



# جامعه ذي قار
# كلية العلوم
# قسم الكيمياء

## الكيمياء العضوية – المرحلة الثالثة
## العام الدراسي 2023- 2024

## مركبات الكاربونيل
## Carbonyl compounds

أ.م. د عذراء حامد مكي

# الكتب المنهجية للمحاضرات

الكيمياء العضوية للمؤلفين هارت وشوتر
الفصل التاسع

كتاب أسس الكيمياء العضوية : المؤلف : وائل غالب محمد

الفصل الرابع / الألدهيدات والكيتونات

اسم الكتاب : ميكانيكية التفاعلات العضوية
ألمؤلف : إبراهيم محمود النجار

Robert Thornton Morrison

اسم الكتاب Organic chemistry

ألمؤلف Francis A. Carey

لكيمياء العضوية المتقدمة للصفوف الثالثة
فهد علي حسين

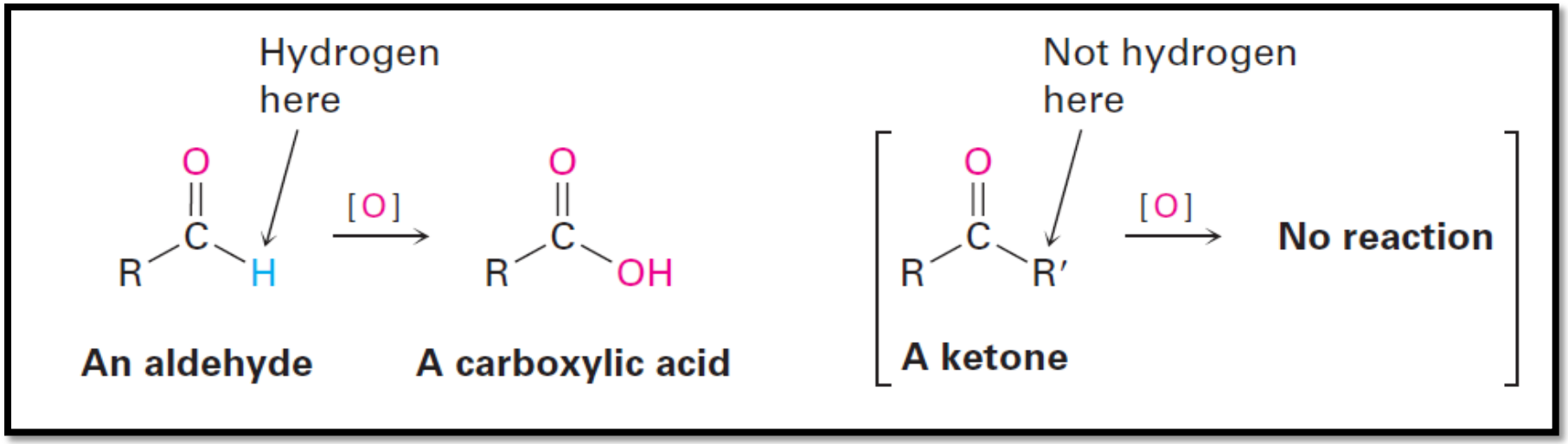
أسس الكيمياء العضوية

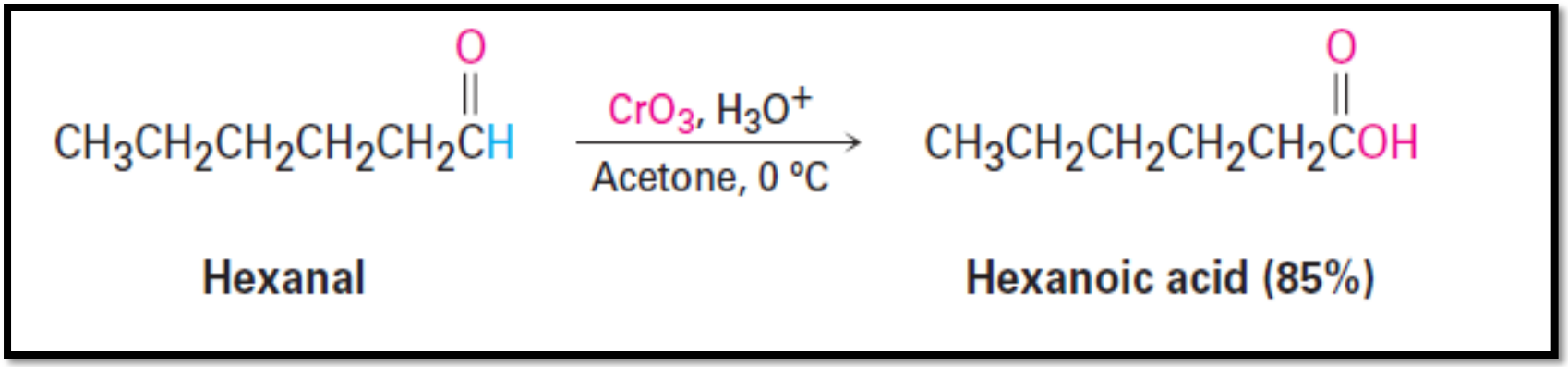
المؤلف : محمد بن ابراهيم الحسن

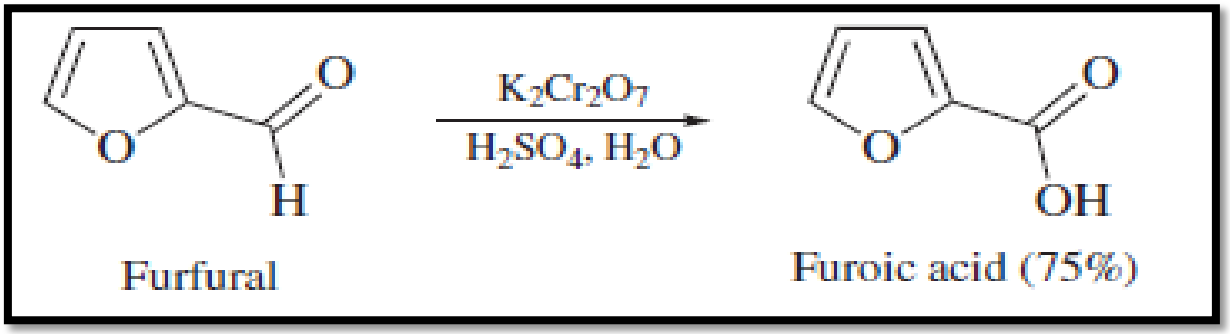
# Oxidation of Aldehydes and Ketones

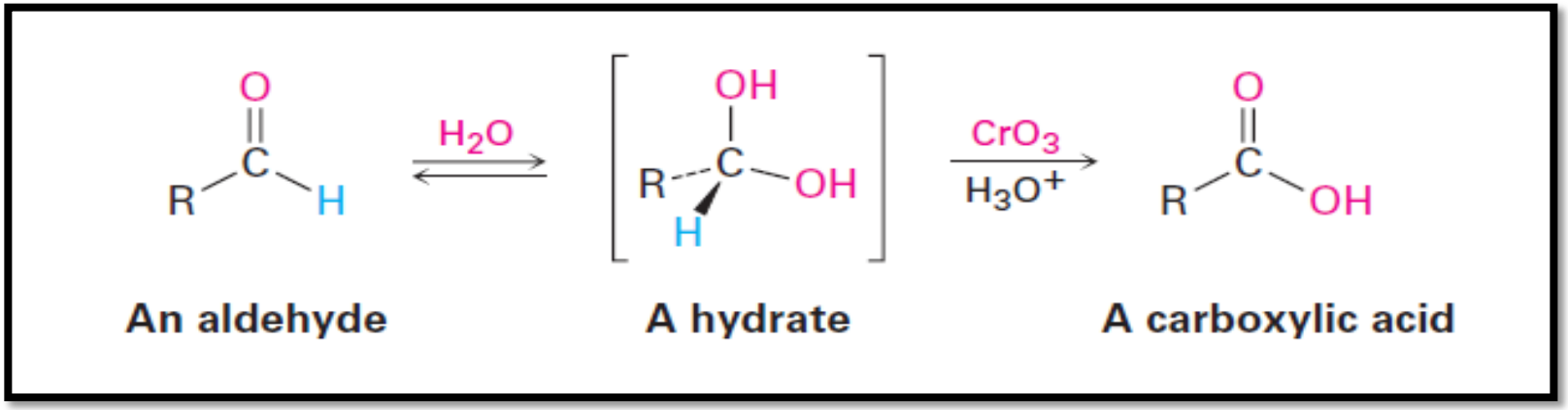
