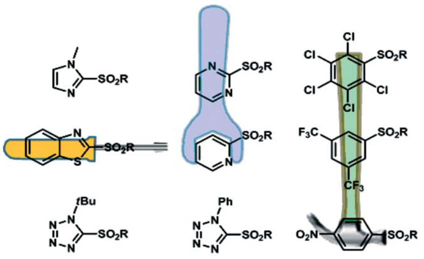
MICROREVIEW

Julia–Kocienski Olefination

C. Aïssa* 1831–1844

Mechanistic Manifold and New Developments of the Julia–Kocienski Reaction

Keywords: Olefination / Modified Julia–Kocienski reaction / Sulfones



The olefination toolbox, already well fitted with heterocyclic sulfones, has recently been further enriched with new electron-poor sulfones. Moreover, results garnered over the past two decades seem to confirm the mechanistic assumptions put forward by S. Julia since his seminal discovery of the Julia–Kocienski olefination.

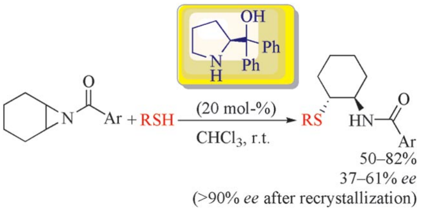
SHORT COMMUNICATIONS

Organocatalysis

A. Lattanzi,* G. Della Sala 1845–1848

Desymmetrization of *meso-N*-Acylaziridines with Benzenethiols Promoted by α,α-Diaryl-L-prolinols

Keywords: Desymmetrization / Aziridines / Organocatalysis / Amino alcohols / Asymmetric catalysis



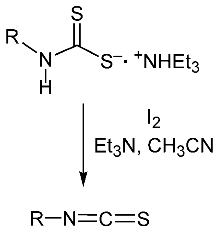
The desymmetrization of *meso-N*-acylaziridines with benzenethiols is provided by using commercially available α,α-L-diphenylprolinol as the organocatalyst. The products are obtained in good yield and moderate enantiontioselectivity, which can be improved to high levels (>90% *ee*) by a single recrystallization.

Isothiocyanate Synthesis

J. Nath, H. Ghosh, R. Yella, B. K. Patel* 1849–1851

Molecular Iodine Mediated Preparation of Isothiocyanates from Dithiocarbamic Acid Salts

Keywords: Iodine / Desulfurization / Oxidation / Sustainable chemistry / Acidity



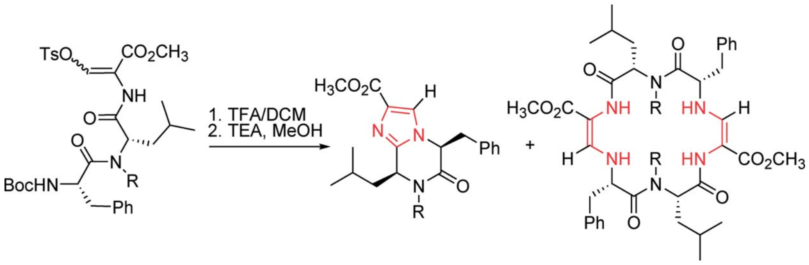
We have developed perhaps the most efficient and simple, environmentally benign method for the preparation of isothiocyanates from the corresponding dithiocarbamic acid salts by using molecular iodine. The reagent is easily available and nontoxic, and the precipitated sulfur can be removed easily; hence, this method is most suitable for large-scale synthesis.

Synthesis of Imidazopyrazines

Y. Kogon, L. Goren, D. Pappo, A. Rudi, Y. Kashman* 1852–1854

Cyclic Endiamino Peptides: A New Synthesis of Imidazopyrazines

Keywords: Cyclization / Peptides / Nitrogen heterocycles / Enols

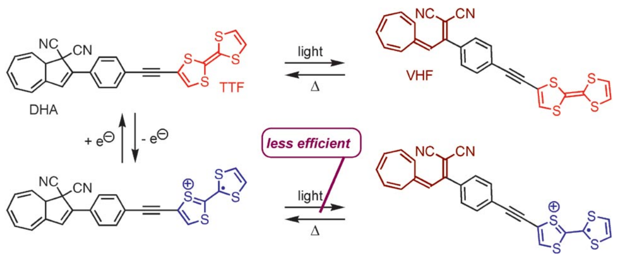


Cyclisation of enol-tosylated tripeptides afforded imidazopyrazines and cyclic endiamino peptides. A possible mechanism is suggested.

