

Abstracts

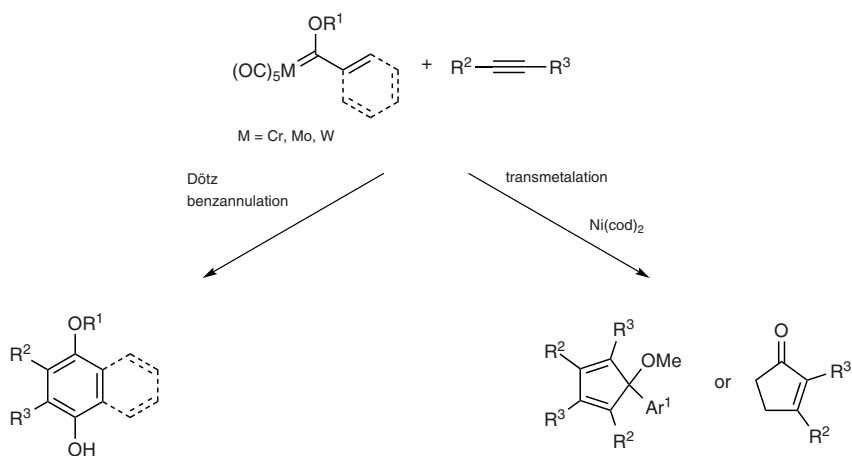
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2.7.10

Carbonyl Complexes of Chromium, Molybdenum, and Tungsten with σ -Bonded Ligands*E. Aguilar and L. A. López*

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 2.7.1) describing the chemistry of Fischer carbene complexes of chromium, molybdenum, and tungsten. The synthesis of acyclic, carbocyclic, and heterocyclic compounds is presented following an approach based on the nature of the starting carbene complex. Relevant mechanistic pathways are also discussed to allow a better understanding of the reactivity displayed.



Keywords: Fischer carbene complexes · Dötz benzannulation · Hegedus photochemistry · cyclopropanation · transmetalation · nonstabilized carbene complexes · chromium compounds · molybdenum compounds · tungsten compounds · heterocycles · carbocycles · metal migration

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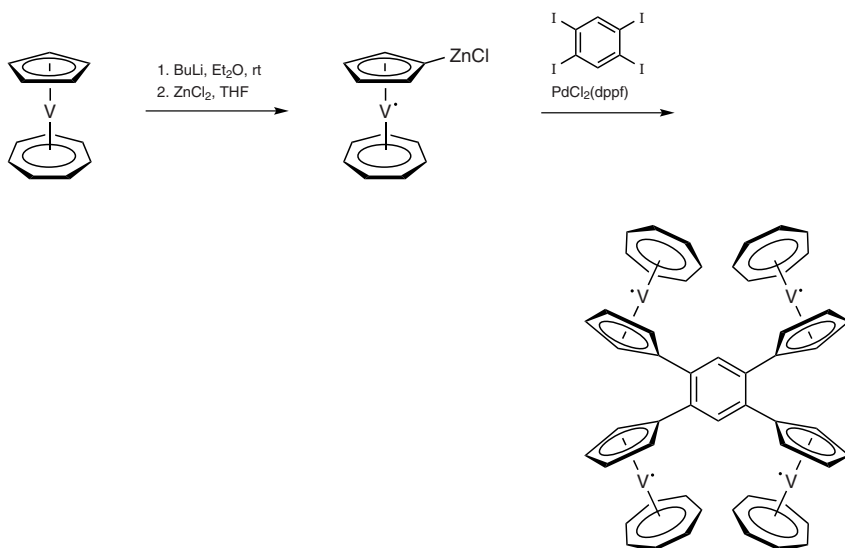
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2.8.10

Organometallic Complexes of Vanadium

O. S. Shneider and A. M. Szpilman

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for synthesis of organometallic complexes of vanadium. It summarizes previous methods and focuses on the literature published in the period 2000–2010.