# اكسدة الالديهايدات والكيتونات

الالديهايدات والكيتونات الالفاتية متشابهة من حيث تفاعلات الاضافة. اما في تفاعلات الاكسدة فالأمر مختلف. تأكسد الالديهايدات بفعل عوامل الاكسدة $KMnO_4$ , $K_2Cr_2O_7$, $CrO_3$ في وسط حامضي الى الحامض الكاربوكسيلية . وتتاكسد الالديهايدات بسرعة مقارنة مع الكيتونات .

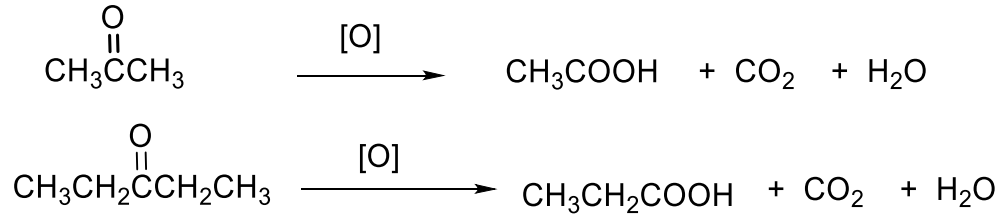


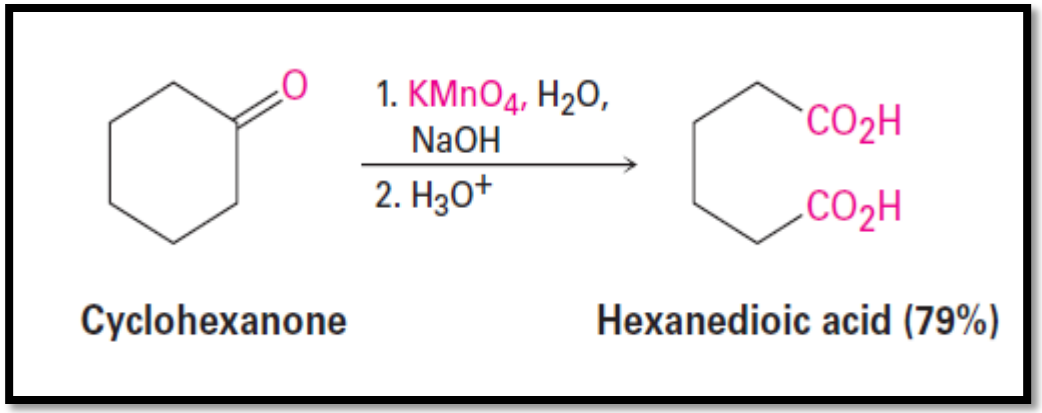





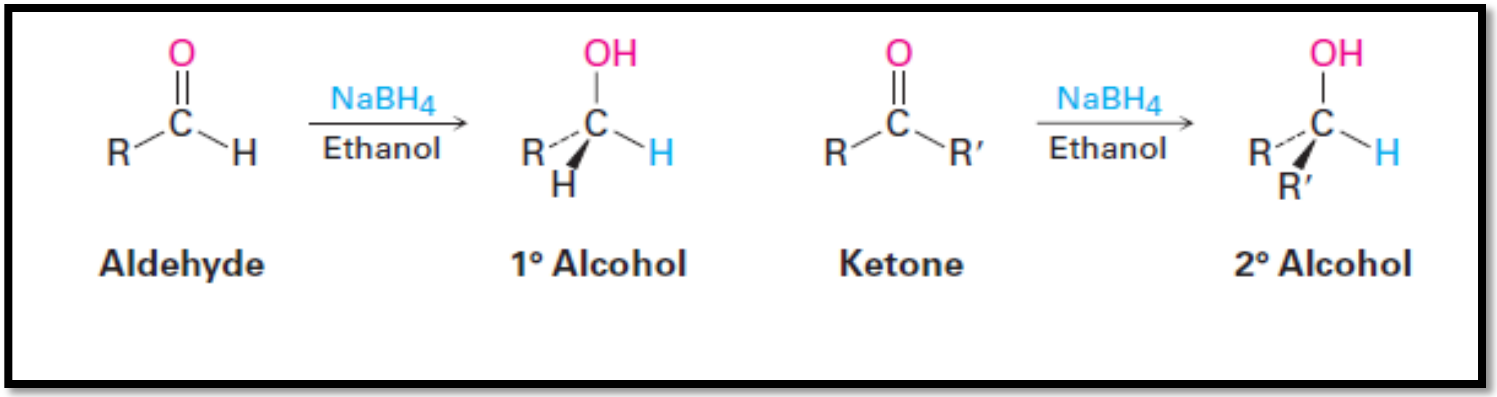

ان اكسدة الكيتونات تتم في ظروف خاصة من عوامل اكسدة قوية من الدايكرومات الحامضية او برمنكنات البوتاسيوم القاعدية , ان اكسدة الكيونات تنتج حوامض كاربوكسيلية تكون فيها ذرات الكاربون اقل من عدد ذرات الكاربون في الكيتون المستخدم في التحضير. حيث ان الاصرة التساهمية بين كاربون مجموعة الكاربونيل واحدى سلاسل الكاربون تنكسر وتتحول سلسلة الكاربون الى غاز ثنائي وكسيد الكاربون وماء اما بالنسبة الى الجزء المتبقى فيتحول الى الحامض الكاربوكسيلى

