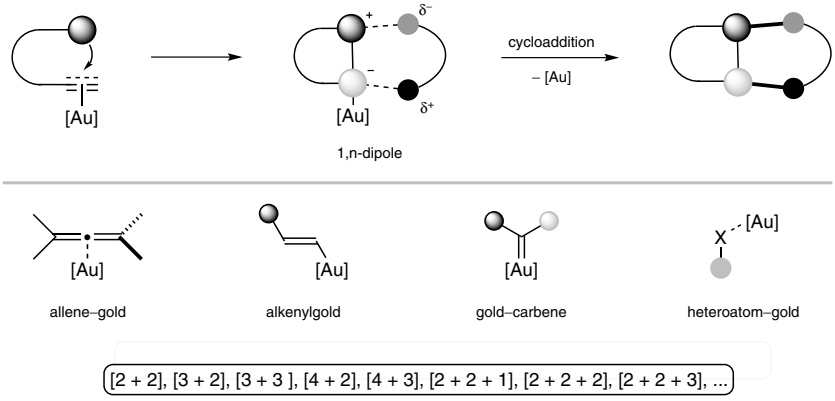
Abstracts

New p 1

3.6.16 Gold-Catalyzed Cycloaddition Reactions

D. Qian and J. Zhang

Since about 2000, a “gold rush” has resulted in the development of numerous gold-catalyzed cycloaddition reactions. Such cycloadditions have now become a powerful and privileged method for the construction of carbo- and heterocycles, in particular those complex polycyclic structures featured in diverse natural products. This chapter is organized according to the key reactive gold intermediate that formally participates in the cycloaddition.



Keywords: gold · cycloaddition · carbocycles · heterocycles · carbophilic activation · alkynes · 1,n-dipolar · allenes · alkenylgold · gold · carbenes · benzopyryliums · furylgold species · cycloisomerization · acyloxy migration · alkyne oxidation · nitrene transfer · carbene transfer · diazo decomposition · σ-Lewis acid · enantioselective

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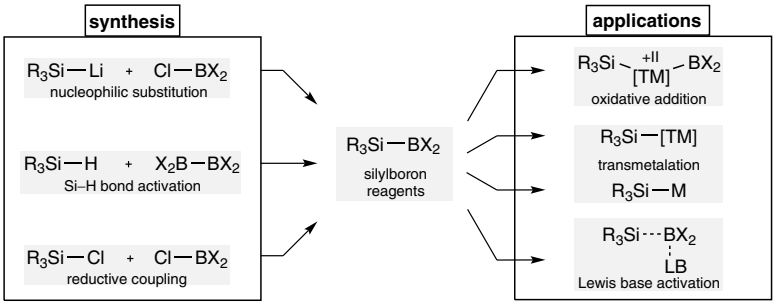
4.4.7 Silylboron Reagents

L. B. Delvos and M. Oestreich

This update describes the development of silylboron chemistry since the initial summary in *Science of Synthesis* by Hemeon and Singer in 2002. In the first part, an overview of the methods to prepare silylboron reagents by nucleophilic substitution, Si—H bond activation, or reductive coupling is provided, and possibilities for further functionalization are presented. The second section comprehensively covers all aspects of the synthetic applications of silylboron compounds, ranging from transition-metal catalysis to transmetalation reactions and Si—B bond activation with Lewis bases. The presented methodologies

include silaboration and silylation of unsaturated carbon–carbon bonds, addition and substitution reactions with nucleophilic silicon reagents, silaboration of strained rings under C—C bond cleavage, and Si—B insertion reactions of carbenoids and related compounds.



Keywords: silicon · boron · interelement compounds · main-group chemistry · silaboration · silylation · borylation · difunctionalization · transition-metal catalysis · asymmetric catalysis · oxidative addition · transmetalation · carbenoid insertion · 1,2-addition · 1,4-addition · allylic substitution · propargylic substitution · aromatic substitution

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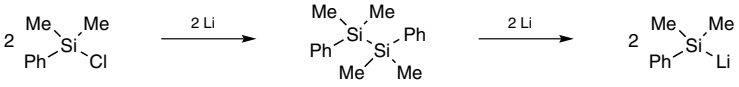
4.4.11 **Silyllithium and Related Silyl Alkali Metal Reagents**

C. Kleeberg

This chapter is a revision of the earlier *Science of Synthesis* contribution describing methods for the synthesis of silyllithium reagents and related compounds of the heavier alkali metals. Various synthetic routes to silyl alkali metal reagents are presented, employing different reaction types including reductive or nucleophilic cleavage of disilanes, reductive metalation of silyl halides, and cleavage of Si—H bonds.



