

Abstracts

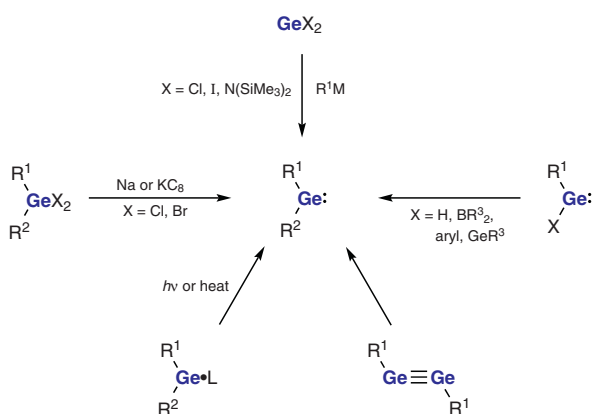
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5.1.7 Product Subclass 7: Germylenes

N. Takeda

This chapter is a revised and updated version of the previous *Science of Synthesis* contribution describing methods for the synthesis of germylenes. As starting materials for the synthesis of germylenes, dihalogermanes and stable germanium(II) compounds {for example, $\text{GeCl}_2 \cdot \text{dioxane}$, GeI_2 , and $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$ } have been used since the 1970s. In recent decades, digermynes and some new stable germanium(II) compounds such as chlorogermynes, aminogermynes, borylgermylenes, and hydrogermylene dimers have been synthesized, and these species have also been used as starting materials for the synthesis of germylenes.



Keywords: germylenes · digermynes · germynes · digermanes · dihalogermanes · substitution · reduction · dissociation · insertion · addition

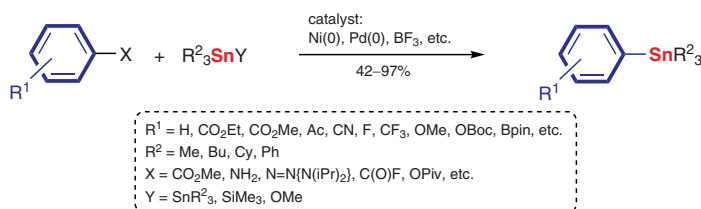
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5.2.24.10 Arylstannanes

J. Vrána and A. Růžicka

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis and uses of arylstannanes. The focus is on the literature published in the period 2001–2020. Novel synthetic methods for the formation of the target compounds are reviewed, including reactions of aryl anions with aryltin halides, reactions of diazonium salts or aryl azo sulfones with distannanes, and various catalyzed processes. The use of arylstannanes as substrates in organic chemistry and radiochemistry is also discussed; these compounds can undergo coupling reactions, destannylations, metal–tin exchange reactions, electrophilic substitutions, and oxidative addition processes.



Keywords: stannanes · aryl compounds · coupling reactions · activation of C–H bonds · oxidative addition

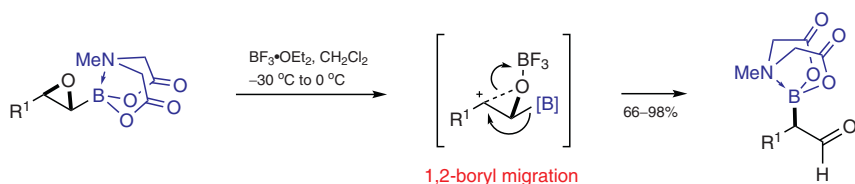
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6.1.29.16 α -Boryl Carbonyl Compounds

A. Trofimova, M. Sirvinskas, and A. K. Yudin

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis and applications of α -boryl carbonyl compounds. It focuses on recent advances in the field in the period 2008–2020 and discusses borylated aldehydes, ketones, carboxylic acids, and carboxylic esters and amides.