Redox-Controlled Switching

M. Å. Petersen, A. S. Andersson, K. Kilså,* M. B. Nielsen* **1855–1858**

Redox-Controlled Dihydroazulene-Vinylheptafulvene Photoswitch Incorporating Tetrathiafulvalene



A novel dihydroazulene (DHA)–tetrathiafulvalene (TTF) conjugate has been synthesized. The photoswitching efficiency to the vinylheptafulvene (VHF) isomer is found to depend on the redox-state of the TTF unit (0 or +1), while the thermal ring closure of VHF to DHA is unaffected.

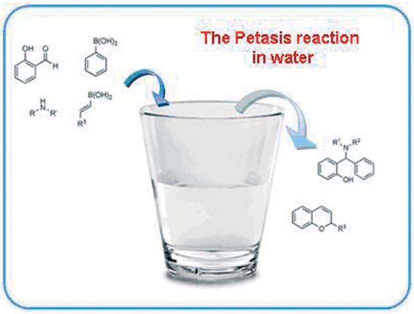
Keywords: Dihydroazulene / Electrocyclic reactions / Photoswitches / Redox chemistry / Tetrathiafulvalene / Photochemistry

Aqueous Petasis Reaction

N. R. Candeias, L. F. Veiros, C. A. M. Afonso, P. M. P. Gois* **1859–1863**

Water: A Suitable Medium for the Petasis Borono-Mannich Reaction

Water was used for the first time as the solvent in the Petasis borono-Mannich reaction, and several alkylaminophenols and 2*H*-chromenes were obtained in considerably high yields. The reaction mechanism was studied by DFT calculations, and the results obtained corroborate the solvent effect experimentally observed.

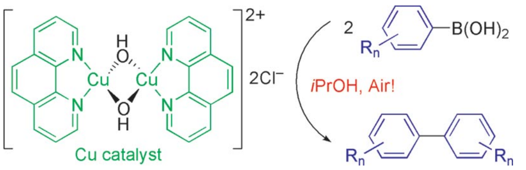


Keywords: Boron / Water chemistry / Multicomponent reactions / Amines / Solvent effects

Aerobic Homocoupling

N. Kirai, Y. Yamamoto* **1864–1867**

Homocoupling of Arylboronic Acids Catalyzed by 1,10-Phenanthroline-Ligated Copper Complexes in Air



The homocoupling of arylboronic acids was achieved at ambient temperature in air with 1,10-phenanthroline-ligated binuclear (μ-hydroxido)copper complex as a catalyst. This method tolerates various substituents on the arylboronic acids. As a result, 25 symmetrical biaryls were obtained from readily available arylboronic acids in 19–92% isolated yield.

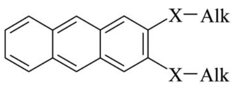
Keywords: Aerobic reactions / Boron / Biaryls / Copper / Homocoupling

Gel Formation by Acenes

H. Hopf,* H. Greiving, H. Bouas-Laurent,* J.-P. Desvergne **1868–1870**

2,3-Di-*n*-undecylanthracene and 2,3-Di-*n*-decyloxyanthracene (DDOA) – on the Connecting Link between the Aromatic Substrate and the Aliphatic Chain in Self-Assembling Systems

The gelling properties of linear acenes **1** (Alk = $C_{10}H_{21}$) depend critically on the atom connecting the aliphatic and the aromatic part of the molecules. Whereas in the case of X = O supergelators result, with X = CH_2 no gelling is observed at all.