Keywords: hydridovanadium complexes · vanadium · vanadium–alkene complexes · vanadium–alkyne complexes · vanadium–arene complexes · vanadium–carbene complexes · vanadocenes

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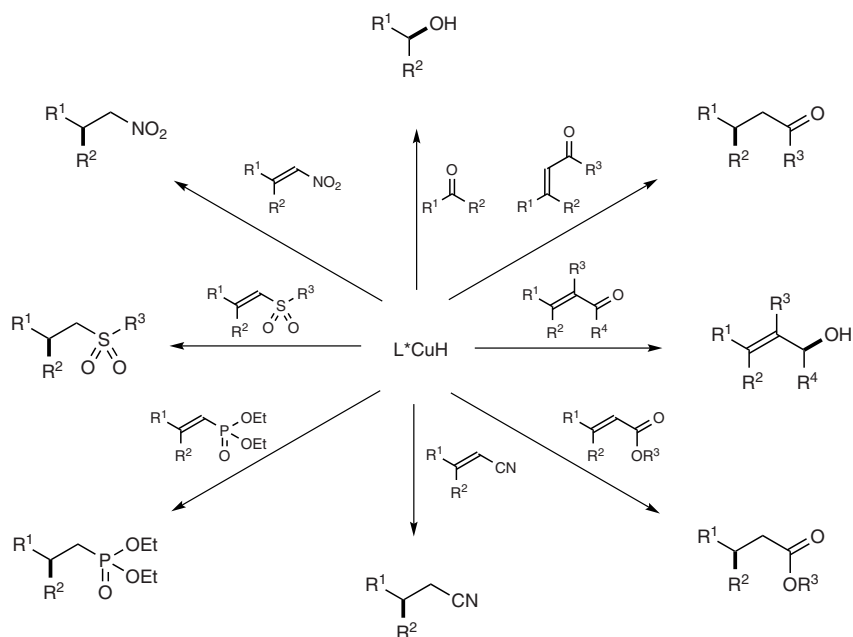
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3.4.8

Organometallic Complexes of Copper*B. H. Lipshutz and S. Ghorai*

The topic of this update chapter is asymmetric copper hydride catalyzed transformations. Copper hydride complexes containing nonracemic ligands catalyze asymmetric 1,2- and 1,4-addition to a variety of unsymmetrical ketones and Michael acceptors.

 L^* = nonracemic ligand

Keywords: activated alkenes · asymmetric catalysis · asymmetric conjugate reduction · copper hydride · hydrosilylation · nonracemic ligands · unsymmetrical ketones

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24.1.1.3

1,1-Dihaloallenes*K. Fuchibe and J. Ichikawa*

This chapter is an update to *Science of Synthesis* Section 24.1.1. Syntheses and applications of 1,1-dihaloallenes reported between 2005 and 2013 are described. 1,1-Difluoroallenes are synthesized by elimination reactions of difluoroallylic compounds (formation of a second C=C bond in fluorinated alkenes) or by nucleophilic and electrophilic substitutions of difluoropropargylic compounds (rearrangement of the C≡C bonds in fluorinated al-

