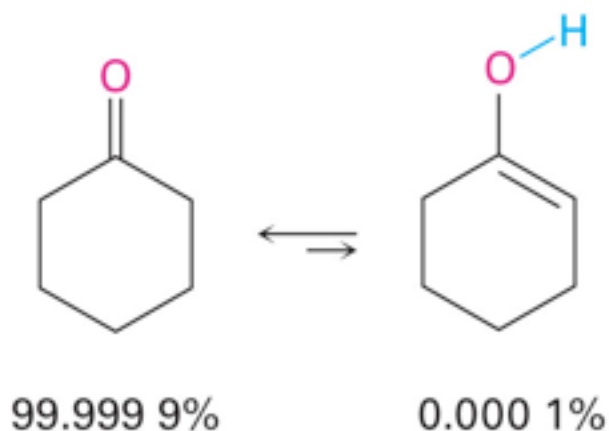
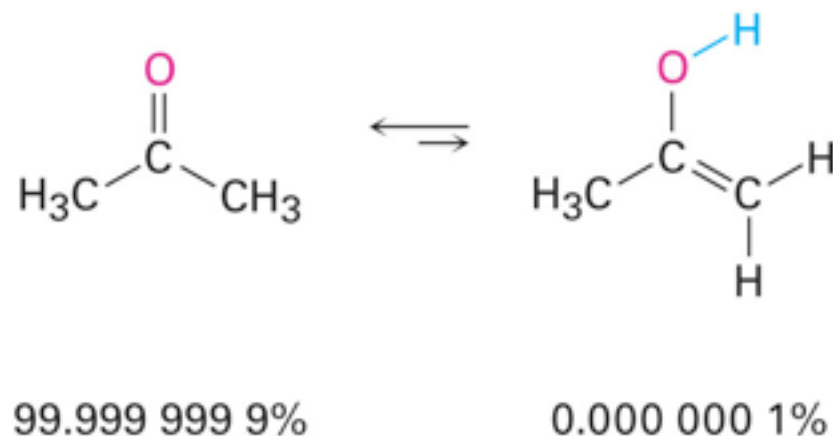


