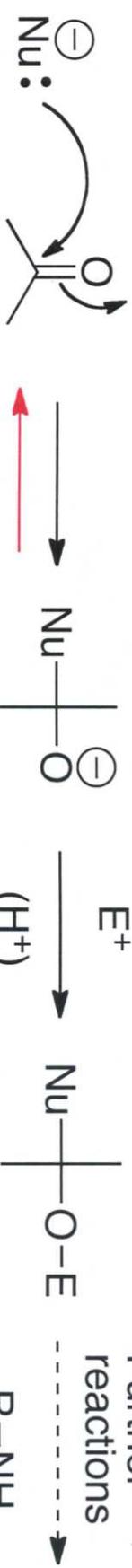


Weak Nucleophiles and Ketones & Aldehydes

191



Irreversible

If Nu: is H- or R-

Reversible for weak Nu:

$$\text{R}-\text{NH}_2$$

Further reactions



R-I-O-I

HCN

R-NH₂

11

Aminal Formation

Cyanohydrin Formation

Hemiacetal Formation → Acetal Formation

12

20

2

1

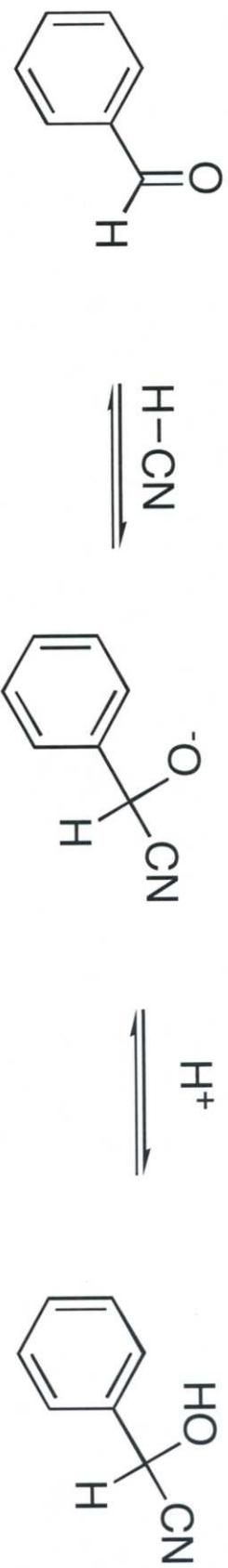
Aminal Formation

Chloral

Chloral Hydrate

Cyanohydrin Formation

Example : cyanide is a good nucleophile



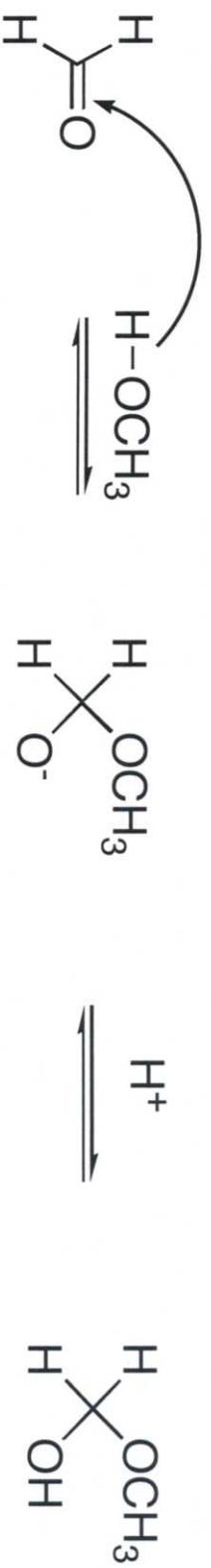
benzaldehyde

toxic gas hydrogen cyanide (HCN) is usually generated by adding an acid (H_2SO_4) to a mixture of carbonyl compound and excess sodium cyanide (NaCN)

