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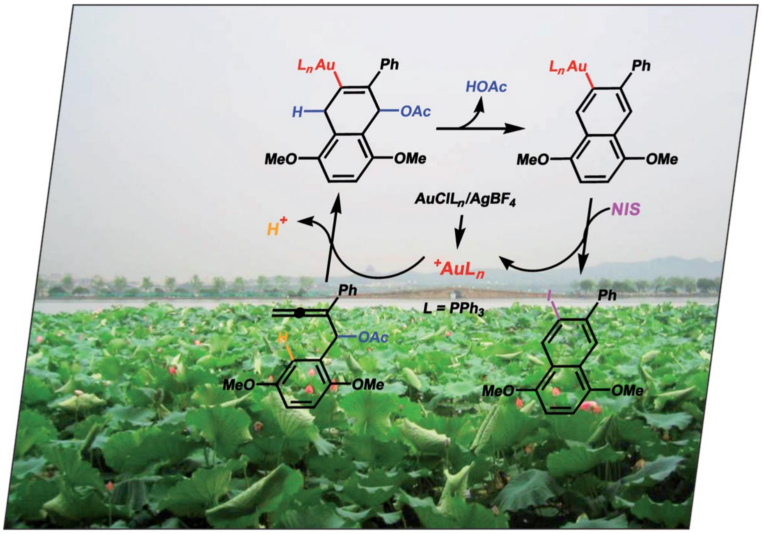
COVER PICTURE

The cover picture shows the efficient synthesis of polysubstituted naphthalene derivatives and the mechanism, which proceeds through the gold-catalyzed cyclization of 1-arylalka-2,3-dienyl acetates. The six-membered cyclohexenyl gold species is formed from the coordination of the allene moiety to the gold followed by nucleophilic attack of the electron-rich benzene to the metal-activated electrophilic C=C bond. Subsequent elimination of acetic acid affords the β-naphthyl gold intermediate, which may be trapped by iodonolysis to release the gold catalyst into the catalytic cycle and afford the target iodonaphthalene. Details are discussed in the article by S. Ma et al. on p. 6545ff. The background picture depicts the typical scenery of West Lake in Hangzhou during the summer season where the lake is covered with lotus leaves. Zhejiang University, a university with a history of over 110 years, is located very close to West Lake.



CONFERENCE REPORT

Conference Report

N. Maulide* **6491–6493**

A Feast and a Reflection on Organocatalysis – Notes from the ISOμ in Mülheim

A short summary on the fruitful conference on organocatalysis, the International Symposium on Organocatalysis, Mülheim (ISOμ 2010), is presented by Nuno Maulide. The conference was held between July 14 and 17 2010 at the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr (Germany) and falls under the priority programme on organocatalysis (Schwerpunktprogramm Organokatalyse) funded by the German Science Foundation (Deutsche Forschungsgemeinschaft, DFG).

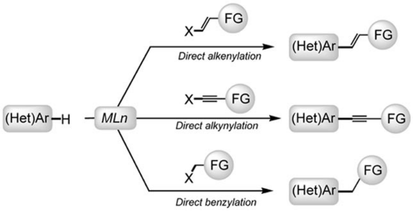
MICROREVIEW

Three-Component Reactions

S. Messaoudi,* J.-D. Brion, M. Alami* **6495–6516**

Transition-Metal-Catalyzed Direct C–H Alkenylation, Alkynylation, Benzylation, and Alkylation of (Hetero)arenes

Keywords: C–H activation / C–C coupling / Alkynes / Alkenylation / Alkynylation / Benzylation / Alkylation / Arenes



Over the last decade, significant efforts have been devoted to transition-metal-catalyzed direct functionalization of (hetero)arenes. We illustrate new protocols for efficient direct alkenylation, alkynylation, benzylation, and alkylation of (hetero)arenes by C–H bond activation with challenging coupling partners – including electrophilic alkenyl-, alkynyl-, and benzyl halides (or pseudohalides).

