

Table of Contents

(For the contents of Volumes 1-19 please visit: https://www.soc.chim.it/it/libri_collane/thc)

Synthesis and reactivity of pyridin-4-ols based on the three-component reaction of alkoxyallenes, nitriles and carboxylic acids	1
<i>Tilman Lechel and Hans-Ulrich Reissig</i>	
1. Introduction	
2. Discovery of a new three-component reaction to pyridine derivatives	
3. Synthesis of fluoroalkyl- and fluoroaryl-substituted pyridin-4-ols or their nonaflates	
4. Scope of the pyridin-4-ol synthesis employing other carboxylic acids	
5. Chiral carboxylic acids and nitriles in the pyridin-4-ol synthesis	
6. Palladium-catalyzed reactions of pyridin-4-yl nonaflates	
7. Sonogashira reactions of pyridin-4-yl nonaflates and synthesis of furopyridines	
8. Synthesis of oligo(thiophen-2-yl)-substituted pyridine derivatives	
9. Miscellaneous reactions of pyridin-4-ol-derived compounds	
10. Conclusions	
List of abbreviations	
Acknowledgements	
References	
 Heterocycles and natural products synthesis through oxidative dearomatization	 33
<i>Gaëtan Maertens and Sylvain Canesi</i>	
1. Introduction	
2. Oxidative cycloadditions with substituted phenols and sulfonamides	
2.1. Formal oxidative cycloadditions between substituted phenols and furan	
2.2. Reactions between substituted phenols and electron-rich alkenes	
2.3. Reactions between substituted phenols and allylsilanes	
2.4. Reactions between substituted phenols and unactivated benzene derivatives	
2.5. Formal oxidative cycloadditions with <i>N</i> -aryl sulfonamides	
3. Heterocyclic natural product synthesis from functionalized dienones	
3.1. Synthesis of <i>Amaryllidaceae</i> alkaloids: mesembrine and dihydro- <i>O</i> -methylsceletenone	
3.2. 3.2. Synthesis of <i>Amaryllidaceae</i> alkaloids: sceletenone and <i>O</i> -methylsceletenone	
3.3. Synthesis of Lycorine alkaloids: (–)-fortucine	
3.4. Synthesis of <i>Aspidosperma</i> alkaloids: aspidospermidine	
3.5. Synthesis of <i>Aspidosperma</i> alkaloids: acetylaspidalbidine	
3.6. Synthesis of <i>Erythrina</i> alkaloid: erysotramidine	
3.7. Synthesis of <i>Strychnos</i> alkaloids: isostrychnine	
3.8. Synthesis of <i>Strychnos</i> alkaloids: (–)-strychnopivotine	
4. Conclusions	
Acknowledgments	
References	
 Progresses for accessing α'-methoxy-γ-pyrone heterocycle: applications to the synthesis of verticipyrene and aureothin	 63
<i>Michaël De Paolis</i>	
1. Introduction	
2. The α' -methoxy- γ -pyrone scaffold in detail	
3. Desymmetrization of α,α' -dimethoxy- γ -pyrone	
4. Synthetic approaches toward verticipyrene (2)	
5. Synthetic approaches toward aureothin (9)	
6. Conclusions	
Acknowledgements	