231

Hemi-Acetal Formation

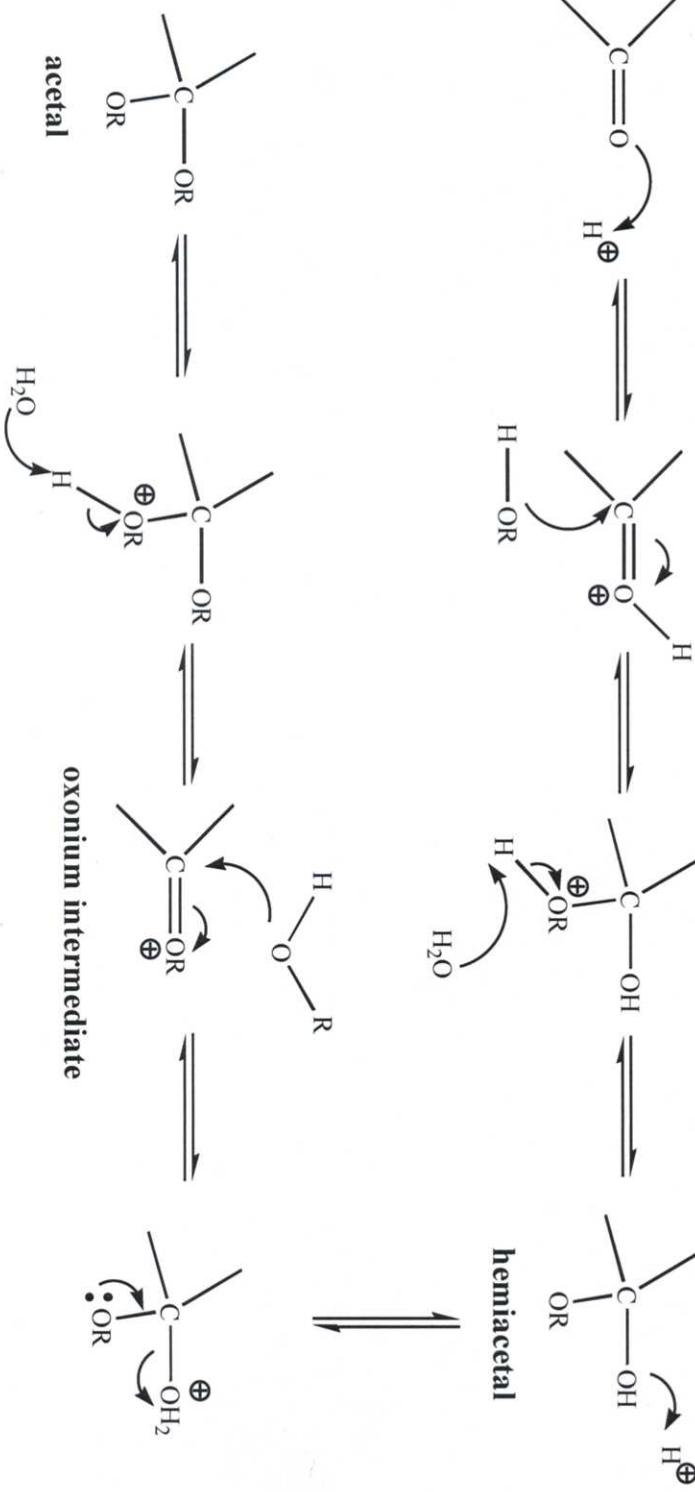
Hemiacetal formation is similar to hydration but alcohols are used instead



Acetal Formation

Hemiacetals can be converted to Acetals: two OR groups instead of one OR and OH

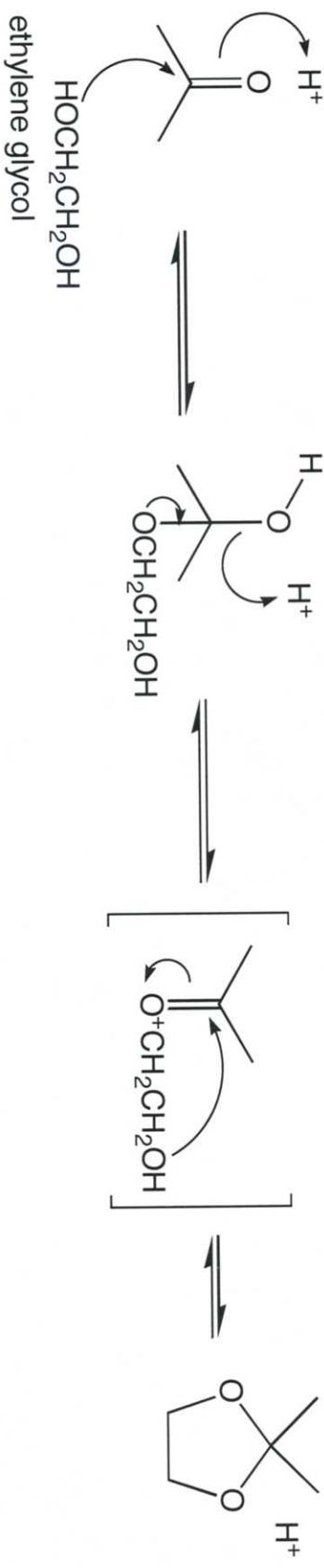
Addition then Elimination then 2nd Addition reaction



