

## Table of contents

<b><math>\alpha</math>-Enolic dithioesters: an attractive platform for the synthesis of functionalized heterocycles</b>	1
<i>Maya Shankar Singh</i>	
1. Introduction	
2. Synthesis of $\beta$ -keto/ $\alpha$ -enolic dithioesters	
3. Reactivity profile of $\beta$ -keto/ $\alpha$ -enolic dithioesters	
4. Functionalization of $\beta$ -keto/ $\alpha$ -enolic dithioesters	
5. Synthetic applications of $\beta$ -keto/ $\alpha$ -enolic dithioesters	
6. Summary and outlook	
7. Conclusion and outlook	
Acknowledgements	
References	
<b>Hypervalent iodine(III) reagents in the synthesis of heterocyclic compounds</b>	27
<i>Rajnish Budhwan, Gaurav Garg, Irishi N. N. Namboothiri, Sandip Murarka</i>	
1. Introduction	
2. <i>De novo</i> synthesis of heterocycles using hypervalent iodine(III) reagents	
2.1. Synthesis of three and four membered heterocycles	
2.1.1. Synthesis of azirines, aziridines, diaziridines and azetidines	
2.1.2. Synthesis of oxiranes and oxetanes	
2.2. Synthesis of five and six membered heterocycles	
2.2.1. Synthesis of pyrroles, pyrrolidines, imidazoles and pyrazoles	
2.2.2. Synthesis of oxazoles, isoxazoles, oxazolines and isooxazolines	
2.2.3. Synthesis of furans, oxadiazoles and thiadiazoles	
2.2.4. Synthesis of six membered heterocycles	
2.3. Synthesis of fused heterocycles	
2.3.1. Synthesis of substituted benzimidazoles	
2.3.2. Synthesis of substituted quinoxalines, quinolinones and isoquinolinones	
2.3.3. Synthesis of substituted carbazoles	
2.3.4. Synthesis of Indoles and Indolines	
2.4. Synthesis of lactones and lactams	
2.4.1. Racemic synthesis of substituted lactones	
2.4.2. Enantioselective synthesis of lactones	
2.4.3. Synthesis of lactams using hypervalent iodine reagents	
2.5. Synthesis of spiro-heterocycles	
3. Conclusions	
Acknowledgements	
References	
<b>Recent progress in the chemistry of polyazidoazines</b>	53
<i>Sergei V. Chapyshev</i>	
1. Introduction	
2. High-energy polyazidoazines	
3. Heterocyclic nanostructures from polyazidoazines	
4. Reactivity of polyazidoazines	
5. Organic molecular magnets from polyazidoazines	
6. Conclusion	
Acknowledgement	
References	

- Synthesis of sugars and steroids conjugates via 1,3-dipolar cycloaddition reactions of nitrile oxides** 70  
*Joaquín Plumet*  
 1. Introduction and objectives  
 2. Sugars conjugates  
   2.1. Intermolecular cycloadditions  
   2.2. Intramolecular cycloadditions  
 3. Steroids conjugates  
 4. Conclusions  
 Acknowledgement  
 References and notes
- Synthesis of heterocyclic compounds by photochemical cyclizations** 92  
*Ana G. Neo*  
 1. Introduction  
 2. Photochemical cyclizations in oxidative conditions  
   2.1. Application for the synthesis of molecules with biological properties  
   2.2. Application for the design of new materials  
 3. Photochemical cyclizations in the presence of a base  
   3.1. Application for the synthesis of molecules with biological properties  
   3.2. Application for the design of new materials  
 4. Cyclization/dehalogenation and related  
 5. Miscellaneous  
 6. Conclusion  
 Acknowledgement  
 References
- Thiazole cores as organic fluorophore units: synthesis and fluorescence** 116  
*Nataliya Belskaya, Irena Kostova, Zhijin Fan*  
 1. Introduction  
 2. Synthesis of fluorescent thiazoles  
   2.1. Main approaches to thiazole core construction  
     2.1.1. Erlenmeyer method for thiazole ring construction  
     2.1.2. Different methods for thiazole ring construction  
   2.2. Modification of the thiazole core  
     2.2.1. Aryl/heteroarylation of the thiazole ring  
     2.2.2. Alkylation of hydroxythiazoles  
     2.2.3. Introduction of substituents containing C=C, C=N, and N=N bonds  
   2.3. Complexation of thiazole derivatives  
 3. Photophysical properties  
   3.1. 4-Hydroxythiazoles as chromophores and fluorophores  
   3.2. Photophysical properties of 2- and 5-aminothiazoles  
   3.3. Thiazoles with flexible conjugated systems  
 4. Photoswitches based on 1,3-thiazole derivatives  
 5. Cation sensors  
 6. pH-sensitive thiazole fluorescence  
 7. Conclusions  
 Acknowledgements  
 References
- 2,1,3-Benzochalcogenadiazoles: regularities and peculiarities over a whole chalcogen pentad O, S, Se, Te and Po** 143  
*Elena A. Pritchina, Nina P. Gritsan, Oleg A. Rakitin, Andrey V. Zibarev*

