

## Abstracts

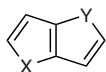
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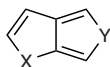
### 10.21 **Product Class 21: Five–Five-Fused Hetarenes with One Heteroatom in Each Ring**

*S. P. Stanforth*

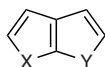
This is a new chapter for *Science of Synthesis* which describes methods for the synthesis of four classes of hetaryl[*n,m-p*]hetarenes from acyclic precursors. The functionalization of these heterocycles by either the introduction of new groups or the modification of existing substituents is also discussed.



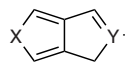
hetaryl[3,2-*b*]hetarene  
(1,4-diheteropentalene)



hetaryl[2,3-*c*]hetarene/  
hetaryl[3,4-*b*]hetarene  
(1,5-diheteropentalene)



hetaryl[2,3-*b*]hetarene  
(1,6-diheteropentalene)



hetaryl[3,4-*c*]hetarene  
(2,5-diheteropentalene)

**Keywords:** heterocycles · hetaryl[*n,m-p*]hetarenes · diheteropentalenes · non-classical heteropentalenes · thieno[*n,m-p*]thiophenes

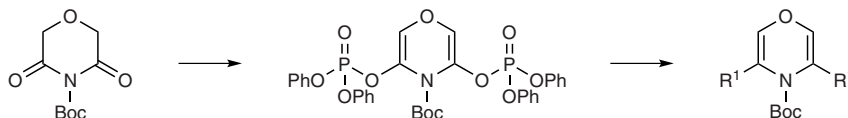
**2014**

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### 17.1.2.5 **One Oxygen and One Nitrogen or Phosphorus Atom**

*R. A. Aitken and A. Meehan*

This chapter is an update of the earlier *Science of Synthesis* contribution (Section 17.1.2) describing methods for the synthesis of 1,4-oxazines and 1,4-benzoxazines. It includes both new methods reported in the period 2004–2013 and older methods not covered in the earlier chapter.



**Keywords:** 1,4-benzoxazines · nitrogen heterocycles · 1,4-oxazines · oxygen heterocycles · ring-closure reactions · substituent modification

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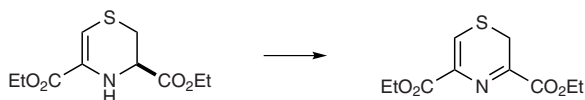
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17.1.3.9 **One Sulfur, Selenium, or Tellurium Atom and One Nitrogen or Phosphorus Atom**

R. A. Aitken and A. Meehan

This chapter is an update of the earlier *Science of Synthesis* contribution (Section 17.1.3) describing methods for the synthesis of 1,4-thiazines and 1,4-benzothiazines. In the absence of significant new methods reported in the period 2004–2013, it focuses on older methods not covered in the earlier chapter.



**Keywords:** 1,4-benzothiazines · nitrogen heterocycles · ring-closure reactions · substituent modification · sulfur heterocycles · 1,4-thiazines

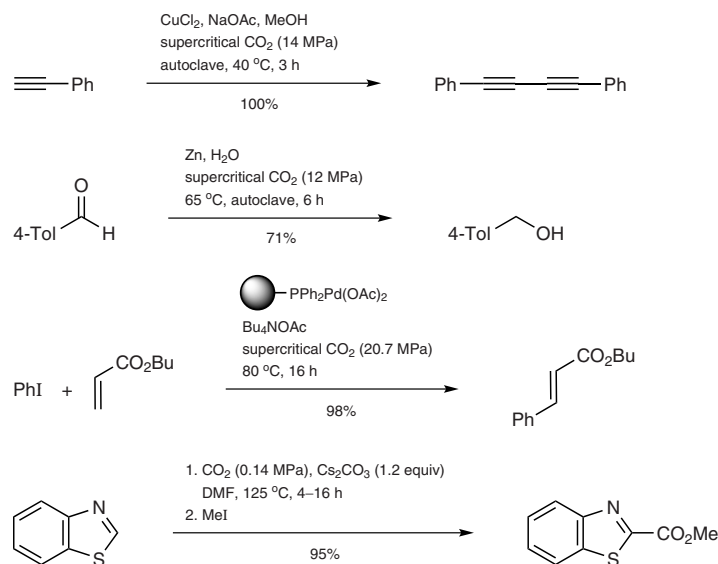
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18.2.16 **Carbon Dioxide, Carbonyl Sulfide, Carbon Disulfide, Isocyanates, Isothiocyanates, Carbodiimides, and Their Selenium, Tellurium, and Phosphorus Analogues**