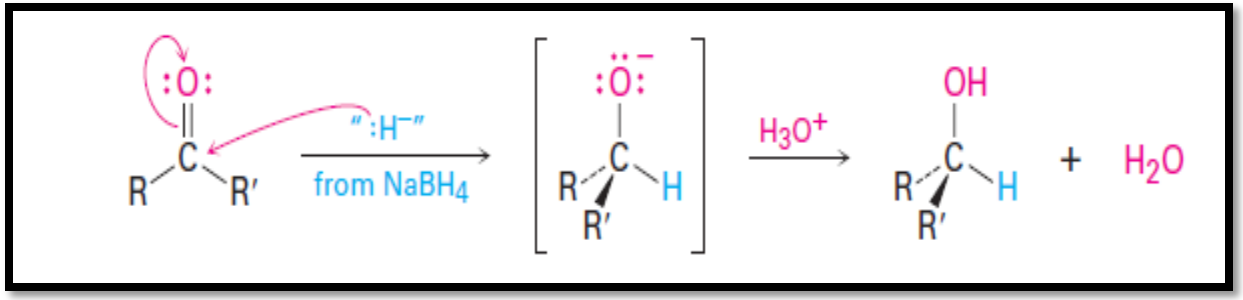



## Nucleophilic Addition of Hydride and Grignard Reagents: Alcohol Formation

### Addition of Hydride Reagents: Reduction

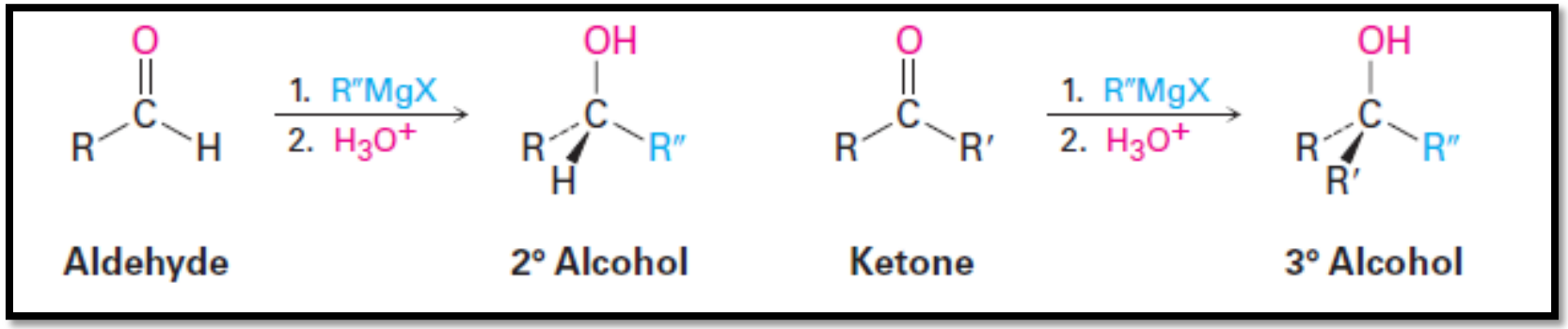





اختزال الالديهايدات والكيتونات

## Addition of Grignard Reagents, RMgX

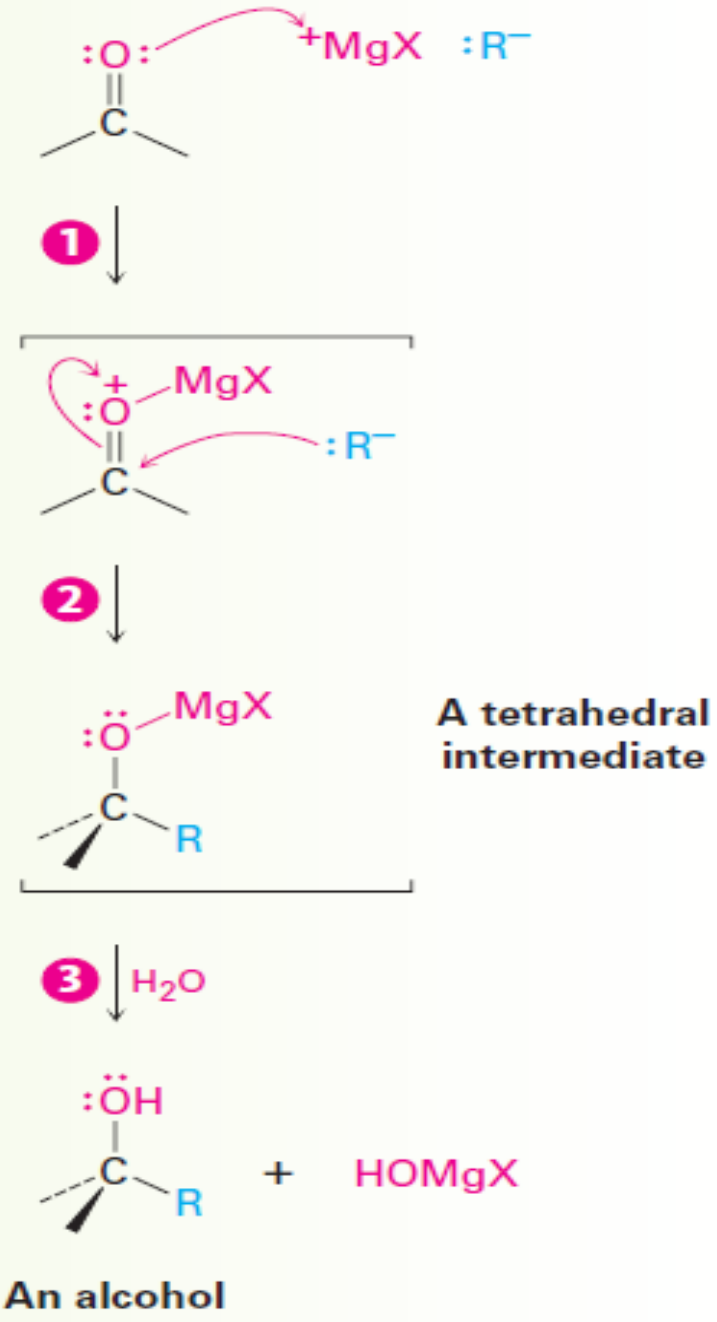
اضافة كاشف كرينارد



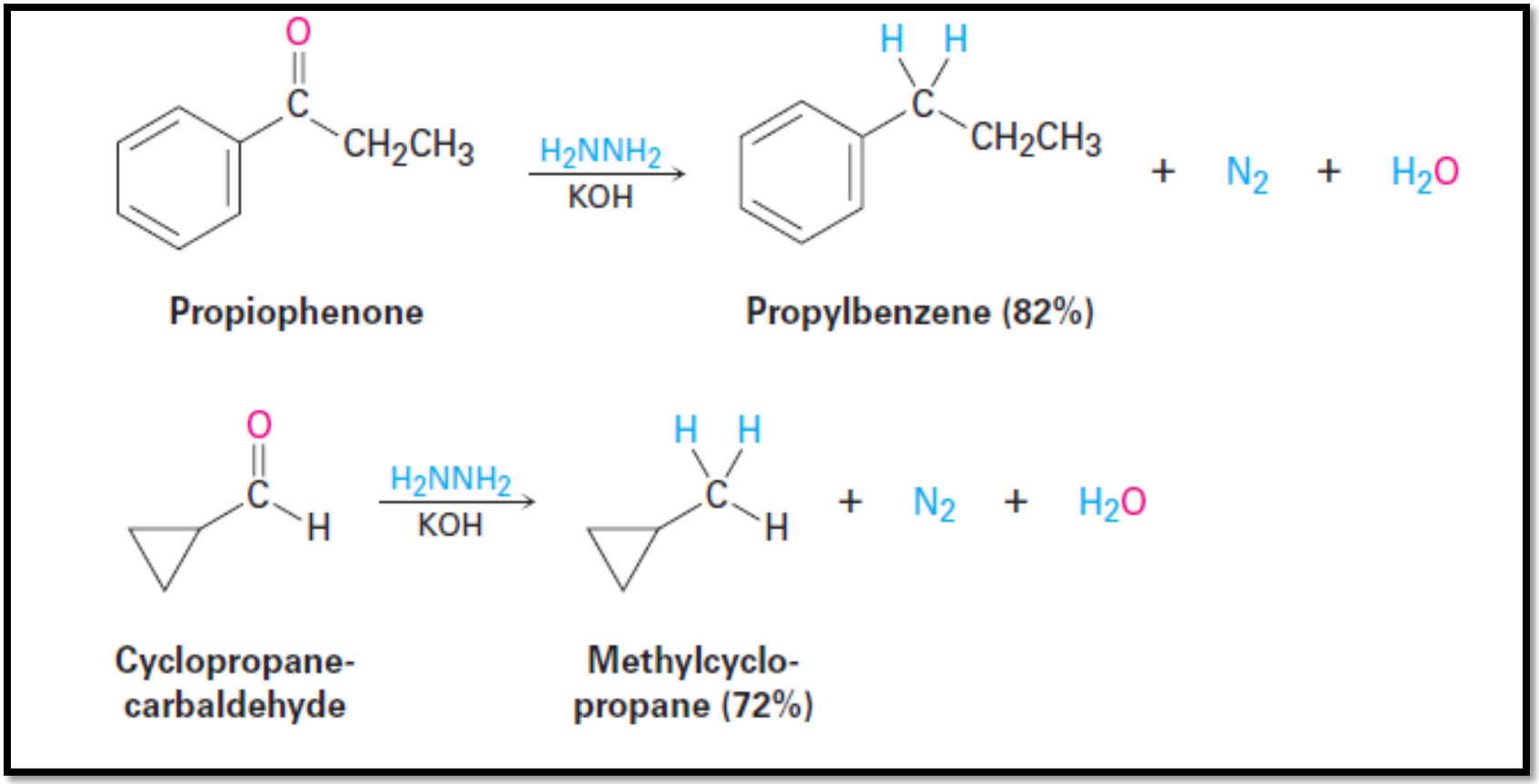
1. The Lewis acid $Mg^{2+}$ first forms an acid–base complex with the basic oxygen atom of the aldehyde or ketone, thereby making the carbonyl group a better acceptor.

2. Nucleophilic addition of an alkyl group $:R^-$ to the aldehyde or ketone produces a tetrahedral magnesium alkoxide intermediate . . .

3. . . . which undergoes hydrolysis when water is added in a separate step. The final product is a neutral alcohol.