1

Keywords: Acenes / Gels / Cycloaddition / Anthracenes / Photochemistry

CONTENTS

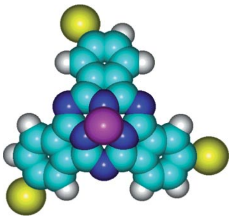
FULL PAPERS

Subphthalocyanine Chemistry

D. González-Rodríguez, T. Torres* **1871–1879**

Peripheral Functionalization of Subphthalocyanines

Keywords: Subphthalocyanines / Phthalocyanines / Chromophores / Macrocycles / Cross-coupling



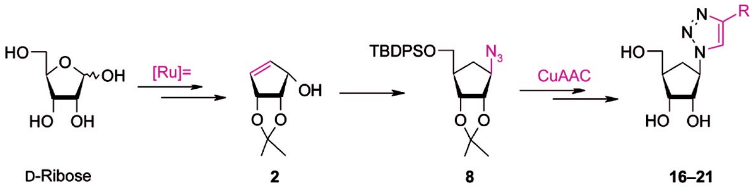
Some useful procedures for the incorporation of diverse functional groups in the periphery of the subphthalocyanine macrocycle are described.

Carbanucleosides

J. Broggi, H. Kumamoto, S. Berteina-Raboin, S. P. Nolan, L. A. Agrofoglio* **1880–1888**

Click Azide-Alkyne Cycloaddition for the Synthesis of D-(−)-1,4-Disubstituted Triazolo-Carbanucleosides

Keywords: Nucleosides / Carbanucleosides / Antiviral agents / Olefin metathesis / Huisgen cycloaddition / Ribavirin / Poxvirus



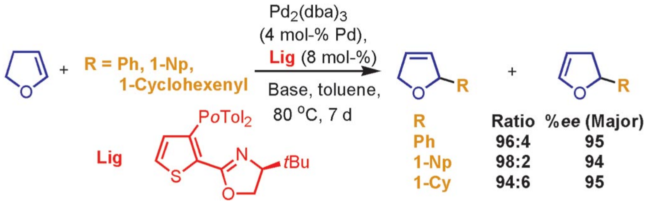
The synthesis of D-(−)-1,4-disubstituted triazolo-carbanucleoside derivatives **16–21** is achieved using high yielding protocols based on ring-closing metathesis and copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC).

Asymmetric Catalysis

M. O. Fitzpatrick, H. Muller-Bunz, P. J. Guiry* **1889–1895**

The Synthesis of New HetPHOX Ligands and Their Application to the Intermolecular Asymmetric Heck Reaction

Keywords: Asymmetric catalysis / Heck reaction / N,P ligands / HetPHOX ligands



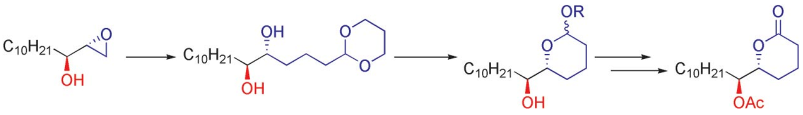
The synthesis of six members of the HetPHOX P,N ligand class, with variation at phosphorus and the oxazoline 4-substituent, has been developed. The ligands provide good levels of enantioselection (*ee* values up to 95%) in a prototypical Pd-catalyzed intermolecular asymmetric Heck reaction employing 2,3-dihydrofuran as substrate. In addition, the kinetic product was favoured up to 98:2.

Pheromone Synthesis

S. Singh, P. J. Guiry* **1896–1901**

A Facile Synthesis of Both Enantiomers of 6-Acetoxy-5-hexadecanolide, a Major Component of Mosquito Oviposition Attractant Pheromones

Keywords: Pheromones / Lactones / Natural products / Total synthesis



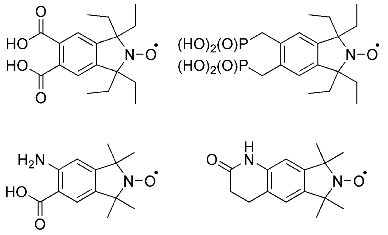
The mosquito attractant pheromone was synthesized in overall 28% yield by using Sharpless asymmetric epoxidation and $ZrCl_4$-catalyzed cyclic acetal formation as key steps.