Acetal Formation - Examples (useful to protect ketone/aldehyde)

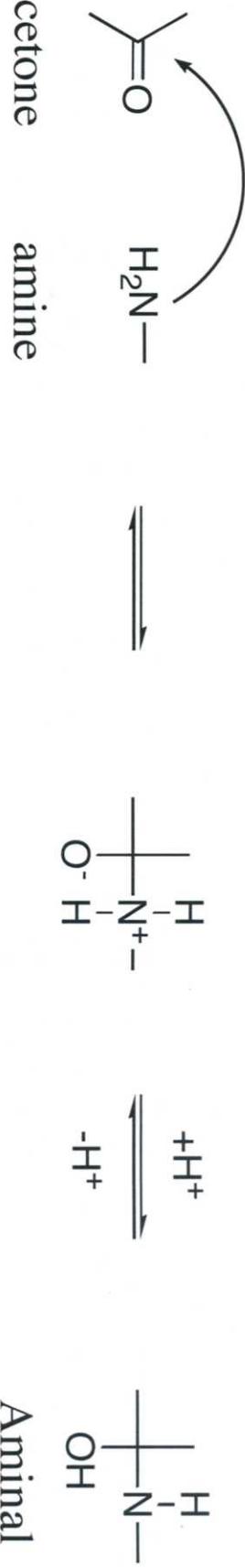


acetals very stable to base



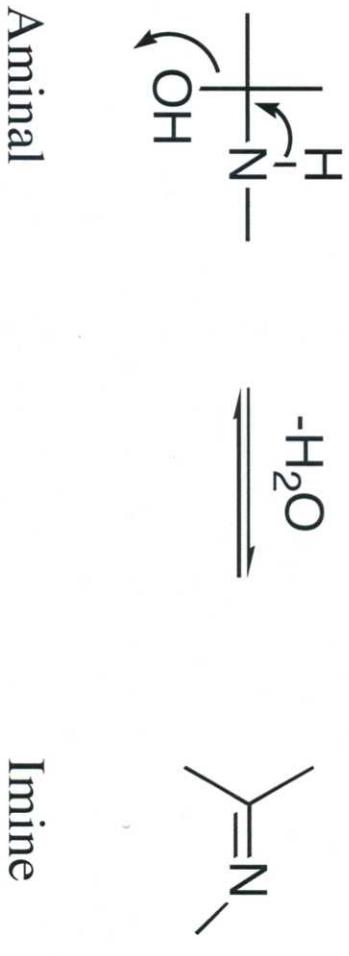
Aminal Formation

171



Aminal formation is similar to that of hydration except the nucleophile is an amine

