Abstracts

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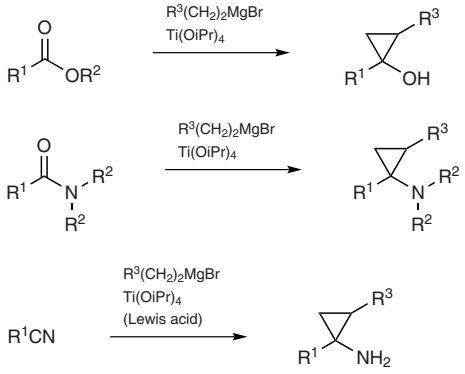
2.10.19 Organometallic Complexes of Titanium (Update 1)

P. Bertus, F. Boeda, and M. S. M. Pearson-Long

This chapter is an update to the earlier *Science of Synthesis* contribution describing the synthesis and application of titanium complexes in organic synthesis. This update focuses on the synthesis of cyclopropane derivatives using titanium reagents, with particular emphasis on the preparation of cyclopropanols from carboxylic esters (Kulinkovich reaction) and cyclopropylamines from carboxylic amides or nitriles.



Keywords: amides · bicyclic compounds · carbonates · cyclopropanes · cyclopropanols · cyclopropylamines · esters · Grignard reagents · imides · magnesium · nitriles · titanium

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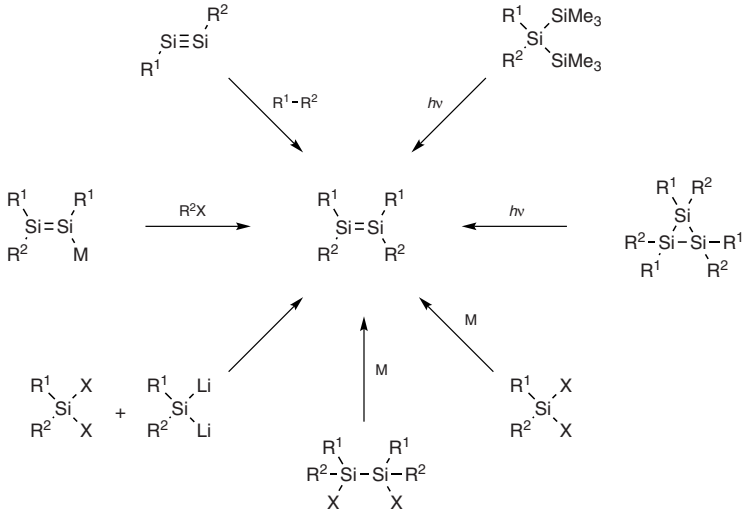
4.4.1 **Product Subclass 1: Disilenes**

A. Meltzer and D. Scheschkewitz

The syntheses of stable and marginally stable compounds with Si=Si bonds, i.e. linear and cyclic disilenes as well as tetrasilabutadienes, are reviewed. Typical procedures are described including detailed special requirements and precautions.



Keywords: alkene analogues · coupling reactions · cyclic compounds · dehalogenation · disilenes · disilenides · disilynes · photolysis · reductive coupling · silanes · silicon compounds · silylenes · silyl halides · unsaturated compounds

New p 69

8.1.31 **Functionalized Organolithiums by Ring Opening of Heterocycles**

M. Yus and F. Foubelo

This manuscript describes the preparation of functionalized organolithium compounds by reductive opening of heterocycles and further reaction of these intermediates with electrophiles.

Keywords: activation of C—O bonds · alkali metal compounds · carbanions · carbon—metal bonds · heterocycles · lithiation · lithium compounds · radical ions · reductive cleavage