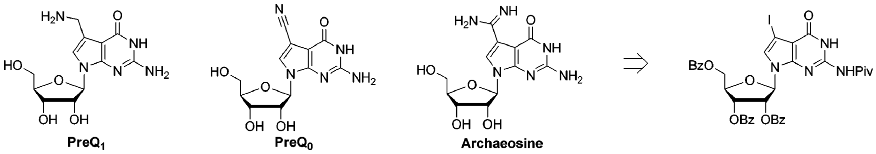
SHORT COMMUNICATIONS

Deazaguanosine Nucleosides

T. Brückl, I. Thoma, A. J. Wagner, P. Knochel, T. Carell* **6517–6519**

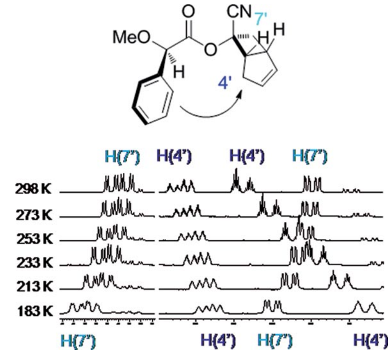
Efficient Synthesis of Deazaguanosine-Derived tRNA Nucleosides PreQ$_0$, PreQ$_1$, and Archaeosine Using the Turbo-Grignard Method

Keywords: Grignard reaction / Nucleosides / tRNA / Natural products



PreQ$_1$, PreQ$_0$, and archaeosine were prepared from a common iododeazaguanosine intermediate by an efficient and divergent route. This approach was facilitated by the development of a novel, functional group tolerating Turbo-Grignard reaction.

Absolute Configuration



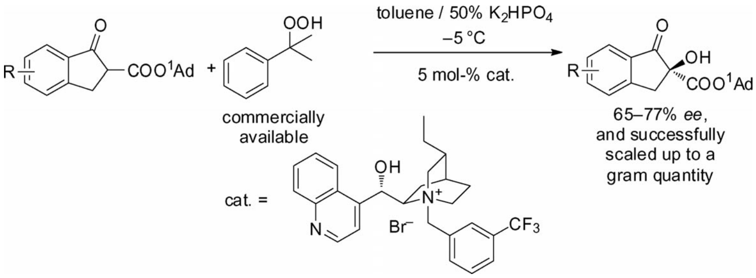
A simple NMR method for the assignment of the absolute configuration of ketone cyanohydrins is presented. The comparison of two ^{1}H NMR spectra recorded at different temperatures of a single MPA derivative constitutes its basis. This procedure allows surpassing the limitation on the amount of sample that is usually found in research areas such as natural product chemistry.

I. Louzao, J. M. Seco, E. Quiñoá, R. Riguera* 6520–6524

The Use of a Single Derivative in the Configurational Assignment of Ketone Cyanohydrins

Keywords: Chirality / Configuration determination / Cyanohydrins / Methoxyphenylacetic acid / NMR spectroscopy

Asymmetric Catalysis



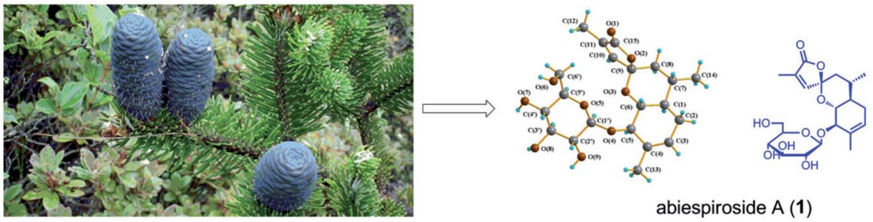
A cinchonine-derived phase-transfer catalyst was employed in the direct α-hydroxylation of β-oxo esters. Catalyst screening showed that substituents in the benzyl moiety and a free secondary alcohol at the C-9 position are important. Equally, the presence of a 1-Ad group in the substrate was found to increase the reaction yield (up to 91 %) and affect the enantioselectivity of the reaction (up to 74 % *ee*).

