

## Abstracts

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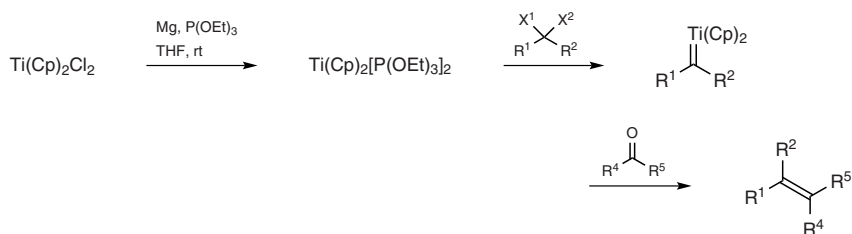
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## 2.10.18 Organometallic Complexes of Titanium

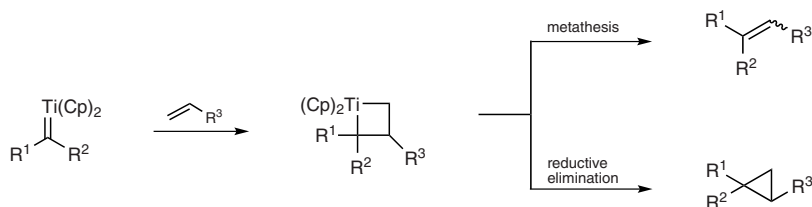
T. Takeda and A. Tsubouchi

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the preparation of organometallic complexes of titanium. Section 2.10.18.1 focuses on the preparation of titanocene alkylidenes by the reductive titaniation of thioacetals, *gem*-dihalides, and alkyl halides, and their synthetic application in carbonyl alkenation reactions.

Section 2.10.18.2 highlights the preparation of titanocene derivatives of metallacyclobutanes derived from titanocene alkylidenes and alkenes, and their synthetic application, mainly in the metathesis reaction. Other types of degradation of titanacyclobutanes such as reductive elimination and  $\beta$ -hydride elimination are also included. In connection with alkene metathesis, titanacyclobutenes, which are intermediates for enyne metathesis, are also discussed.



$\text{X}^1 = \text{SR}^3$ , halogen;  $\text{X}^2 = \text{SR}^3$ , halogen, H



**Keywords:** alkenation · alkene metathesis · alkenes · alkenylcyclopropanes · carbene complexes · conjugate dienes ·  $\beta$ -hydride elimination · reductive titaniation · titanacyclobutanes · titanacyclobutenes · titanium complexes · titanocenes

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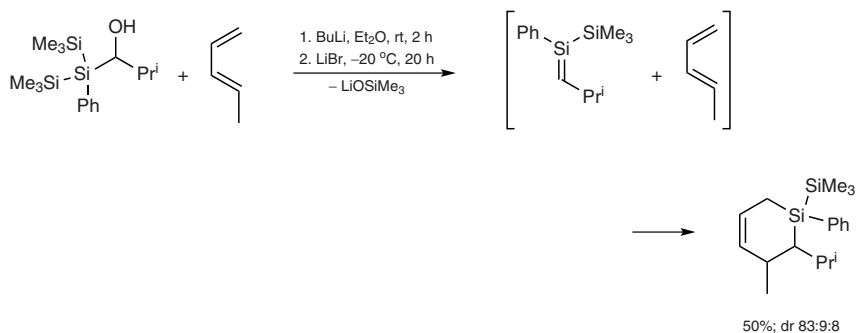
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## 4.4.2.5 Silenes (Update 1)

H. Ottosson and A. M. Rouf

The topic of this update is synthesis of silenes, compounds with Si=C bonds, which are generally highly reactive and sensitive to the ambient atmosphere. Synthetic routes published since 2001 yielding either persistent silenes or transient silenes that can be trapped by suitable reagents are discussed. Both novel routes and modifications of earlier established routes, now employing less forcing conditions than previously reported, are covered.



**Keywords:** silicon compounds · silenes · unsaturated compounds · lithium compounds · rearrangement · Peterson alkenation · elimination · isomerization

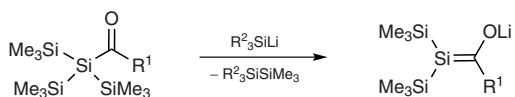
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## 4.4.2.6 Silenes (Update 2)

H. Ottosson and J. Ohshita

This section describes the synthesis of silen-2-olates, silicon analogues of enolates with formal Si=C bonds, for example through trimethylsilyl–metal exchange of acylpolysilanes using organolithium or organopotassium reagents. The fundamental reactions of silenolates and the structural differences between silenolates dominated by keto-form versus enol-form resonance structures are also presented.