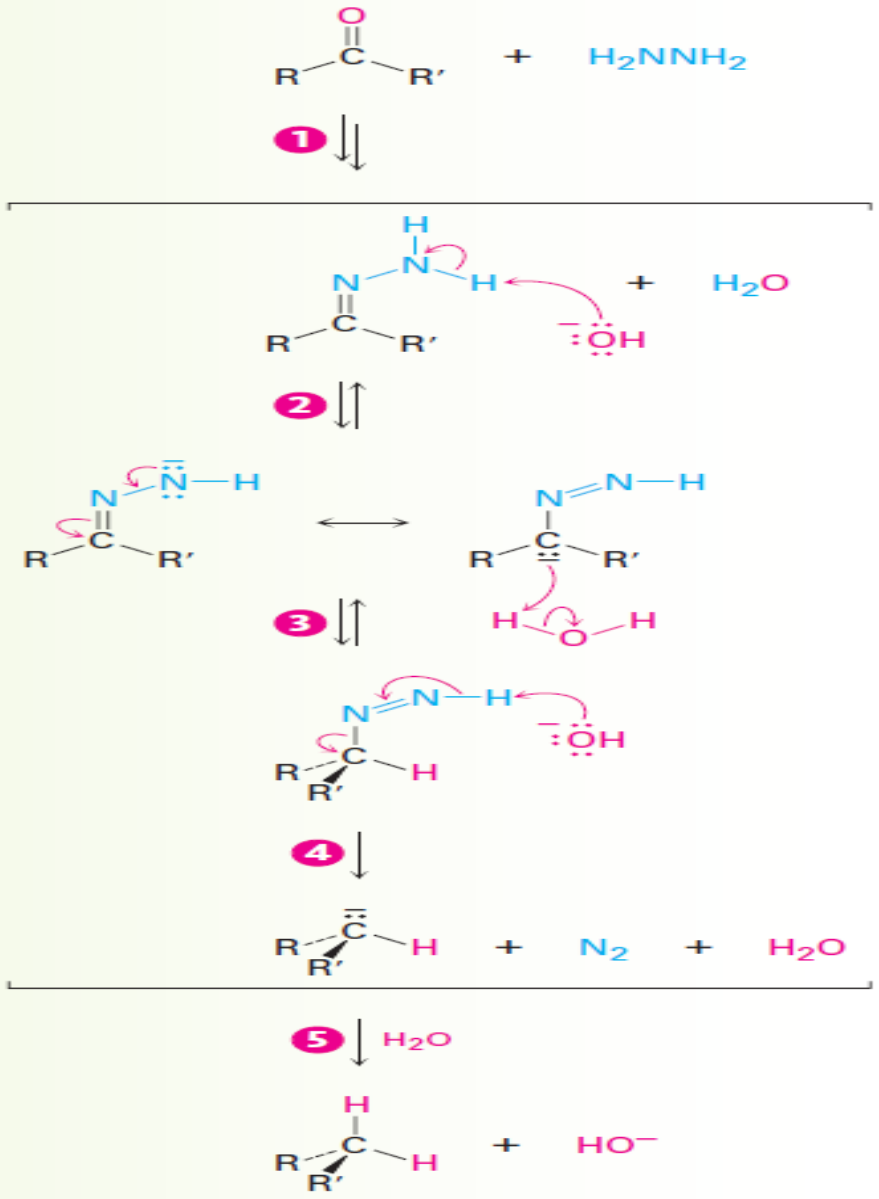


# Nucleophilic Addition of Hydrazine: The Wolff–Kishner Reaction



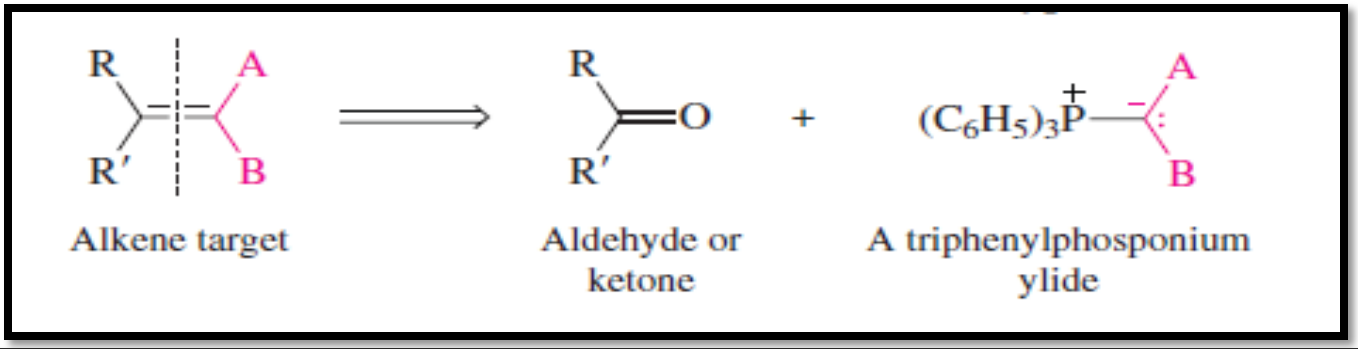
## MECHANISM

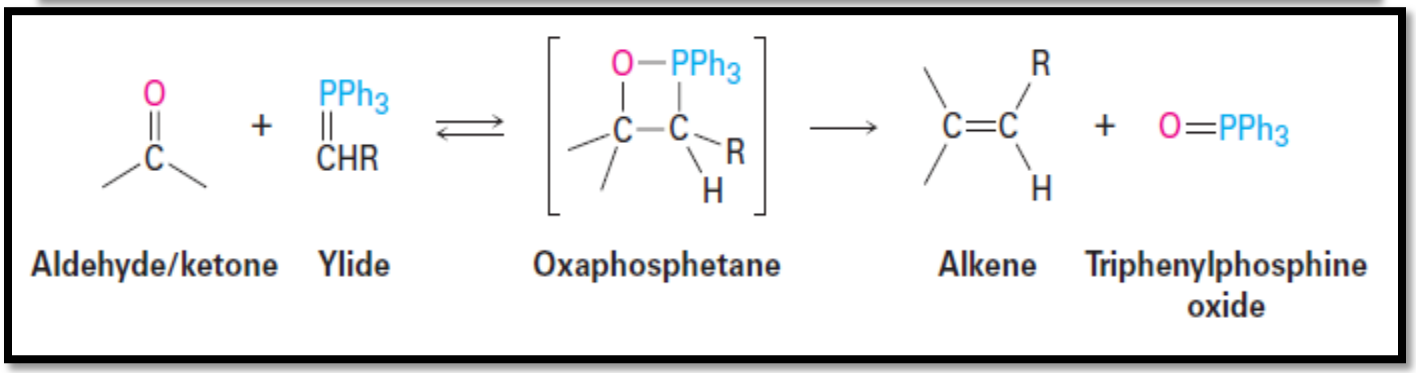
Mechanism for the Wolff–Kishner reduction of an aldehyde or ketone to yield an alkane.