M. Lian, Z. Li, J. Du, Q. Meng,* Z. Gao 6525–6530

Asymmetric Direct α-Hydroxylation of β-Oxo Esters by Phase-Transfer Catalysis Using Chiral Quaternary Ammonium Salts

Keywords: Asymmetric catalysis / Phase-transfer catalysis / Hydroxylation / β-Oxo esters

Sesquiterpenoid with 6/6/5 Ring System



abiespiroside A (**1**)

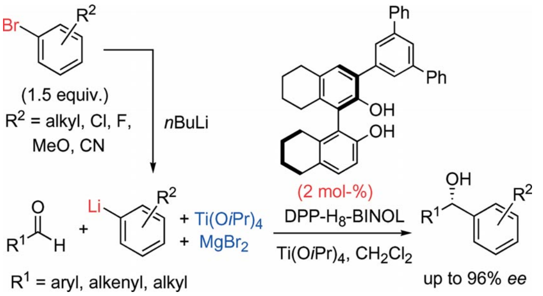
Abiespiroside A (**1**), a unique sesquiterpenoid spirolactone with a novel 6/6/5 ring system, was isolated from the plant *Abies delavayi*. Its absolute stereochemistry was established as (1*R*,5*R*,6*R*,7*S*,9*R*)-6,9α-epoxy-9,15-bisabolanolide-5-*O*-β-D-glucopyranoside. It inhibits the production of nitric oxide in RAW264.7 macrophages induced by lipopolysaccharides.

X. W. Yang, S. M. Li, Y. L. Li, J. H. Xia, L. Wu, Y. H. Shen, J. M. Tian, N. Wang, Y. Liu, W. D. Zhang* 6531–6534

Abiespiroside A, an Unprecedented Sesquiterpenoid Spirolactone with a 6/6/5 Ring System from *Abies delavayi*

Keywords: Natural products / Terpenoids / Spiro compounds / Lactones / *Abies delavayi* / Nitric oxide

Enantioselective Arylation



The catalytic enantioselective arylation of aldehydes is realized by starting from readily available aryl bromides. Mixed titanium reagents, derived from aryllithium intermediates, titanium tetraisopropoxide, and magnesium bromide, underwent highly enantioselective addition to aldehydes in the presence of 2 mol-% of DPP-H$_8$-BINOL.

Y. Nakagawa, Y. Muramatsu, T. Harada* 6535–6538

Catalytic Enantioselective Synthesis of Diarylmethanols from Aryl Bromides and Aldehydes by Using Organolithium Reagents

Keywords: Alcohols / Aldehydes / Asymmetric catalysis / Lithium / Titanium

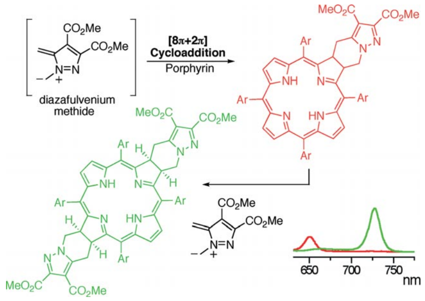
CONTENTS

Chlorins and Bacteriochlorins

N. A. M. Pereira, A. C. Serra, T. M. V. D. Pinho e Melo* **6539–6543**

Novel Approach to Chlorins and Bacteriochlorins: [8π+2π] Cycloaddition of Diazafulvenium Methides with Porphyrins

Keywords: Cycloaddition / 1,7-Dipoles / Porphyrin / Chlorin / Bacteriochlorin



Cycloaddition of diazafulvenium methides with porphyrin and chlorins is reported for the first time.