Imine Formation Addition then Elimination then 2nd Addition reaction

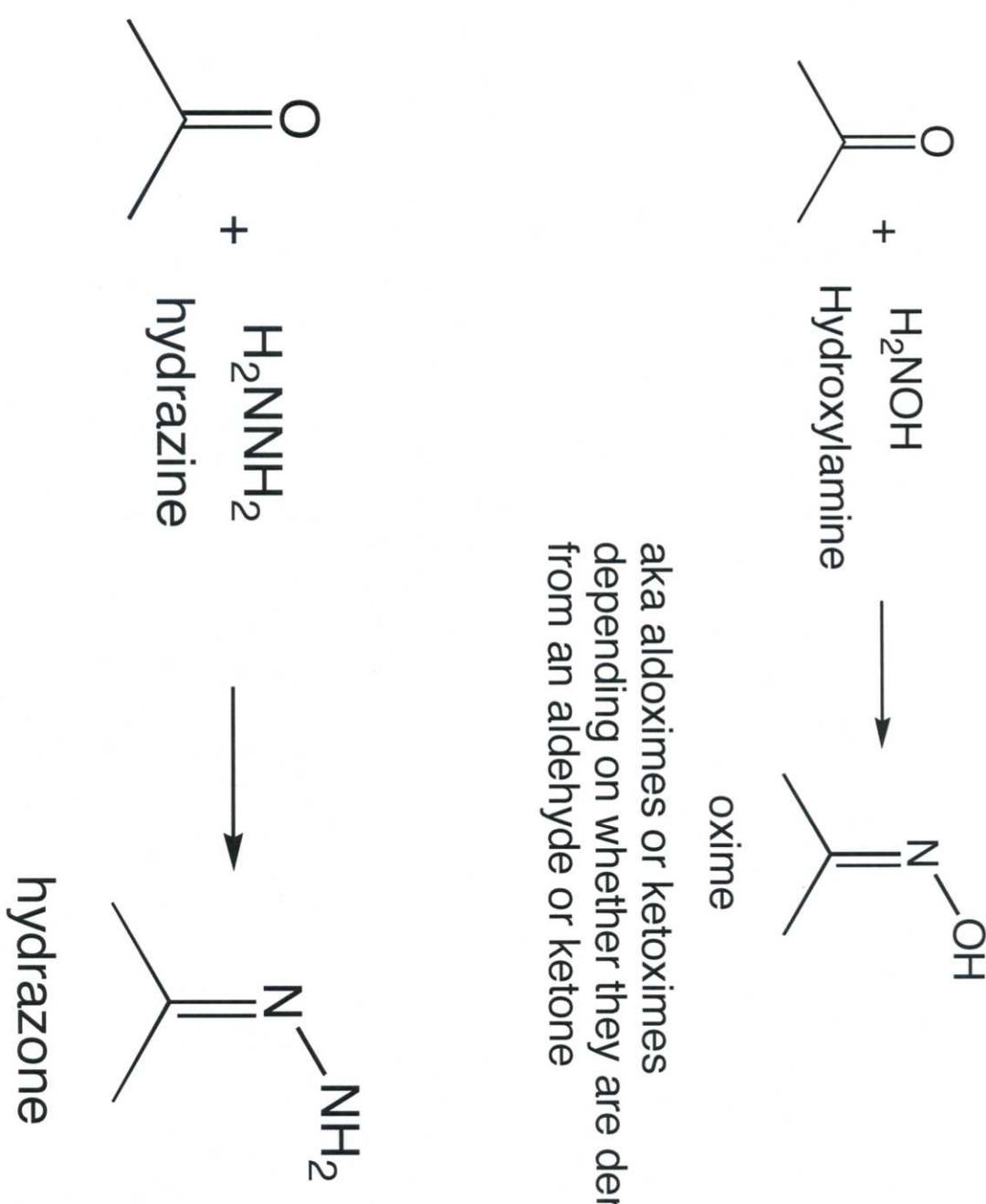


Imine

Aminal

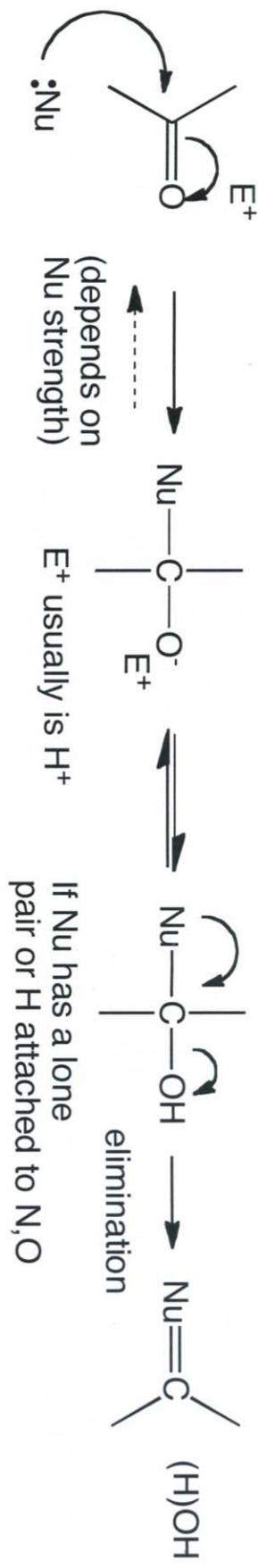
Imine Bond Formation - addition, elimination, addition