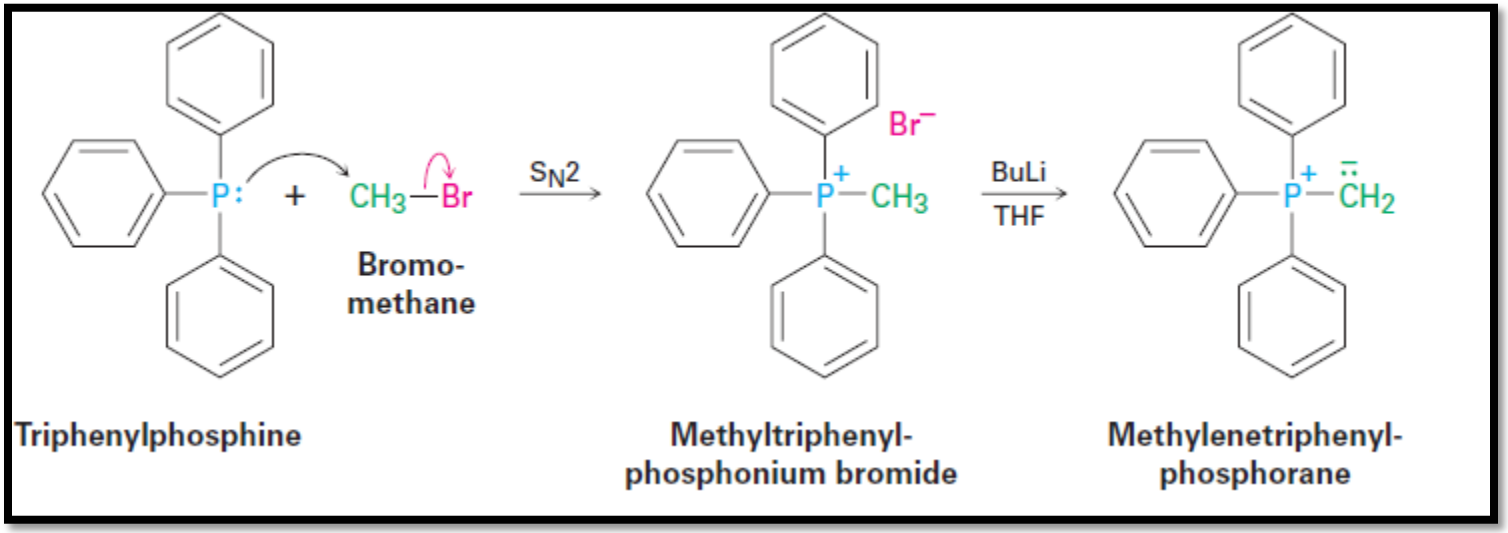


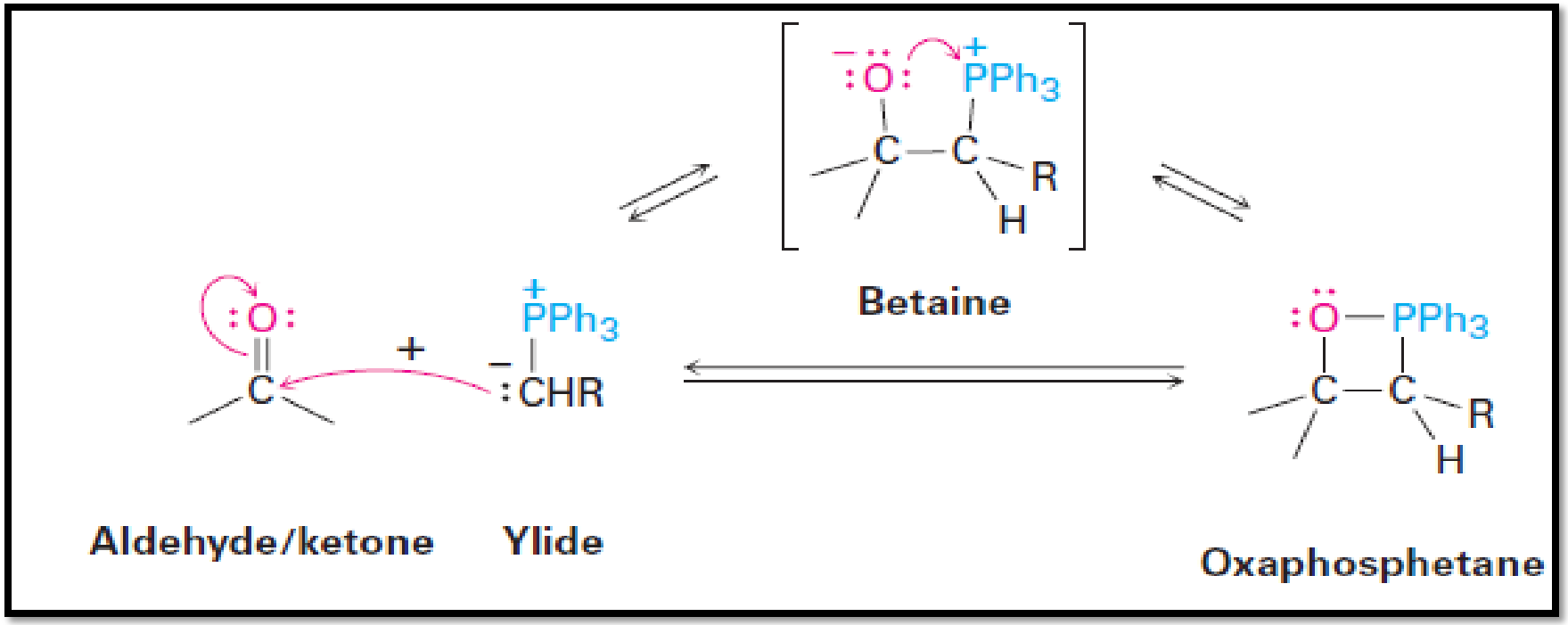

1. Reaction of the aldehyde or ketone with hydrazine yields a hydrazone in the normal way.
2. Base abstracts a weakly acidic N–H proton, yielding a hydrazone anion. This anion has a resonance form that places the negative charge on carbon and the double bond between nitrogens.
3. Protonation of the hydrazone anion takes place on carbon to yield a neutral intermediate.
4. Deprotonation of the remaining weakly acidic N–H occurs with simultaneous loss of nitrogen to give a carbanion . . .
5. . . . which is protonated to give the alkane product.

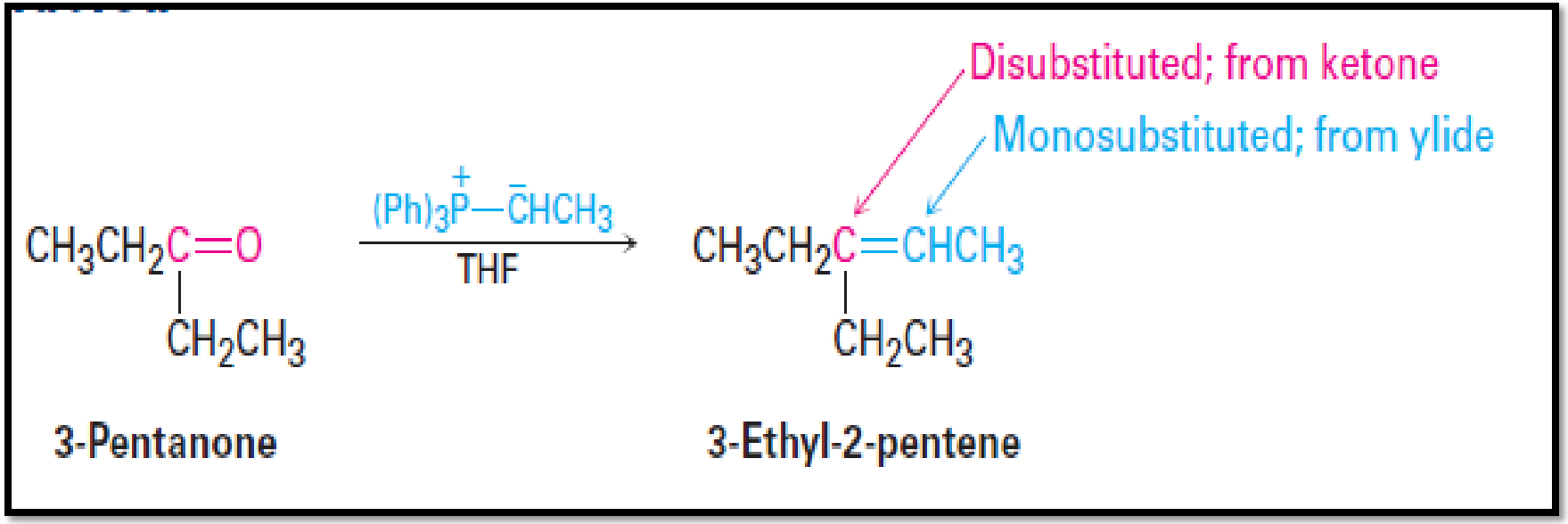
# Nucleophilic Addition of Phosphorus Ylides: The Wittig Reaction.



