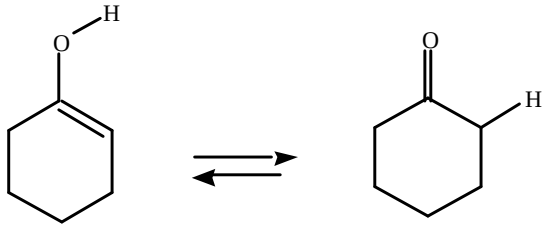
I. ENOLS AND ENOLATES

A. ENOLS (22.1-22.2)

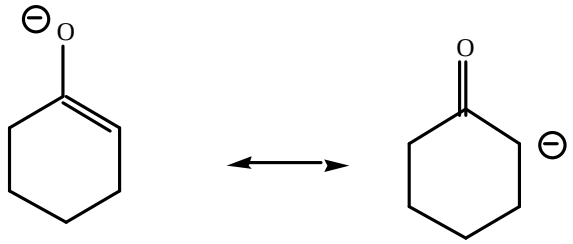


ENOL KETO

1. An enol is an organic compound which contains a C-C double bond with an -OH group bonded to one of the carbon atoms of the double bond.
2. Enols are in equilibrium with a carbonyl isomer, referred to as the "keto" form of the enol. The interconversion of enols to the carbonyl form is referred to as tautomerization
3. The enol-keto interconversion involves transfer of an α-proton from the α–carbon in the keto form to the oxygen in the enol form.
4. Acid catalyzes the conversion of keto to enol form.
5. At neutral pH, the keto form is *usually* more stable than the enol form.
6. Enhanced stabilization of the enol form occurs if the double bond of the enol is in conjugation with other double bonds or part of an aromatic ring.
7. β-dicarbonyls form enols easily
8. There are two stereochemical factors to consider in the keto-enol isomerization.
   a. Configuration of a chiral α-carbon in the keto form
   b. Configuration of the double bond in the enol form.

B. ENOLATES (22.5-22.6)

1. An enolate is an anionic organic compound with an oxygen atom bonded to an alkene. There are two resonance forms associated with enolates.

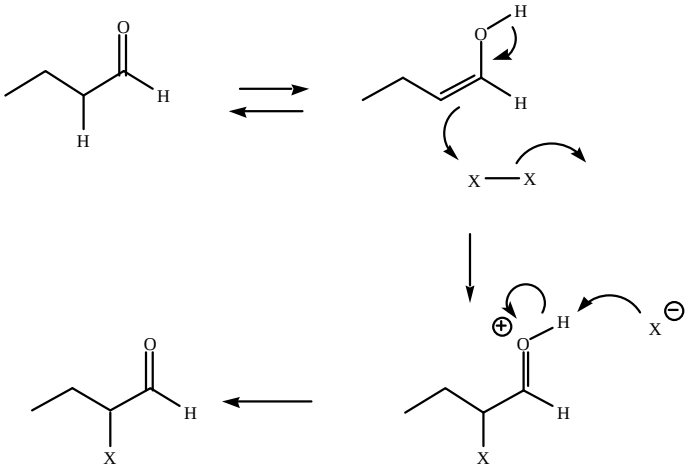


ENOLATE

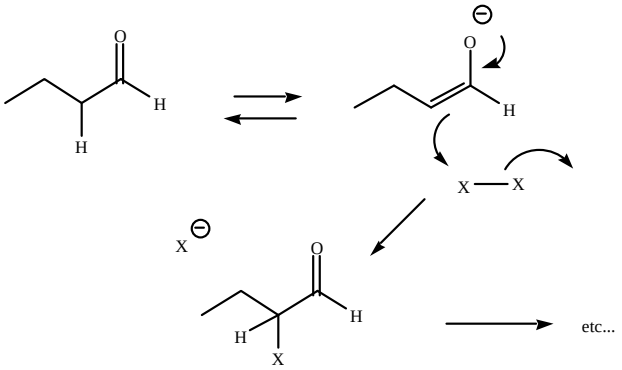
2. Enolates are derived from α-hydrogen deprotonation of a carbonyl compound,1,4-addition to an α,ß-unsaturated carbonyl compound or decarboxylation of a ß-dicarbonyl compound
   a. Deprotonation of an α-hydrogen
      i.. α-Hydrogens are relatively acidic (pKa 16-20) and react with strong bases(eg. NaH, LDA, or tert-BuLi).
      ii. ß-Dicarbonyls form enolates readily. (pKa ~9)
   b. Nucleophilic attack of an α,ß-unsaturated carbonyl at the 4-position gives rise to an enolate.
   c. Enolates themselves are nucleophilic.
   3. Enolates usually react through the carbon anion as opposed to the oxygen anion.
   4. Stereochemistry of Enolates: There are two stereochemical features of enolates.
      a. Configuration of a chiral α-carbon atom in the carbonyl compound
      b. Configuration of the double bond of the enolate.