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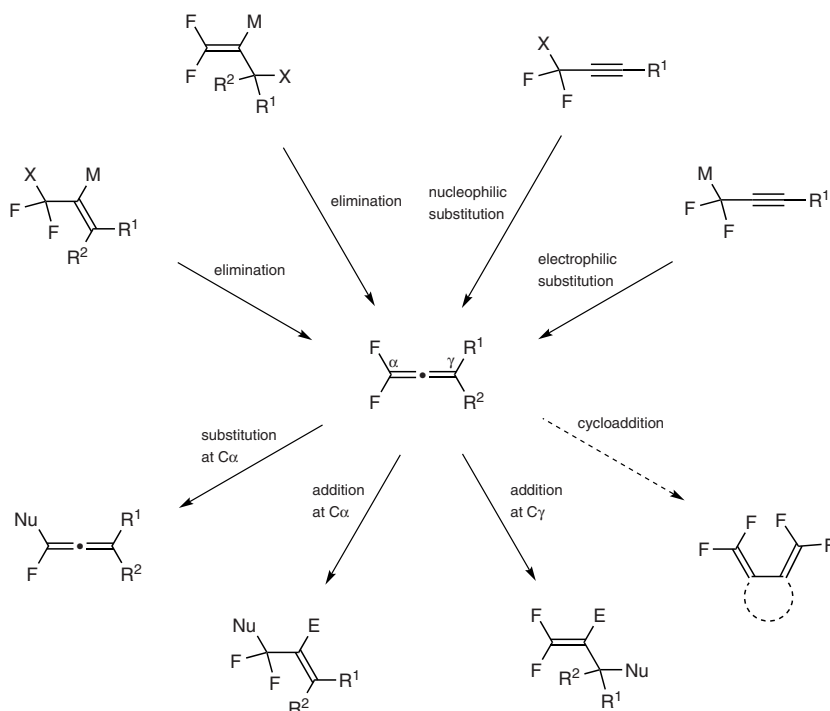
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Science of Synthesis Knowledge Updates 2014/2

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kynes). 1,1-Difluoroallenes are used for the syntheses of unsaturated fluorine-containing compounds, mainly by nucleophilic substitutions and additions at the positions α and/ or γ to the fluorine substituents. Cycloadditions of tetrafluorobuta-1,2,3-triene are also described.



Keywords: allenes · alkenes · cumulenes · cycloaddition · domino reaction · electrophilic substitution · elimination · fluorine compounds · metalation · nucleophilic addition · nucleophilic substitution · propargylic compounds

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24.1.16 1,1-Bis(heteroatom-functionalized) Allenes

C. Ibis

This chapter updates *Science of Synthesis* Sections 24.1.3, 24.1.10, 24.1.14, and 24.1.15. Mono-, bis-, tris-, and tetrakis(sulfanyl-substituted) butatrienes are obtained from alkyl-sulfanyl- or arylsulfanyl-substituted buta-1,3-dienes in the presence of base in petroleum ether at room temperature. The treatment of 1,1,4,4-tetrakis[4-(dimethylamino)pyridin-1-ium]-2,3-dichlorobuta-1,3-diene with thiolates with thiolates in dimethyl sulfoxide leads to the formation of tetrakis(sulfanyl-substituted) butatrienes. Allenylphosphonates are synthesized by the reaction of aliphatic- or aromatic-substituted propargylic alcohols and chlorophosphites in the presence of triethylamine. The reaction of 1-bromo-1-silylallenes with butyllithium and then chlorodiphenylphosphine in tetrahydrofuran gives 1,1-bis(diphenylphosphino)allenes.

