

Abstract

“Organometallic Chemistry directed towards Organic Synthesis” (OMCOS) is the topic of current interest. In several cases the concept is applied for the coupling between an organometallic intermediate with an organic halide or its surrogates leading to synthetically meaningful carbon-carbon and carbon-heteroatom bond formation. Among the reactive organotin(IV) intermediates, allylstannanes are widely exploited in organic synthesis. The recent trend pays attention towards in-situ generation of allylstannane catalyzed by a transition metal, and subsequent coupling with organic electrophile in one-pot, which has proven utility for the synthesis of important structural subunits. Generation of organotin(IV) under Schlenk-free condition, and in presence of water and air continues to evoke interest from the view of Green chemistry and processes. Mechanistic elaboration towards tin-carbon bond formation under such conditions is yet another area of active interest.

The thesis entitled “**Tuning The Reactivity Of Tin(II) By Transition Metal Catalysts: An Organometallic Approach Towards C-C, C-S, & C-Se Bond Formation**” is primarily an effort towards the development of new synthetic strategies for the formation of carbon-carbon and carbon-heteroatom bond by exploiting the reactivity of tin(II) under the aegis of a transition metal catalyst. Efforts have also been made to understand the initial steps in the catalytic cycles. The deliberations are presented in four major chapters:

- Chapter 1.** Allylstannanes via transient or catalytic organotransition metal intermediates: Recent developments in carbon-carbon bond forming reactions
- Chapter 2.** Carbon-carbon bond formation mediated by tin(II) & transition metal catalysts

- Part A:** Barbier like carbonyl allylation over an oxide reagent comprising of β -SnO & catalytic palladium(0) or platinum(II) complex
- Part B:** Barbier like carbonyl allylation over an all-oxide reagent comprising of β -SnO & catalytic Cu_2O
- Chapter 3.** Barbier like allylation of epoxides mediated by SnCl_2 & catalytic palladium(0) complex
- Chapter 4.** Carbon-heteroatom bond formation mediated by tin(II) & transition metal catalyst
- Part A:** Activation of sulfur via novel copper(II)/tin(II) reagent
- Part B:** Activation of selenium via novel copper(II)/tin(II) reagent

Chapter 1. Allylstannanes via transient or catalytic organotransition metal intermediates: Recent developments in carbon-carbon bond forming reactions

This chapter consists of a brief overview on recent developments in transition metal catalyzed generation of allylstannanes and their applications in organic synthesis. Available literature on spectroscopic diagnosis of in-situ generated allylstannanes is also discussed.

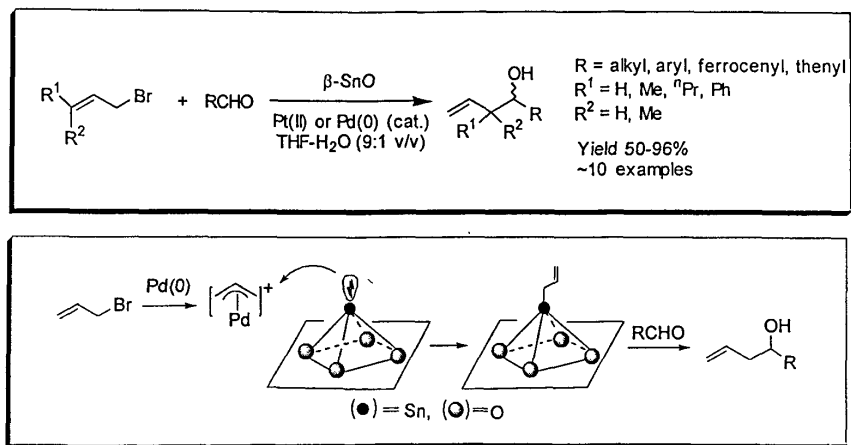
Chapter 2. Carbon-carbon bond formation mediated by tin(II) & transition metal catalysts

This chapter delineates the synthesis of homoallylic alcohols, an important class of organic compounds, using allyl halides and carbonyl compounds mediated by tetragonal blue-black tin(II) oxide (β -SnO) and catalytic platinum(II), palladium(0), copper(I), salts/complexes using Barbier-like protocol. The work is presented in two sub-chapters.