Chapter 22

Carbonyl Alpha-Substitution Reactions



Cyclohexanone

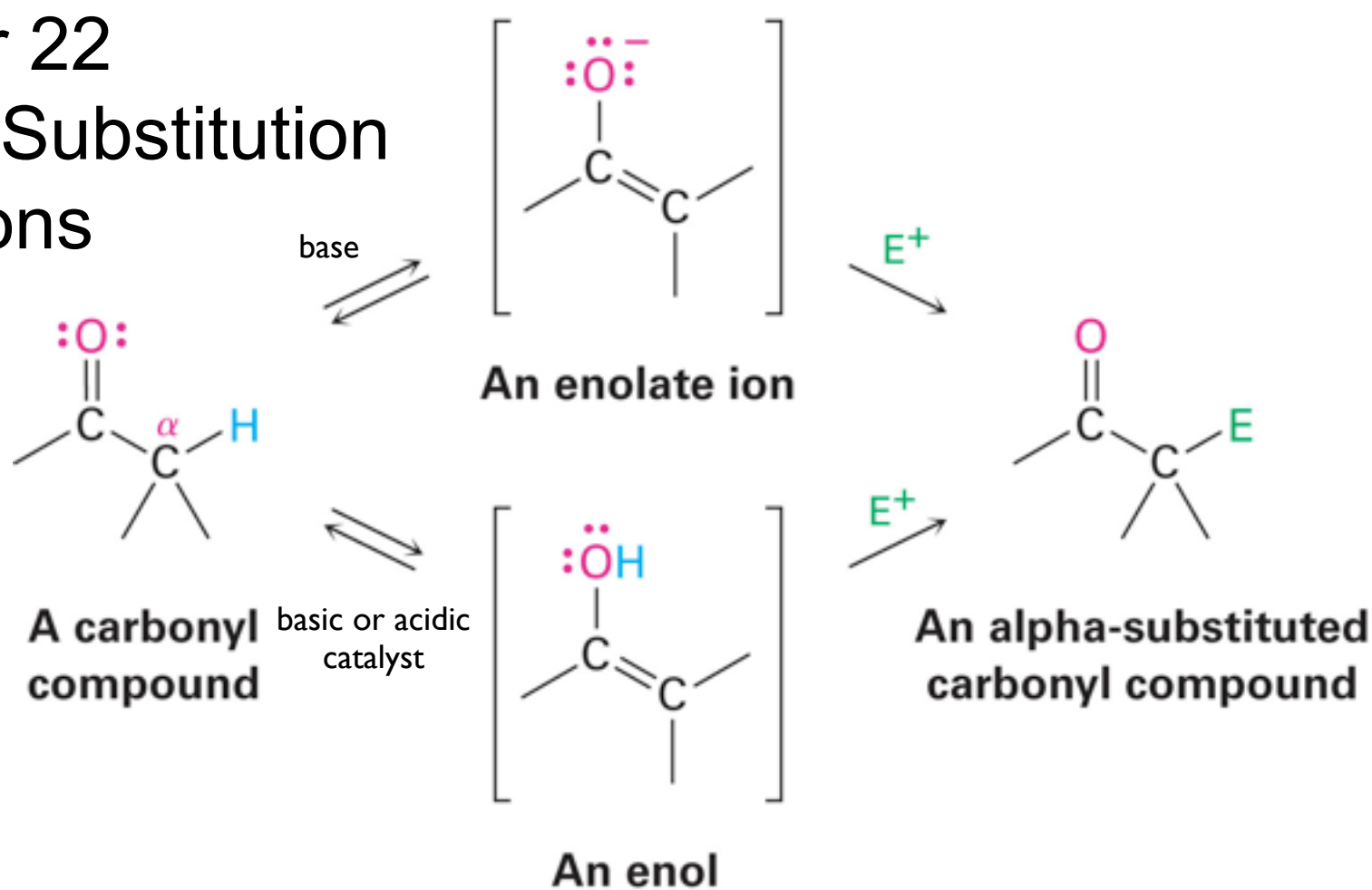


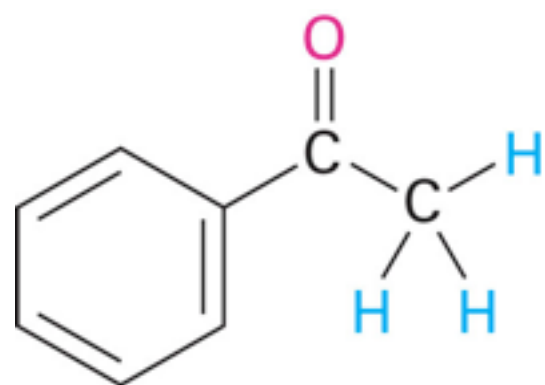
Acetone

enols are not resonance structures
they are TAUTOMERS

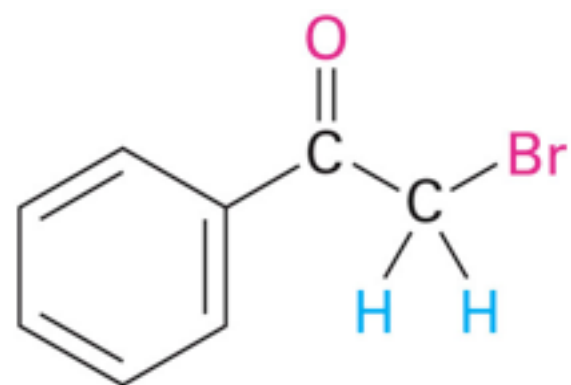
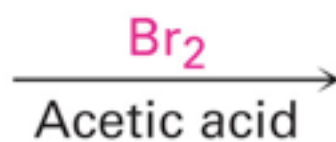
Chapter 22