Water-Soluble Nitroxides

K. E. Fairfull-Smith, F. Brackmann, S. E. Bottle* 1902–1915

The Synthesis of Novel Isoindoline Nitroxides Bearing Water-Solubilising Functionality

A number of novel tetramethyl- and tetraethylisoindoline nitroxides possessing water-solubilising functionalities were synthesised. The increased steric bulk of the tetraethyl structures should limit bioreduction and these compounds may have potential as antioxidants.



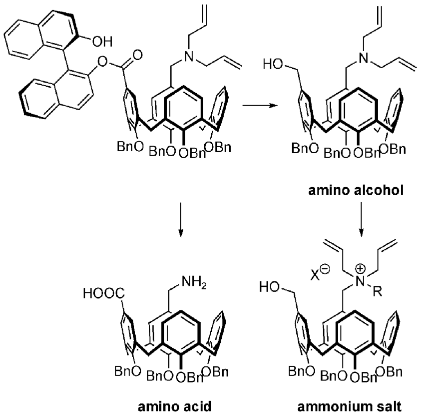
Keywords: Nitroxide / Isoindoline / Radicals / Antioxidant / Medicinal chemistry

Inherently Chiral Calixarenes

S. Shirakawa, S. Shimizu* 1916–1924

Synthesis of an Inherently Chiral Calix[4]arene Amino Acid and Its Derivatives: Their Application to Asymmetric Reactions as Organocatalysts

The synthesis of an inherently chiral calix[4]arene amino acid as a chiral building block has been achieved. Different types of optically pure calix[4]arene amino acid derivatives were obtained and these were applied to asymmetric reactions as organocatalysts.



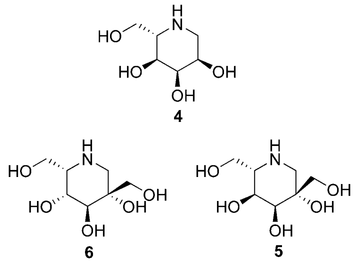
Keywords: Calixarenes / Amino acids / Asymmetric catalysis / Michael addition / Phase-transfer catalysis

Facile Aza-Claisen Rearrangement

P. Gupta, Y. D. Vankar* 1925–1933

Facile Aza-Claisen Rearrangement of Glycals: Application in the Synthesis of 1-Deoxy-L-iminosugars

L-*allo*-Deoxynojirimycin (**4**) and two new *C*-5-(hydroxymethyl) analogues of L-*altro*-deoxynojirimycin and L-*ido*-deoxynojirimycin, **5** and **6**, respectively, have been synthesized by a strategy that involves an aza-Claisen rearrangement and an intramolecular N-heterocyclization as the key steps.

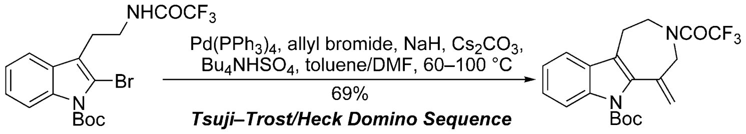


Keywords: Carbohydrates / Iminosugars / Azasugars / Rearrangement / Enzymes / Inhibitors

Domino Reactions

S. G. Stewart,* C. H. Heath, E. L. Ghisalberti 1934–1943

Domino or Single-Step Tsuji–Trost/Heck Reactions and Their Application in the Synthesis of 3-Benzazepines and Azepino[4,5-*b*]indole Ring Systems



3-Benzazepines and azepino[4,5-*b*]indoles are readily prepared in one pot by utilizing domino Tsuji–Trost/Heck reactions. Through this methodology, and the single-step equivalent, complex 6-7-6 and 6-5-7 ring heterocycles have been prepared. In addition, a domino Heck/Heck sequence of reactions that produces the azepinobenzindolizine tetracyclic ring system from *N*-diallylated precursors is described.

