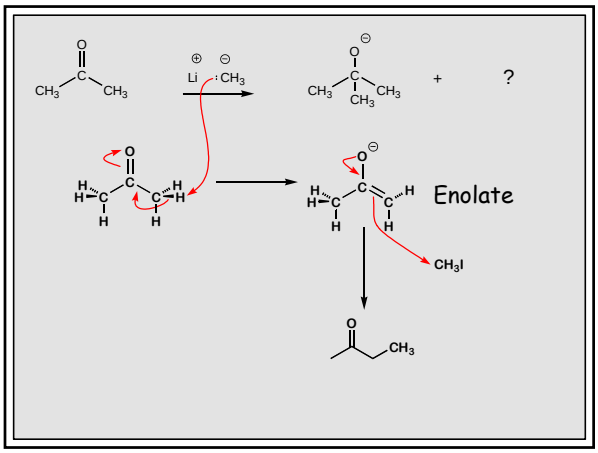
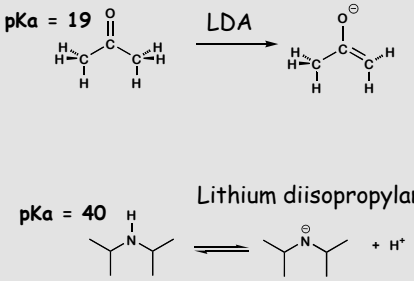
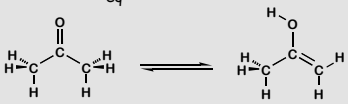


To make the enolate in a stoichiometric amount you need a strong non nucleophlic base.