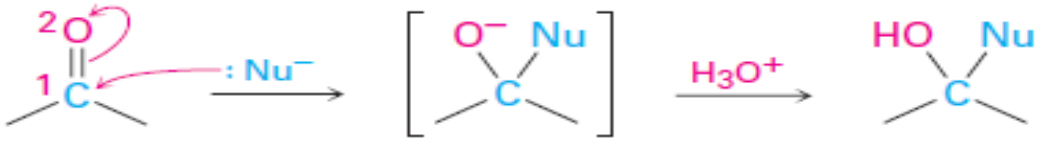




Betaine
Aldehyde/ketone
Ylide
Oxaphosphetane

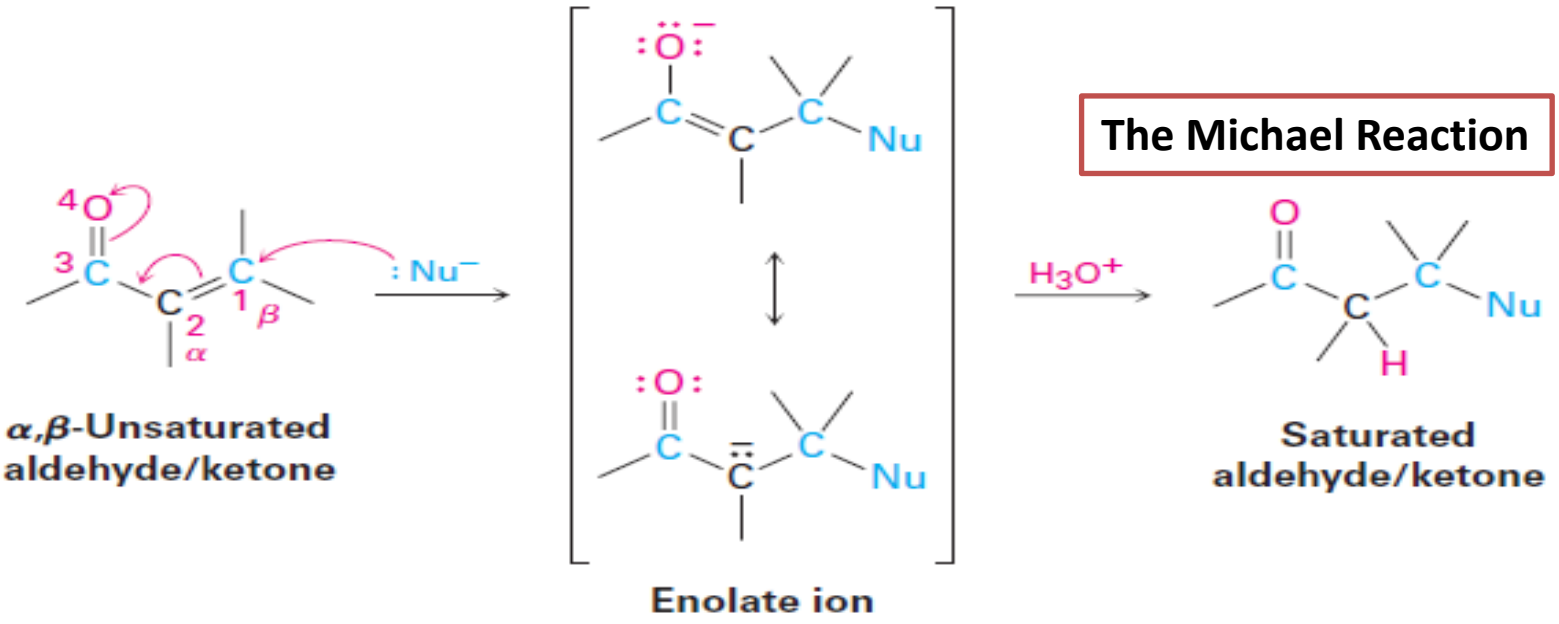

Disubstituted; from ketone
Monosubstituted; from ylide
THF
3-Pentanone
3-Ethyl-2-pentene