Carbonyl Alpha-Substitution Reactions

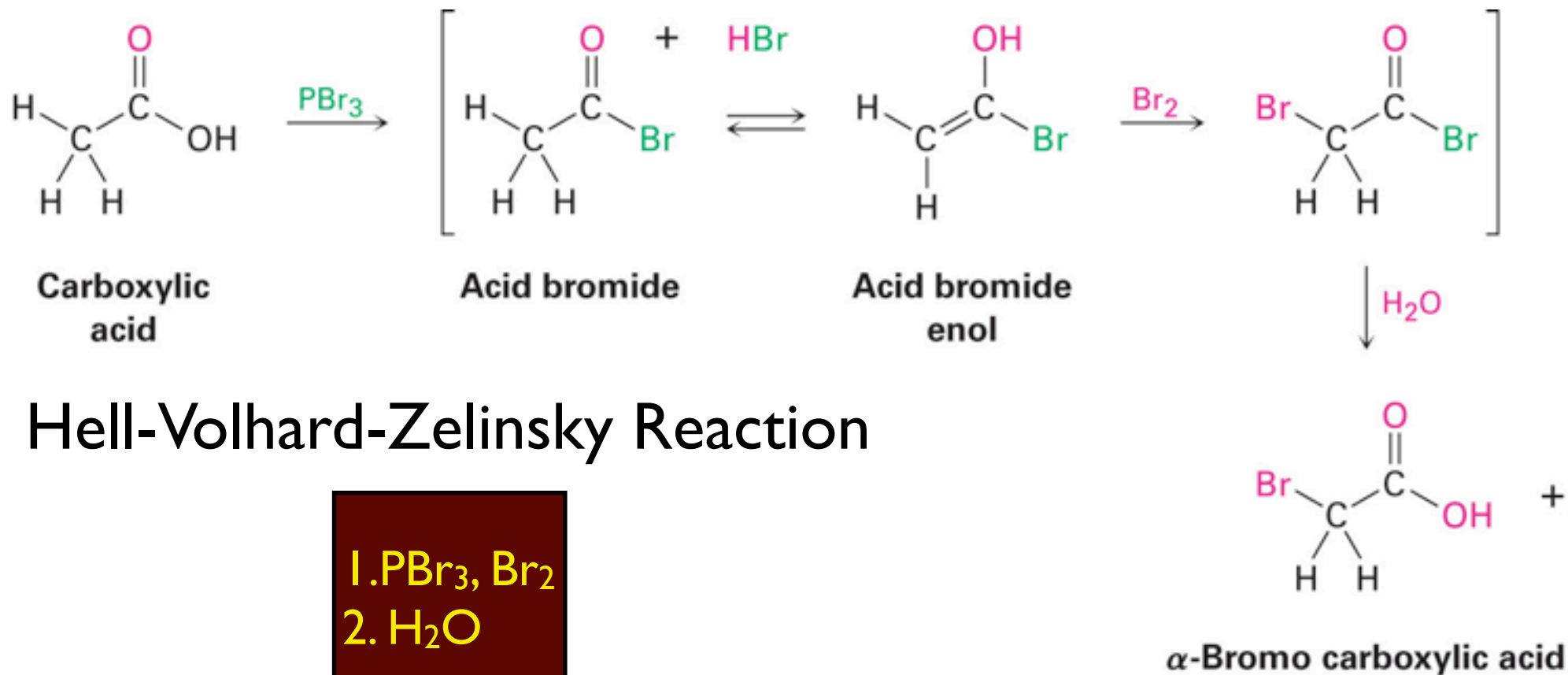




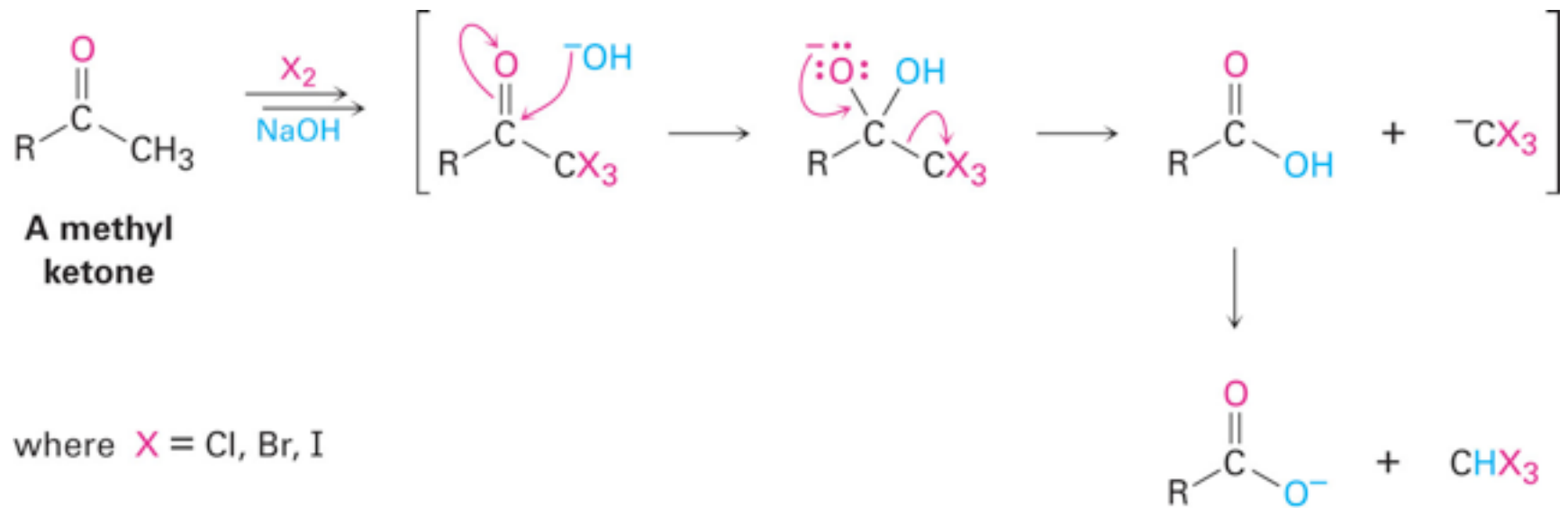
Acetophenone