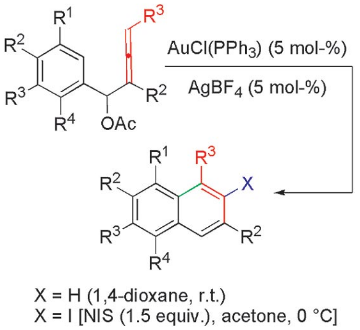
FULL PAPERS

Naphthylenes

W. Kong, C. Fu, S. Ma* **6545–6555**

An Efficient Synthesis of Polysubstituted Naphthalene Derivatives by Gold-Catalyzed Cyclization of 1-Arylalka-2,3-dienyl Acetates

Keywords: Allenes / Naphthalene / Gold / Cyclization / Reaction mechanisms



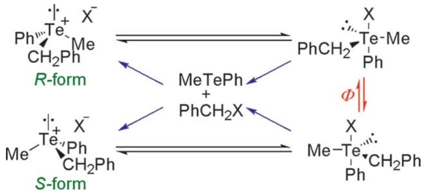
Differently polysubstituted naphthalenes and iodonaphthalenes have been efficiently prepared through a gold-catalyzed cyclization reaction of 1-arylalka-2,3-dienyl acetates. A possible mechanism involving the formation of alkenyl and naphthyl Au species was proposed for this reaction

Racemization Mechanism

T. Shimizu,* R. Sakurai, Y. Azami, K. Hirabayashi, N. Kamigata **6556–6562**

Isolation and Racemization Mechanism of Optically Active Benzylmethylphenyltelluronium Salts

Keywords: Chirality / Configuration determination / Circular dichroism / Racemization mechanism / Tellurium



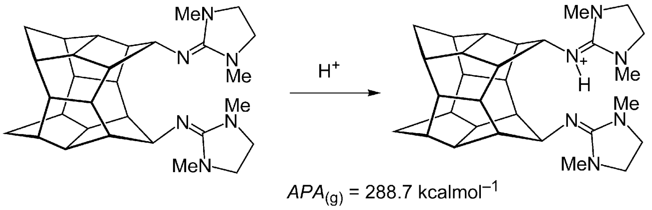
Enantiomeric benzylmethylphenyltelluronium salts were isolated with several counteranions. The racemization was found to proceed either through the formation of a tellurane followed by decomposition into achiral methyl phenyl telluride and benzyl halide or by several pseudorotations (*Φ*) of the tellurane intermediate.

Basicity

D. Margetić,* T. Ishikawa, T. Kumamoto **6563–6572**

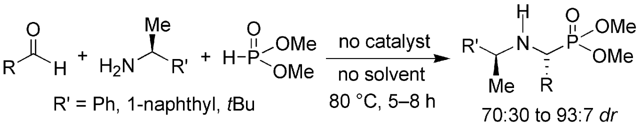
Exceptional Superbasicity of Bis(guanidine) Proton Sponges Imposed by the Bis(secododecahedrane) Molecular Scaffold: A Computational Study

Keywords: Guanidines / Basicity / Heterocycles / Dodecahedranes / Density functional calculations



Density functional calculations (B3LYP/6-311+G**//B3LYP/6-31G*) have shown that the 3-*syn*,13-*syn*-disubstituted bis(secododecahedrane) skeleton is a suitable polycyclic scaffold for anchoring organic functionalities such as guanidines, which give exceptionally basic proton sponges (see scheme). Their absolute proton affinity and basicity in the gas phase and in acetonitrile exceed most of the known superbases.

α-Amino Phosphonates



Three-component reactions (aldehyde, chiral amine, and dimethyl phosphite) under uncatalyzed solvent-free conditions afforded mixtures of the corresponding α-amino phosphonates in good yields and with excellent diastereoselectivities.

G. D. Tibhe, S. Lagunas-Rivera, E. Vargas-Díaz, O. García-Barradas, M. Ordoñez* 6573–6581

Uncatalyzed One-Pot Diastereoselective Synthesis of α-Amino Phosphonates Under Solvent-Free Conditions

Keywords: Diastereoselectivity / α-Amino phosphonates / Kabachnik–Fields reaction / α-Amino phosphonic acids / Phosphorus / Multicomponent reactions

Domino Synthesis

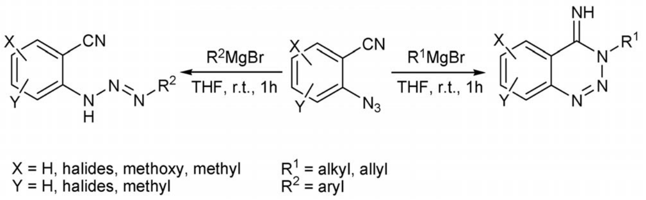
Functionalized alkyl nicotinates can be obtained from propargyl vinyl ether scaffolds through a microwave-assisted domino manifold comprising a complex network of reactions with at least five distinct chemical steps. The obtained alkyl nicotinates incorporate two diversity points at the ring and one ester functionality as convenient handles for further elaboration.