Keywords: silyllithium reagents · lithium compounds · alkali metal compounds · sodium compounds · potassium compounds · reductive cleavage · cleavage reactions · silicon compounds · silanes

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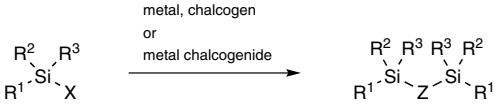
4.4.19.4 **Silyl Sulfides and Selenides**

A. Baker and T. Wirth

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of silyl sulfides and silyl selenides. Various efficient synthetic routes to these compounds are shown. The use of disilyl sulfides and disilyl selenides as versatile reagents in synthesis is highlighted.



X = halogen; Z = S, Se

Keywords: silyl sulfides · silyl selenides · sulfur · silanes

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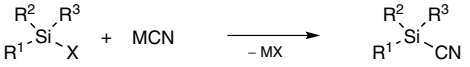
4.4.24.3 **Silyl Cyanides**

Y. Nishimoto, M. Yasuda, and A. Baba

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of silyl cyanides. It focuses on the literature published in the period 1997–2015.



Keywords: silanes · silenes · silicon compounds · cyanides · silyl halides

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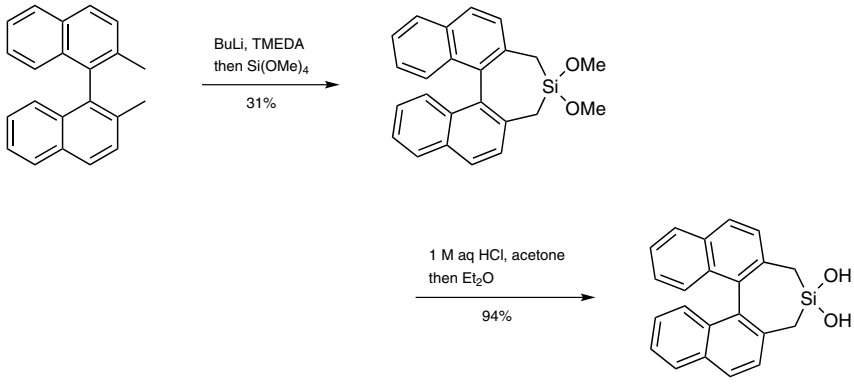
4.4.47 **Silanols**

A. M. Hardman-Baldwin and A. E. Mattson

This chapter covers synthetic approaches toward and selected applications of organosilanols. The focus is on the literature published in the period 2000–2015.



Keywords: silanols · silanediols · silanes · metal catalysis · organocatalysis · directing groups

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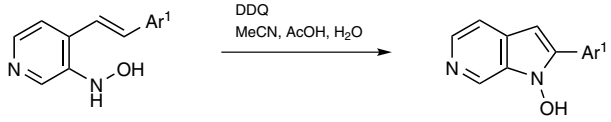
10.22.2 **Azaindol-1-ols**

J.-Y. Mérour and B. Joseph

This chapter presents the little-known azaindol-1-ol family. Methods for the preparation as well as the reactivity of each isomer are covered.



Keywords: azaindol-1-ols · cyclization · reduction · oxidation · O-alkylation

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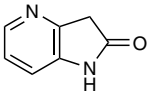
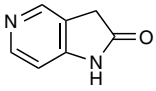
10.22.3 1,3-Dihydroazaindol-2-ones

J.-Y. Mérour and B. Joseph

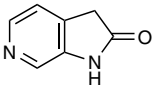
This chapter reviews the synthesis and reactivity of 1,3-dihydroazaindol-2-ones described in the literature until mid-2014. Synthetic methods and substituent modifications are reviewed for each isomer.



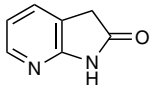
1,3-dihydropyrrolo[3,2-*b*]pyridin-2-one
(4-azaoxindole)



1,3-dihydropyrrolo[3,2-*c*]pyridin-2-one
(5-azaoxindole)



1,3-dihydropyrrolo[2,3-*c*]pyridin-2-one
(6-azaoxindole)



1,3-dihydropyrrolo[2,3-*b*]pyridin-2-one
(7-azaoxindole)

Keywords: 1,3-dihydroazaindol-2-ones · azaoxindoles · cyclization · reduction · rearrangement · radical cyclization · C3-alkylation · C3-aldolization

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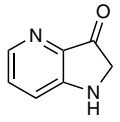
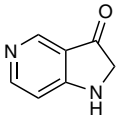
10.22.4 1,2-Dihydroazaindol-3-ones

J.-Y. Mérour and B. Joseph

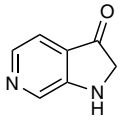
This chapter reviews the synthesis and reactivity of 1,2-dihydroazaindol-3-ones (azaindoxyls) and related 1,2-dihydroazaindol-3-yl acetates. Synthetic preparations are reviewed for all isomers except for 1,2-dihydro-3*H*-pyrrolo[2,3-*c*]pyridin-3-ones.