172

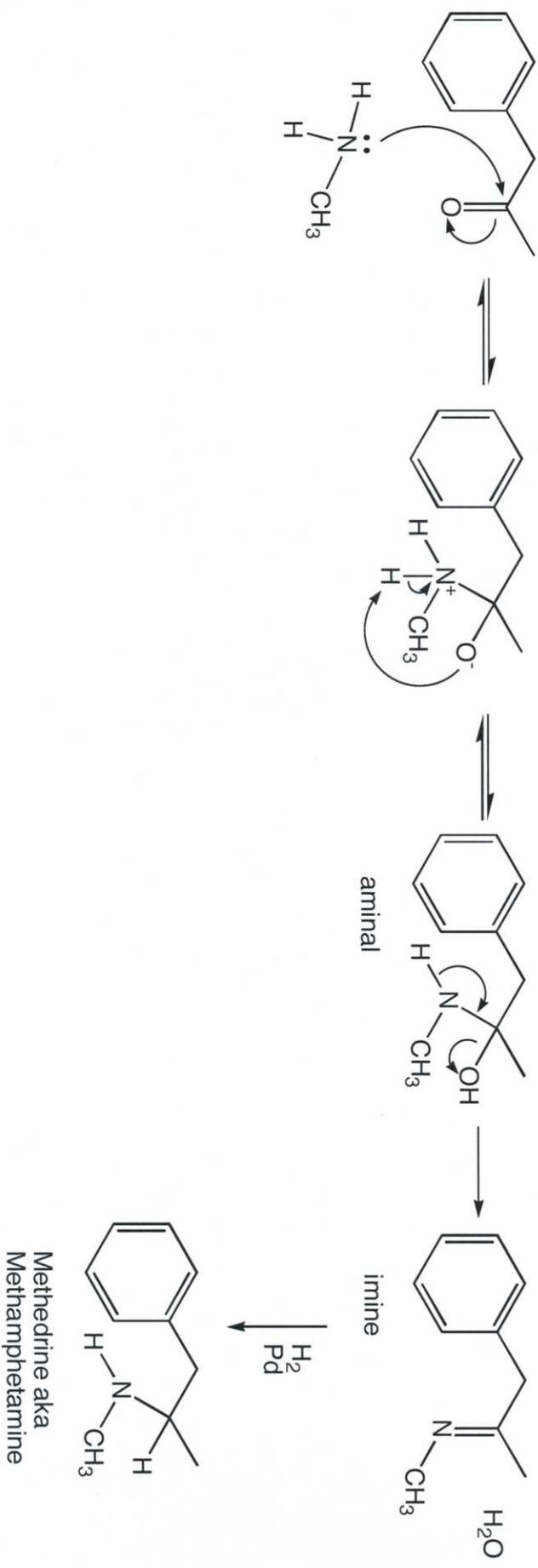


aka aldoximes or ketoximes
depending on whether they are derived
from an aldehyde or ketone