Keto $K_{eq} = 1.5 \times 10^{-4}$ Enol

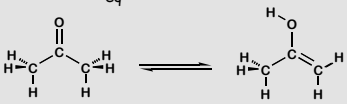


These two compounds are tautomers

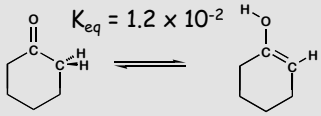
tautomerization

isomerization by moving an acidic H^+

Keto $K_{eq} = 1.5 \times 10^{-4}$ Enol



$K_{eq} = 1.2 \times 10^{-2}$

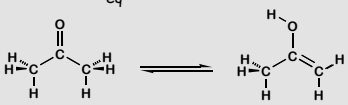


More highly substituted

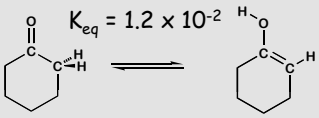
Will K_{eq} be larger or smaller

A. Larger
B. Smaller

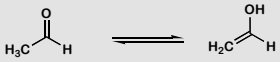
Keto $K_{eq} = 1.5 \times 10^{-4}$ Enol



$K_{eq} = 1.2 \times 10^{-2}$



More highly substituted

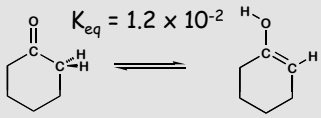


Will K_{eq} be larger or smaller

A. Larger
B. Smaller

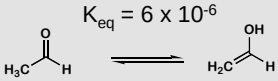
Keto $K_{eq} = 1.5 \times 10^{-4}$ Enol

$K_{eq} = 1.2 \times 10^{-2}$



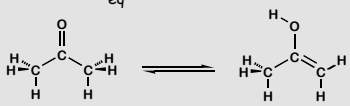
More highly substituted

$K_{eq} = 6 \times 10^{-6}$



Aldehydes form less enol

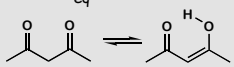
Keto $K_{eq} = 1.5 \times 10^{-4}$ Enol



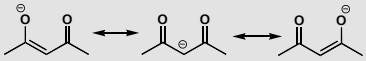
$pK_a = 19$

$K_{eq} = 3.2$

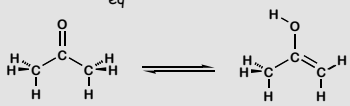
Acetyl acetone



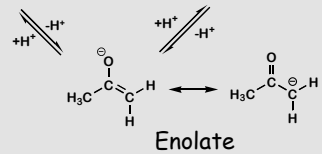
$pK_a = 9$



Keto $K_{eq} = 1.5 \times 10^{-4}$ Enol



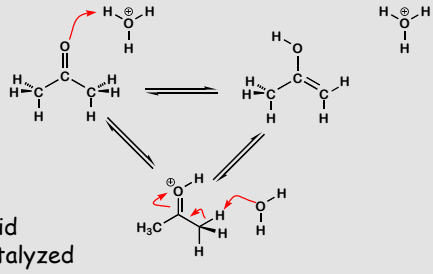
$pK_a = 19$



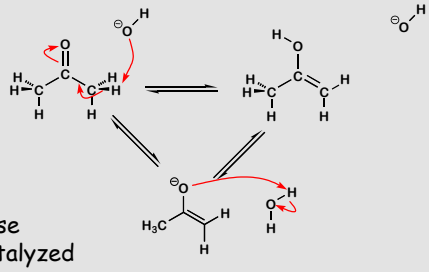
Enolate

Two sites of basicity, O and C

Most reactions will take place at C because stronger bonds are the result.

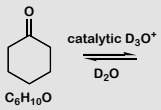


Acid Catalyzed Tautomerization



Base Catalyzed Tautomerization

Many reactions of carbonyl compounds can be catalized by both acid or base



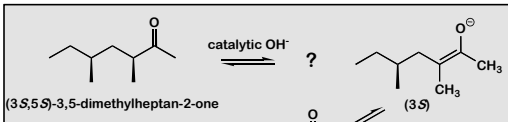
?

Deuterium exchange

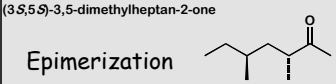
What is the formula of the expected product?

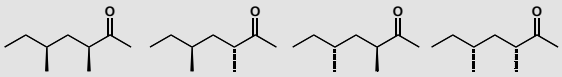
A. $C_6D_1H_9O$ B. $C_6D_2H_8O$ C. $C_6D_4H_6O$

D. $C_6D_6H_4O$ E. $C_6D_8H_2O$ F. $C_6D_{10}O$



Epimerization

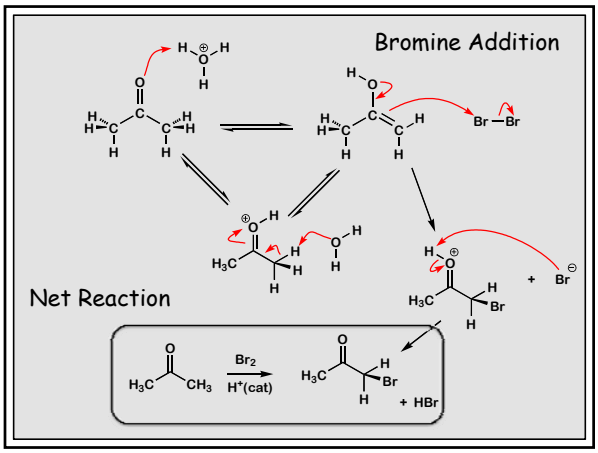


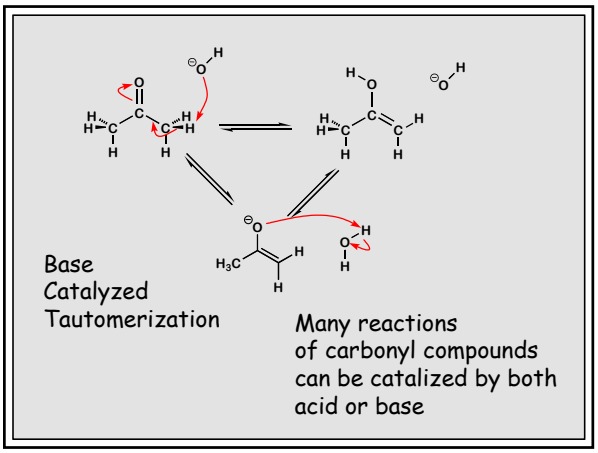


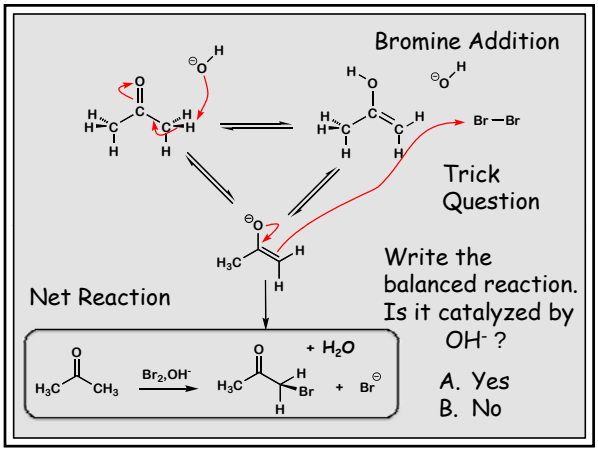
(3*S*,5*S*) i. (3*R*,5*S*) ii. (3*S*,5*R*) iii. (3*R*,5*R*) iv.