1,2-dihydro-3*H*-pyrrolo-
[3,2-*b*]pyridin-3-one



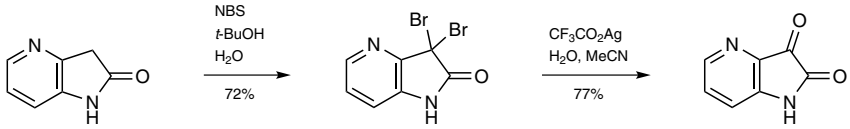
1,2-dihydro-3*H*-pyrrolo-
[3,2-*c*]pyridin-3-one



1,2-dihydro-3*H*-pyrrolo-
[2,3-*c*]pyridin-3-one

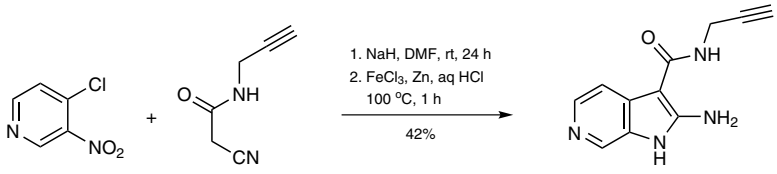
Keywords: 1,2-dihydroazaindol-3-ones · azaindoxyls · 1,2-dihydroazaindol-3-yl acetates · cyclization · C2-aldolization

This chapter reviews the synthesis and reactivity of 1*H*-azaindole-2,3-diones (azaisatins). It focuses on the literature published until mid-2014. Synthetic preparations are reviewed for 1*H*-pyrrolo[3,2-*b*]pyridine-2,3-diones, 1*H*-pyrrolo[3,2-*c*]pyridine-2,3-diones, and 1*H*-pyrrolo[2,3-*b*]pyridine-2,3-diones.



Keywords: 1*H*-azaindole-2,3-diones · azaisatins · cyclization · bromination · oxidation · 1*H*-pyrrolo[3,2-*b*]pyridine-2,3-diones · 1*H*-pyrrolo[3,2-*c*]pyridine-2,3-diones · 1*H*-pyrrolo[2,3-*b*]pyridine-2,3-diones

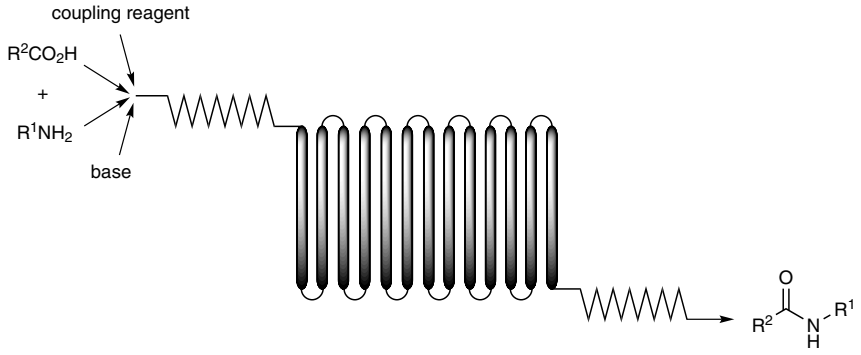
This chapter presents methods for the preparation of azaindol-2-amines and azaindol-3-amines published in the literature until mid-2014. Synthetic methods are described for each isomer.



Keywords: azaindol-2-amines · azaindol-3-amines · cyclization · nitrosation · reduction

Microreactors are powerful tools which present excellent mass- and heat-transfer performance properties for various kinds of chemical reaction. In this chapter, we present a brief introduction to microreactors, followed by an overview of the different microfluidic methods available for the synthesis of amides (including peptides). The range of peptides obtained via microreactor use includes di- to pentapeptides and also some cyclic analogues. Other continuous-flow reactions involving amide-bond formation are also illus-

trated, including examples of carbonylation, dendrimer preparation, and drug synthesis. The noteworthy features of these microfluidic reactions include shorter reaction times, high yields, and significantly less wastage. They are thus a step toward environmentally friendly, green reactions.



