

Abstracts

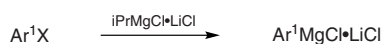
2010

p 1

7.6.5.6 Aryl Grignard Reagents

H. Yorimitsu

Halogen–magnesium exchange between aryl iodides or bromides and an isopropylmagnesium chloride–lithium chloride complex or lithium trialkylmagnesates is now recognized as a useful method for the preparation of aryl Grignard reagents in addition to the conventional Grignard method. The exchange reactions lead to a wide variety of functionalized aryl Grignard reagents containing, for example, a carbonyl or a cyano group. Directed *ortho*-magnesiation reactions of arenes with bulky magnesium amide complexes, such as (2,2,6,6-tetramethylpiperidin-1-yl)magnesium chloride–lithium chloride complex and bis(2,2,6,6-tetramethylpiperidin-1-yl)magnesium–bis(lithium chloride) complex, are also useful.



X = I, Br

Keywords: amination · “ate” complexes · carbomagnesiation · carbometalation · Grignard reagents · homocoupling · magnesates · magnesium compounds · metalation

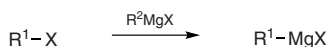
2010

p 11

7.6.10.9 Alkyl Grignard Reagents

H. Yorimitsu

While the conventional preparation of Grignard reagents from alkyl halides and metallic magnesium remains reliable, halogen–magnesium and sulfoxide–magnesium exchange have emerged as useful methods for the preparation of functionalized alkyl Grignard reagents that are otherwise difficult to synthesize. Carbomagnesiation reactions of alkenes are also useful for preparing alkyl Grignard reagents of some complexity. The formation of “ate” complexes gives a significant improvement in the utility of alkyl Grignard reagents and can lead to higher efficiency in nucleophilic addition to carbonyl compounds.

X = I, Br, SOAr; R² = Et, iPr

Keywords: “ate” complexes · carbomagnesiation · carbometalation · cyclization · magnesium compounds · magnesates · metalation · Grignard reagents · nucleophilic addition · sulfoxides

2010

Updated Section ·

2010

Completely Revised Contributions ·

New

New Contributions

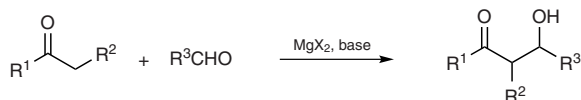
2010

p 21

7.6.12.13 **Magnesium Halides**

M. Shimizu

This manuscript is an update to the earlier *Science of Synthesis* contribution describing reactions involving magnesium halides. It focuses on the literature published in the period 2001–2009. In particular, magnesium bromide and magnesium iodide are used frequently as promoters for specific transformations of important molecules.



Keywords: Friedel–Crafts reaction · Knoevenagel reaction · magnesium bromide · magnesium chloride · magnesium enolates · magnesium fluoride · magnesium iodide · Morita–Baylis–Hillman reaction

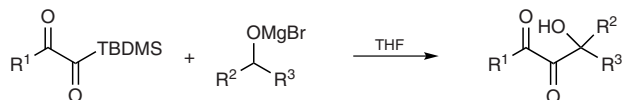
2010

p 31

7.6.13.17 **Magnesium Oxide, Alkoxides, and Carboxylates**

M. Shimizu

This manuscript is an update to the earlier *Science of Synthesis* contribution describing reactions involving magnesium oxide, alkoxides, and carboxylates. It focuses on the literature published in the period 2001–2009. In particular, magnesium oxide and magnesium alkoxides are used for useful chemoselective transformations.



Keywords: Baeyer–Villiger oxidation · Diels–Alder reaction · ethyl magnesium malonate · magnesium alkoxides · magnesium bis[2-(alkoxycarbonyl)acetate] · magnesium carboxylates · magnesium monoperoxyphthalate · magnesium oxide · Mannich-type reaction · Michael addition · Oppenauer oxidation

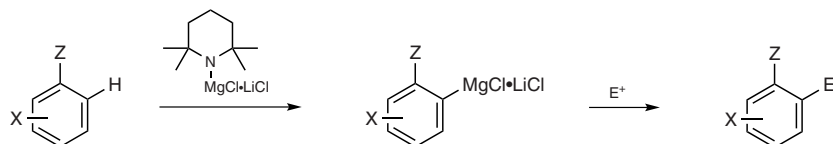
2010

p 41

7.6.14 **Product Subclass 14: Magnesium Amides**

M. Shimizu

This manuscript is a revision of the earlier *Science of Synthesis* contribution describing reactions involving magnesium amides. Synthesis of a series of magnesium amides, bis(amides), and their lithium chloride complexes is described. The use of magnesium amides as bases enables the regioselective deprotonation of a variety of molecules. Chiral magnesium amides are also discussed.