α -Bromoacetophenone (72%)



Haloform Reaction



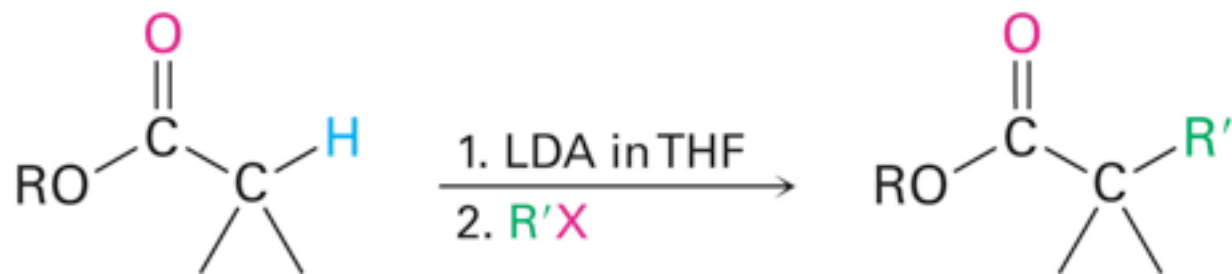
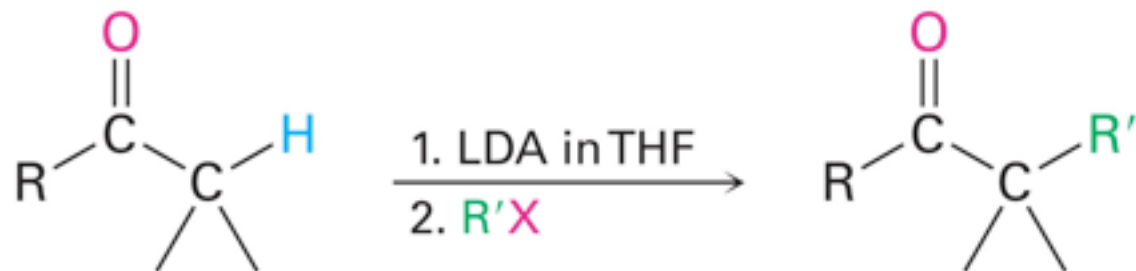
A methyl
ketone