- Part A:** Barbier like carbonyl allylation over an oxide reagent comprising of β -SnO & catalytic palladium(0) or platinum(II) complex

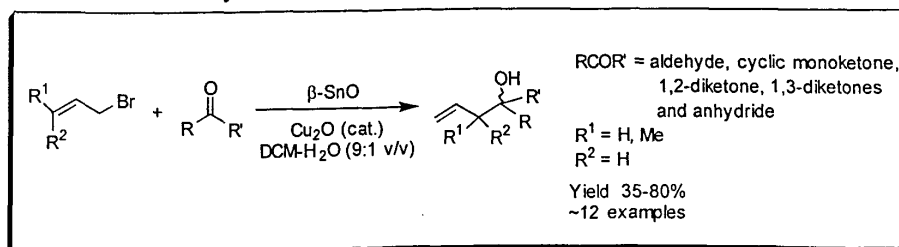
This chapter delineates our efforts in executing a redox-transmetallation

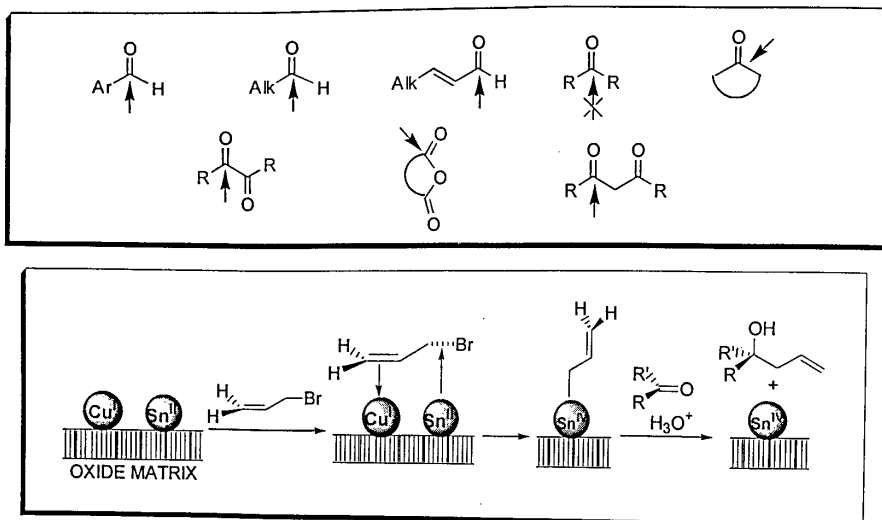
strategy to promote allyl transfer from allyl-palladium and platinum to tetragonal tin(II) oxide (β -SnO), and further utilizing the in-situ generated allylstannane towards carbonyl allylation. The reaction leads to the facile formation of homoallylic alcohols by a γ -regioselective SE2' allylation pathway. The pronounced effect of water in promoting the reaction is noteworthy. The formation of a σ -allyltin species via π -allylpalladium intermediate is suggested by ^1H NMR, and EIMS studies.



Part B: Barbier like carbonyl allylation over an all-oxide reagent comprising of β -SnO & catalytic Cu_2O

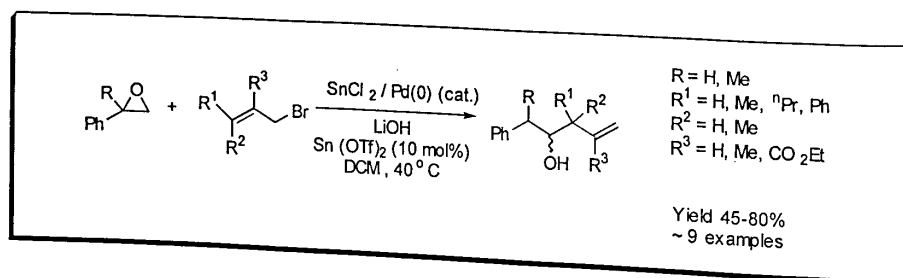
Further extension of the above methodology to β -SnO/catalytic copper(I) oxide affords an *all-oxide* reagent in Barbier allylation. The intermediate allylstannane shows interesting carbonyl selectivity. The interaction of allyl halide with β -SnO in presence or absence of Cu_2O has been studied by XPS and XRD, which indicates the prior interaction of allyl bromide with copper(I) and tin(II).

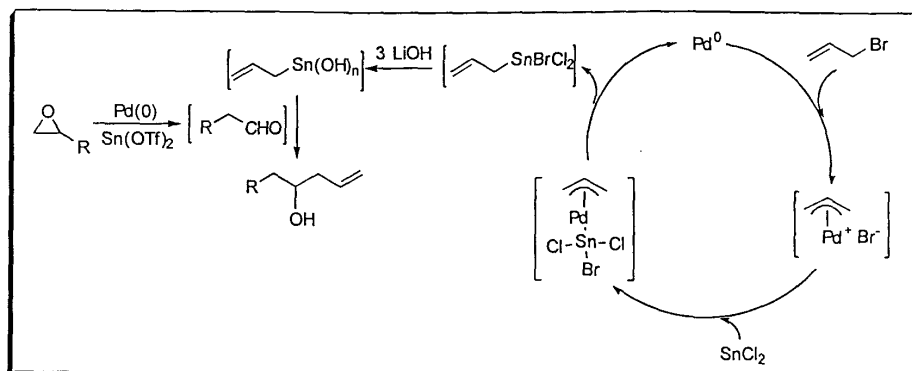




Chapter 3. Barbier like allylation of epoxides mediated by of SnCl₂ & catalytic palladium(0) complex

Presented in this chapter is an one pot protocol for the allylation of epoxides from allyl halide using SnCl₂ and catalytic palladium(0). A dramatic effect of lithium hydroxide is observed in promoting the reactivity of allyltin(IV) leading to formation of homoallylic alcohols. The plausible mechanism includes (a) the formation of allylhydroxytin(IV) species, and (b) rearrangement of 1-aryl-oxiranes to corresponding benzylic aldehydes.