1. Introduction
  2. Neutral molecules
  3. Radical anions
  4. Radical cations
  5. Conclusion
- Acknowledgements  
References

**Heteroaromatic motifs in resorcinarene-derived cavitand receptors: structural and functional** 155

*David Lozano, Agustí Lledó*

1. Introduction
  2. Synthesis of resorcin[4]arene derived cavitands
  3. Cavitands with 1,3-diazine walls
    - 3.1. Quinoxaline-type cavitands
    - 3.2. Stimuli-responsive cavitands
    - 3.3. Self-assembling pyrazine-based cavitands
  4. Cavitands with benzo-fused heterocyclic walls
    - 4.1. 1,3-Dihydro-2*H*-benzo[*d*]imidazol-2-one walls
    - 4.2. 1*H*-Benzo[*d*]imidazole walls
  5. Functionalized cavitands
    - 5.1. Functionalized cavitands with 1,3-diazine walls
    - 5.2. Dissymmetric cavitands with singular 1*H*-benzo[*d*]imidazole walls
    - 5.3. The introverted acid cavitand
    - 5.4. Metal-functionalized cavitands with heterocyclic coordination motifs
  6. Conclusions
- Acknowledgements  
References

**Synthesis and synthetic applications of *o*-benzenedisulfonimide and its derivatives** 178

*Margherita Barbero, Stefano Dughera*

1. Introduction
  2. *o*-Benzenedisulfonimide as Brønsted acid catalyst in acid-catalysed organic reactions
    - 2.1. Theoretical and experimental studies on *o*-benzenedisulfonimide pK<sub>a</sub>
    - 2.2. *o*-Benzenedisulfonimide as catalyst in multicomponent heterocycle syntheses
    - 2.3. *o*-Benzenedisulfonimide as catalyst in common acid-catalysed organic syntheses
  3. Synthesis and synthetic applications of *o*-benzenedisulfonimide derivatives
    - 3.1. Chiral derivatives of *o*-benzenedisulfonimide
    - 3.2. Silica-supported *o*-benzenedisulfonimide
    - 3.3. Miscellaneous studies
  4. Synthesis and synthetic applications *o*-benzenedisulfonimide salts
    - 4.1. Arenediazonium *o*-benzenedisulfonimides
      - 4.1.1. Sandmeyer cyanation
      - 4.1.2. Palladium catalysed cross-coupling reactions
      - 4.1.3. Gold catalysed cross-coupling reactions
      - 4.1.4. Azo-coupling reactions
    - 4.2. Aryl (or heteroaryl) indol-3-ylmethylum *o*-benzenedisulfonimides
    - 4.3. *o*-Benzenedisulfonimide-based ionic liquids
  5. Miscellaneous studies on *o*-benzenedisulfonimide derivatives
  6. Conclusion
- Acknowledgement  
References