Keywords: Domino reactions / Cross-coupling / Tsuji–Trost reaction / Heck reaction / N-Heterocycles

CONTENTS

Natural Product Analogues

H. Guthmann, D. Conole, E. Wright,
K. Körber, D. Barker,
M. A. Brimble* 1944–1960

Synthesis of AE and BE Ring Analogues of the Alkaloid Methyllycaconitine

Keywords: Alkaloids / Olefination / Hydrogenation / Nicotinic acetylcholine receptors

Ar = Ph, 2-ClC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4, 3-$MeOC_6H_4$, 4-$MeOC_6H_4$, 3-MeC_6H_4, 4-MeC_6H_4
AE ring analogues

R = $(CH_2)_3Ph$, CH_2Ph, $(CH_2)_3CH_3$, (*R*)-$CH(CH_3)Ph$
BE ring analogues

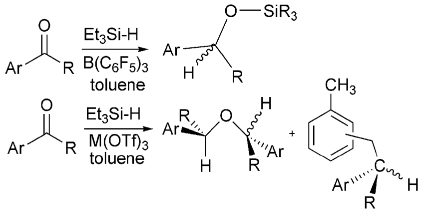
The synthesis of AE and BE analogues of the alkaloid methyllycaconitine is reported. The analogues contain the two key 2-(2-methylmaleimido)benzoate ester pharmacophores embedded in an octahydroquinoline motif that mimics the EB-rings of methyllycaconitine.

Hydrosilylation

P. Bach, A. Albright,
K. K. Laali* 1961–1966

Influence of Lewis Acid and Solvent in the Hydrosilylation of Aldehydes and Ketones with Et_3SiH; Tris(pentafluorophenyl)borane $B(C_6F_5)_3$ versus Metal Triflates [$M(OTf)_3$; M = Sc, Bi, Ga, and Al] – Mechanistic Implications

Keywords: Tris(pentafluorophenyl)borane / Hydrosilylation / Aldehydes / Ketones / Metal triflates / Dibenzyl ether formation / Solvent benzylation products



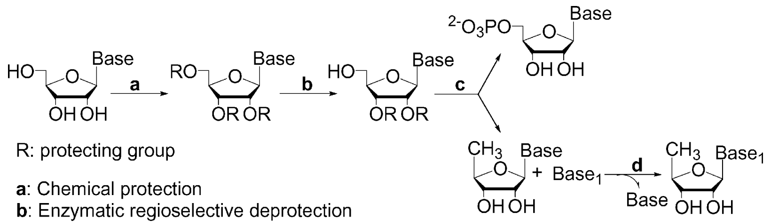
The $Et_3SiH/M(OTf)_3$ (M = Sc, Bi, Ga, Al) systems exhibit very different chemoselectivity as compared to the $Et_3SiH/B(C_6F_5)_3$ system in the reaction with aromatic aldehydes and ketones.

Regioselective Enzymatic Deprotection

T. Bavaro, S. Rocchietti, D. Ubiali,*
M. Filice, M. Terreni,
M. Pregnolato* 1967–1975

A Versatile Synthesis of 5′-Functionalized Nucleosides Through Regioselective Enzymatic Hydrolysis of Their Peracetylated Precursors

Keywords: Immobilization / Lipases / Nucleosides / Regioselectivity / Enzymes



R: protecting group

a: Chemical protection
b: Enzymatic regioselective deprotection
c: Chemical fuctionalization
d: Enzymatic transglycosylation

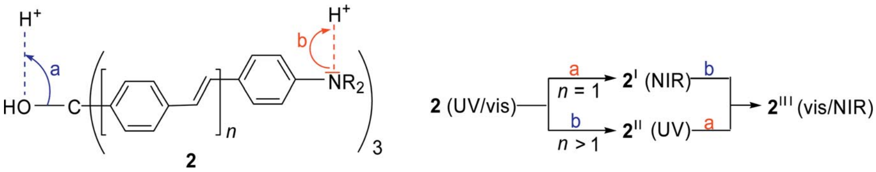
Screening of immobilized lipases against natural and modified peracetylated nucleosides provided a set of biocatalysts with different regioselectivities. Selectively deprotected nucleosides were prepared with these lipases by enzymatic reaction and were then used for the chemo-enzymatic synthesis of 5′-functionalized nucleosides and mononucleotides in high yields and purities.