References

- Multicomponent strategies for the diversity-oriented synthesis of blue emissive heterocyclic chromophores** 85
Renata Riva, Lisa Moni and Thomas J. J. Müller
1. Introduction
 2. Multicomponent Sonogashira alkynylation–cyclization syntheses of blue emitters
 - 2.1. Michael-type cyclocondensations of *N*-nucleophiles with the alkynone
 - 2.2. Michael-type cyclocondensations of *S*-nucleophiles with the alkynone
 - 2.3. Miscellaneous alkynylation–cyclization syntheses
 3. Ugi substrates for accessing blue emitters
 4. Conclusions
- Acknowledgements
References
- Advances in *N*- and *O*-demethylation of opiates** 113
Aleš Machara and Tomáš Hudlický
1. Introduction
 2. *N*-Demethylations
 - 2.1. *N*-Demethylations with hard electrophiles
 - 2.2. *N*-Demethylations with dialkyl azodicarboxylates
 - 2.3. *N*-Demethylations through *N*-oxides
 - 2.4. Oxidative *N*-demethylations mediated by palladium
 3. *O*-Demethylation
 - 3.1. *O*-Demethylations with Brønsted acids
 - 3.2. *O*-Demethylations with Lewis acids
 - 3.3. *O*-Demethylations with combination of acids and nucleophiles
 - 3.4. *O*-Demethylations with strongly nucleophilic reagents
 4. Biological methods
 5. Conclusions and outlook
- Acknowledgments
References
- Green synthesis of 1,3,5-triazines with applications in supramolecular and material chemistry** 139
Antonio de la Hoz and Ana M. Sánchez-Migallón
1. Introduction
 2. Synthesis of 1,3,5-triazines
 - 2.1. Preparation of symmetrically substituted 1,3,5-triazines
 - 2.2. Preparation of amino-1,3,5-triazines
 - 2.2.1. Preparation of 2,4-diamino-1,3,5-triazines
 - 2.2.2. Preparation of mono-, di- or triamino-substituted-1,3,5-triazines
 3. NMR structure determination and dynamic behaviour of 1,3,5-triazines
 4. 1,3,5-Triazinyl mono- and bisureas
 5. Optoelectronic and electrochemical properties
 - 5.1. Bistriazines with 4-aminobenzylamine as a spacer
 - 5.2. Bistriazines with phenylenediamine as a spacer
 - 5.3. Bistriazines with 1,5-diaminonaphthalene as a spacer
 - 5.4. Imine-derived triazine amines
 - 5.5. Bistriazines with streptocyanine as a spacer
 - 5.6. Star-shaped triazines with 2,5-dimethoxyaniline as a donor
 6. Complexes of 1,3,5-triazines with Pd(II) and Ag(I)
 7. 2,4-Diamino-1,3,5-triazines in molecular recognition

8. Conclusions

References

A journey through the oxadiazole-based compounds: from synthesis to applications 174

Codruța C. Paraschivescu, Anca Păun and Mihaela Matache

1. Introduction

2. Synthesis of the 1,3,4-oxadiazole compounds

3. Applications of the 1,3,4-oxadiazole derivatives

3.1. Medicinal chemistry

3.2. Materials chemistry

3.2.1. Organic-Light Emitting Diodes

3.2.2. Liquid crystals

3.2.3. Sensors for cations and anions, metal-ion complexes and coordination polymers

3.2.4. Others

4. Conclusions

Acknowledgments

References

Microwave and mechanochemistry: tools for the sustainable synthesis of pyrroles, porphyrins and related macrocycles 197

Marta Pineiro

1. Introduction

2. Pyrroles

2.1. Introduction

2.2. Microwave-assisted synthesis

2.3. Mechanochemical synthesis

3. Porphyrins

3.1. Introduction

3.2. Microwave-assisted synthesis

3.2.1. Solventless reaction conditions

3.2.2. Synthesis in solution

3.3. Mechanochemical synthesis

4. Related compounds

5. Conclusions

References

Enyne metathesis reactions in the synthesis of small ring heterocycles 222

Daniele Castagnolo

1. Introduction

2. Synthesis of nitrogen heterocycles

2.1. Synthesis of pyrrolines

2.1.1. Ring-closing enyne metathesis (RCEYM)

2.1.2. Enyne cross-metathesis (EYCM)

2.2. Synthesis of indolines and pyrroles

2.3. Synthesis tetrahydropyridines and tetraisoquinolines

2.4. Synthesis of other nitrogen heterocycles

3. Synthesis of oxygen-heterocycles

3.1. RCEYM approaches to oxygen-heterocycles

3.2. EYCM approaches to oxygen-heterocycles

4. Conclusions

References

Recent developments in the synthesis of aromatic heterocycles by S_{RN}1 and related mechanisms