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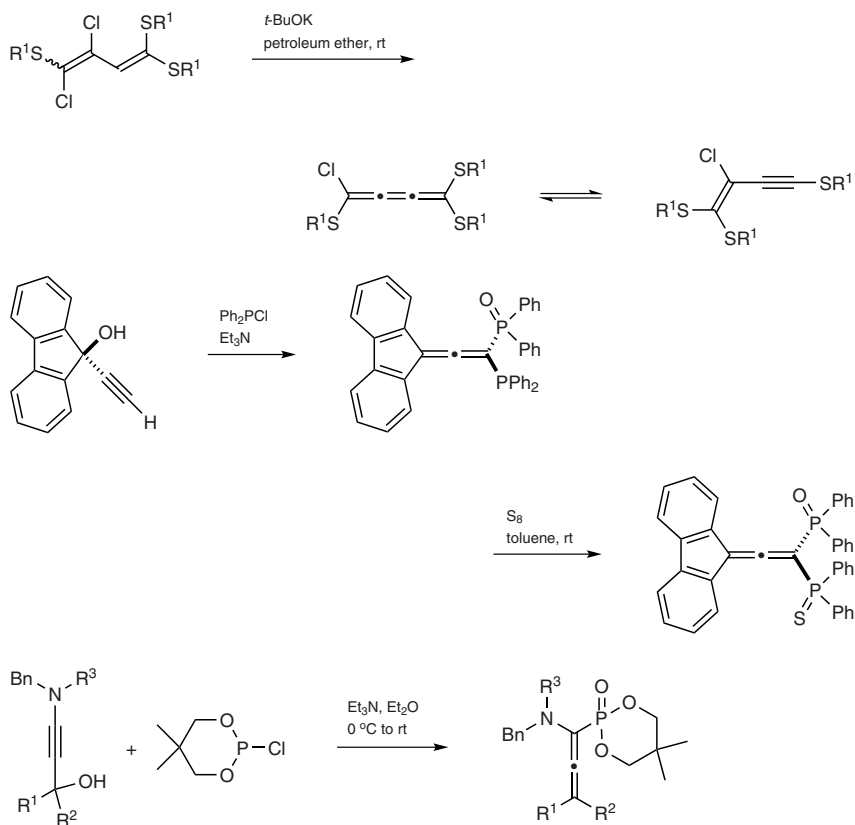
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Keywords: butadienes · butatrienes · butenyne · elimination · allenylphosphonates · allenylphosphine oxides · silyllallenes · diphenylphosphines · diphenylphosphine oxides · propargylic alcohols

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24.2.11.3 1,1-Bis(organothio)alk-1-enes (Ketene S,S-Acetals)

Q. Liu

This chapter is an update to *Science of Synthesis* Section 24.2.11 describing methods for the synthesis of 1,1-bis(organothio)alk-1-enes (ketene S,S-acetals). It focuses on the literature published in the period 2000-2013 and gives several examples of the use of ketene S,S-acetals as versatile intermediates for organic synthesis.

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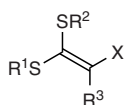
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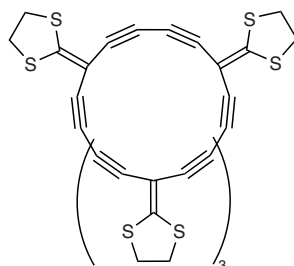
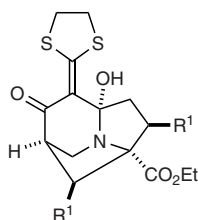
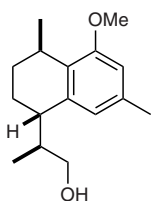
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X = Br, I, NO₂, N₂Ar¹, CH(OH)R³, CCl=CH₂, CBr=CH₂, CN, CF₃, acyl, alkenoyl, ethynyl
 sulfonyl, phosphonyl;
 R¹ = alkyl, aryl, CF₃;
 R² = alkyl, aryl, CF₃;
 R¹, R² = (CH₂)_n, CH=CH, CH=CMe;



Keywords: [5 + 1]-annulation reactions · [7 + 1]-annulation reactions · 1,1-bis(organosulfanyl)alk-1-enes · carbonyl condensation reactions · domino reactions · α -functionalization · substitution–cycloaromatization reactions

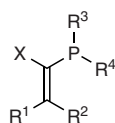
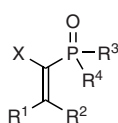
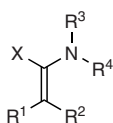
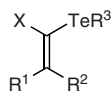
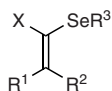
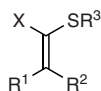
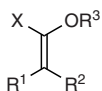
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24.2.20 1,1-Bis(heteroatom-functionalized) Alk-1-enes (Update 1)

P. Beier

This chapter is an update to the earlier *Science of Synthesis* contributions describing 1-haloalk-1-enes that bear an oxygen (Section 24.2.2), chalcogen (Section 24.2.3), nitrogen (Section 24.2.4), or phosphorus substituent (Section 24.2.5) at the 1-position. This review focuses on literature published in the period 2005–2013.