Imine Formation - addition, elimination, addition

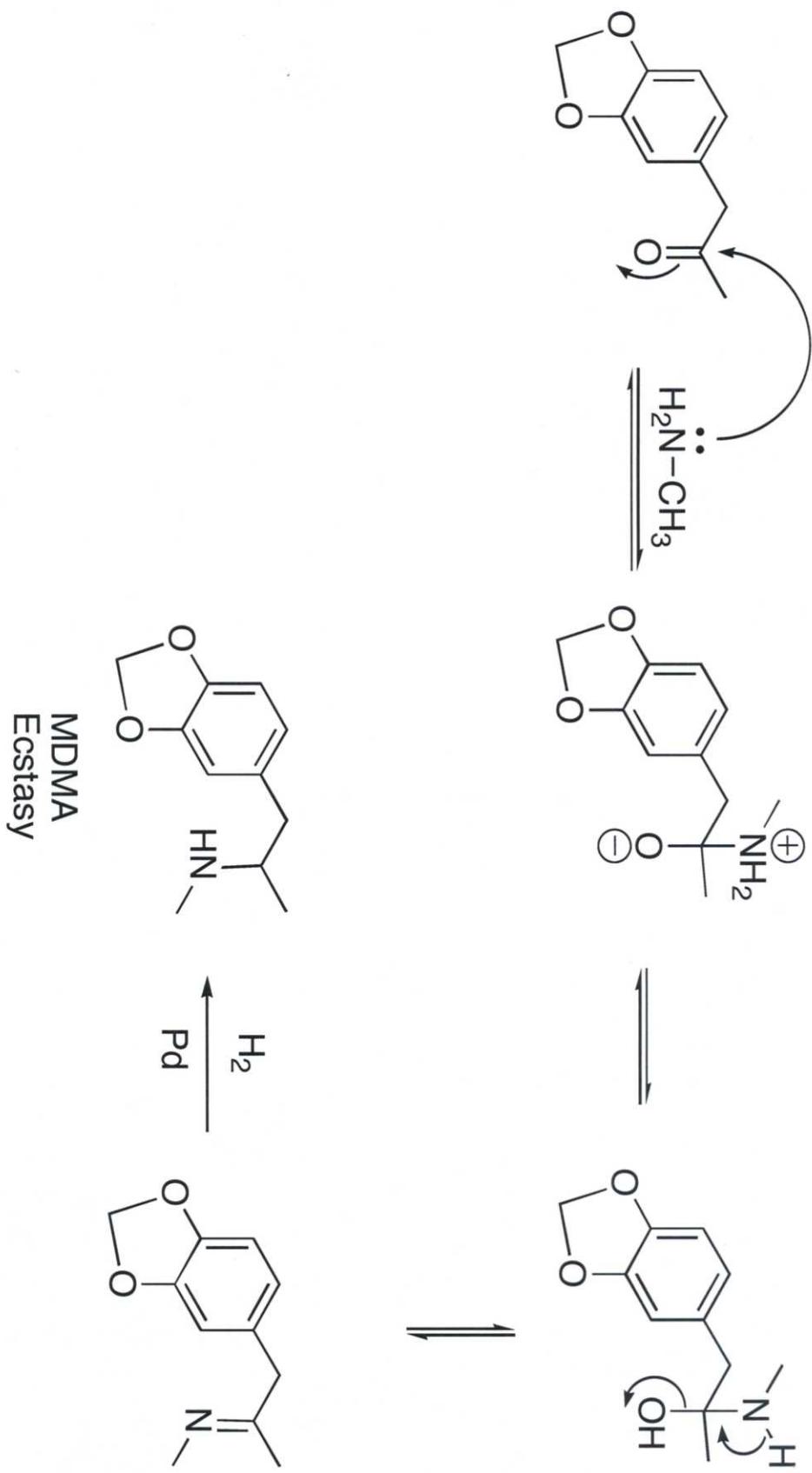


Example (Imines can be reduced to amines)