where $X = Cl, Br, I$

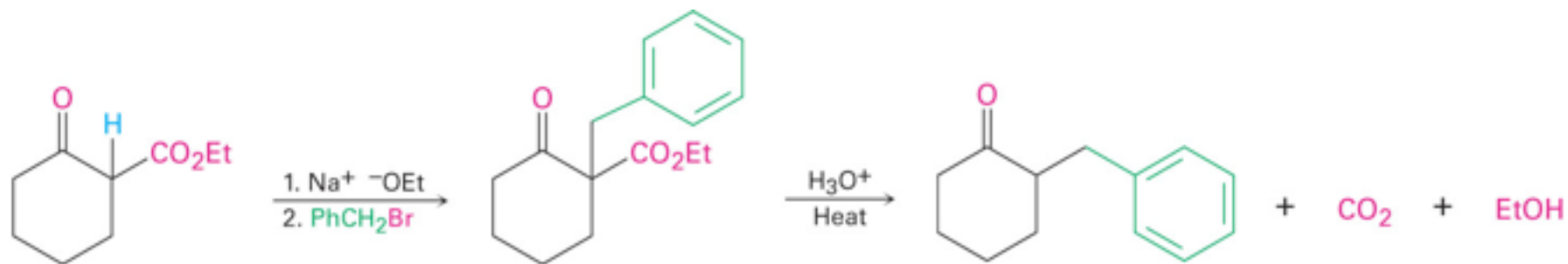
Table 22.1 Acidity Constants for Some Organic Compounds

Functional group	Example	pK _a
Carboxylic acid	$\text{CH}_3\overset{\text{O}}{\parallel}\text{COH}$	5
1,3-Diketone	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_2\overset{\text{O}}{\parallel}\text{CCH}_3$	9
3-Keto ester	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_2\overset{\text{O}}{\parallel}\text{COCH}_3$	11
1,3-Diester	$\text{CH}_3\overset{\text{O}}{\parallel}\text{OCCH}_2\overset{\text{O}}{\parallel}\text{COCH}_3$	13
Alcohol	CH_3OH	16
Acid chloride	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCl}$	16
Aldehyde	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CH}$	17
Ketone	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_3$	19
Thioester	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CSCH}_3$	21
Ester	$\text{CH}_3\overset{\text{O}}{\parallel}\text{COCH}_3$	25
Nitrile	$\text{CH}_3\text{C}\equiv\text{N}$	25
<i>N,N</i> -Dialkylamide	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CN}(\text{CH}_3)_2$	30
Dialkylamine	$\text{HN}(i\text{-C}_3\text{H}_7)_2$	36

Alkylation



enolate formation, alkylation, hydrolysis/decarboxylation



Ethyl 2-oxocyclohexane-
carboxylate
(a cyclic β -keto ester)

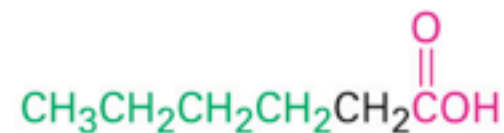
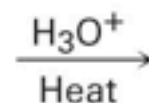
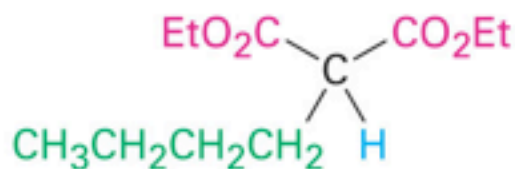
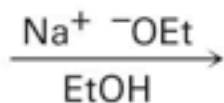
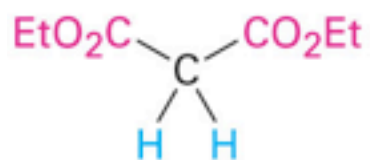
2-Benzylcyclohexanone
(77%)

