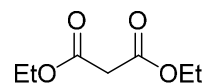
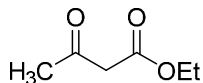
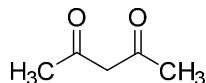
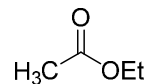
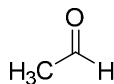
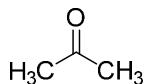
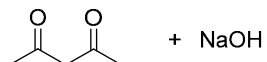
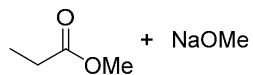
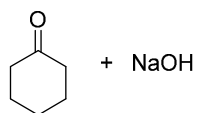
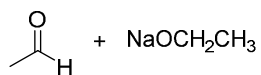


**Chapter 15: Enolate Anions****15.1 Acidity of  $\alpha$ -Hydrogens and Enolate Formation****a) Acidity of  $\alpha$ -Hydrogens**

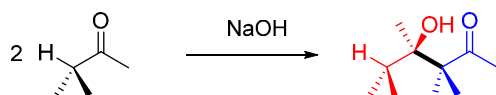
15.1

**b) Formation of enolate anions**

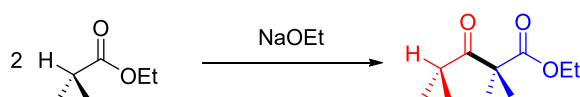
15.2

**c) Use of Enolates to Form New C-C Bonds**

Enolate anions can act as nucleophiles in carbonyl addition reactions (Aldol reaction).



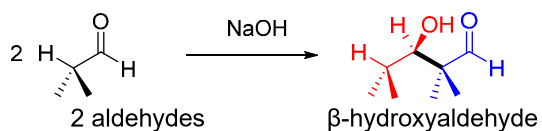
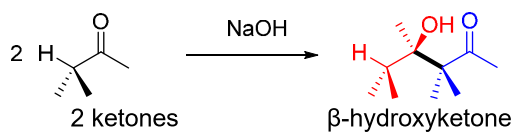
Enolate anions can act as nucleophiles in nucleophilic acyl substitution reactions (Claisen condensation).



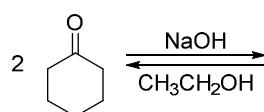
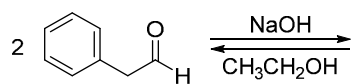
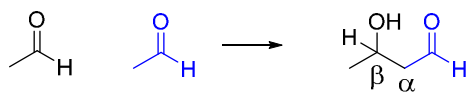
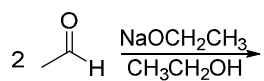
15.3

**15.2 Aldol Reaction and Aldol Condensation****a) Aldol Reaction**

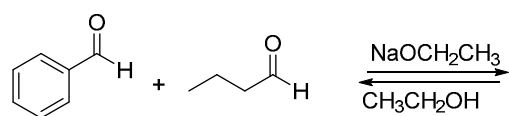
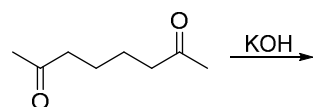
Enolate anions of aldehydes and ketones act as nucleophiles in carbonyl addition reactions.



15.4

**Examples:**

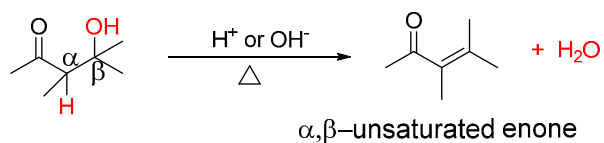
15.5

**b) Crossed Aldol Reaction****c) Intramolecular Aldol Reaction**

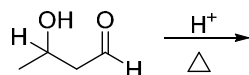
15.6

**d) Dehydration of Aldol Product (Aldol Condensation)**

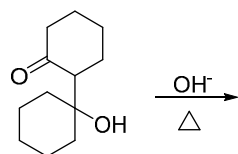
Dehydration of the aldol product is either acid or base catalyzed and generally requires heating. The result is an  $\alpha,\beta$ -unsaturated carbonyl compound.



**Acid catalyzed mechanism:**



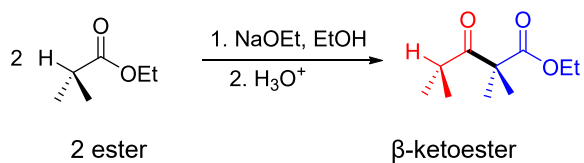
**Base catalyzed mechanism:**



15.7

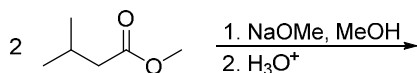
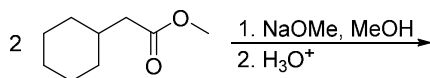
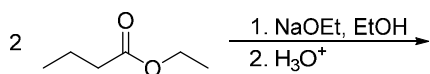
**15.3 Claisen Condensation and Dieckmann Condensation****a) Claisen Self-Condensation**

In the Claisen condensation two esters react under basic conditions to form a new C-C-bond.

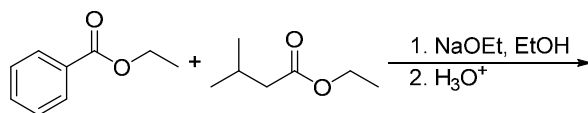


Note: Aqueous base such as NaOH cannot be used. Why not?

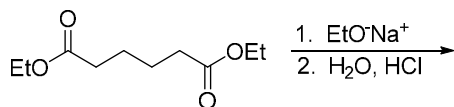
15.8



15.9

**b) Crossed Claisen Condensation****c) Dieckmann Condensation**

The Dieckmann Condensation is an intramolecular Claisen condensation. 5- or 6-membered rings are formed preferentially.



15.10

**d) Hydrolysis and Decarboxylation of  $\beta$ -Ketoesters**

Claisen condensation gives a  $\beta$ -ketoester:

Hydrolysis (Saponification) of the  $\beta$ -ketoester followed by acidification results in a  $\beta$ -ketoacid:

$\beta$ -Ketoacids undergo decarboxylation upon heating:

15.11

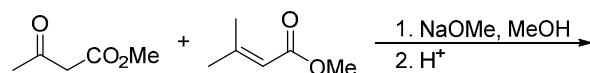
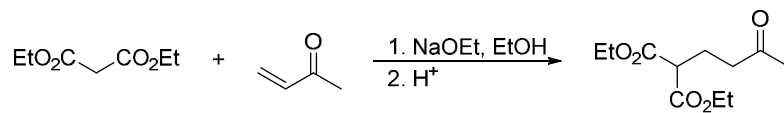
**15.4 Michael Addition Reaction**

Michael addition reactions are conjugate additions to  $\alpha,\beta$ -unsaturated carbonyl compounds. They are also called 1,4-additions to  $\alpha,\beta$ -unsaturated carbonyl compounds.

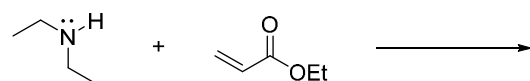
**a) 1,4-Additions versus 1,2-Additions to  $\alpha,\beta$ -Unsaturated Carbonyl Compounds**

Michael  
Acceptor

15.12

**b) Michael Addition (1,4-Addition) of Enolate Anions to  $\alpha,\beta$ -Unsaturated Carbonyl Compounds**

15.13

**c) Michael Addition (1,4-Addition) of Amines to  $\alpha,\beta$ -Unsaturated Carbonyl Compounds**

15.14