S. Braverman and M. Cherkinsky

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 18.2) describing methods for the synthesis and synthetic application of heterocumulenes ( $X=C=Y$ ) with particular emphasis on supercritical carbon dioxide as a reaction medium for organic synthesis. It focuses on the literature published in the period 2002–2013.



**Keywords:** carbon dioxide · supercritical carbon dioxide · carbonyl sulfide · carbon disulfide · carbonyl selenide · isocyanates · isothiocyanates · isoselenocyanates · carbodiimides

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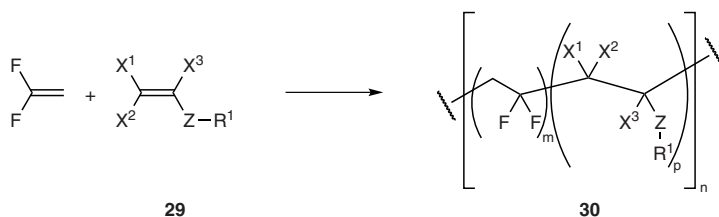
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24.2.1.3 **1,1-Dihaloalk-1-enes**

B. Ameduri

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods and strategies for the synthesis of 1,1-dihaloalk-1-enes. This update focuses on the preparation and polymerization of 1,1-difluoroalk-1-enes, including trifluorovinyl functional monomers. Radical additions of chain-transfer agents onto commercially available fluoroalkenes are described, followed by their chemical modification to yield original fluorinated monomers. These monomers are further involved in radical (conventional or controlled) copolymerizations with vinylidene fluoride (1,1-difluoroethene) or chlorotrifluoroethene to achieve high-value-added materials.



$X^1 = X^2 = X^3 = \text{H, F, CF}_3$ ;  $R^1 = \text{SO}_3\text{H, PO(OEt)}_2, \text{Br, CO}_2\text{H, Si(OEt)}_3, \text{NR}_2^+$ ,  $(\text{OCH}_2\text{CH}_2)_x\text{OMe}$ ;  
 $Z = (\text{CH}_2)_x, \text{O}(\text{CH}_2)_x, \text{O}(\text{CF}_2)_x$ , or none

**Keywords:** 1,1-dihaloalk-1-enes · chlorotrifluoroethene · fluoropolymers · fuel-cell membranes · NMR · radical copolymerization · trifluorovinyl functional monomers · vinylidene fluoride · 1,1-difluoroethene

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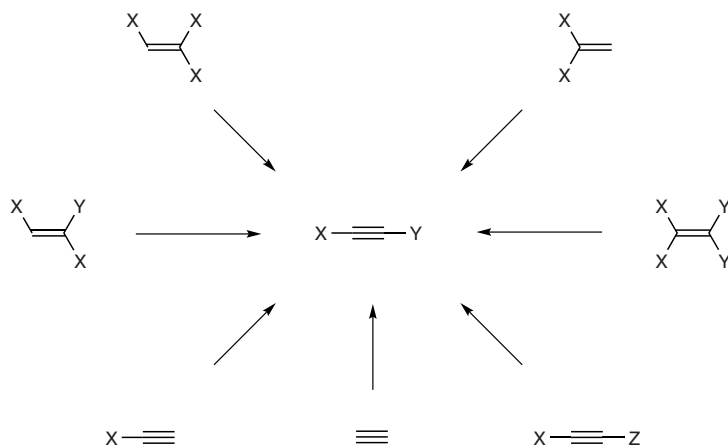
New Contributions

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24.3.12 **Bis(heteroatom-functionalized) Acetylenes***J. Udmark and M. Brøndsted Nielsen*

This chapter provides an update to the earlier *Science of Synthesis* contribution (Section 24.3) describing methods for the synthesis of bis(heteroatom-functionalized) acetylenes. Selected applications are also included. It focuses on the literature published since the original report in 2006 up until the end of 2013.