247

Javier I. Bardagí, María E. Budén and Roberto A. Rossi

1. Introduction
 2. Mechanism of S_{RN}1 reactions
 - 2.1. Initiation step
 - 2.2. Propagation steps
 - 2.3. Termination steps
 3. Intermolecular S_{RN}1 reactions followed by spontaneous polar ring closure reaction
 - 3.1. Synthesis of five member heterocycles
 - 3.2. Synthesis of six member heterocycles
 4. S_{RN}1 reaction followed by functional group transformation-ring closure reactions
 5. Intramolecular S_{RN}1 and related reactions
 - 5.1. Ring closure with formation of a C-C bond with carbanions
 - 5.2. Ring closure with formation of a C-C bond with aromatic nitranions
 - 5.3. Ring closure with formation of a C-C bond with aromatic oxianions
 - 5.4. Ring closure with formation of a C-N bond
 - 5.5. Ring closure with formation of a C-O or C-S bonds
 6. *Endo* or *exo* ring closure reaction followed by a S_{RN}1 reaction
 7. Miscellaneous ring closure reactions
 - 7.1. Heterocyclic synthesis by S_{RN}1-BHAS reactions
 - 7.2. Heterocyclic synthesis by S_{RN}1 reaction followed by nitrous acid elimination-electrocyclic ring closure reaction
 - 7.3. Ring closure reactions by formation of a radical-anion/radical cation pair under irradiation
 - 7.4. Heterocyclic synthesis by oxidation of a carbanion followed by coupling reaction
- Acknowledges
References

Galanthamine

283

Uwe Rinner, Christian Dank and Tomas Hudlicky

1. Introduction
 2. Biological properties
 3. Biosynthesis
 4. Syntheses
 - 4.1. Landmark achievements reported prior to 2006
 - 4.2. Recent syntheses of galanthamine
 5. Conclusion
- References
Acknowledgements

Regiospecific preparation of substituted furans from some 5-substituted derivatives of 1,1-diethoxyalk-3-yn-2-ones

316

Leiv K. Sydnes

1. Introduction
2. Syntheses of furans; a condensed overview
3. Interlude
4. Synthesis of 5-substituted 1,1-diethoxyalk-3-yn-2-ones
5. Furans from 1,1-diethoxy-5-hydroxyalk-3-yn-2-ones
 - 5.1. With secondary amines
 - 5.2. With the ethyl acetoacetate monoenolate
 - 5.3. With the diethyl malonate enolate
6. Furans from 1,1-diethoxy-5-trialkylsilyloxyalk-3-yn-2-one with dialkylcuprates

7. Furans from 1,1-diethoxy-5-hydroxyalk-3-yn-2-one esters with dialkylcuprates
 8. Furans from 5,5-disubstituted 1,1-diethoxy-5-hydroxypent-3-yn-2-ones generated *in situ*
 9. Concluding remarks
- Acknowledgements
References

Regiocontrolled 1,3-dipolar cycloadditions of nitrile imines with acetylenes and α,β -unsaturated systems: synthesis of polysubstituted and ring fused pyrazoles with pharmaceutical activity

337

Giulio Bertuzzi, Mariafrancesca Fochi and Mauro Comes Franchini

1. Introduction
 2. 1,3-Dipolar cycloaddition of nitrile imines with acetylenes
 - 2.1. 1,3-Dipolar cycloaddition of nitrile imines with activated acetylenes: regiocontrolled synthesis of 4- and 5-substituted pyrazoles
 - 2.2. 1,3-Dipolar cycloaddition with sulphur-based acetylenes: regiocontrolled synthesis of thieno[2,3-*c*]pyrazoles
 - 2.3. 1,3-Dipolar cycloaddition with ynamide *tert*-butyl *N*-ethynyl-*N*-phenylcarbamate: experimental and theoretical investigation
 3. 1,3-Dipolar cycloaddition of nitrile imines with cyclic dipolarophiles
 - 3.1. 1,3-Dipolar cycloaddition of nitrile imines with α,β -unsaturated ketones: regiocontrolled synthesis of ring-fused pyrazoles
 - 3.2. 1,3-Dipolar cycloaddition of nitrile imines with α,β -unsaturated lactones, thiolactones and lactams: regiocontrolled synthesis of ring-fused pyrazoles
 4. Pyrazole derivatives through 1,3-dipolar cycloadditions for applications in medicinal chemistry
 - 4.1. Polysubstituted pyrazoles
 - 4.2. Ring fused pyrazoles
 5. Conclusions
- References