II. REACTIONS OF ENOLS AND ENOLATES

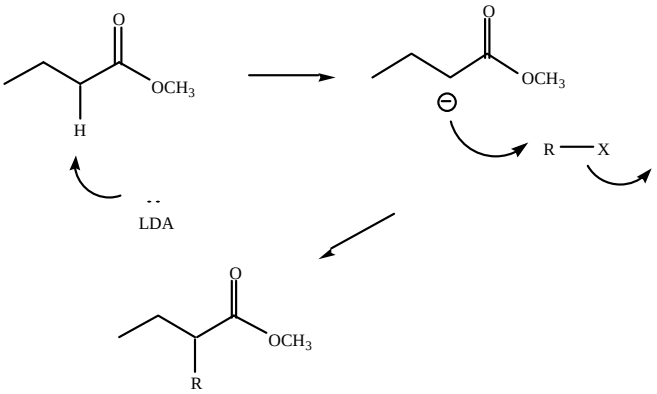
A. Halogenation (22.3)
1. Halogenation of Enols
   a. Enols react with halogen molecules through a reaction mechanism that is similar to the electrophilic addition of alkenes. This reaction occurs under acidic conditions.



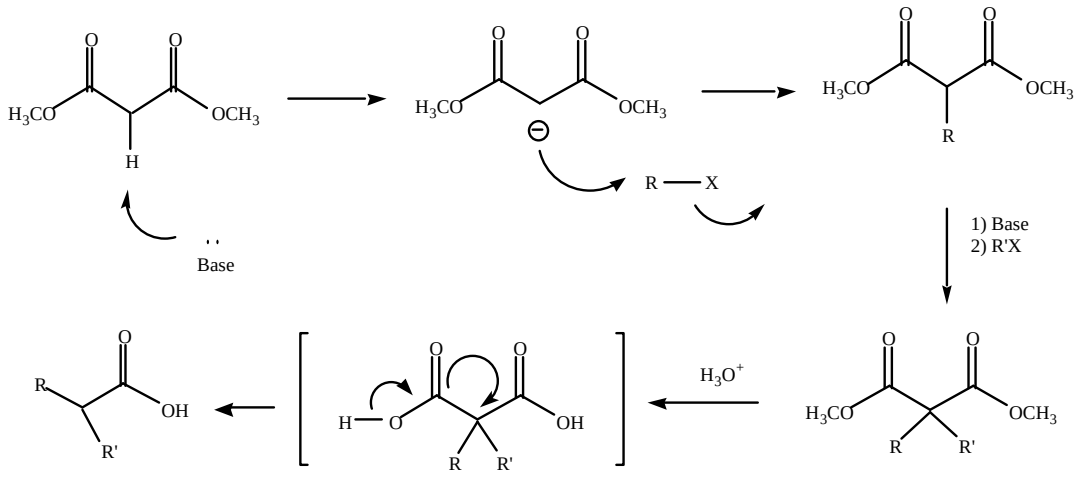
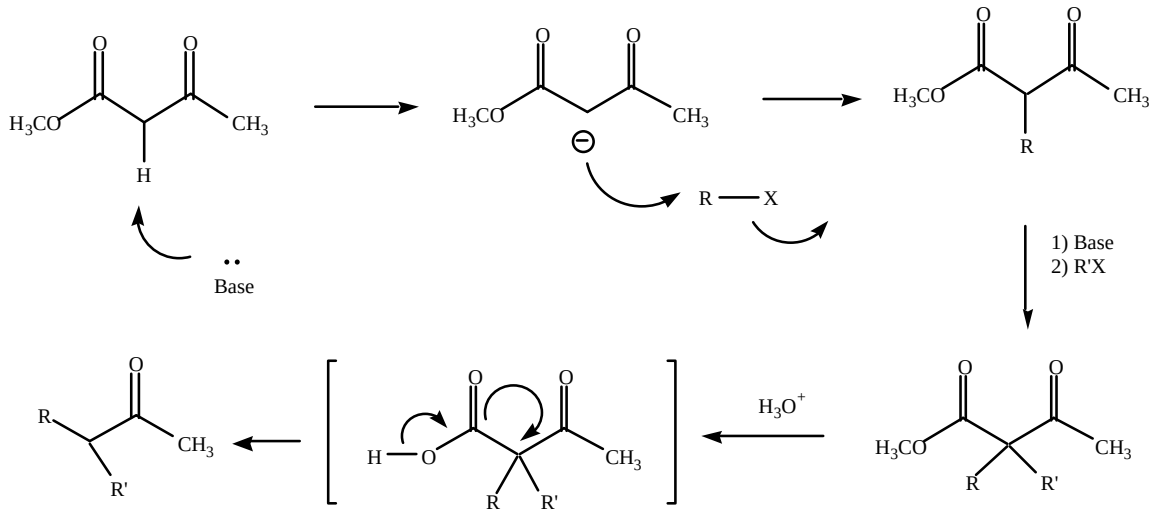
2. Halogenation of Enolates
   Enolates react with halogens under basic conditions
3. If there is more than one α-hydrogen, additional halogenation can occur



B. Alkylation of Enolates (22.7)
1. Direct Alkylation
   Treatment of carbonyl compounds with a sterically hindered base, followed by an alkylkation agent (usually an alkyl halide) gives a product substituted at the α-carbon.



2. Malonic Ester Synthesis
   a. Treatment of a β-diester (malonic ester)with base and an alkylating agent gives a product substituted at the α-carbon.
   b. Acid catalyzed hydrolysis and decarboxylation gives a substituted carboxylic acid.



3. Acetoacetic Ester Synthesis
   Treatment of a β-ketoester with base and an alkylating agent, followed by decarboxylation gives a substituted ketone.