R<sup>1</sup> = tertiary alkyl, aryl, acyl

**Keywords:** silicon compounds · silenes · silenolates · silyl anions · lithium compounds · potassium compounds · mercury compounds · silyl–metal exchange

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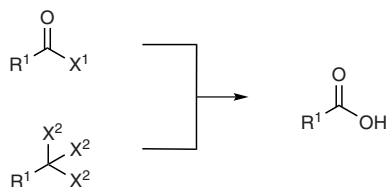
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20.2.1.2.10 **Synthesis from Carboxylic Acid Derivatives**

A. K. Mourad and C. Czekelius

This manuscript is an update to the earlier *Science of Synthesis* contribution describing general methods to synthesize carboxylic acids from their derivatives. This update addresses more specific methods, new developments, and transformations of carboxylic acid derivatives which were not covered in the original contribution.



$X^1 = OR^2, OSiR^2_3, NHNHR^2, NHNR^2_2$   
 $X^2 = F, Cl, Br$

**Keywords:** acid catalysts · carboxylic acid derivatives · carboxylic acids · enzyme catalysis · esters · halo compounds · hydrazides · hydrolysis · oxidative cleavage · photolysis · reductive cleavage · silyl esters

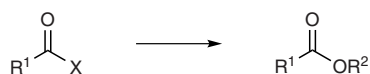
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20.5.1.2.8 **Synthesis from Carboxylic Acids and Derivatives**

A. K. Mourad and C. Czekelius

This manuscript is an update to the earlier *Science of Synthesis* contribution describing general methods to synthesize esters from carboxylic acids and their derivatives. This update addresses more specific methods, new developments, and transformations of carboxylic acid derivatives which were not covered in the original contribution.



$X = OH, SR^2, NHNHR^2$

**Keywords:** alkylations · carboxylic acid derivatives · carboxylic acids · enzyme catalysis · esters · halo compounds · hydrazides · oxidative cleavage · thioesters

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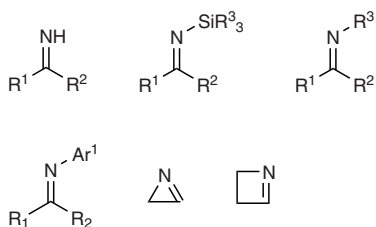
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27.7.6

**Imines***S. Dekeukeleire, M. D'hooghe, and N. De Kimpe*

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of imines. It focuses on the literature published in the period 2004–2010.



**Keywords:** 2*H*-azirines · imines · *N*-unsubstituted imines · *N*-silyl imines · *N*-alkyl imines · *N*-aryl imines · 2,3-dihydroazetes · imino esters · nitrogen heterocycles · synthesis design

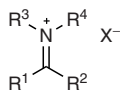
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27.8.2

**Iminium Salts***S. Dekeukeleire, M. D'hooghe, and N. De Kimpe*

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of iminium salts. It focuses on the literature published in the period 2004–2010.



**Keywords:** iminium salts · nitrogen heterocycles · synthesis design

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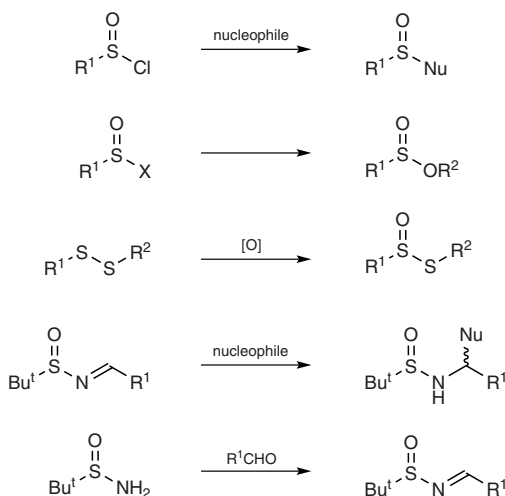
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## 39.3.9 Alkanesulfinic Acids and Acyclic Derivatives

R. Kawęcki

This chapter is an update to the earlier *Science of Synthesis*, Section 39.3, describing the synthesis and applications of alkanesulfinic acids and acyclic derivatives. It includes discussion of the applications of alkanesulfinyl halides and the synthesis of alkanesulfinic acid esters, alkanethiosulfinic acid esters, and alkanesulfinamides, focusing on the literature in the period 2006–2010.

It also contains an extension of the coverage of the previous contribution describing the synthesis and applications of *N*-alkylidenealkanesulfinamides, here focusing on literature in the period 1997–2010.