D. Tejedor,* G. Méndez-Abt, F. García-Tellado* 6582–6587

Microwave-Assisted Diversity-Oriented Domino Synthesis of Functionalized Nicotinic Acid Derivatives

Keywords: Domino reactions / Electrocyclic reactions / Microwave chemistry / Nitrogen heterocycles / Nicotinic acid

Grignard Reactions of Azides



The reactions of 2-azidobenzonitrile derivatives with Grignard reagents have been investigated. These reactions, depending on the type of Grignard reagent and the substituents on the 2-azidobenzonitrile derivatives, resulted in benzotriazines and triazenes.

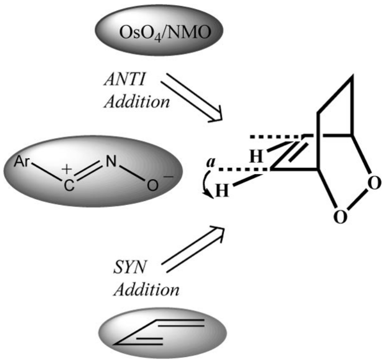
A. Nakhai, B. Stensland, P. H. Svensson, J. Bergman* 6588–6599

Synthesis of Benzotriazine and Aryltriazene Derivatives Starting from 2-Azidobenzonitrile Derivatives

Keywords: Nitrogen heterocycles / Grignard reaction / Substituent effects / Azides / Nitriles

Facial Selectivity

Facial selectivity in cycloaddition reactions to 2,3-dioxabicyclo[2.2.2]oct-5-ene is variable. Osmilation takes place on the face *anti* to the dihetero bridge. Cycloaddition of butadiene affords exclusively the *syn* cycloadduct, while cycloadditions of nitrile oxides are unselective. DFT calculations give insights into the origin of the variable facial selectivity.



P. Quadrelli,* S. Romano, P. Caramella* 6600–6608

Nonbonded Interactions Tune Selectivities in Cycloadditions to 2,3-Dioxabicyclo[2.2.2]oct-5-ene

Keywords: Facial selectivity / Density functional calculations / Cycloaddition / Osmilation / Regioselectivity

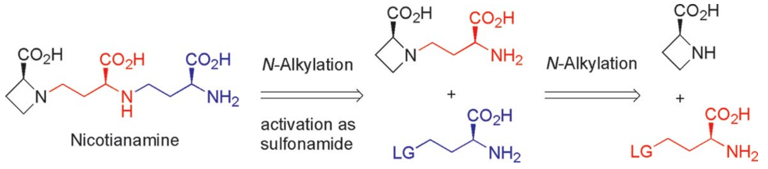
CONTENTS

Natural Product Synthesis

M. Bouazaoui, M. Larrouy, J. Martinez, F. Cavelier* 6609–6617

Efficient Synthesis of Nicotianamine and Non-Natural Analogues

Keywords: Alkylation / Sulfonamides / Natural products / Nucleophilic substitution



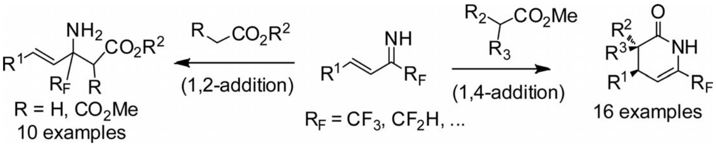
An efficient synthesis of nicotianamine, a natural product found in plants, has been achieved by using a new strategy based on *N*-alkylation. This strategy was applied to the synthesis of new synthetic analogues.

