Abstracts



This manuscript is an update to the existing *Science of Synthesis* chapter on organometallic complexes of lanthanides. It summarizes the synthesis of β -hydroxycarbonyl compounds using lanthanide-containing catalysts in Mukaiyama aldol reactions. Early investigations as well as recent improvements to lanthanide-containing catalysts with respect to substrate scope and enantioselectivity are included.

Keywords: aldol reaction \cdot catalysis \cdot β -hydroxycarbonyl \cdot lanthanide \cdot Mukaiyama

T. Beweries and U. Rosenthal

This manuscript describes the methods for the synthesis and application of group 4 metallocene–bis(trimethylsilyl)acetylene complexes. Recent interest in this area has been generated by the fact that metallocenes play an important role in numerous catalytic and stoichiometric applications, including the formation of metallacycles, which can serve as model compounds for such highly interesting reactions as the oligomerization of ethene to linear alpha alkenes.

$$M(Cp)_2Cl_2 + Mg + TMS \xrightarrow{\qquad} TMS$$
 $M = Ti; \text{ no L};$
 $M = Zr; L = THF, py, PMe_3, acetone;$
 $M = Hf; L = py, PMe_3$

Keywords: alkyne complexes · titanocenes · zirconocenes · hafnocenes · metallacycles

X = Br, I



6.1.7.11 Hydroxyboranes

D. G. Hall and H. Zheng

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the preparation and application of organoboronic acids (hydroxyboranes) in organic synthesis. It focuses on the literature published in the period 2002–2011.

$$\begin{array}{c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$$

Keywords: boronic acids \cdot boronic esters \cdot borylation \cdot boronic ester hydrolysis \cdot boronic acid catalysis \cdot cross-coupling reaction \cdot C—C bond formation \cdot C—X bond formation \cdot C—H borylation \cdot hydroxyboranes \cdot organoboronic acids \cdot phase-switch purification

7.1.4.7 Aluminum Alkoxides and Phenoxides

K. Ohmatsu and T. Ooi

This manuscript is an update to the earlier *Science of Synthesis* contribution describing the synthesis of aluminum alkoxides and phenoxides. It focuses on the literature published in the period 1999–2010.

Keywords: alkoxides \cdot aluminum compounds \cdot asymmetric catalysis \cdot carbonyl compounds \cdot Lewis acid catalysis \cdot phenoxides

______ p 131 —

7.1.7.15 Aluminum Amides

K. Ohmatsu and T. Ooi

This manuscript is an update to the earlier *Science of Synthesis* contribution on the synthesis of aluminum amides. It focuses on the literature published in the period 1999–2010.

Keywords: aluminum compounds \cdot amides \cdot asymmetric catalysis \cdot carbonyl compounds \cdot coupling reactions \cdot Lewis acid catalysis

<u>New</u> p 139 —

8.1.29 **Dearomatization Reactions Using Organolithiums**

G. Lemière and J. Clayden

Addition of organolithiums to aromatic rings has emerged as a convenient method for the rapid construction of functionalized carbocyclic and heterocyclic compounds. These dearomatization reactions of readily available activated or unactivated aromatic rings often occur with a high degree of selectivity. Developments in the intramolecular version of this process known as dearomatizing cyclization have allowed access to various polycyclic frameworks with well-defined relative stereochemistry. Several strategies have been employed to carry out asymmetric organolithium-mediated dearomatizations efficiently and some of them have been used as key steps in the synthesis of natural compounds.

Keywords: organolithium \cdot dearomatization \cdot dearomatizing addition \cdot dearomatizing cyclization \cdot rearrangements \cdot stereospecificity



Carbolithiation of Carbon–Carbon Multiple Bonds

p 191 -

E. Lete and N. Sotomayor

This chapter describes relevant synthetic applications of carbolithiation reactions of alkenes and alkynes. Both inter- and intramolecular reactions are discussed, including also enantioselective transformations.

Keywords: carbolithiation \cdot lithiation \cdot lithium compounds \cdot carbanions \cdot carbon–carbon double bonds \cdot carbon–carbon triple bonds \cdot cyclization \cdot diastereoselectivity \cdot enantioselectivity \cdot intramolecular reactions

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of pyrazines. It focuses on the literature published in the period 2002–2010, together with some selected references for 2011.

 R^1 = aryl, Pr; R^2 = H, Et; R^1 , R^2 = (CH₂)₃, (CH₂)₄, (CH₂)₆

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Keywords: pyrazines \cdot cyclocondensation \cdot dimerization \cdot cyclization \cdot metalation \cdot halo compounds \cdot cross-coupling reactions \cdot Suzuki coupling \cdot palladium catalyst \cdot microwave irradiation





17.3.4 Six-Membered Hetarenes with More than Three Heteroatoms

S. L. Castle

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of aromatic tetrazines. It focuses on the literature published in the period 2003–2010.

$$O = \begin{pmatrix} N - N \\ N - N \end{pmatrix}$$

$$O = \begin{pmatrix} N - N \\ N - N \end{pmatrix}$$

$$O = \begin{pmatrix} N - N \\ N - N \end{pmatrix}$$

$$O = \begin{pmatrix} N - N \\ N - N \end{pmatrix}$$

$$O = \begin{pmatrix} N - N \\ 200 \text{ °C}, 2 \text{ h} \\ 28 - 67\% \end{pmatrix}$$

$$O = \begin{pmatrix} N - N \\ N - N \\ N - N \end{pmatrix}$$

$$O = \begin{pmatrix} N - N \\ N - N \\ N - N \end{pmatrix}$$

$$O = \begin{pmatrix} N - N \\ N - N \\ N - N \end{pmatrix}$$

Keywords: nitrogen heterocycles \cdot tetrazines \cdot annulation \cdot aromatization \cdot cross-coupling reactions \cdot dimerization \cdot nucleophilic aromatic substitution

19.5.16 Asymmetric Synthesis of Nitriles
W. T. Wang, L. L. Lin, X. H. Liu, and X. M. Feng

vv. 1. vvang, L. E. Em, A. H. Ela, and A. W. Peng

This manuscript provides an update to the methods for the synthesis of chiral nitriles previously covered in *Science of Synthesis*, Section 19.5. It focuses on the literature published in the period 2003–2011.

 $X = O, NR^3, CR^4R^5$

Keywords: asymmetric synthesis · cyanation · nitriles · cyanohydrins · cyanosilylation · α -amino nitriles · hydrocyanation · conjugate addition.



27.15

p 445 —

Product Class 15: Oximes

S. Chiba and K. Narasaka

The chemical reactions of oximes are much more diverse than those of N-substituted imines and carbonyl compounds such as ketones. This wide range in the chemical reactivity of oximes is derived from their unique chemical structure, which includes three different atoms (carbon, nitrogen, and oxygen) and a polarized C=N bond. In this chapter, preparation methods and synthetic reactions of oximes and their derivatives are reviewed, covering not only classical but also more-recent literature precedents.

Keywords: oximes \cdot amination \cdot amino compounds \cdot azaheterocycles