Keywords: amides · continuous-flow reactions · flow chemistry · green chemistry · microfluidics · microreactors · peptides

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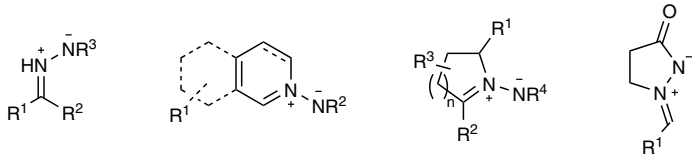
27.19.5 **Azomethine Imines**

I. Atodiresei and M. Rueping

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of azomethine imines and focuses on the literature published in the period 2003–2014. As azomethine imines are commonly generated in situ, and subsequently trapped with suitable reaction partners, their applications in synthesis are also presented herein.



Keywords: azomethine imines · cycloaddition reactions · dipolar cycloaddition · hydrazones · intramolecular cycloaddition

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35.1.5.1.12 **Synthesis of 1-Chloro-n-Heteroatom-Functionalized Alkanes by Addition across C=C Bonds**

T. Wirth and F. V. Singh

Chlorination of alkenes is an important synthetic process in organic chemistry. Several approaches for the chlorination of alkenes have been developed, including dichlorination, aminochlorination, halochlorination, oxychlorination, sulfanylchlorination, trihalomethylchlorination, and azidochlorination. Various inorganic and organic chlorides have been used as the source of chlorine, including alkali metal chlorides, tetrabutylam-

monium chloride, *N*-chlorosuccinimide, and (dichloroiodo)benzene. In this section, numerous approaches for the chlorination of alkenes using different inorganic and organic chlorides as source of chlorine, to give 1-chloro-n-heteroatom-functionalized alkanes, are discussed.

X = Cl, Br, I, NR^5_2, OR^5, SR^5, SeR^5, trihalomethyl, N_3

Keywords: alkenes · chlorination · aminochlorination · halochlorination · oxychlorination · sulfanylchlorination · trihalomethylchlorination · azidochlorination

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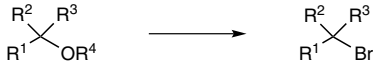
35.2.1.5.7 **Synthesis of Bromoalkanes by Substitution of Oxygen Functionalities**

M. Braun

This chapter is an update to the earlier *Science of Synthesis* contribution describing the synthesis of bromoalkanes by substitution of oxygen functionalities. In this update, the focus is the substitution of free hydroxy groups, silyl ethers, tetrahydropyran-2-yl ethers, and sulfonates.



R^4 = H, THP, SO_2R^5

Keywords: bromoalkanes · alcohols · tetrahydropyran-2-yl ethers · silyl ethers · sulfonates · substitution · bromination

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35.2.2.2 **Propargylic Bromides**

M. Braun

This chapter is an update to the earlier *Science of Synthesis* contribution describing the synthesis of propargylic bromides. The focus in this update is on synthesis by substitution of propargylic alcohols and protected derivatives thereof.

Keywords: propargylic bromides · substitution · propargylic alcohols · bromination

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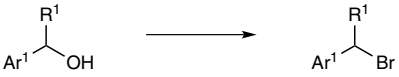
35.2.3.3.3 **Synthesis of Benzylic Bromides by Substitution of σ-Bonded Heteroatoms**

M. Braun

This chapter is an update to the earlier *Science of Synthesis* contribution describing the synthesis of benzylic bromides by substitution of σ-bonded heteroatoms. In this update, the focus is on the substitution of hydroxy groups.



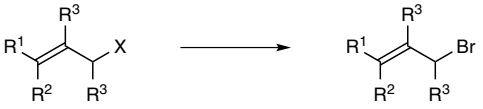
Keywords: benzylic bromides · substitution · benzylic alcohols · bromination

2017 p 469

35.2.4.2.3 **Synthesis of Allylic Bromides by Substitution of σ-Bonded Heteroatoms**

M. Braun

This chapter is an update to the earlier *Science of Synthesis* contribution describing the synthesis of allylic bromides by substitution of σ-bonded heteroatoms. In this update, the focus is on the substitution of other halogens and of hydroxy groups.



X = Cl, OH

Keywords: allylic bromides · substitution · allylic alcohols · allylic chlorides · bromination