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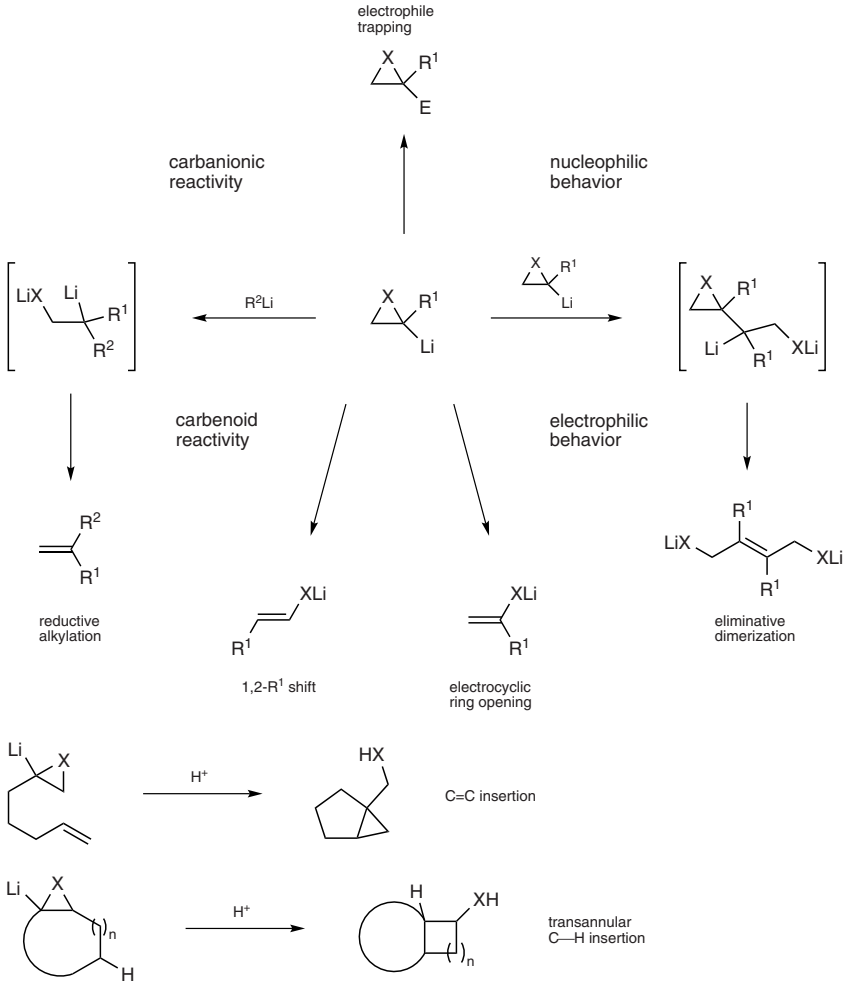
8.1.32 **Syntheses Mediated by α-Lithiated Epoxides and Aziridines**

L. Degennaro, F. M. Perna, and S. Florio

Three-membered ring heterocycles such as epoxides and aziridines, whose structural motif occurs frequently in natural products and biologically active substances, are an uncommon combination of reactivity, synthetic flexibility, and atom economy. Readily accessible, also in enantioenriched form, they are mainly used as electrophiles, undergoing

highly regioselective ring-opening reactions when reacted with nucleophiles. There are, however, many other less conventional but useful reactions these small-ring heterocycles may undergo. This chapter surveys a selection of the most recent advances in the chemistry of α-lithiated epoxides and aziridines, which can be simply generated by treatment of the parent epoxide or aziridine with strong bases such as organolithiums or lithium amides. Such lithiated species are relatively stable and can be captured with a number of electrophiles to give more functionalized oxiranes and aziridines or undergo other transformations including 1,2-organo shifts to enolates, eliminative dimerization, β-elimination, intramolecular cyclopropanation onto a double bond (C=C insertion), transannular C—H insertion, and reductive alkylation.



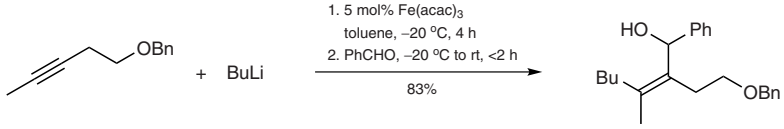
Keywords: oxiranes · aziridines · small-ring heterocycles · α-lithiation · carbenoids · organolithiums · configurational stability · asymmetric synthesis

New p 215

8.1.33 **Transition-Metal-Catalyzed Carbon—Carbon Bond Formation with Organolithiums**

G. Manolikakes

Transition-metal-catalyzed reactions with organolithiums are a useful tool for the formation of carbon—carbon bonds. This chapter covers reactions with organolithium compounds catalyzed by various transition metals such as copper, palladium, or iron.



Keywords: lithium compounds · cross coupling · copper catalysis · palladium catalysis · iron catalysis · carbolithiation · asymmetric catalysis

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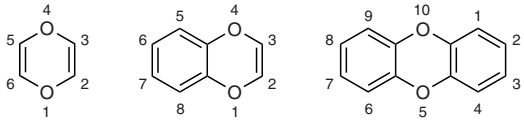
16.2.4 **1,4-Dioxins and Benzo- and Dibenzo-Fused Derivatives**

S. M. Sakya and J. Yang

This manuscript concerns three types of compound: 1,4-dioxins, 1,4-benzodioxins, and dibenzo[*b*,*e*][1,4]dioxins, and covers recent syntheses of these substrates that have not previously been highlighted in Section 16.2 of *Science of Synthesis*.