- Synthetic strategies for the synthesis of indoloquinoline natural products** 201  
*Magne O. Sydnes*  
 1. Introduction  
 2. Quinindoline  
 3. Neocryptolepine  
 4. Quindoline  
 5. Cryptolepine  
 6. 11-Isopropylcryptolepine  
 7. Quindolinone  
 8. Cryptolepinone  
 9. Isocryptolepine  
 10. Conclusion  
 Acknowledgment  
 References
- Synthesis of biologically relevant heterocyclic compounds through the chemistry of selenium** 220  
*Luana Bagnoli*  
 1. General considerations of selenium chemistry applied to the synthesis of heterocycles  
 2. Synthesis of heterocyclic compounds through asymmetric cyclization induced by chiral substrates  
 2.1. Asymmetric synthesis of nitrogen heterocyclic compounds  
 2.2. Asymmetric cyclization reactions for the synthesis of pseudo- oligosaccharides  
 3. Domino processes for the synthesis of heterocycles using vinyl selenones  
 3.1. Asymmetric domino processes for the synthesis of enantiopure 1,4-dioxanes, morpholines, thiomorpholines and piperazines.  
 3.2. Domino processes for the synthesis of six and seven-membered benzo-1,4-heterocyclic compounds  
 3.3. Domino processes for the synthesis of heterocycle-fused indoles  
 4. Conclusion  
 Acknowledgement  
 References
- [3+2]-Annulation reactions with nitroalkenes in the synthesis of aromatic five-membered nitrogen heterocycles** 237  
*Vladimir A. Motornov, Sema L. Ioffe, Andrey A. Tabolin*  
 1. Introduction  
 2. Classification of nitroalkene-based annulation reactions  
 3. Annulations with nitroalkenes in the synthesis of five-membered rings  
 3.1. Synthesis of pyrroles  
 3.1.1. Barton-Zard pyrrole synthesis  
 3.1.2. Annulation with enamines  
 3.1.3. Annulation with azomethine ylides  
 3.2. Synthesis of pyrazoles  
 3.2.1. Nitroalkene-diazocompounds [3+2]-cycloadditions  
 3.2.2. Oxidative annulation of nitroalkenes with hydrazones  
 3.3. Synthesis of imidazoles and imidazo[1,2-a]pyridines  
 3.4. Synthesis of indolizines and related heterocycles  
 3.5. Synthesis of 1,2,3-triazoles  
 3.5.1. Synthesis of *NH*-1,2,3-triazoles  
 3.5.2. Synthesis of 1,5-disubstituted 1,2,3-triazoles  
 4. Conclusions  
 Acknowledgement  
 References

- 1,3-Dipolar cycloadditions to cyclopropenes: convenient way for the synthesis of heterocyclic systems** 261  
*Vitali M. Boitsov, Sergey Yu. Vyazmin, Alexander V. Stepanov*
1. Introduction
  2. Diazocompounds
  3. Azides
  4. Azomethine imines
  5. Nitrile imines
  6. Nitrile oxides
  7. Nitrones
  8. Carbonyl ylides
  9. Azomethine ylides
  10. Immonium ylides
  11. Asymmetric formal [3+3]-cycloaddition reactions
  12. Conclusions
- Acknowledgement  
References
- The double reductive amination approach to the synthesis of polyhydroxypiperidines** 283  
*Camilla Matassini, Francesca Clemente, Francesca Cardona*
1. Introduction
  2. Sugar-derived substrates
    - 2.1. Dialdehydes
    - 2.2. Ketoaldehydes
    - 2.3. Diketones
  3. Not sugar-derived substrates
  4. Conclusions
- Acknowledgements  
References
- Palladium catalyzed syntheses of fused tricyclic heterocycles: a personal account** 302  
*Alessandra Casnati, Elena Motti, Raffaella Mancuso, Bartolo Gabriele, Nicola Della Ca'*
1. Introduction
  2. Palladium/norbornene cooperative catalysis (Catellani Reactions)
    - 2.1. Synthesis of carbazoles and phenanthridines
    - 2.2. Synthesis of dibenzofurans and dibenzopyrans
    - 2.3. Synthesis of dibenzoazepines
      - 2.3.1. DFT studies
  3. Pd<sub>2</sub>/KI-catalyzed oxidative carbonylation processes
    - 3.1. Synthesis of dibenzooxazocinones
    - 3.2. Synthesis of furoindolones and furobenzofuranones
    - 3.3. Synthesis of benzimidazopyrimidinones, benzimidazoimidazoles and benzimidazothiazoles
  4. Conclusion
- Acknowledgement  
References
- Synthesis of octahydrobenzo-1,2,3-diazaphospholidine-2-oxides and their derivatives: applications in asymmetric synthesis** 324  
*Carlos Cruz-Hernández, José M. Landeros, Eusebio Juaristi*
1. Introduction
  2. Synthesis of the octahydrobenzo-1,3,2-diazaphospholidine-2-oxides
    - 2.1. Conformational and configurational assignments