Fluorine Compounds

F. Palacios,* A. M. Ochoa de Retana, S. Pascual, G. F. de Trocóniz, J. M. Ezpeleta* 6618–6626

Fluoroalkylated α,β-Unsaturated Imines: Efficient and Versatile Substrates for the Synthesis of Fluorinated Vinylogous β-Amino Esters and 3,4-Dihydropyridin-2-ones

Keywords: Amino acids / Fluorine / Nitrogen heterocycles / Lactams / Spiro compounds



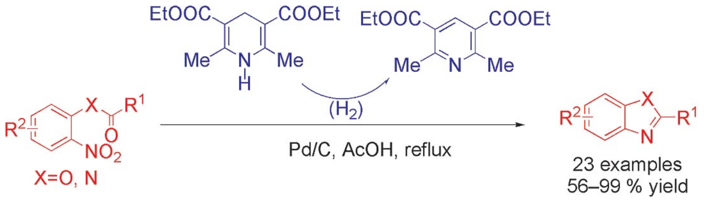
The synthesis of vinylogous fluoroalkylated β-amino esters by the 1,2-addition of enolates of alkyl acetates or diethyl malonate to fluoroalkylated α,β-unsaturated imines is described. These imines were used in the regioselective synthesis of fluorine-containing *trans*-3,4-dihydro- and 3,3-spiro-3,4-dihydropyridin-2-ones by conjugate (1,4-) addition of enolates derived from substituted esters.

Reductive Cyclizations

R.-G. Xing, Y.-N. Li, Q. Liu,* Q.-Y. Meng, J. Li, X.-X. Shen, Z. Liu, B. Zhou, X. Yao, Z.-L. Liu 6627–6632

Facile and Efficient Synthesis of Benzoxazoles and Benzimidazoles: The Application of Hantzsch Ester 1,4-Dihydropyridines in Reductive Cyclization Reactions

Keywords: Fused-ring systems / Heterocycles / Biomimetic synthesis / Reduction / Cyclization



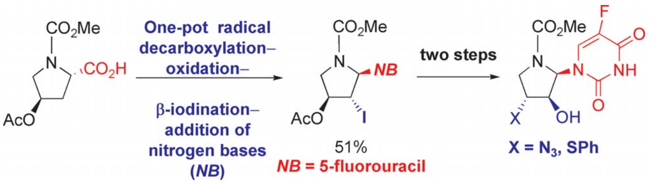
An efficient reductive cyclization of *ortho*-substituted nitrobenzenes was achieved by employing Hantzsch ester 1,4-dihydropyridines as a biomimetic reducing agent in the presence of catalytic Pd/C. This approach was applied with spectacular success to synthesize various benzoxazoles and benzimidazoles.

Nucleoside Analogues

A. Boto,* D. Hernández, R. Hernández* 6633–6642

One-Pot Conversion of Proline Derivatives into Iodinated Iminosugar-Based Nucleosides, Useful Precursors of Highly Functionalized Nucleoside Analogues

Keywords: Radical reactions / Amino acids / Nucleosides / Nitrogen heterocycles / Sequential processes

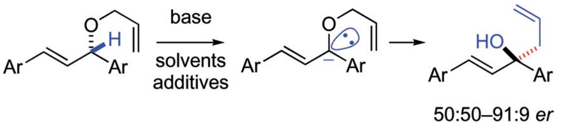


Readily available proline derivatives can be directly converted into β-iodinated iminosugar-based nucleosides by using a sequential radical decarboxylation–oxidation–β-iodination–addition of nitrogen base process. The iodo group is introduced into a previously unfunctionalized position. These iodo derivatives are useful precursors of highly functionalized nucleoside analogues.