X = halogen

Keywords: alkenes · halo compounds · oxygen compounds · chalcogen compounds · nitrogen compounds · phosphorus compounds

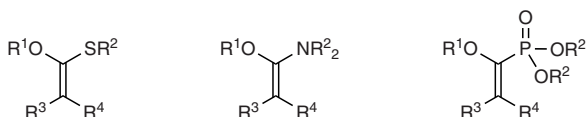
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24.2.21 **1,1-Bis(heteroatom-functionalized) Alk-1-enes (Update 2)**

M. H. Vilhelmsen

This chapter is an update to the existing *Science of Synthesis* contributions on the synthesis of ketene *O,S*-acetals (Section 24.2.7), ketene *O,N*-acetals (Section 24.2.9), and (1-alkoxyalk-1-enyl)phosphonates (enolphosphonates, Section 24.2.10). The reviewed synthetic methodologies are from literature published since 2005.



Keywords: (1-alkoxyalk-1-enyl)phosphonates · ketene *O,S*-acetals · ketene *O,N*-acetals · enolphosphonates · ring-opening reactions · carbohydrates · heterocycles

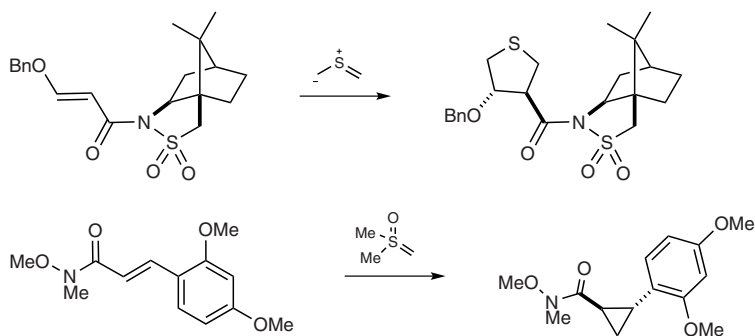
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27.1.6 **Sulfur Ylides**

G. Mlostoń and H. Heimgartner

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the in situ generation of thiocarbonyl ylides and Corey–Chaykovsky reagents (sulfonium and sulfoxonium methylides). Whereas thiocarbonyl ylides react as electron-rich 1,3-dipoles, Corey–Chaykovsky reagents act as methylene-transfer agents. The most relevant application of thiocarbonyl ylides relates to the synthesis of tetrahydrothiophene (thiolane) and 1,3-dithiolane derivatives, via [3 + 2]-cycloaddition reactions with electron-deficient C,C and C,S dipolarophiles, respectively. In the last decade, Corey–Chaykovsky reagents have been widely applied for cyclopropanation, epoxidation, and aziridination, as well as for diverse heterocyclization reactions. In all cases, asymmetric versions of the applied protocols are of great interest.



Keywords: aziridination · cyclopropanation · cycloaddition · five-membered rings · sulfur heterocycles · sulfides · sulfur ylides · thiiranes · thiones