3. Applications in asymmetric synthesis
- 3.1. Octahydrobenzo-1,3,2-diazaphospholidine-2-oxide as chiral auxiliary
    - 3.1.1. Phosphoryl group as a carbanion stabilizer in  $\alpha$ - and  $\gamma$ -functionalization
    - 3.1.2. Phosphoryl moiety as activating group for electrophilic addition in  $\beta$ -functionalization
  - 3.2. Chiral phosphoramides as Lewis bases
  - 3.3. Phosphoramides as chiral organocatalysts
    - 3.3.1. Asymmetric aldol reactions
    - 3.3.2. Asymmetric Michael addition reactions
    - 3.3.3. Asymmetric cascade processes
4. Conclusions  
 Acknowledgement  
 References
- Intramolecular Mizoroki-Heck reaction in the synthesis of heterocycles: strategies for the generation of tertiary and quaternary stereocenters** 340  
*Iratxe Barbolla, Esther Lete, Nuria Sotomayor*
1. Introduction
  2. Intramolecular Mizoroki-Heck reaction for the generation of stereocenters
    - 2.1. Approaches based on blocking the  $\beta$ -hydride elimination: cyclic alkenes as coupling partners
    - 2.2. Approaches based on blocking the  $\beta$ -hydride elimination: tri- and tetrasubstituted acyclic alkenes as coupling partners
    - 2.3. Approaches based on the use of a leaving group: allylsilanes, ethers, esters, and boronates as coupling partners
  3. Cascade reactions initiated by intramolecular carbopalladation
    - 3.1. Reductive Heck cyclizations
    - 3.2. Carbopalladation followed by nucleophilic trapping
    - 3.3. Heck/Heck processes
    - 3.4. Carbopalladation followed by other couplings
  4. Conclusion  
 Acknowledgements  
 References
- Cobalt catalyzed ( $sp^2$ ) C-H activation reactions with multi-unsaturated substrates for five- and six-membered nitrogen heterocycle synthesis** 363  
*Subban Kathiravan, Ian A. Nicholls*
1. Introduction
  2. C-H activation with carboxamides
  3. C-H activation with phosphinamides
  4. C-H activation with sulfonamides
  5. C-H activation for five membered heterocycles
  6. Conclusion  
 Acknowledgement  
 References
- Synthesis and use of halodifluoromethyl heterocycles** 384  
*Marco Colella, Pantaleo Musci, Renzo Luisi, Leonardo Degennaro*
1. Introduction
  2. Synthesis and use of halodifluoromethyl-substituted pyrazoles
    - 2.1. *N*-CXF<sub>2</sub> substituted pyrazoles
    - 2.2. *C*-CXF<sub>2</sub> substituted pyrazoles
  3. Synthesis and use of *N*-halodifluoromethyl-substituted imidazoles
  4. Synthesis and use of 5-(bromodifluoromethyl)-1,2,4-oxadiazoles

5. Synthesis and use of halodifluoromethyl-substituted pyridines
    - 5.1. C-CXF<sub>2</sub> substituted pyridines
    - 5.2. N-CXF<sub>2</sub> substituted pyridines
  6. Synthesis and use of halodifluoromethyl-substituted thiazoles
  7. Synthesis and use of 2-(bromodifluoromethyl)benzoxazoles
  8. Synthesis and use of N-bromo- and N-chlorodifluoromethyl benzimidazoles
  9. Synthesis and use of bromodifluoromethyl benzofurans
  10. Synthesis and use of bromodifluoromethyl substituted 1,3-imidazolines and 1,3-oxazolines
  11. Synthesis and use of bromodifluoromethyl substituted  $\beta$ -lactams
  12. Synthesis and use of bromodifluoromethyl substituted sugars
  13. Conclusions
- References