Keywords: α -boryl carbonyl compounds · boron compounds · boranes · borates · borohydrides · carbon–boron bonds · borylation · hydroboration

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Updated Section ·

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Completely Revised Contributions ·

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New Contributions

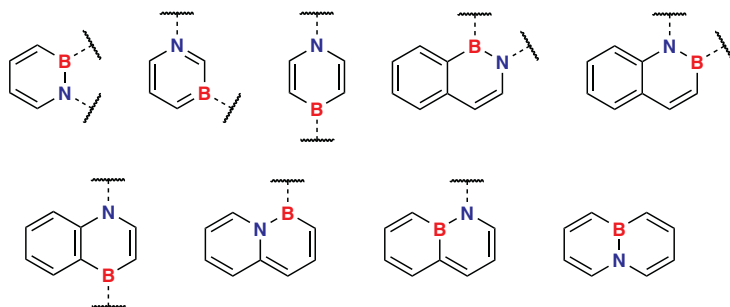
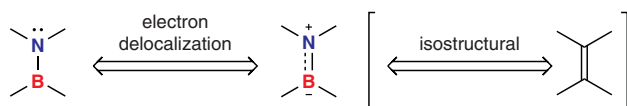
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6.1.43 **Product Subclass 43: Azaborines (Borazines)**

G. H. M. Davies and S. R. Wisniewski

Azaborines (or borazines) represent an interesting class of heterocycles incorporating a boron–nitrogen structural motif within an aromatic ring system. This creates a system that is isosteric to traditional all-carbon ring systems, as the lone pair on nitrogen can donate into the empty orbital at boron to afford aromatic properties. Reviewed herein are synthetic strategies to access mono- and bicyclic azaborine cores, along with subsequent functionalization strategies, some of which are uniquely applicable due to the inherent dipole imparted on these ring systems.



Keywords: azaborines · aromaticity · bicyclic compounds · borazarenes · borazines · boron compounds · cyclization · heterocycles · isosteres

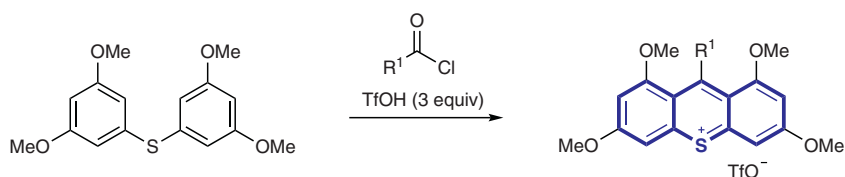
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14.6.5 **Thiopyrylium Salts**

M. Wang and X. Jiang

This is an update to the original *Science of Synthesis* chapter from 2003 (Section 14.6) on thiopyrylium salts. This update covers articles from the literature that were published between 2003 and 2020. Several methods for the synthesis of thiopyrylium salts that were covered in the previous chapter are also included in this update, because some new applications of thiopyrylium salts were explored in those works.



Keywords: thiopyrylium salts · thioxanthylum · thiopyrylium dyes · photocatalysts · ring enlargement · elimination · dehydrogenation

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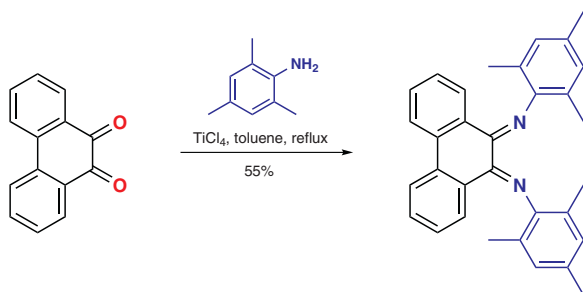
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27.27

Product Class 27: 1,2-Diimines*R. Isovitsch*

The utility of 1,2-diimines (α -diimines, 1,4-diazabutadienes) stems from the ease with which their steric and electronic properties can be tailored to a specific use. Current interest in this area involves using 1,2-diimines as precursors for novel bioactive compounds, as well as transition-metal ligands for the formation of novel polymerization catalysts and chemotherapeutic agents. In this review, the fundamental approaches for the synthesis of 1,2-diimines are described, as well as a current sampling of the unique ways that they are used to solve research problems. The chapter is organized based on the ways that 1,2-diimines are synthesized: condensation reactions and metal-promoted methods.