**Keywords:** sulfinyl halides · sulfinic acid esters · sulfinates · sulfinylation · sulfoxides · aziridines · asymmetric synthesis · boron trichloride complexes · thiosulfinic acid esters · thiosulfinates · disulfides · asymmetric oxidation · sulfinamides · *N*-sulfinylimines · sulfinimines · 1,2-addition · allylation · nucleophilic addition · imines

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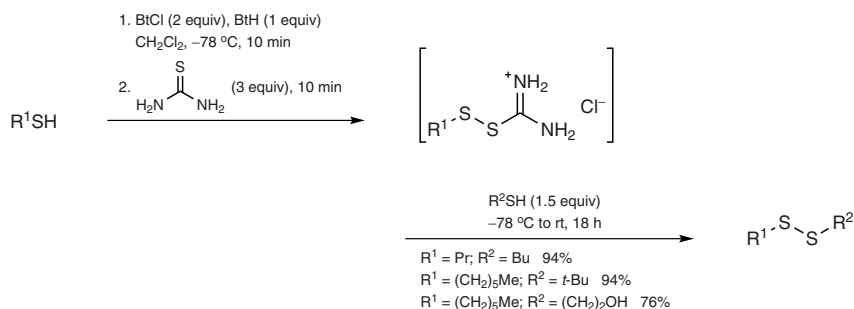
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## 39.5.2 Alkanethiols

D. Witt

This manuscript is an update to the earlier *Science of Synthesis* contribution on alkanethiols, and describes applications of alkanethiols as a starting material in organic synthesis. Thiols can be converted into sulfonic, sulfinic, and sulfenic acids and their derivatives, as well as sulfides, disulfides, polysulfides, sulfonium salts, and thiiranes, etc. These transformations are accomplished by nucleophilic displacement or addition, oxidation, condensation, or coupling reactions involving the thiol group.



**Keywords:** alkanethiols · organosulfur compounds · sulfur electrophiles · sulfur functional groups · sulfur nucleophiles · sulfur oxidation states

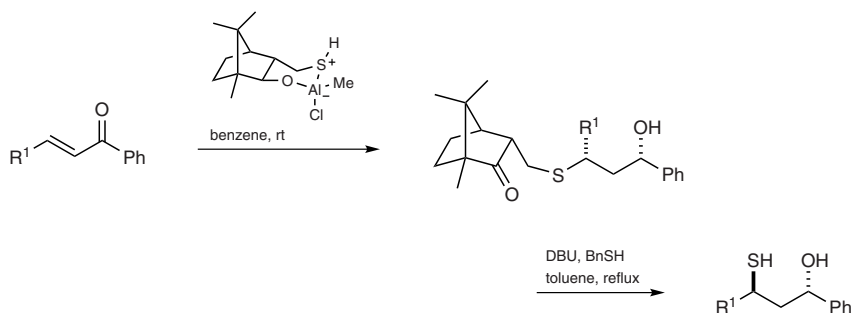
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## 39.6.1.2 Alkanethiolates of Group 1, 2, and 13–15 Metals

D. Witt

This update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of alkanethiolates of group 1, 2, and 13–15 metals focuses on applications of these compounds in organic synthesis. Alkanethiolates can be converted into *S*-alkyl thiocarboxylates, 1-thioglycosides, *S*-alkyl thiosulfonates, tetrahydro-1,4-thiazin-3-ones, sulfides, disulfides, sulfonium salts, dithioacetals, and dithioketals. These transformations are accomplished by nucleophilic displacement or addition, condensation, or coupling reactions involving the thiolate group.



**Keywords:** alkanethiolates · *S*-alkyl thiocarboxylates · disulfides · dithioacetals · dithioketals · organosulfur compounds · sulfur electrophiles · sulfides · sulfonium salts · sulfur nucleophiles · thioacetals · 1-thioglycosides

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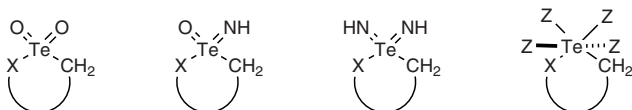
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39.39.1 **Product Subclass 1: Cyclic Alkanetelluronic Acid Derivatives***T. Kimura*

The topic of this section is cyclic compounds with one or more tellurium atoms, where the tellurium atom bears one  $sp^3$  carbon atom, two tellurium–heteroatom double bonds ( $Te=O$  or  $Te=N$ ), and one  $Te-X$  single bond ( $X = O, NR^1, S, \text{etc.}; R^1 = H$  or other substituent); or one  $sp^3$  carbon atom and five single bonds: one  $Te-X$  and four  $Te-Z$  ( $Z = OR^1, NR^1_2, SR^1$ , halogen, etc.;  $R^1 = H$  or other substituent). Thus, this product subclass contains cyclic telluronic acid esters, cyclic telluronic acid thioesters, cyclic telluronic acid amides, and their derivatives. However, at present, no examples of such compounds have been prepared in a stable form.