X = Y = Z = F, Cl, Br, I, NR<sup>1</sup><sub>2</sub>, N<sub>3</sub>, PR<sup>1</sup><sub>2</sub>, P(OR<sup>1</sup>)<sub>2</sub>, P(NR<sup>1</sup><sub>2</sub>)(OR<sup>2</sup>), OR<sup>1</sup>, SR<sup>1</sup>, S(O)R<sup>1</sup>, SO<sub>2</sub>R<sup>1</sup>, SiR<sup>1</sup><sub>3</sub>

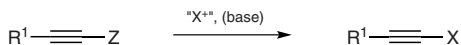
**Keywords:** alkynes · cross-coupling reactions · dehydrohalogenation · halogenation · nucleophilic substitution

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24.4.1.3 **1-Haloalk-1-ynes and Alk-1-yn-1-ols***A. U. Petersen and M. Brøndsted Nielsen*

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 24.4.1) describing methods for the synthesis of 1-haloalk-1-ynes. It focuses on the literature published since the original report in 2006 up until the end of 2013.



Z = H, TMS, TIPS, SnMe<sub>3</sub>, BF<sub>3</sub>K, CO<sub>2</sub>H; X = F, Cl, Br, I

**Keywords:** alkynes · cross-coupling reactions · dehydrohalogenation · halogenation · succinimides

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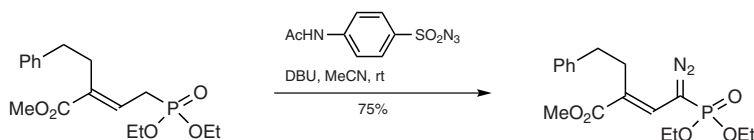
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27.21.3 **Diazo Compounds**

H. Heydt

This chapter is an update to *Science of Synthesis* Section 27.21 and deals with the synthesis of diazo compounds and their applications in organic synthesis. The current chapter covers the literature published between 2004 and 2013. The focus of the work presented here is on new methods for the synthesis of diazoalkanes, improvement of established methods (including new variations and examples), and on some important applications of these compounds, especially relating to stereoselective synthesis.



**Keywords:** diazo compounds · diazotization · diazo group transfer · hydrazones · cyclopropanation · Bamford–Stevens reaction · continuous-flow methods · diazotates · diazenolates · diazoalkane substitution

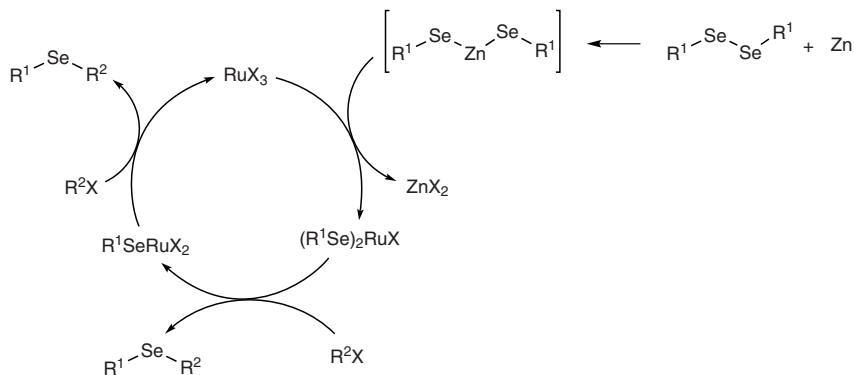
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39.19.2.3 **Alkaneselenolates of Group 3–12 Metals**

A. Polo and J. Real

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 39.19.2) describing methods for the synthesis of transition metal selenolates and their applications in organic synthesis. Synthetic methods developed in recent years concern both terminal and bridging alkaneselenolates. New applications for this class of compounds in organic synthesis have not been proposed. However, compounds of this class have been postulated as catalytic intermediates in some reactions, such as transition-metal-catalyzed Se–C bond formation via cross-coupling reactions.