X = CO²R, CN, COR
Z = directing group

2010

Updated Section · 2010 Completely Revised Contributions · New

New Contributions

Keywords: amidomagnesium halide–lithium chloride complexes · amidomagnesium halides · magnesium bis(amide)–lithium chloride complexes · magnesium bis(amides) · magnesium dialkylamides · deprotonation

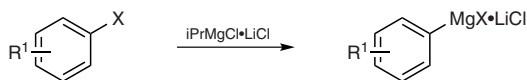
2010

p 57

11.12.5 Oxazoles

A. Khartulyari and M. E. Maier

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of oxazoles. This heterocyclic system is of particular interest, since many oxazole-containing natural products and their synthetic analogues possess interesting biological activities. In addition, oxazoles and related compounds serve as building blocks and reagents for organic synthesis.



X = I or Br

Keywords: oxazoles · cyclization · multicomponent reaction · gold catalysis · heterocycles · *N*-propargylamides · cycloisomerization · coupling reactions

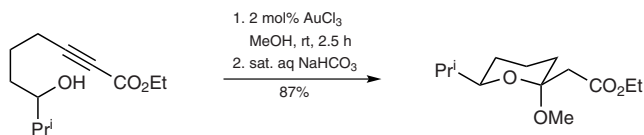
2010

p 121

29.6.2 Acyclic and Semicyclic OJO Acetals

L. S. Fowler and A. Sutherland

This manuscript is an update to the previous *Science of Synthesis* contribution describing methods for the synthesis of acyclic and semicyclic acetals. It focuses on the literature published in the period 2007 to mid-2010.



Keywords: acyclic acetals · semicyclic acetals · aldehydes · ketones · trialkyl orthoformates · enol ethers · cycloaddition · dehydration · acetalization

2010

Updated Section ·

2010

Completely Revised Contributions ·

New

New Contributions

2010

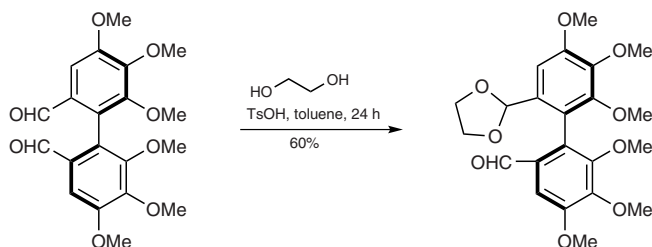
p 151

29.7.3

1,3-Dioxetanes and 1,3-Dioxolanes

D. Carbery

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of 1,3-dioxetanes and 1,3-dioxolanes. It focuses on the synthesis and synthetic applications of 1,3-dioxolanes covered in the literature over the period 2008–2010.



Keywords: dioxolane · carbonyls · diols · protecting groups · deprotection

2010

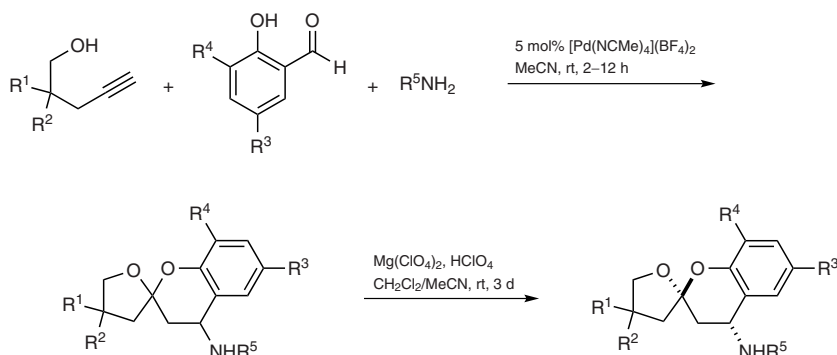
p 173

29.9.2

Spiroketal

E. A. Anderson and B. Gockel

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of spiroketals. It focuses on the literature published in the period 2005–2010.