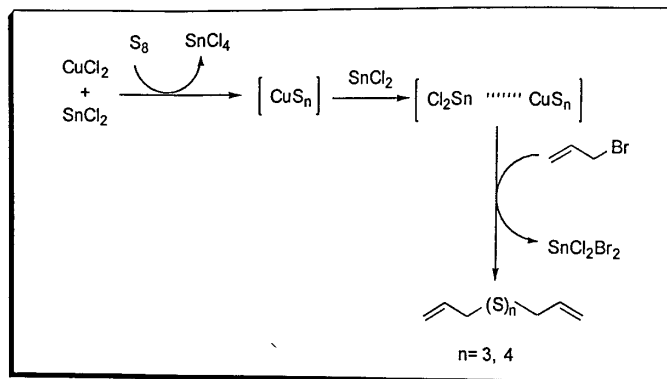
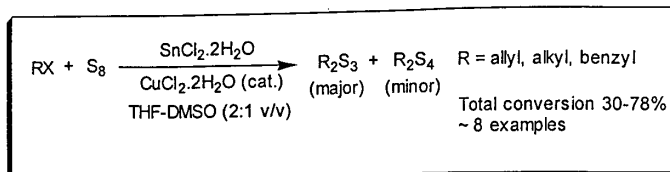


Chapter 4: Carbon-heteroatom bond formation mediated by tin(II) & transition metal catalyst

The metal assisted cleavage of dichalcogenide bond is an area of significant mechanistic and synthetic interests among organic and inorganic chemists alike. In continuation to our ongoing interest in exploring the bimetallic reactivity of tin(II)/copper(II) reagent towards carbon-chalcogenide bond formation, the present work describes the activation of elemental sulfur and selenium. The work is presented in two sub-chapters.

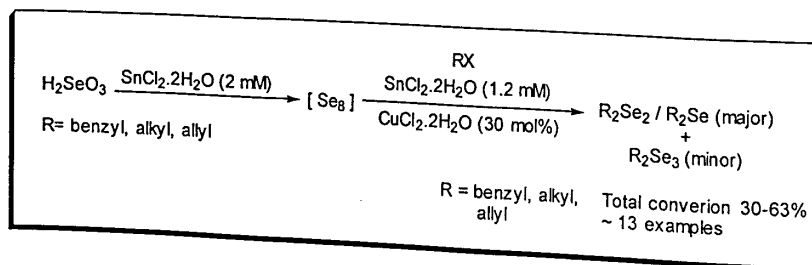
Part A: Activation of sulfur via novel copper(II)/tin(II) reagent

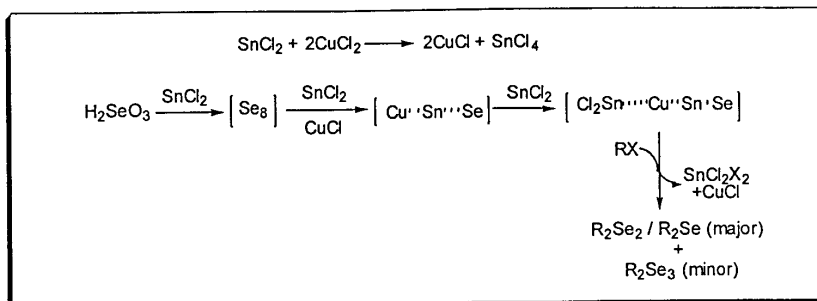
In this chapter, we present a novel finding pertaining to the reactivity of copper(II)/tin(II) reagent towards the activation of elemental sulfur leading to the facile formation of trisulfides as the major product and tetrasulfides as minor product. Based upon mechanistic investigations and EPR, IR, XRD studies a distinct “copper effect” is observed in controlling the reactivity, and the reaction is believed to mediate via a copper-thiolate intermediate.



Part B: Activation of selenium via novel copper(II)/tin(II) reagent

The success in S-S cleavage reaction prompted us to study the activation of red-selenium with organic halides in presence of copper(II)/tin(II) reagent leading to the formation of symmetrical diorganoselenide and diorganodiselenide as the major product and diorganotriselenide as minor product. Elemental red-selenium was generated in-situ from selenous acid. Preliminary study establishes the catalytic role of copper and demonstrates that generation of a trimetallic 'Cu-Sn-Se' intermediate is the key step for the selenium-transfer reaction.





Finally a summary of the main results of the work and scope for the future investigation is presented.