

## Chapter 21 Review

### β-Ketoesters -- Preparation

Claisen	$\text{RCH}_2\text{COOEt} \xrightarrow{\text{NaOEt}} \xrightarrow[\text{H}_2\text{O}]{\text{H}^+} \text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{R}}{\text{CH}}-\text{COOEt}$
Dieckmann	$\begin{array}{c} \text{COOEt} \\ \diagup \\ (\text{CH}_2)_n \\ \diagdown \\ \text{COOEt} \end{array} \xrightarrow{\text{NaOEt}} \xrightarrow[\text{H}_2\text{O}]{\text{H}^+} \begin{array}{c} \text{C}=\text{O} \\ \diagup \\ (\text{CH}_2)_{n-1} \\ \diagdown \\ \text{CH}-\text{COOEt} \end{array}$
Mixed Claisen	$\text{RCH}_2\text{COOEt} + \text{R}'\text{COOEt} \xrightarrow{\text{NaOEt}} \xrightarrow[\text{H}_2\text{O}]{\text{H}^+} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{R}}{\text{CH}}-\text{COOEt}$
Ketone Acylation	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3 + \text{EtO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OEt} \xrightarrow{\text{NaOEt}} \xrightarrow[\text{H}_2\text{O}]{\text{H}^+} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{COOEt}$

### β-Ketoesters -- Reactions

Alkylation	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{C}}\text{H}-\text{COOEt} \xrightarrow{\text{R}'\text{CH}_2\text{X}} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{R}'-\text{CH}_2}{\text{CH}}-\text{COOEt}$
Michael additions	$\begin{array}{c} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{C}}\text{H}-\text{COOEt} \\ + \\ \text{R}'-\text{CH}=\text{CH}-\text{COOEt} \end{array} \longrightarrow \begin{array}{c} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{R}'-\text{CH}-\text{CH}_2-\text{COOEt}}{\text{CH}}-\text{COOEt} \end{array}$
( Note - the products above are still β-ketoesters )	
Hydrolysis	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{COOEt} \xrightarrow[\text{H}_2\text{O}]{\text{H}^+} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{COOH}$
Decarboxylation	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{COOH} \xrightarrow{\square} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$

( Note - many of the above reactions also work with β-diketones )

### Ester enolates

	$\text{R-CH}_2\text{-COOEt} \xrightarrow{\text{LDA}} \text{R-}\overset{\ominus}{\text{C}}\text{H-COOEt}$ <p style="text-align: center;">( no Claisen )</p>
Alkylation	$\text{R-}\overset{\ominus}{\text{C}}\text{H-COOEt} \xrightarrow{\text{R}'\text{CH}_2\text{X}} \begin{array}{c} \text{R-}\overset{\ominus}{\text{C}}\text{H-COOEt} \\   \\ \text{R}'\text{-CH}_2 \end{array}$
Carbonyl addition	$\text{R-}\overset{\ominus}{\text{C}}\text{H-COOEt} \xrightarrow[\text{H}_2\text{O}]{\text{R}'\text{CH=O, H}^+} \begin{array}{c} \text{R-}\overset{\ominus}{\text{C}}\text{H-COOEt} \\   \\ \text{R}'\text{-CH-OH} \end{array}$

### Acetoacetic Ester Synthesis and Malonic Ester Synthesis