$X = O, NR^1, S; Z = OR^1, NR^1_2, SR^1, \text{halogen}$

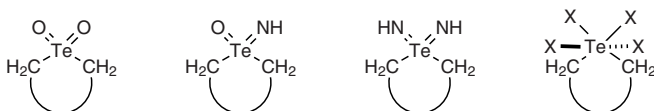
**Keywords:** tellurium · telluronic acid esters · telluronic acid thioesters · telluronic acid amides

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39.39.2 **Product Subclass 2: Cyclic Dialkyl Tellurones and Derivatives***T. Kimura*

This section describes the synthesis of cyclic compounds with one or more tellurium atoms, where a tellurium atom bridges two  $sp^3$  carbon atoms to form a cyclic structure and this tellurium atom has two tellurium–heteroatom double bonds ( $Te=O$  or  $Te=N$ ). Thus, this product subclass contains cyclic tellurones, cyclic telluroximides, cyclic telluronediiimines, and cyclic dialkyl tetrasubstituted  $\lambda^6$ -tellanes. At present, no examples of cyclic telluroximides or cyclic telluronediiimines have been prepared in a stable form.



$X = O, NR^1_2, SR^1_2, \text{halogen}$

**Keywords:** tellurium · cyclic tellurones · cyclic telluroximides · telluronic acid amides · cyclic dialkyl- $\lambda^6$ -tellanes

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40.1.1.5.5 **Metal-Mediated Cyclizations of Amines***J. Ipaktschi and M. R. Saidi*

This review summarizes the transition-metal-catalyzed reactions of N-tethered 1,n-enynes, 1,n-diyne, and 1,n-dienes. The emphasis of the review is on the presentation of useful methods for the synthesis of nitrogen-containing heterocycles. Enyne cycloisomerization without and with skeletal reorganization, metathesis of N-tethered dienes and

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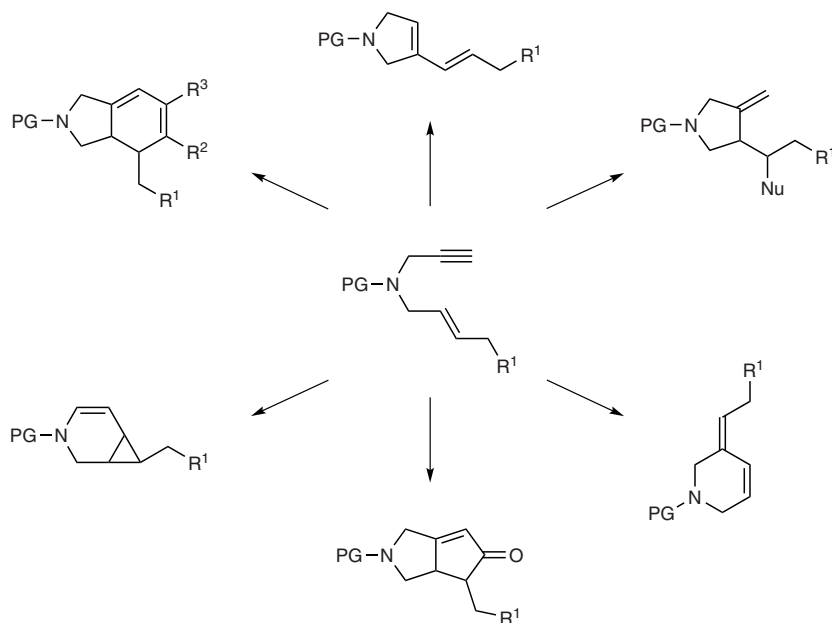
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enynes, and transition-metal-catalyzed cycloaddition reactions are discussed in the earlier parts of the review. In later parts, the Mizoroki–Heck reactions of amines and amides and palladium-mediated cascade cross coupling/electrocyclization are discussed with regard to construction of fused bi- and tricyclic nitrogen-containing systems.



**Keywords:** nitrogen heterocycles · enynes · cycloisomerization · rearrangement · homogeneous catalysis · asymmetric catalysis · aqueous media · alkene metathesis · enantioselectivity · metallacycles · reductive cyclization · natural products · transition metals · nickel · iron · palladium · rhodium · ruthenium · molybdenum · silver · gold