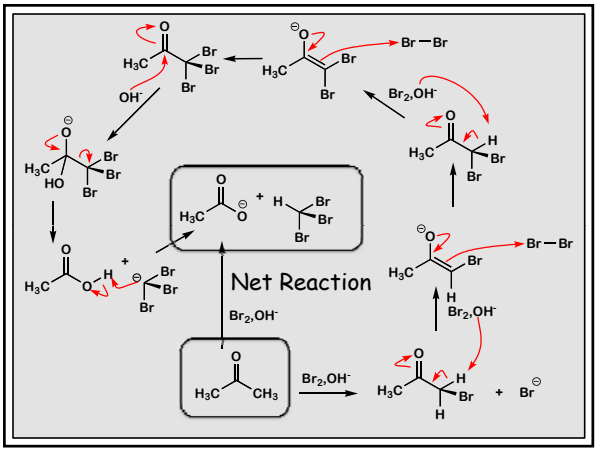
A. i B. ii C. i + ii D. iii E. iv

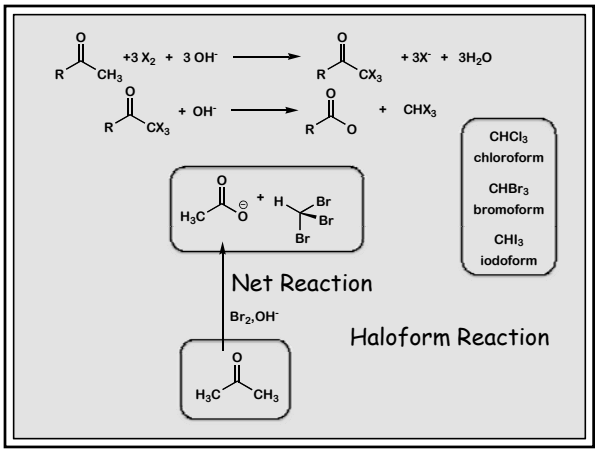
F. iii + iv G. all four

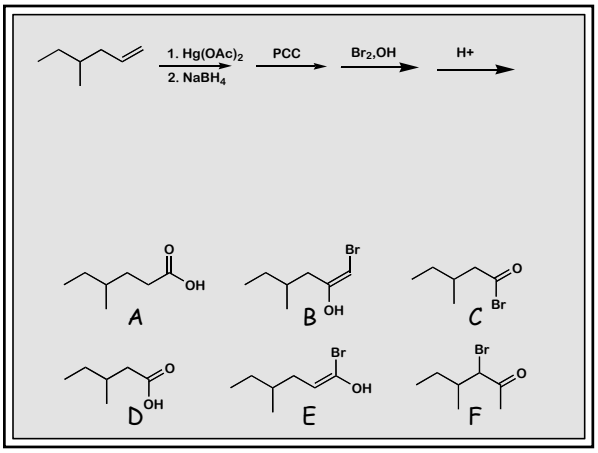

Bromine Addition
Net Reaction
Br2
H+(cat)
+ HBr

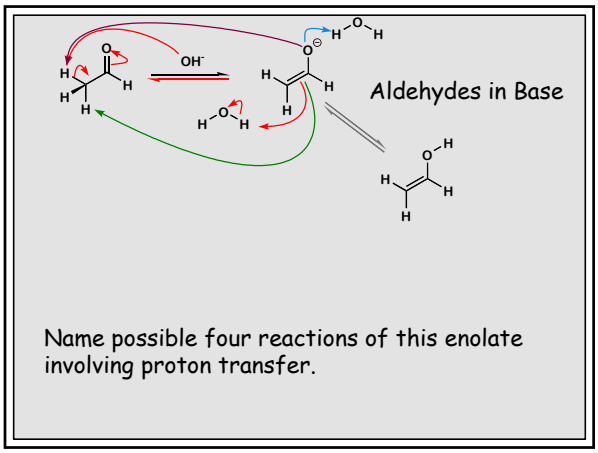

Base
Catalyzed
Tautomerization
Many reactions
of carbonyl compounds
can be catalized by both
acid or base


Bromine Addition
Trick
Question
Write the
balanced reaction.
Is it catalyzed by
OH- ?
A. Yes
B. No
Net Reaction
Br2,OH-
+ H2O