**Keywords:** transition metals · bridged compounds · selenium compounds · selenides · selenols · oxidative addition · cross-coupling reactions

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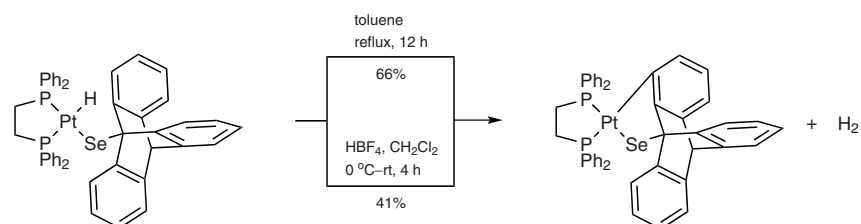
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39.26.6.2 **Cyclic Alkaneselenolates of Group 3–12 Metals**

A. Polo and J. Real

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 39.26.6) describing methods for the synthesis of cyclic alkaneselenolates of transition metals and their applications in organic synthesis. Synthetic methods developed in recent years concern diselenolates, aminoselenolates, and selenolates with a metal–carbon bond. New applications for this class of compounds in organic synthesis have not been proposed.



**Keywords:** transition metals · bridged compounds · cyclic compounds · selenium compounds · selenides · selenols · oxidative addition · cycloaddition

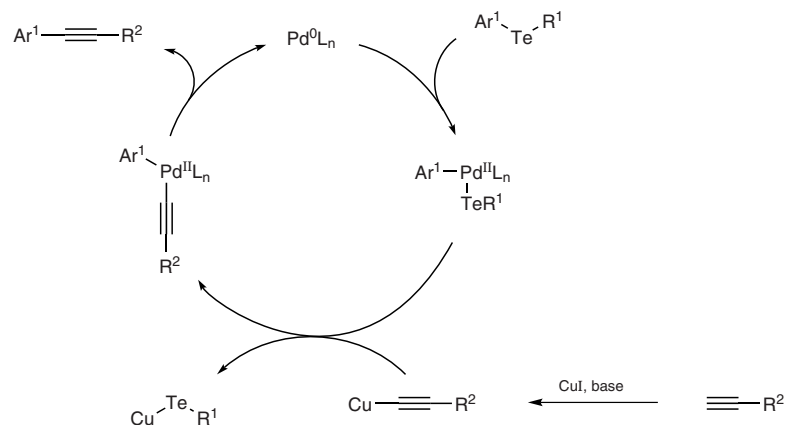
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39.32.2.2 **Alkanetellurolates of Group 3–12 Metals**

A. Polo and J. Real

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 39.32.2) describing methods for the synthesis of transition metal alkanetellurolates and their applications in organic synthesis. Synthetic methods developed in recent years concern both terminal and bridging alkanetellurolates. New applications for this class of compounds in organic synthesis have not been proposed. However, they have been postulated as catalytic intermediates in some transition-metal-mediated cross-coupling reactions.



**Keywords:** transition metals · bridged compounds · tellurium compounds · tellurides · oxidative addition · cross-coupling reactions

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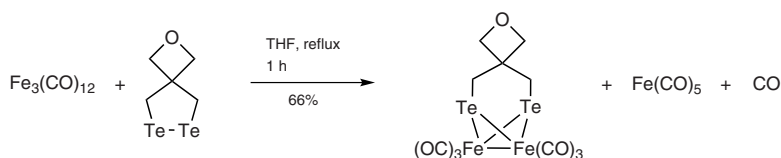
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39.39.6.2 **Cyclic Alkanetellurolates of Group 3–12 Metals**

A. Polo and J. Real

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 39.39.6) describing methods for the synthesis of cyclic alkanetellurolates of transition metals and their applications in organic synthesis. Synthetic methods developed in recent years focus principally on the synthesis of ditellurolates and aminotellurolates. New applications for this class of compounds in organic synthesis have not been proposed.



**Keywords:** transition metals · bridged compounds · cyclic compounds · tellurium compounds · tellurides · oxidative addition

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