Recent synthetic developments and reactivity of aromatic indolizines

365

Camila R. de Souza, Augusto C. Gonçalves, Monica F. Z. J. Amaral, Alcindo A. Dos Santos and Giuliano C. Clososki

1. Introduction
2. Preparation of aromatic indolizines
 - 2.1. From 2-alkylazarenes
 - 2.2. From heterocyclic *N*-ylides
 - 2.3. From propargylic pyridines
 - 2.4. From alkynyl pyridines
 - 2.5. From 2-pyridylesters
 - 2.6. From pyrroles
3. Reactivity of aromatic indolizines
 - 3.1. Protonation of aromatic indolizines
 - 3.2. Nitration of aromatic indolizines
 - 3.3. Nitrosation and diazo coupling of aromatic indolizines
 - 3.4. Alkylation of aromatic indolizines
 - 3.5. Acylation of aromatic indolizines
 - 3.6. Halogenation of aromatic indolizines
 - 3.7. Oxidation of aromatic indolizines
 - 3.8. Metalation of aromatic indolizines
 - 3.9. Palladium-catalyzed coupling reactions of aromatic indolizines
 - 3.10. Aromatic nucleophilic substitution
 - 3.11. Reduction of aromatic indolizines

4. Conclusion
 Acknowledgements
 References

Carbopalladation cascades to access heterocyclic compounds: our endeavors

393

Daniel B. Werz

1. Introduction
 2. A carbohydrate-based chroman and isochroman synthesis
 3. Towards the synthesis of anthracycline aglycone
 4. Dispiro compounds as unexpected products of helicene formation
 5. Preparation of dibenzopentafulvalenes
 6. Formal *anti*-carbopalladation cascades
 6.1. Reaction design
 6.2. Mechanistic studies
 6.3. Different terminating processes
 7. Conclusion
 Acknowledgement
 References

Iminosugars and related heterocycles with quaternary carbon adjacent to nitrogen: synthesis and biological properties

409

Tomasz Rowicki

1. Introduction
 2. Construction of quaternary centre at an existing heterocycle
 2.1. Addition to imine-type precursor
 2.2. Addition to enamine-type precursor
 2.3. Alkylation of EWG substituted compounds
 3. Cyclization with simultaneous formation of quaternary centre
 3.1. Intramolecular aldol-type reaction
 3.2. Cycloaddition
 3.3. Intramolecular addition to imine
 4. Cyclization of precursors already possessing quaternary centre
 4.1. Cycloaddition
 4.2. Metathesis
 4.3. Reductive aminocyclization
 4.4. Intramolecular alkylation of amines
 5. Biological activity
 6. Conclusions
 Acknowledgment
 References

Synthesis of azachrysenes and multi-nitrogenated derivatives

448

Elina Marinho and Fernanda Proença

1. Introduction
 2. Synthesis of monoazachrysene derivatives
 2.1. 2-Azachrysene
 2.2. 5-Azachrysene
 2.3. 6-Azachrysene
 3. Synthesis of diazachrysene derivatives
 3.1. 1,7-Diazachrysene
 3.2. 5,6-Diazachrysene
 3.3. 5,7-Diazachrysene

- 3.4. 5,8-Diazachrysene
- 3.5. 5,10b-Diazachrysene
- 3.6. 5,11-Diazachrysene
- 3.7. 5,12-Diazachrysene
- 3.8. 6,12-Diazachrysene
- 3.9. 7,11- and 8,11-Diazachrysene
- 4. Synthesis of triazachrysene derivatives
 - 4.1. 1,5,10-, 2,5,9- and 3,5,8-Triazachrysene
 - 4.2. 4b,6,11-Triazachrysene
 - 4.3. 5,6,11-Triazachrysene
 - 4.4. 7,10a,11-Triazachrysene
 - 4.5. 7,13,13d-Triazachrysene
- 5. Synthesis of pentaazachrysene derivatives
 - 5.1. 1,3,5,8,10-Pentaazachrysene
- 6. Conclusions
- Acknowledgments
- References