

CHAPTER OVERVIEW

23: ALPHA SUBSTITUTIONS AND CONDENSATIONS OF CARBONYL COMPOUNDS

LEARNING OBJECTIVES

After reading this chapter and completing ALL the exercises, a student can be able to

- predict the relative acidity of the α -hydrogens on various carbonyl compounds (section 23.1)
- explain or predict the equilibrium of enol-keto tautomers (section 23.2)
- predict the products and specify the reagents for the following reactions
 - Halogenation of the α -carbon of aldehydes and ketones (section 23.3 and 23.4)
 - Halogenation of the α -carbon of carboxylic acids (Hell-Vollhard-Zelinski) (section 23.3 and 23.5)
 - Alkylation of the α -carbon of carbonyl compounds via the LDA pathway (section 23.3 and 23.6)
 - Alkylation of the α -carbon of aldehydes and ketones via the enamine intermediate (section 23.3 and 3.7)
 - Aldol addition and condensation reactions – 2 aldehydes, 2 ketones, 1 aldehyde with 1 ketone (section 23.3 and 23.8)
 - Claisen condensation reactions – 2 esters or 1 ester with 1 ketone (section 23.3 and 23.9)
 - Dieckmann condensation reactions (intramolecular Claisen) - (section 23.9)
 - Conjugate Addition a.k.a. Michael reaction (section 23.3 and 23.10)
 - Robinson annulation (section 23.10)
 - Decarboxylation of 3-oxocarboxylic acids (section 23.3 and 23.12)
 - Malonic ester synthesis of carboxylic acids
 - Acetoacetic ester synthesis of methyl ketones

Designing synthesis using all of the reactions through this chapter with an emphasis on increasing the size of the carbon backbone by forming new carbon-carbon bonds

Topic hierarchy

- [23.1: Relative Acidity of alpha-Hydrogens](#)
- [23.2: Enols, Enolate Ions and Tautomerization](#)
- [23.3: Reaction Overview](#)
- [23.4: Alpha Halogenation of Carbonyls](#)
- [23.5: Bromination of Acids- The HVZ Reaction](#)
- [23.6: Alkylation of the alpha-Carbon via the LDA pathway](#)
- [23.7: Alkylation of the Alpha-Carbon via the Enamine Pathway](#)
- [23.8: The Aldol Reaction and Condensation of Ketones and Aldehydes](#)
- [23.9: The Claisen Condensation Reactions of Esters](#)
- [23.10: Conjugate Additions- The Michael Reaction](#)
- [23.11: Decarboxylation Reactions](#)
- [23.12: Additional Exercises](#)
- [23.13: Solutions to Additional Exercises](#)

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