Keywords: diimines · azomethines · Schiff bases · diketones · anilines · condensation reactions

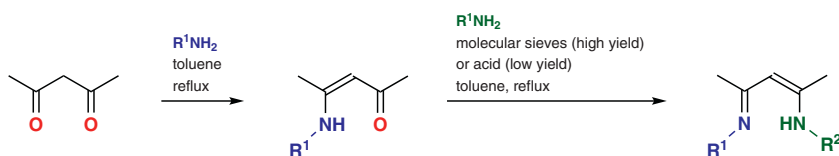
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27.28

Product Class 28: β -Diketimines (1,3-Diimines)*K. Chand, Umesh, D. P. Dorairaj, and S. C. N. Hsu*

β -Diketimines, encountered frequently as “nacnac” ligands, have emerged as popular motifs among other ancillary supports. There has been a great deal of interest in these compounds as supporting ligands because of their strong binding to metal ions, their tunable steric and electronic effects, and their diversity in terms of bonding modes. A classical synthetic approach towards β -diketimines is direct condensation of pentane-2,4-diones (and 1,3-diketone analogues) with suitable amines in the presence of an acid source. Recent developments involve the use of molecular sieves to avoid purification problems and to improve yields. Herein, a thorough survey of the synthetic approaches to β -diketimine ligands and their metal complexes, and applications in coordination chemistry, has been compiled.



Keywords: β -diketimines · 1,3-diimines · nacnac ligands · β -diketiminate ligands · condensation reactions · 1,3-diketones · amines · coordination chemistry

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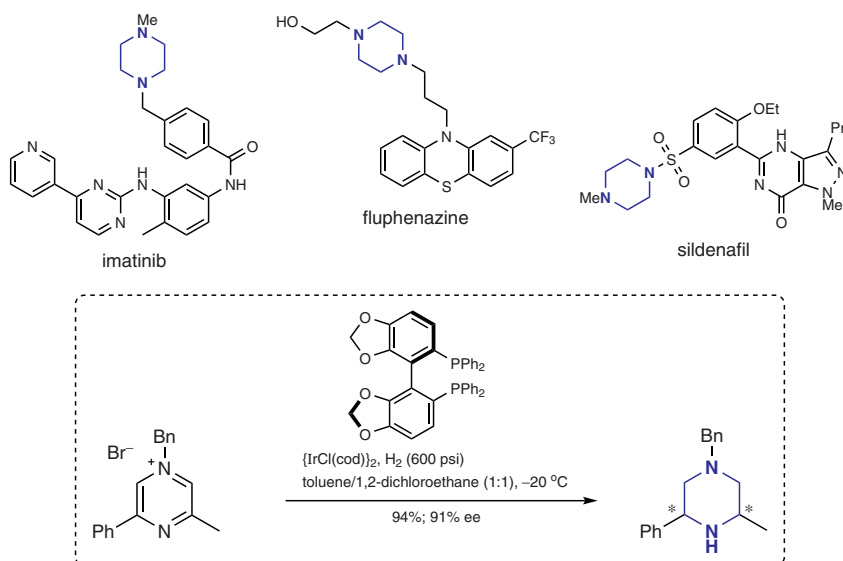
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40.1.8 Product Subclass 8: Piperazines

Z.-S. Ye

The piperazine unit is widely distributed in natural products and life-saving small-molecule pharmaceuticals. It is the third most common nitrogen heterocycle occurring in pharmaceuticals approved by the U. S. Food and Drug Administration. This chapter covers strategies for the synthesis and transformations of piperazines, with both classical methods and recent developments reviewed. A major focus is on cyclization reactions such as intramolecular hydroaminations, multicomponent approaches, and routes from ethane-1,2-diamine substrates. Also discussed are approaches based on hydrogenation of (hydro)pyrazines by heterogeneous catalysis and by (asymmetric) homogeneous catalysis. Finally, a variety of transformations involving modification of a substituent on a piperazine ring are surveyed, including arylations, alkylations, and oxidations.

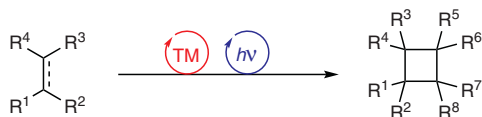


Keywords: piperazines · cyclization · hydroamination · Ugi reaction · allylation · arylation · hydrogenation · dearomatization · asymmetric synthesis · lithiation · activation of C–H bonds · cross-coupling reactions

Cyclobutanes

Y. Xiong, R. Guo, and G. Z. Zhang

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 48.3), and describes methods for the formation of cyclobutanes reported in the period 2009–2019. The focus is on recent advances in the synthetic preparations and applications of cyclobutanes via transition-metal-catalyzed and photochemical processes.



R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ = carbon- or heteroatom-based group

Keywords: alkenes · cyclization · cycloaddition · cyclobutanes · photocycloaddition · photochemistry · stereoselective synthesis · transition metals · total synthesis