

## **Roadmap Reaction Legend**

#### Reaction 19.1 NaOH or acid

- The aldol reaction

- The reaction is catalytic in either acid or base
  In base the reaction involves formation of an
- enolate that attacks the carbonyl group of another molecule
- In acid, the reaction involves enol attack
- on a protonated carbonyl.

- Makes a new C-C bond

## Reaction 19.2 Acid or base

Action black - Aldol products readily dehydrate to create conjugated  $\alpha_{\alpha}\beta_{-unsaturated}$  carbonyl products - The new C=C pi bond forms toward the carbonyl group because of conjugation

## Reaction 19.3 1. NaOR 2. Mild HCl, H<sub>2</sub>O

The Claisen condensation
The ""R group of the NaOR reagent should match the OR group of the starting ester
The reaction involves formation of an enolate that attacks the carbonyl group of another molecule.
Makes a new C-C bond

# Reaction 19.5

## 1. 2° amine 2. RX 3. HCl, H<sub>2</sub>O

- The initially formed enamine reacts as a

nucleophile at the  $\alpha$ -carbon atom

- Following reaction with the haloalkane, the 2° amine is removed in aqueous acid

- Makes a new C-C bond

### Reaction 19.7

# NaOEt 2. RX 3. NaOH, H<sub>2</sub>O 4. HCl, H<sub>2</sub>O 5. Heat The acetoester synthesis The acetoester enolate reacts with the haloalkane followed by ester hydrolysis and decarboxlyation of the β-ketoacid

- Makes a new C-C bond

## Reaction 19.9

Various enolates or amines - The Michael reaction - An example of conjugate addition - The reaction involves attack by the enolate or

amine nucleophile on the carbon-carbon double bond to give an enolate intermediate that protonates to give an enol that undergoes keto-enol tautomerism

- Makes a new C-C bond

## Reaction 19.4 1. NaOR 2. Mild HCl, H<sub>2</sub>O

The Dieckmann condensation
A cyclic version of the Claisen condensation involving an intramolecular reaction of a diester
The R group of the NaOR reagent should match the OR group of the starting diester
Makes a new C-C bond

# Reaction 19.6

## 1.2° amine 2. Acid chloride 3. HCl, H<sub>2</sub>O

The initially formed enamine reacts as a nucleophile at the α-carbon atom
Following reaction with the acid chloride, the 2° amine is removed in aqueous acid
Makes a new C-C bond

## Reaction 19.8

1. NaOEt 2. RX 3. NaOH, H<sub>2</sub>O 4. HCl, H<sub>2</sub>O

5. Heat

- The malonic ester synthesis The acetoester enolate reacts with the haloalkane followed by ester hydrolysis and decarboxlyation of the β-diacid `Makes a new C-C bond

## Reaction 19.11

**1.** R<sub>2</sub>CuLi **2.** HCl, H<sub>2</sub>O - The conjugate addition of a Gilman reagent

- Makes a new C-C bond