#### **Abstracts**

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#### 3.6.11 Organometallic Complexes of Gold (Update 1)

V. López-Carrillo and A. M. Echavarren

The topic of this update is gold-catalyzed cycloisomerization of enynes.

Gold(I) catalysts are the most alkynophilic amongst the electrophilic metals that catalyze the cyclization of 1,n-enynes leading to a wide diversity of cyclic structures under mild conditions. This section reviews the major gold-catalyzed cycloisomerization pathways as well as cyclization reactions that occur with concomitant addition of heteroand carbonucleophiles.

$$Z \xrightarrow{R^3} \xrightarrow{AuL^+} \xrightarrow{S-exo-dig} Z \xrightarrow{R^2} \xrightarrow{AuL^+} \xrightarrow{AuL^+} \xrightarrow{G-endo-dig} Z \xrightarrow{R^1} \xrightarrow{R^3} \xrightarrow{R^3} \xrightarrow{R^2} \xrightarrow{R^4}$$

**Keywords:** gold  $\cdot$  enynes  $\cdot$  alkynes  $\cdot$  cyclization  $\cdot$  cycloisomerization  $\cdot$  rearrangement

### 3.6.12 Organometallic Complexes of Gold (Update 2) L. Zhang

The topic of this update is gold-catalyzed propargylic rearrangement.

Gold-catalyzed 3,3-rearrangements of propargylic carboxylates lead to the formation of carboxyallenes, which can subsequently undergo a range of fascinating in situ transformations, leading to various versatile functional structures.

**Keywords:** gold  $\cdot$  catalysis  $\cdot$  rearrangement  $\cdot$  oxidation  $\cdot$  cross coupling  $\cdot$  cyclization  $\cdot$  nucleophile  $\cdot$  electrophile  $\cdot$  oxocarbenium  $\cdot$  propargyl  $\cdot$  allene  $\cdot$  enyne  $\cdot$  diene



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### 3.6.13 Organometallic Complexes of Gold (Update 3)

M. N. Hopkinson and V. Gouverneur

The topic of this update is gold-catalyzed coupling reactions.

This chapter covers homo- and cross-coupling reactions mediated by gold complexes under homogeneous conditions. In the first two sections, coupling reactions mediated by stoichiometric gold(III) complexes and catalytic cross-coupling reactions involving oxidative addition to gold(I) are presented. This is followed in the subsequent two sections by a discussion of recently developed gold-catalyzed homo- and cross-coupling processes using external oxidants.

**Keywords:** gold  $\cdot$  cross coupling  $\cdot$  homocoupling  $\cdot$  carbon—carbon bond formation  $\cdot$  oxidation  $\cdot$  cascade reactions  $\cdot$  C—H functionalization  $\cdot$  cyclization  $\cdot$  rearrangement  $\cdot$  fluorination

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### 5.2.27 **Product Subclass 27: Benzylstannanes**

I. S. Snaith

This manuscript is a revision of an earlier *Science of Synthesis* contribution describing methods for the synthesis of benzylstannanes. The principal routes to benzylstannanes are discussed, the most important being those involving stannyl metal species and benzyl halides or benzyl metal species and stannyl halides, including Barbier reactions. Also discussed are methods for the synthesis of enantiomerically enriched benzylstannanes via enantioselective deprotonation and stannylation at benzylic centers.

$$Ar^{1} X \xrightarrow{R^{1}_{3}SnLi} Ar^{1} SnR^{1}_{3} \xrightarrow{R^{1}_{3}SnCl} Ar^{1} Li$$
 $X = Cl, Br$ 

**Keywords:** Barbier reaction  $\cdot$  benzylic compounds  $\cdot$  C—Sn bonds  $\cdot$  Grignard reagents  $\cdot$  lithium compounds  $\cdot$  stannanes  $\cdot$  Stille coupling  $\cdot$  transmetalation  $\cdot$  tin compounds



# 5.2.28 **Product Subclass 28: AllyIstannanes** *I. S. Snaith*

This manuscript is a revision of an earlier *Science of Synthesis* contribution describing methods for the synthesis of allylstannanes. The principal routes to allylstannanes are discussed, with the most important being those involving stannylmetal species and allyl halides or allylmetal species and stannyl halides, including Barbier reactions. Other important methods discussed include palladium-catalyzed reactions with allylic acetates, reactions of allylic sulfur derivatives, eliminations, stannylation of allenes, and the reaction of stannyl anion equivalents with carbonyls.

X = CI, Br

**Keywords:** allylstannanes  $\cdot$  stannanes  $\cdot$  Barbier reaction  $\cdot$  carbon—tin bonds  $\cdot$  allylic compounds  $\cdot$  Grignard reagents  $\cdot$  lithium compounds  $\cdot$  tin compounds  $\cdot$  Stille coupling  $\cdot$  transmetalation  $\cdot$  allylation  $\cdot$  radicals

X.-L. Hou, X.-S. Peng, K.-S. Yeung, and H. N. C. Wong

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of substituted furans. It focuses on the literature published between 1999 and early 2010.

**Keywords:** substituted furans  $\cdot$  cyclization  $\cdot$  cycloisomerization  $\cdot$  electrophilic  $\cdot$  nucleophilic  $\cdot$  replacement  $\cdot$  catalytic  $\cdot$  multicomponent reaction  $\cdot$  coupling reaction  $\cdot$  regioselectivity  $\cdot$  rearrangement



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### Thiophenes, Thiophene 1,1-Dioxides, and Thiophene 1-Oxides

J. Schatz and M. Seßler

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of thiophenes. The main focus lies on modern synthetic transformations, such as transition-metal-mediated coupling reactions, leading to functionalized thiophenes. Owing to the increasing interest in organic materials based on the thiophene skeleton, oligothiophenes are discussed separately within this manuscript, in Section 9.10.4.2.

**Keywords:** thiophenes  $\cdot$  five-membered rings  $\cdot$  ring formation  $\cdot$  halogenation  $\cdot$  oxidation  $\cdot$  cross-coupling reactions  $\cdot$  oligomerizations

# 20.5.1.7.15 Synthesis with Retention of the Functional Group

G. Landelle and J.-F. Paquin

This manuscript is an update to the earlier *Science of Synthesis* contribution describing methods for the conjugate addition to unsaturated esters. It focuses on the literature published in the period 1990–2010.

 $R^1 = H$ , Me, Ph, 4-MeOC<sub>6</sub>H<sub>4</sub>, 4-BrC<sub>6</sub>H<sub>4</sub>;  $R^2 = Me$ , Et;  $R^3 = Bn$ , 4-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>, CHPhMe

**Keywords:** conjugate addition  $\cdot$  carboxylic esters  $\cdot$  unsaturated compounds  $\cdot$  organometallic reagents  $\cdot$  stereoselectivity  $\cdot$  regioselectivity

# 39.1.15 Alkanesulfonic Acids and Acyclic Derivatives P. Łyżwa

This section describes the applications of alkanesulfonyl halides in organic synthesis, for example their use as protecting groups, in the synthesis of thiols, disulfides, sulfinic acids, sulfones, in C—C and C=C bond-forming reactions, epoxidation, and lactone inversion.

 $R^1$  = Bn,  $CH_2CMe=CH_2$ ;  $R^2$  = H,  $NO_2$ ;  $R^3$  = H, Me

**Keywords:** alcohols  $\cdot$  amines  $\cdot$  alkanethiols  $\cdot$  dialkyl disulfides  $\cdot$  sulfones  $\cdot$  cyclization  $\cdot$  inversion  $\cdot$  aldehydes  $\cdot$  thioacetals