β -keto ester



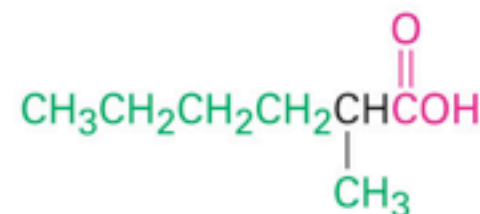
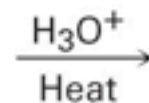
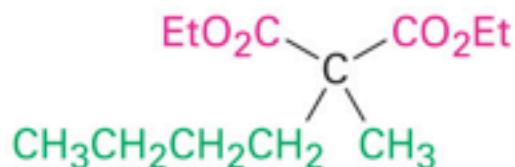
1-Bromobutane

+

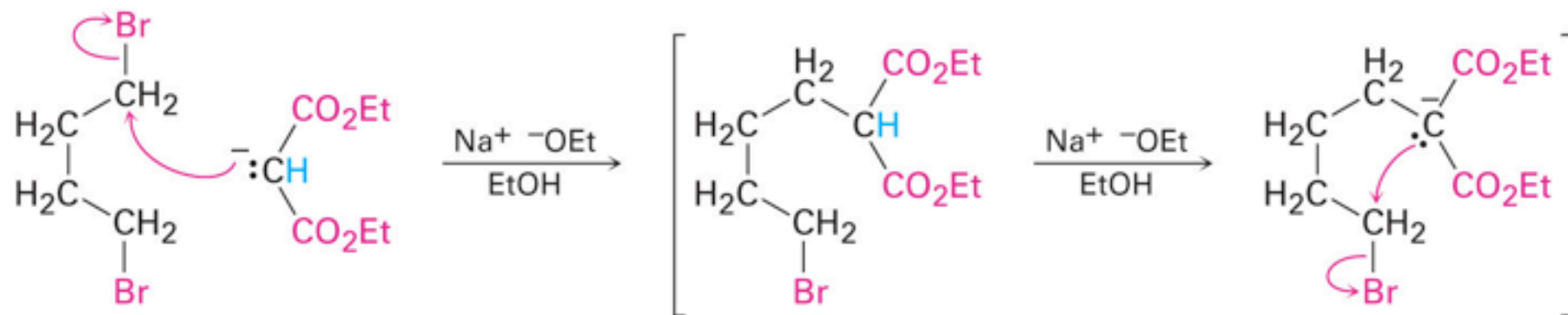


Hexanoic acid (75%)