Functional Dyes

S. Kim, H. Kalbitz, S. Hillmann,
H. Meier* 1976–1983

Tris[oligo(1,4-phenylenevinylene)]methylium Dyes

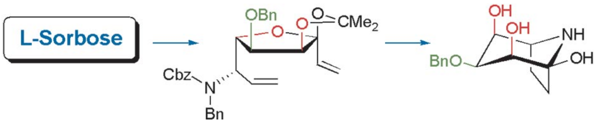
Keywords: Conjugation / Carbocations / Dyes/pigments / Oligomers / Protonation / Push–pull effects



2

Tris[oligo(1,4-phenylenevinylene)]carbinols **2** form methylium dyes, the absorptions of which depend strongly on the different protonation processes for *n* = 1 and *n* > 1.

Calystegines, Azasugars



The 3-*O*-benzyl derivative of the polyhydroxylated *nor*-tropane alkaloid 1,3,5-tri-*epi*-calystegine B$_2$ was prepared from L-sorbose by a Wittig and magnesium-mediated alkylation methodology, followed by a ring-closing olefin metathesis (RCM) reaction.

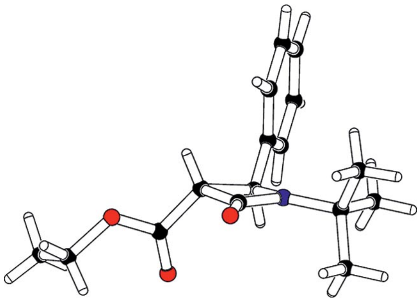
D. Lo Re, F. Franco, F. Sánchez-Cantalejo, J. A. Tamayo* .... 1984−1993

Total Synthesis of 3-*O*-Benzyl-1,3,5-tri-*epi*-calystegine B$_2$ from L-Sorbos

Keywords: Total synthesis / Calystegines / Alkaloids / Alkylation / Metathesis / Azasugars

One-Pot β-Lactam Synthesis

The effective one-pot synthesis of *N-tert*-butyl-*trans*-α-ethoxycarbonyl-β-phenyl-β-lactam by the octacarbonyldicobalt-catalyzed carbonylation of ethyl diazoacetate in the presence of *N-tert*-butylbenzaldimine is described.



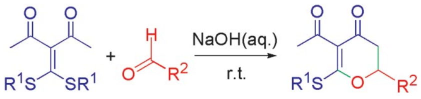
E. Fördős, R. Tuba, L. Párkányi, T. Kégl, F. Ungváry .... 1994−2002

Application of the Octacarbonyldicobalt-Catalyzed Carbonylation of Ethyl Diazoacetate for the One-Pot Synthesis of *N-tert*-Butyl-*trans*-α-ethoxycarbonyl-β-phenyl-β-lactam 💻

Keywords: Cobalt / Carbene ligands / Carbonyl ligands / C−C coupling / Lactams / Density functional calculations

Substituted Dihydropyranones

A series of substituted dihydropyranones were synthesized by a formal [4+2] annulation of α-acetyl ketene S,S-acetals with aldehydes in the presence of NaOH in water.



Y. Ouyang, J. Huang, W. Pan, Y. Liang, Y. Yang, D. Dong* .... 2003−2009

[4+2] Annulation − Convenient Synthesis of Substituted Dihydropyranones in Aqueous Media

Keywords: Aldol reactions / Annulation / α-Oxo ketene S,S-acetals / Dihydropyranones / Water

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* Author to whom correspondence should be addressed.

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