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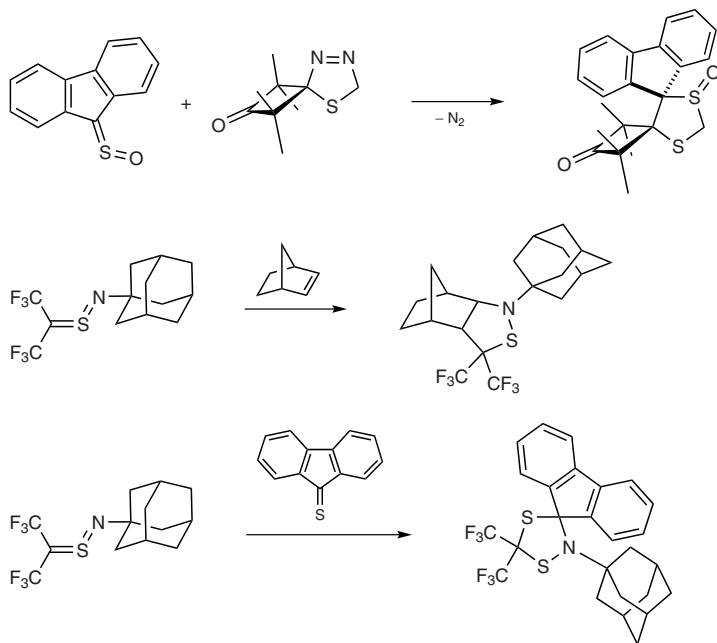
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27.4.3

Thioaldehyde and Thioketone S-Oxides and S-Imides (Sulfines and Derivatives)

G. Mlostoń and H. Heimgartner

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods of synthesis and new applications for thiocarbonyl S-oxides (sulfines) and thiocarbonyl S-imides. In general, thiocarbonyl S-oxides are more stable and in many instances can be isolated. The in situ generated thiocarbonyl S-imides are efficient “sulfur-transfer agents” via the isomeric thiaziridines, formed as products of electrocyclic ring closure. Stable thiocarbonyl S-imides, derived from hexafluorothioacetone, are useful 1,3-dipoles and are applied in the preparation of fluorinated five-membered heterocycles.



Keywords: thiazolidines · cycloaddition · five-membered rings · oxidation · small-ring systems · thiones

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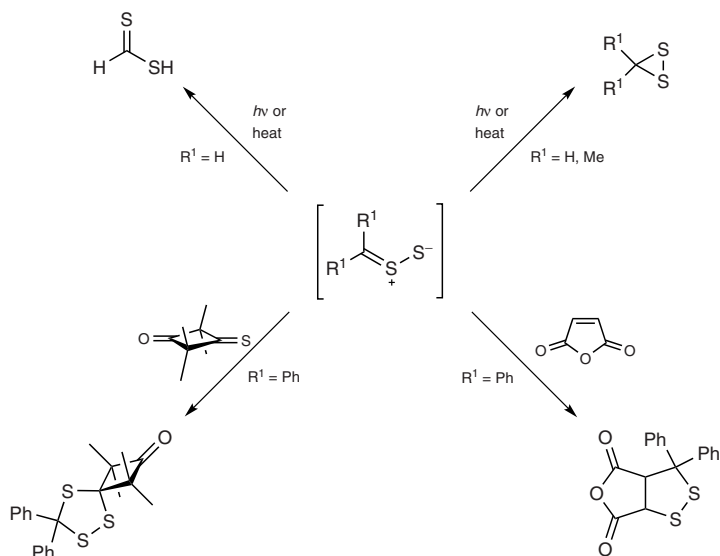
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27.26

Product Class 26: Thioaldehyde and Thioketone S-Sulfides (Thiosulfines)*G. Mlostoń and H. Heimgartner*

This chapter is an overview of methods for the in situ generation and application of highly reactive thiocarbonyl *S*-sulfides. Typically, thiocarbonyl *S*-sulfides react as sulfur-rich 1,3-dipoles and trap both electron-deficient C,C-dipolarophiles and thiocarbonyl substrates, yielding the corresponding five-membered cycloadducts. In some instances, intermediate thiocarbonyl *S*-sulfides and/or their cyclic isomers (i.e., dithiiranes) act as sulfur-transfer agents leading to sulfur-rich heterocycles such as pentathiepanes and hexathiepanes.



