

**CHEM 3021 3.0** – Intermediate Organic Chemistry II  
Course Director: Dr. Arturo Orellana

**Learning Outcomes**

1. Understand the bonding in conjugated organic molecules. Apply the 'linear combination of atomic orbitals' approach to predict the molecular orbitals of conjugated systems.
2. Appreciate the consequences of conjugation on the stability of organic molecules.
3. Predict the reaction outcome of conjugated systems with electrophiles based on the relative stabilities of reactive intermediates.
4. Understand the electronic structure of conjugated organic molecules, and use this to predict and understand the electronic transitions in conjugated systems.
5. Understand the concept of aromaticity. Apply the 'linear combination of atomic orbitals' approach to constructing molecular orbitals of cyclic conjugated systems. Use the polygon rule to predict the stability of cyclic conjugated systems (aromatic? conjugated? antiaromatic?).
6. Understand the concept of pericyclic reactions. Be familiar with the main families of pericyclic reactions: cycloadditions (Diels-Alder reactions, 3+2 dipolar cycloaddition, 2+2 photocycloadditions, electrocyclizations and cycloreversions ( $4\pi$ ,  $5\pi$  (i.e. the Nazarov reaction) and  $6\pi$  systems), sigmatropic rearrangements (Cope, Claisen, Ireland-Claisen, Eschenmoser-Claysen, Fisher indole synthesis, oxidative rearrangements) group transfer reactions (ene, carbonyl-ene).
7. Predict the viability of a proposed pericyclic reaction based on the orbital symmetry requirements (allowed or forbidden processes) and the electronic properties of the reactants (e.g. the nature of dienes and dienophiles in Diels-Alder reactions).
8. Predict the regiochemical and stereochemical outcome of pericyclic reactions based on their mechanism and the structure of the reagents. Use this predictive power to devise the synthesis of more complex molecules.
9. Appreciate the reactivity of amines. Apply their reactivity profile in extraction and purification schemes.
10. Understand and apply a variety of methods for the synthesis of amines and related functional groups (exhaustive alkylation, Gabriel synthesis, Cope elimination, Hoffmann elimination,  $S_N2$  with azide and reduction of azides with  $PPh_3$ , substitution and addition reactions with cyanide and reduction of nitriles, reductive amination, the Mannich reaction, carbodiimide couplings in synthesis of amides, reductive amidation, the Schotten-Bauman method for amide synthesis, the Ritter reaction, the Strecker amino acid synthesis, synthesis and reduction of oximes, diazotization of amines, synthesis and use of diazonium salts, the Sandmeyer reaction, the Beckmann rearrangement)
11. Understand and apply reactions involving rearrangements to electron poor centers (the Schmidt reaction, the Tiffeneau-Demjanov rearrangement, the pinacol rearrangement, the Baeyer-Villiger oxidation)
12. Understand the structure and reactivity of carbenes, appreciate the connection with rearrangement reactions (see above).
13. Understand and apply a variety of methods for the synthesis of carbenes (photochemical, thermal), carbenoids (transition metal catalyzed reactions) and carbene precursors (diazo transfer reactions, tosyl hydrazones).
14. Apply reactions involving carbene intermediates in the preparation of more complex products (e.g. Simmons-Smith reaction, Reimer-Tiemann reaction, Wolff rearrangement)
15. Understand the structure and reactivity of nitrenes. Understand and apply reactions involving nitrene intermediates in the synthesis of complex molecules (Curtius rearrangement)

16. Understand the structure and reactivity of Ylides. Appreciate the connection of Ylides to carbene and carbenoid intermediates.
17. Apply reactions involving ylides (sulfonium, sulfoxonium and phosphonium ylides in the Corey Chaykovsky epoxidation and cyclopropanation, and Wittig reactions respectively) and ylide precursors (sulfonium and phosphonium salts) in the synthesis of complex molecules.

**Assessment** Theory (100%): Unannounced quizzes (3-4, 10%), midterm exams (2 x 25%), final exam (40%).