

# Organic Functional Group Transformations

CHM3A2-II

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## Course Synopsis

The vast majority of transformations in organic chemistry involve bond-forming processes between carbon, hydrogen, oxygen and nitrogen atoms. Organic chemists, however, are not restricted to using just these elements for carrying out a reaction; on the contrary they have the whole periodic table at their disposal for ensuring a desired transformation is accomplished with the requisite high levels of chemo-, regio- and stereoselectivity. Main group elements in particular boron, silicon, tin, sulfur and phosphorus, are widely exploited in organic synthesis for effecting a variety of reactions. This eight-lecture course will discuss some of the more important uses of these elements in key functional group manipulations. Since most transformations can be achieved in a number of ways using a variety of elements, the course will be taught according to reaction type. This approach will allow the similarities and, perhaps more importantly, the differences between various strategies to be highlighted, enabling a judicious choice of reagent and reaction conditions for any given situation. Although many of the reactions, which will be discussed, have been known for many years, the development of new, improved versions remains an active area of investigation, especially in the development of catalytic and asymmetric processes. Some of the most significant recent developments in these areas will be discussed, bringing many of the 'old' reactions into the context of modern organic synthesis where issues of atom economy, efficiency and selectivity are paramount.

## Course Contents

### Lectures 1-2      **Properties of two main-group elements**

How can a simple understanding of the behaviour of main group elements be used to account for their reactivity and uses in synthesis? The first two lectures will introduce the key properties of silicon and boron that govern their application in synthesis. Using simple electronic and stereoelectronic arguments, most of the reactions (including their mechanisms) discussed in later lectures can be readily rationalised or even predicted.

#### Lectures 3-4

#### Olefination

- *Phosphorus* - Wittig reaction and Horner-Wadsworth-Emmons reaction - reaction mechanism, stereocontrol.
- *Silicon*-mediated olefination - acid- and base-induced pathways - stereospecificity

#### Lectures 5-6

#### Allylation

- *Type I allyl metals* - allylboranes - reaction mechanism, stereospecificity, asymmetric allylation (Brown)
- *Type II allyl metals* - allylstannanes - stereoselectivity, reaction mechanism, asymmetric allylation (chiral Lewis acids - Keck)

#### Lectures 7

#### Forming $sp^3$ -Carbon-Metal bonds

- *Carbon-Silicon*      Silylcuprates
- *Carbon-Boron*      Hydroboration - reaction mechanism

#### Reactions of Organosilanes and Organoboranes

- $C-Si \rightarrow C-O$       Tamao and Fleming oxidations
- $C-B \rightarrow C-O$

#### Lecture 8

#### Use of Sulfur in Organic Synthesis

- Dithianes as Umpolung reagents

### **General Aims**

- 1) to convey the diversity and utility of reactions involving main-group elements.
- 2) to consolidate and build on the ideas and issues involved in controlling selectivity (chemo-, regio- and stereo-).
- 3) to emphasise that reaction mechanisms and issues of selectivity can often be readily rationalised if you have a good grasp of basic electronic and stereoelectronic principles involved in structure and bonding.

### **General Objectives**

- 1) to understand the reactivity of main-group compounds and be able to rationalise stereo- and regioselectivities using steric, electronic and stereoelectronic arguments.
- 2) to appreciate the use of main-group elements in synthetic transformations.
- 3) to be flexible and be able to use different routes for carrying out the same synthetic transformation.
- 4) to understand the similarities and the differences between different reactions and know which process to use in a given situation.
- 5) to use a variety of drawing representations for rationalising the stereochemical outcome of reactions.