Keywords: spiroketal · acetalization · benzannulation · carbon–oxygen bonds · cyclic compounds · diastereoselectivity · intramolecular reactions · oxiranes · oxygen heterocycles · synthesis design · spiro compounds

2010

Updated Section ·

2010

Completely Revised Contributions ·

New

New Contributions

2010

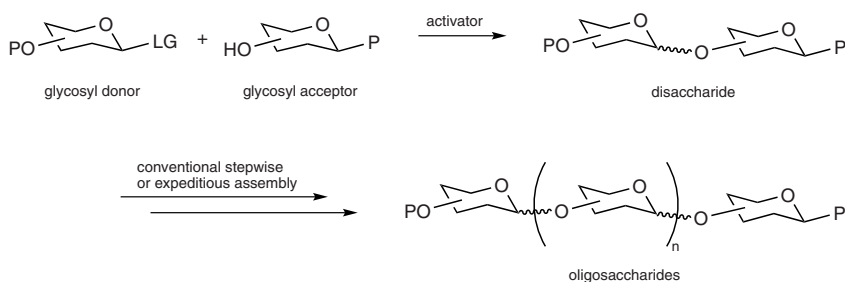
p 229

29.16

Product Class 16: Glycosyl Oxygen Compounds (Di- and Oligosaccharides)

A. V. Demchenko and C. De Meo

This manuscript is a revision of the earlier *Science of Synthesis* contribution describing methods for the synthesis of di- and oligosaccharides. Recent new developments and important improvements of fundamental concepts are the particular focus of this update.



LG = leaving group; P = protecting group

Keywords: carbohydrates · enzyme catalysis · glycosidases · glycosidation · glycosides · glycosylation · halides · imidates · neighboring-group participation · neuraminic acids · nucleophilic substitution · oligosaccharides · protecting groups · solid-phase synthesis · saccharides · stereoselective synthesis · sugars · thioglycosides · thioimidates

New

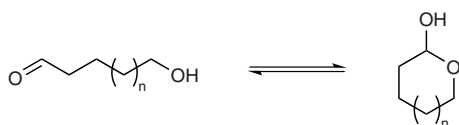
p 417

29.17

Product Class 17: Acyclic Hemiacetals, Lactols, and Carbonyl Hydrates

S. C. Coote, L. H. S. Smith, and D. J. Procter

Acyclic hemiacetals are in most cases unstable and exist only as transient intermediates, in contrast with cyclic hemiacetals (lactols), which are often stable, isolable compounds. Lactols may be prepared using various different methods, including the reduction of lactones, reduction of dicarbonyl compounds, or the selective oxidation of diols, as well as by addition of carbon nucleophiles to lactones or dicarbonyl compounds, deprotection of O-protected cyclic hemiacetals, or from enol ethers. Carbonyl hydrates are generally short-lived intermediates, although a limited number of stable carbonyl hydrates (generally derived from strained carbonyl compounds or carbonyl compounds bearing electron-withdrawing groups) have been documented.



Keywords: carbonyl additions · carbonyl compounds · dicarbonyl compounds · diols · hydroxycarbonyl compounds · lactols · lactonization · oxidation · reduction

2010

Updated Section ·

2010

Completely Revised Contributions ·

New

New Contributions

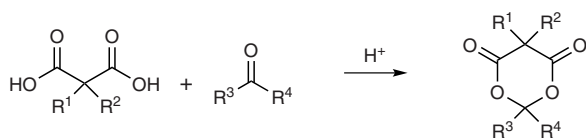
New

p475

29.18

Product Class 18: 1,1-Diacyloxy Compounds*L. H. S. Smith, S. C. Coote, and D. J. Procter*

1,1-Diacyloxy compounds can be accessed from a variety of starting materials including aldehydes, ketones, and O/O, O/Hal, and Hal/Hal acetals under a variety of reaction conditions. This product class encompasses Meldrum's acid, several natural products, and acyloxy ester prodrugs; in addition, acyl acetals are useful protecting groups for aldehydes and can be cleaved orthogonally to alkyl acetals.



Keywords: acetals · acylation · alkylation · carbonyl compounds · carboxylic acids · esters · Lewis acid catalysts · oxidation