Keywords: aromatization · base-induced coupling · 1,4-benzodioxins · Diels–Alder reaction · 1,4-dioxins · dibenzo[*b*,*e*][1,4]dioxins · lithium–halogen exchange · ring-closing metathesis · ring-closure reactions · Stille coupling · substituent modification · Vilsmeier reaction

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16.3.5 **1,2-Dithiins**

F. K. Yoshimoto and Q. Li

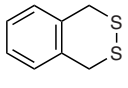
1,2-Dithiins are six-membered rings with two double bonds and two sulfur atoms within the ring. Related compounds include 3,6-dihydro-1,2-dithiins, 1,4-dihydrobenzo[*d*][1,2]dithiins, and dibenzo[*c*,*e*][1,2]dithiins. A wide variety of compounds observed in nature are found to contain the dithiin motif and the group is implicated in a wide range of biological activity. 1,2-Dithiins have also been used in other fields, for example as organic tran-

sistors and ligands for transition metals. This section updates previously published material in *Science of Synthesis* and in particular focuses on synthesis by ring-closure reactions and applications of the group in reactions with transition metals, Lewis acids, diazo compounds, alkynes, and enzymes.

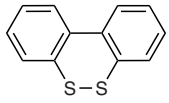
1,2-dithiin

3,6-dihydro-1,2-dithiin

1,2-dithiane



1,4-dihydrobenzo[*d*][1,2]dithiin



dibenzo[*c*,*e*][1,2]dithiin

Keywords: cyclization · diazo compounds · dibenzo[*c*,*e*][1,2]dithiins · Diels–Alder reaction · 1,4-dihydrobenzo[*d*][1,2]dithiins · 3,6-dihydro-1,2-dithiins · dimerization · 1,2-dithianes · 1,2-dithiins · enzymes · Lewis acids · phase-transfer catalysis · photolysis · ring-closing metathesis · ring-closure reactions · sulfonation · transition metals

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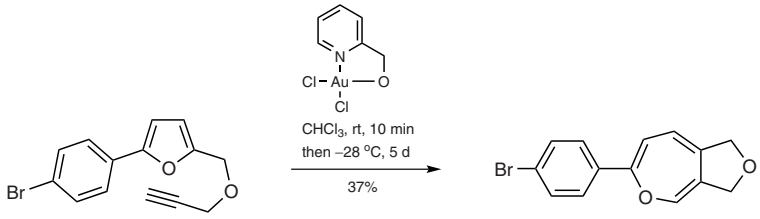
17.4.1.5 Oxepins

J. Hong

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of oxepins. It focuses on the literature published in the period 2003–2011.



Keywords: cycloaddition · dehydrogenation · isomerization · Michael addition · nucleophilic substitution · ring expansion

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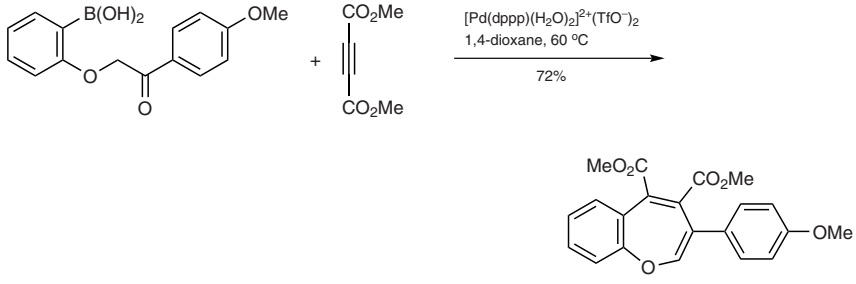
17.4.2.5 **Benzoxepins**

J. Hong

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of benzoxepins. It focuses on the literature published in the period 2003–2011.