Keywords: dipolar cycloaddition · dithiolanes · five-membered rings · multicomponent reactions · sulfur heterocycles · thiones

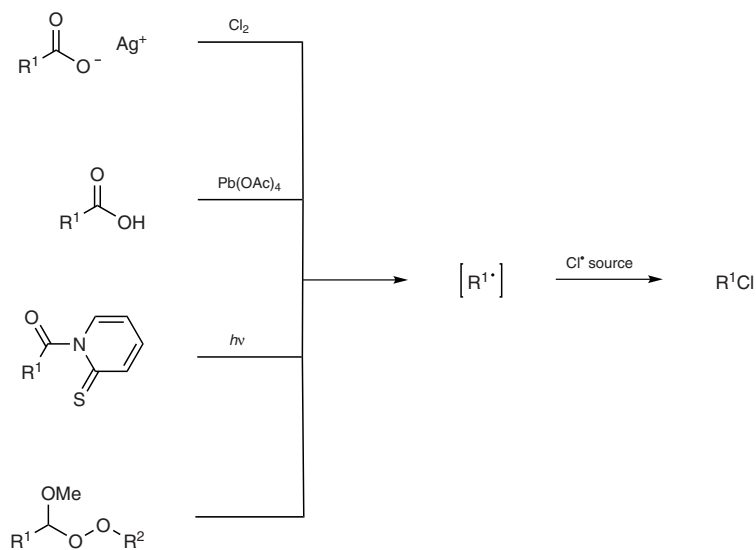
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35.1.1.3.5 **Synthesis by Substitution of Carbon Functionalities**

P. Margaretha

This update summarizes reactions wherein an alkyl radical is formed by cleavage of an appropriately functionalized C—C bond, followed by trapping of this intermediate by a chlorine atom source to afford a chloroalkane. It covers the literature up until late 2013.



Keywords: chlorination · radicals · carboxylic acids · silver carboxylates · decarboxylation · Hunsdiecker reaction · Kochi reaction · Barton reaction · 1-(acyloxy)pyridine-2-(1H)-thiones · Barton esters · peroxyacetals

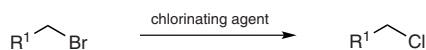
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35.1.1.4.3 **Synthesis by Substitution of Other Halogens**

P. Margaretha

This is an update to *Science of Synthesis* Section 35.1.1.4, describing the synthesis of chloroalkanes from other haloalkanes, and covers the literature up until late 2013.



Keywords: chlorination · substitution · halogen exchange

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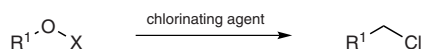
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35.1.1.5.13 **Synthesis by Substitution of Oxygen Functionalities**

P. Margaretha

This update summarizes reactions wherein compounds containing C–O bonds are transformed into chloroalkanes via nucleophilic substitution at the sp³-hybridized carbon atom. It covers the literature up until late 2013.

X = H, SO₂R²

Keywords: substitution · chlorination · chloroformates · decarboxylation · sulfonates · alcohols · chlorodehydroxylation

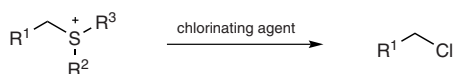
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35.1.1.6.2 **Synthesis by Substitution of Sulfur, Selenium, or Tellurium Functionalities**

P. Margaretha

This is an update to *Science of Synthesis* Section 35.1.1.6, describing the synthesis of chloroalkenes from sulfur-, selenium-, or tellurium-substituted alkyl compounds and covers the literature up until late 2013.



Keywords: chlorination · substitution · halogen exchange · halogenase · methionine

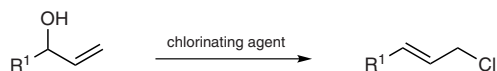
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35.1.4.2.4 **Synthesis by Substitution of σ-Bonded Heteroatoms**

P. Margaretha

This update summarizes reactions wherein allylic alcohols (or their anions) are transformed into rearranged allylic chlorides via an S_N2'-reaction. It covers the literature up until late 2013.