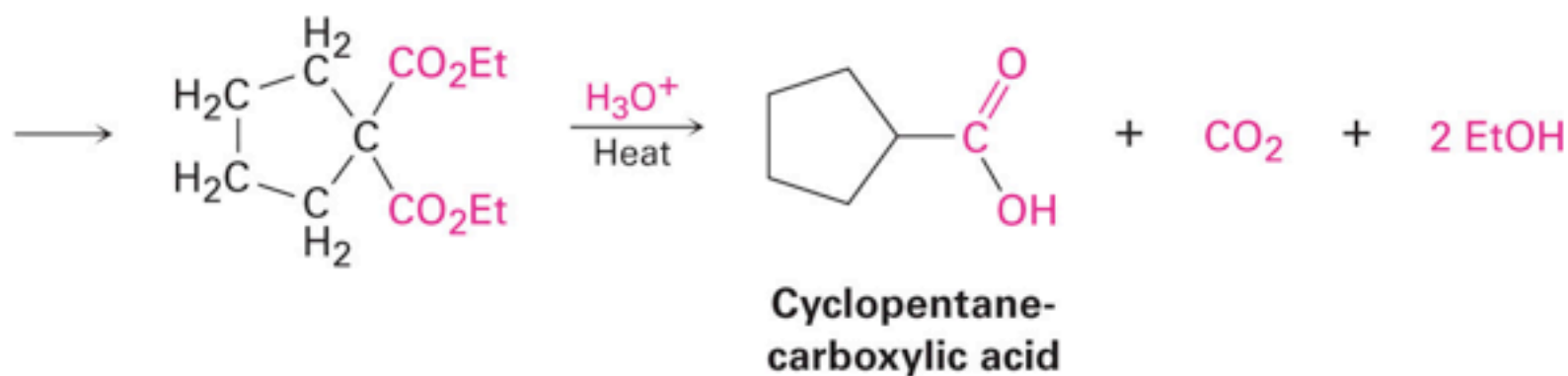
1. $\text{Na}^+ \text{ } ^-\text{OEt}$
2. CH_3I

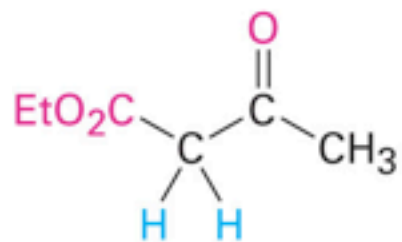


2-Methylhexanoic acid (74%)

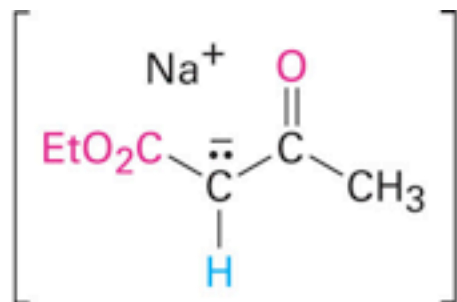
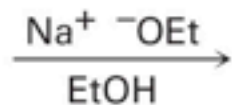


1,4-Dibromobutane

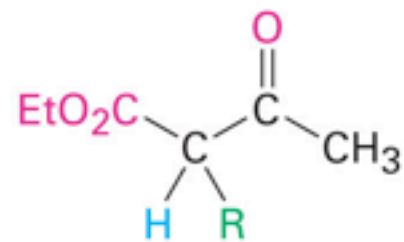




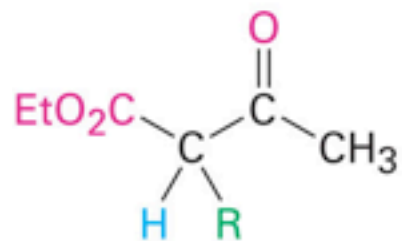
**Ethyl acetoacetate
(acetoacetic ester)**



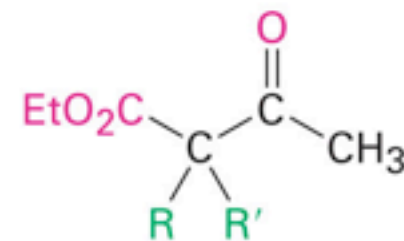
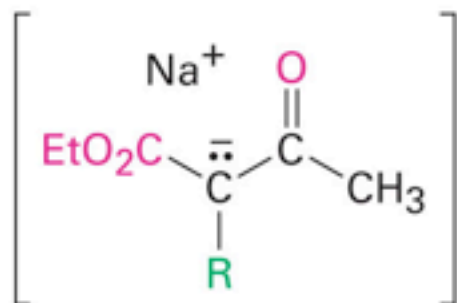
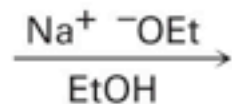
**Sodio acetoacetic
ester**



**A monoalkylated
acetoacetic ester**



**A monoalkylated
acetoacetic ester**



**A dialkylated
acetoacetic ester**