Chiral Carbanions

H. Ikemoto, M. Sasaki, K. Takeda* 6643–6650

Solvent Effects on the Steric Course of the [2,3]-Wittig Rearrangement of (*S*,*E*)-[3-(Allyloxy)prop-1-ene-1,3-diyl]dibenzene and Derivatives



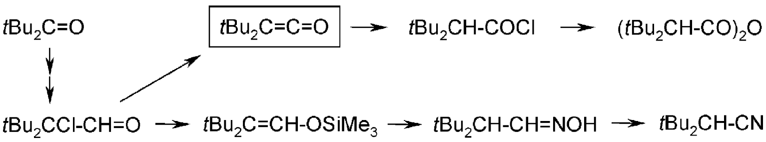
The effect of solvents and additives on the configurational stability of chiral carbanions was examined by assessing the extent of chirality transfer by intramolecular trapping in the [2,3]-Wittig rearrangement of the chiral 1,3-diphenyl-1-propenyloxy-2-propen-1-yl carbanion and its derivatives.

Keywords: Carbanions / Chirality / Configuration determination / Rearrangement / Wittig reactions

gem-Di-*tert*-butyl Compounds

R. Knorr,* K.-O. Hennig, B. Schubert, P. Böhrer 6651–6664

Shorter and Easier Syntheses of Di-*tert*-butylketene and Related *gem*-Di-*tert*-butyl Compounds



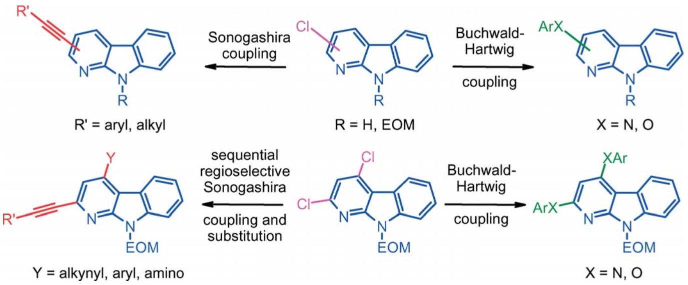
A simplified procedure converts $t\mathrm{Bu_2C{=}O}$ into the key compound $t\mathrm{Bu_2CCl{-}CH{=}O}$, the unusual 1,2-elimination of HCl from which affords $t\mathrm{Bu_2C{=}C{=}O}$ and leads to derivatives of that compound. Electron transfer from lithium metal or *t*BuMgCl to $t\mathrm{Bu_2CCl{-}CH{=}O}$ provides $t\mathrm{Bu_2C{=}CH{-}OSiMe_3}$ and its descendants.

Keywords: Aldehydes, α-chloro / Electron transfer / Oxiranes, chloro / Ketenes / Strained molecules / Steric hindrance

Heterocyclic Chemistry

C. Schneider, D. Goyard, D. Gueyrard, B. Joseph, P. G. Goekjian* 6665–6677

Synthesis of 2-, 3-, and 4-Substituted Pyrido[2,3-*b*]indoles by C–N, C–O, and C–C(sp) Bond Formation



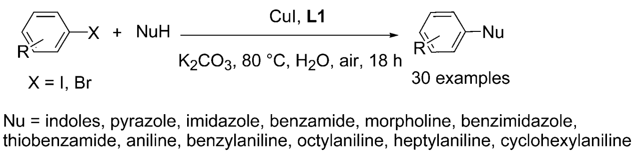
The synthesis of 2-, 3-, and 4-substituted α-carbolines is described starting from the corresponding chloropyrido[2,3-*b*]indoles by Buchwald–Hartwig and Sonogashira cross-coupling reactions. Regioselective Sonogashira reactions on 2,4-dichloropyrido[2,3-*b*]indoles are also presented as an efficient route to unsymmetrically 2,4-disubstituted α-carbolines.

Keywords: Natural products / Nitrogen heterocycles / Palladium / Polycycles / Cross-coupling

Green *N*-Arylation

K. Swapna, S. N. Murthy, Y. V. D. Nageswar* 6678–6684

Copper Iodide as a Recyclable Catalyst for Buchwald *N*-Arylation



Different arylated amines are prepared by *N*-arylation of indoles with aryl halides in water. This is an efficient green protocol that avoids hazardous and moisture-sensitive catalysts. The catalytic system can be recycled up to four times without loss of catalytic activity.

Keywords: Amines / Aryl halides / Copper / Green chemistry / Nitrogen heterocycles / Recyclability

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* Author to whom correspondence should be addressed.

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