Keywords: annulation · condensation reactions · cyclization · cyclocondensation · rearrangement · ring closure · ring expansion · transition metals

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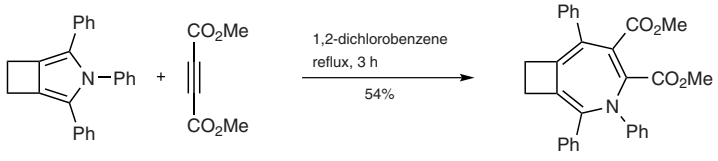
17.4.5.5 **Azepines, Cyclopentazepines, and Phosphorus Analogues**

J. E. Camp

This manuscript is an update of the earlier *Science of Synthesis* contribution describing methods for the synthesis of fully unsaturated azepines, cyclopentazepines, and their phosphorus analogues. It focuses on the literature published between 2003 and 2010.



Keywords: azepines · cyclopentazepines · electrocyclization · Diels–Alder · photolytic decomposition · rearrangement · C-amination · C-alkoxylation · Friedel–Crafts · azepinium ion

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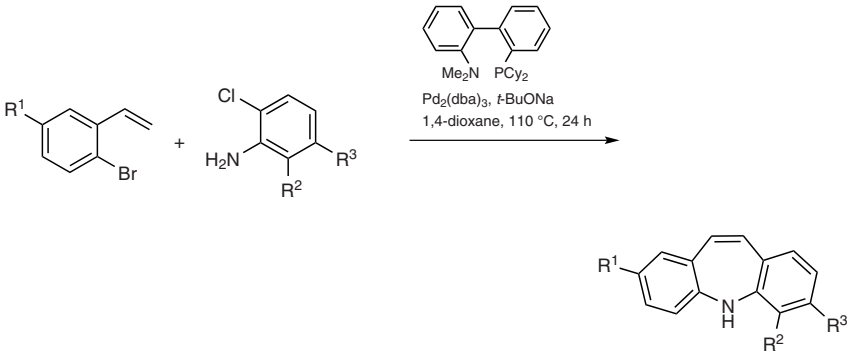
17.4.6.10 **Benzazepines and Their Group 15 Analogues**

J. E. Camp

This manuscript is an update of the earlier *Science of Synthesis* contribution describing methods for the synthesis of fully unsaturated benzazepines and their group 15 analogues. It focuses on the literature published between 2003 and 2010.



Keywords: benzazepines · dibenzoheterepins · tribenzoheterepins · condensation · Bischler–Napieralski · tandem reaction · phase-transfer catalysis · ring enlargement · photodimerization · benzoheterepins · Friedel–Crafts

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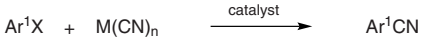
19.5.17 **Synthesis of Nitriles Using Cross-Coupling Reactions**

D. M. Rudzinski and N. E. Leadbeater

The synthesis of aryl and hetaryl nitriles by metal-catalyzed cross-coupling reactions is presented. Attention is focused mainly on key methodologies published in the period 2003–2011. As well as the use of alkali metal cyanide salts as sources of cyanide, the application of the less toxic and increasingly popular potassium hexacyanoferrate(II) is also discussed.



X = halogen, OMs, OTf; $M(CN)_n$ = alkali metal cyanide, $K_4Fe(CN)_6$

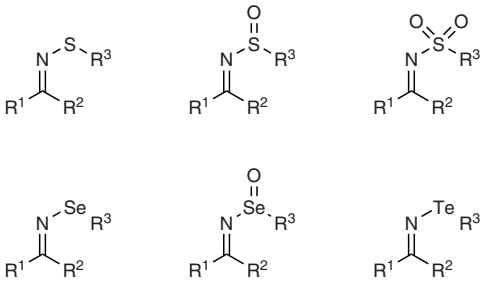
Keywords: nitriles · cyanide · cyanation · cross coupling · palladium · nickel · copper · aryl halides · hetaryl halides · aryl trifluoromethanesulfonates · aryl methanesulfonates

New p 417

27.25 **Product Class 25: *N*-Sulfanyl-, *N*-Selanyl-, and *N*-Tellanylimines, and Their Oxidation Derivatives**

F. Chemla, F. Ferreira, and A. Pérez-Luna

This chapter is devoted to synthetically useful methods for the preparation of *N*-sulfanylimines and their oxidation derivatives (*N*-sulfinylimines and *N*-sulfonylimines), as well as of *N*-selanylimines and *N*-tellanylimines and their oxidation derivatives. *N*-Sulfinylimines and *N*-sulfonylimines are important compounds which have raised considerable interest over the past 20 years.



Keywords: imines · sulfanylimines · sulfenimines · sulfinylimines · sulfonylimines · sulfinyl compounds · sulfonyl compounds · selanylimines · selenium compounds · tellurium compounds