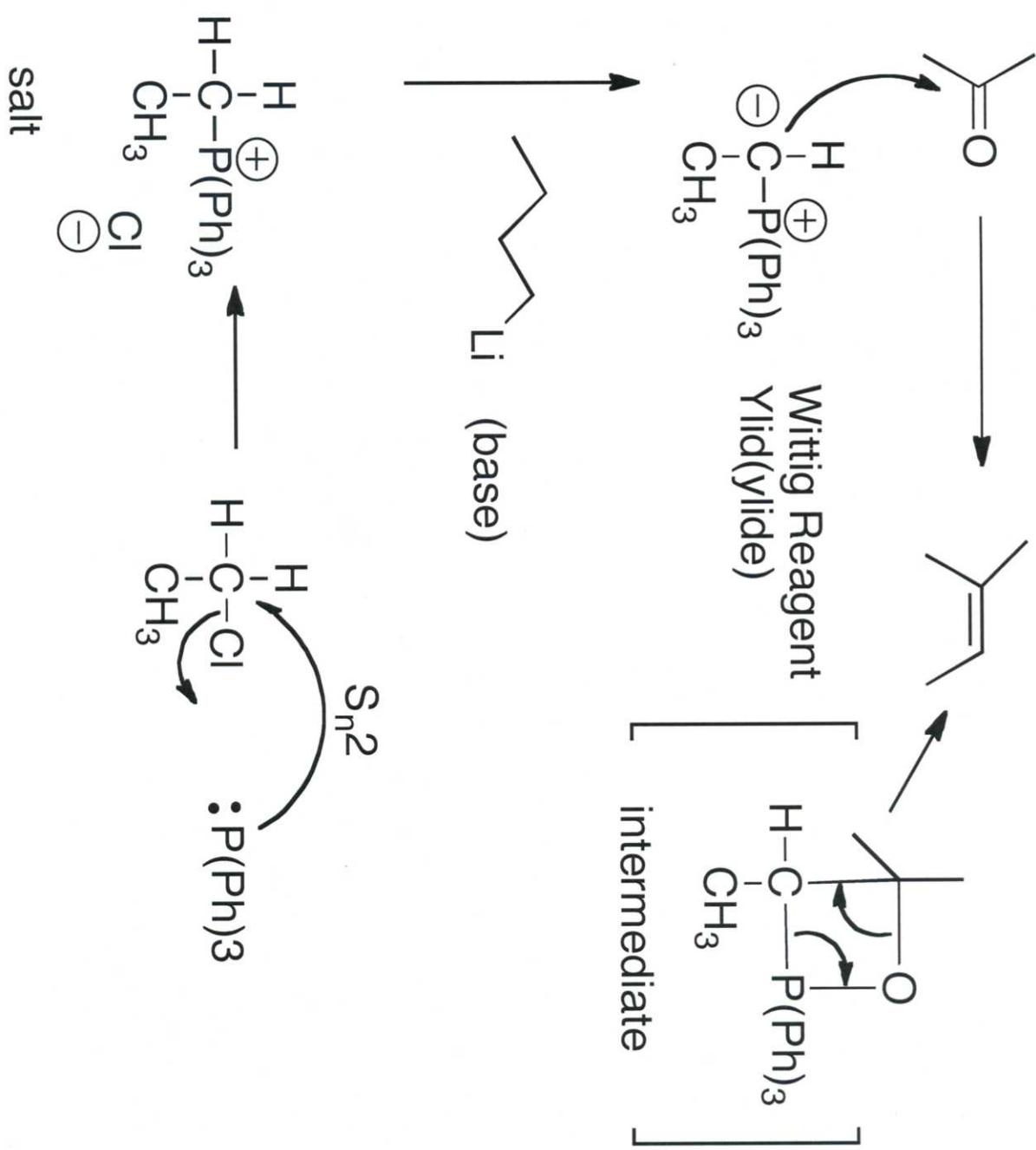


Imine Formation Example - addition, elimination, addition

174

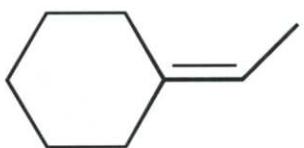


Wittig Reaction: an Addition-Elimination Reaction

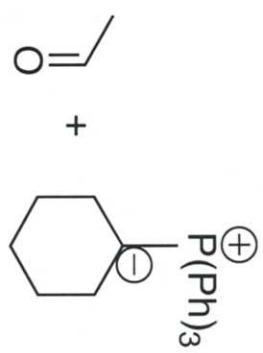


Wittig Reaction: an Addition-Elimination Reaction - Example

Consider how to make

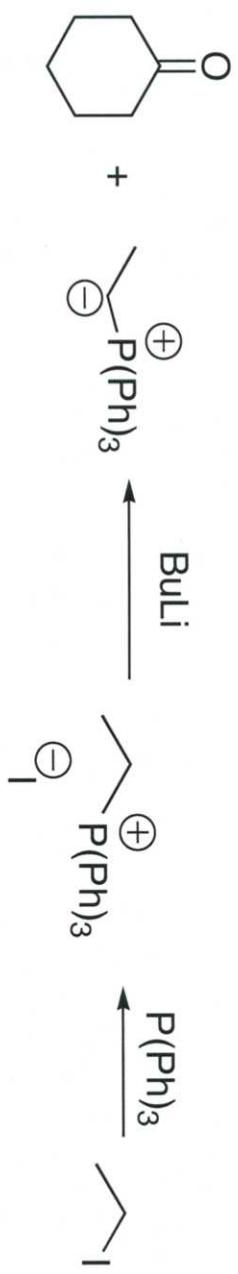


synthetic route A:



(but this wittig reagent is more hindered than the one in route B,
so, route B is better)

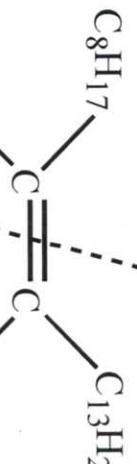
synthetic route B:



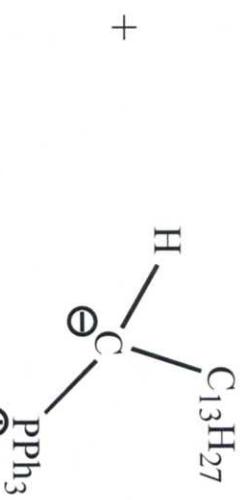
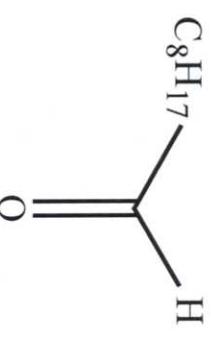
172

Wittig Reaction: an Addition-Elimination Reaction - Example

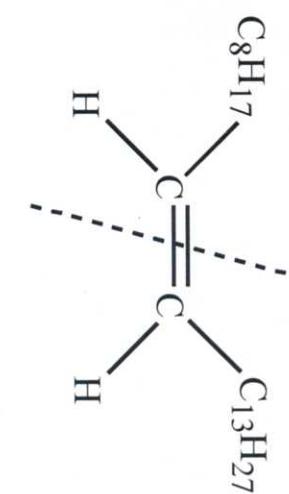
Consider how to make housefly pheromone $\text{C}_8\text{H}_{17}\text{C}=\text{C}\text{C}_{13}\text{H}_{27}$



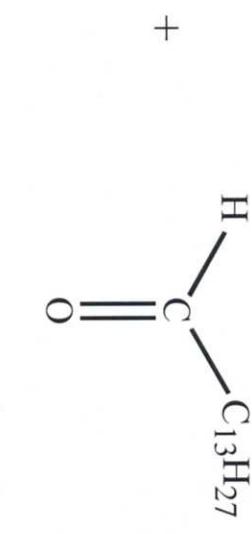
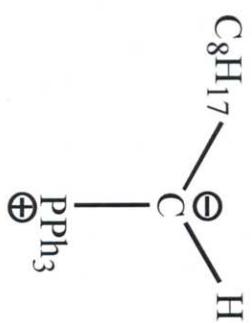
From



or (will also work) :

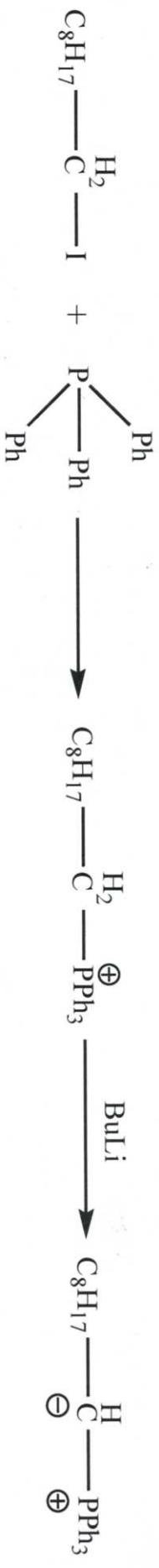


From



Wittig Reaction: an Addition-Elimination Reaction - Example

To make housefly pheromone



add