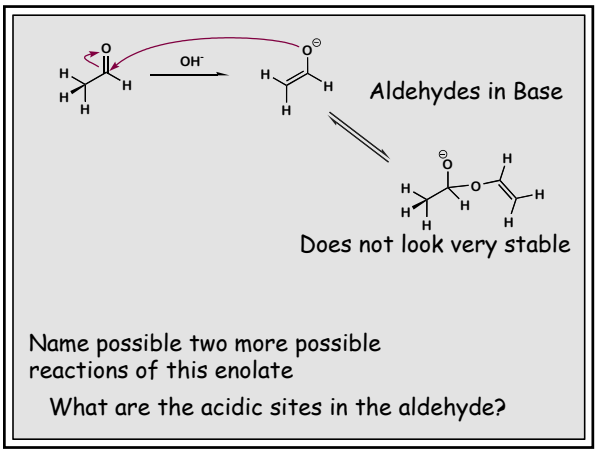

Net Reaction
Br2,OH-


+3 X2 + 3 OH-
+ 3X- + 3H2O
+ OH-
+ CHX3
CHCl3
chloroform
CHBr3
bromoform
CHI3
iodoform
Net Reaction
Br2,OH-
Haloform Reaction


1. Hg(OAc)2
2. NaBH4
PCC
Br2,OH
H+
A
B
C
D
E
F

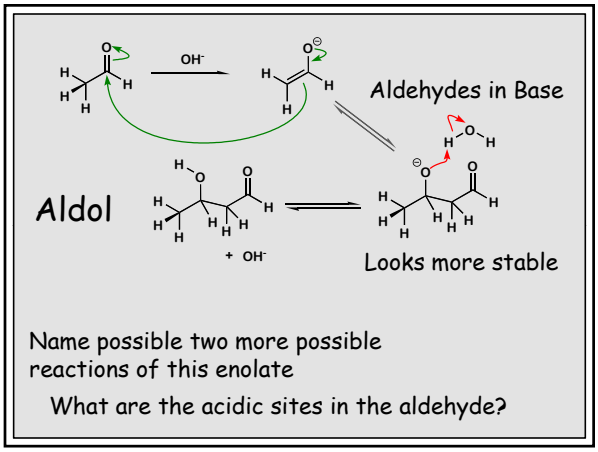


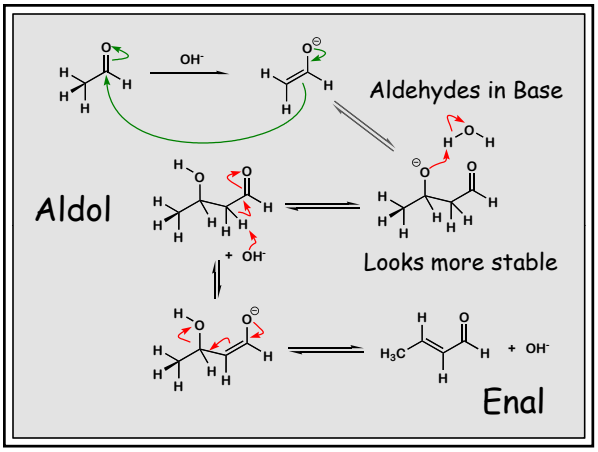
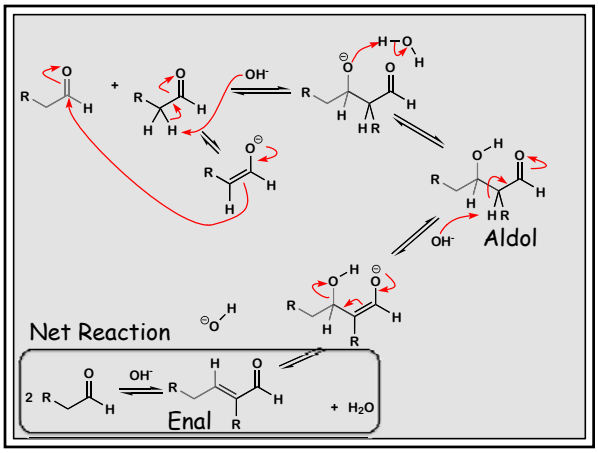
Name possible four reactions of this enolate involving proton transfer.



Name possible two more possible reactions of this enolate

What are the acidic sites in the aldehyde?



Name possible two more possible reactions of this enolate

What are the acidic sites in the aldehyde?