Keywords: chlorination · allylic alcohols · allylic chlorides · substitution · rearrangement · methylenecyclohexanes · cyclohexenes · alkoxides

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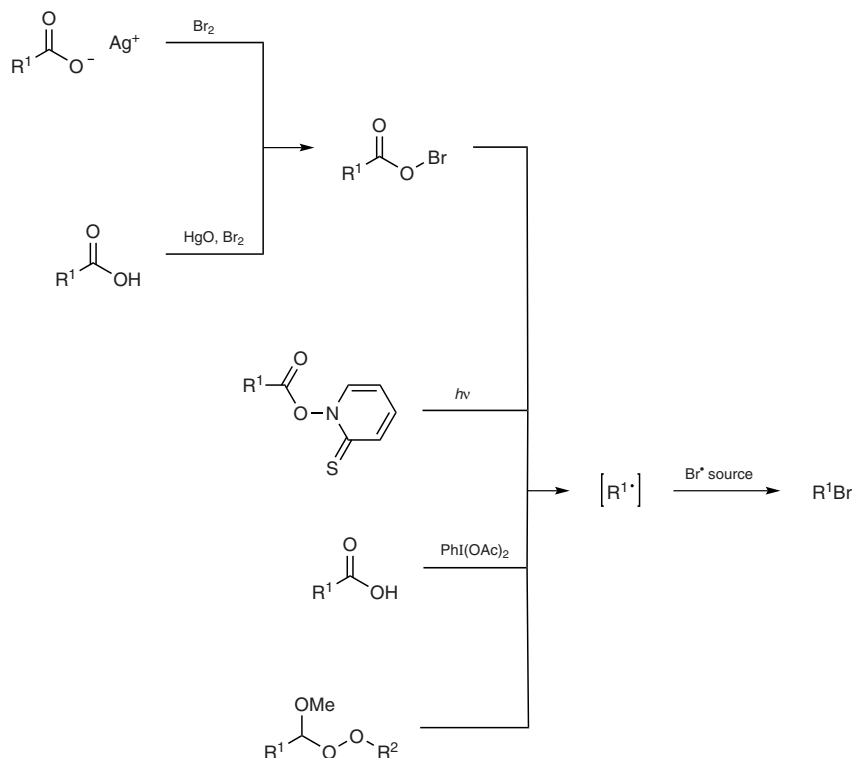
New Contributions

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35.2.1.3.5 **Synthesis by Substitution of Carbon Functionalities***P. Margaretha*

This update summarizes reactions wherein an alkyl radical is formed by cleavage of an appropriately functionalized C–C bond, followed by trapping of this intermediate by a bromine atom source to afford a bromoalkane. It covers the literature up until late 2013.



Keywords: bromination · radicals · carboxylic acids · silver carboxylates · decarboxylation · Hunsdiecker reaction · Cristol–Firth reaction · Barton reaction · 1-(acyloxy)pyridine-2-(1H)-thiones · Barton esters · peroxyacetals

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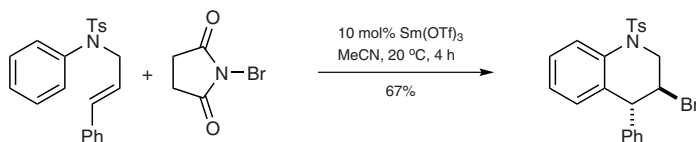
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35.2.1.8.10 **Synthesis by Addition to π -Type C—C Bonds**

Q. Yin and S.-L. You

This is an update to the earlier *Science of Synthesis* contribution (Section 35.2.1.8) on the preparation of bromoalkanes by additions to π -type C—C bonds, covering material published from 2004 to the end of 2013. Methods for carbobromination, including bromocyclization and asymmetric intramolecular carbobromination, are presented.



Keywords: bromocyclization · enantioselective · Friedel–Crafts · oxindole · polyene · spirocyclohexadienone · semipinacol rearrangement

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