# Conjugate Nucleophilic Addition to α,β-Unsaturated Aldehydes and Ketones

**Direct (1,2) addition**




**Conjugate (1,4) addition**

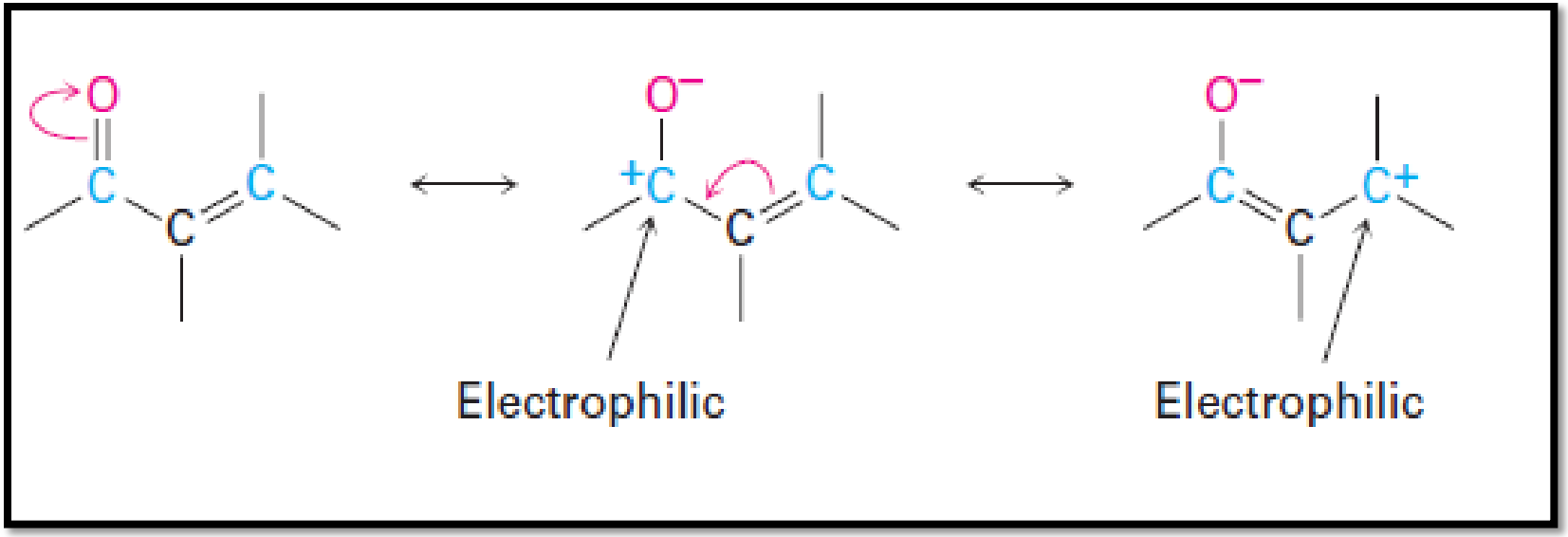


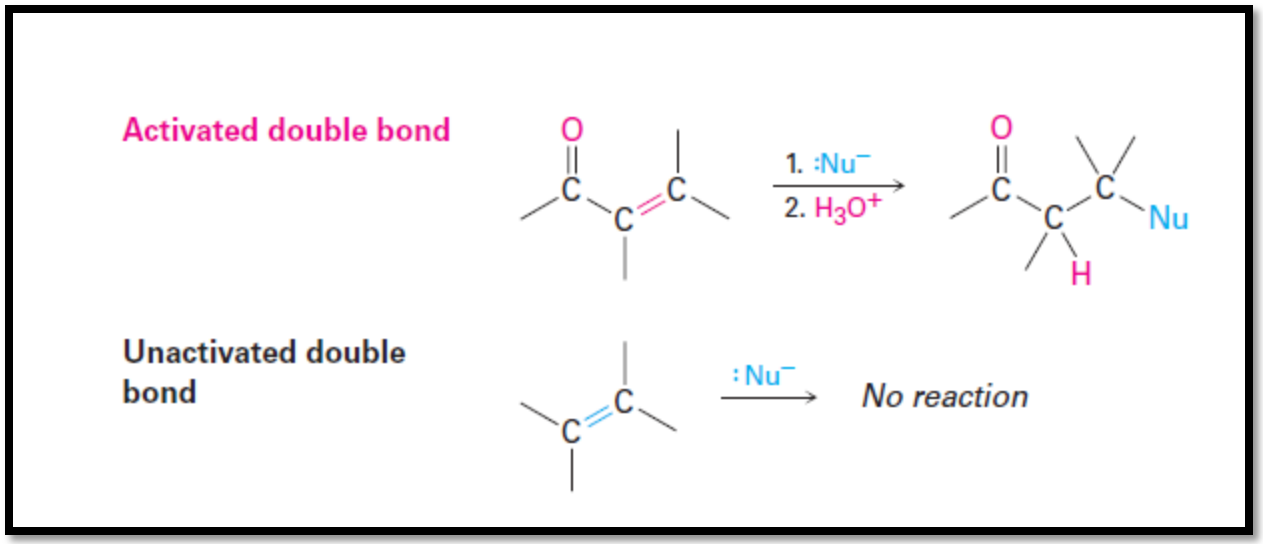

**α,β-Unsaturated aldehyde/ketone**

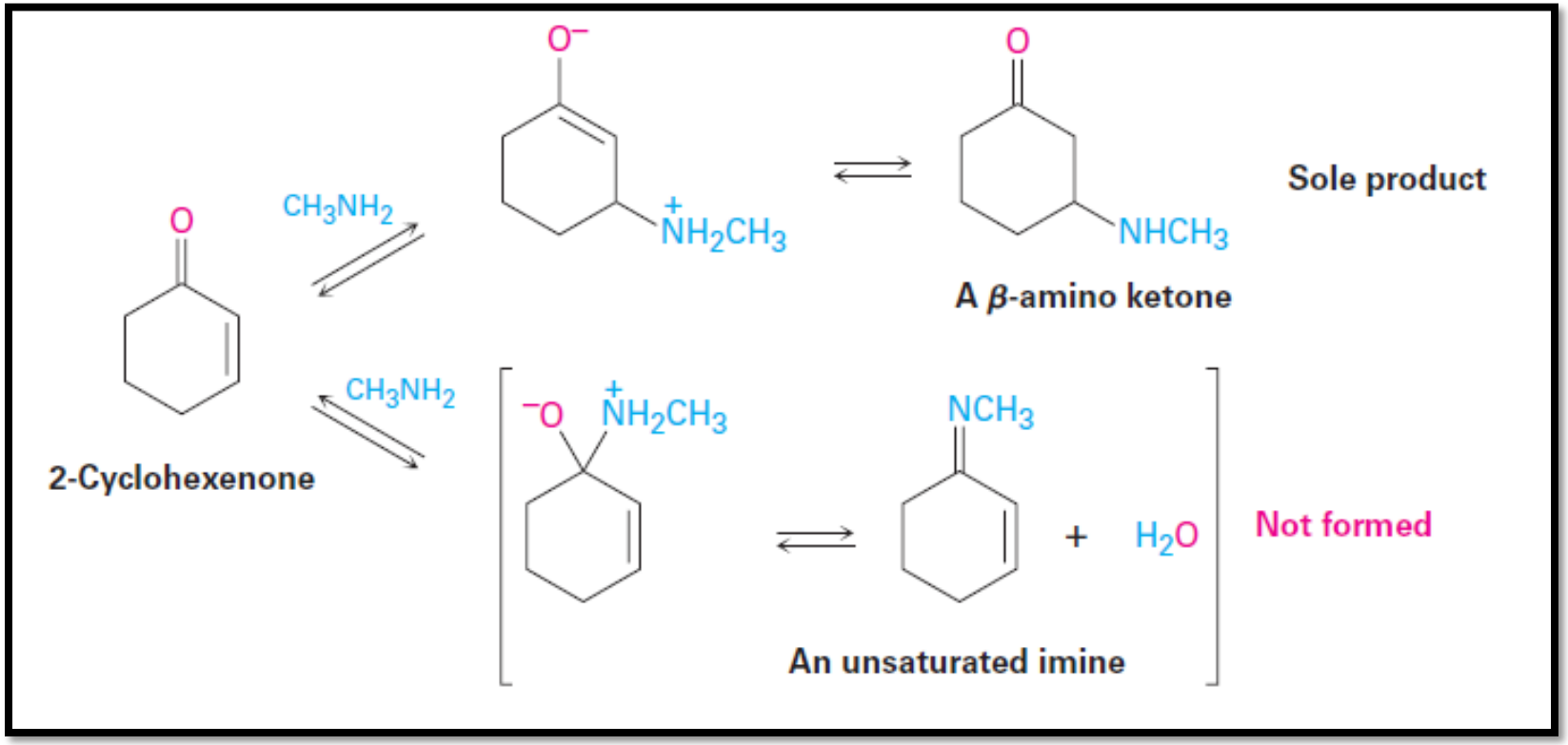
**Enolate ion**

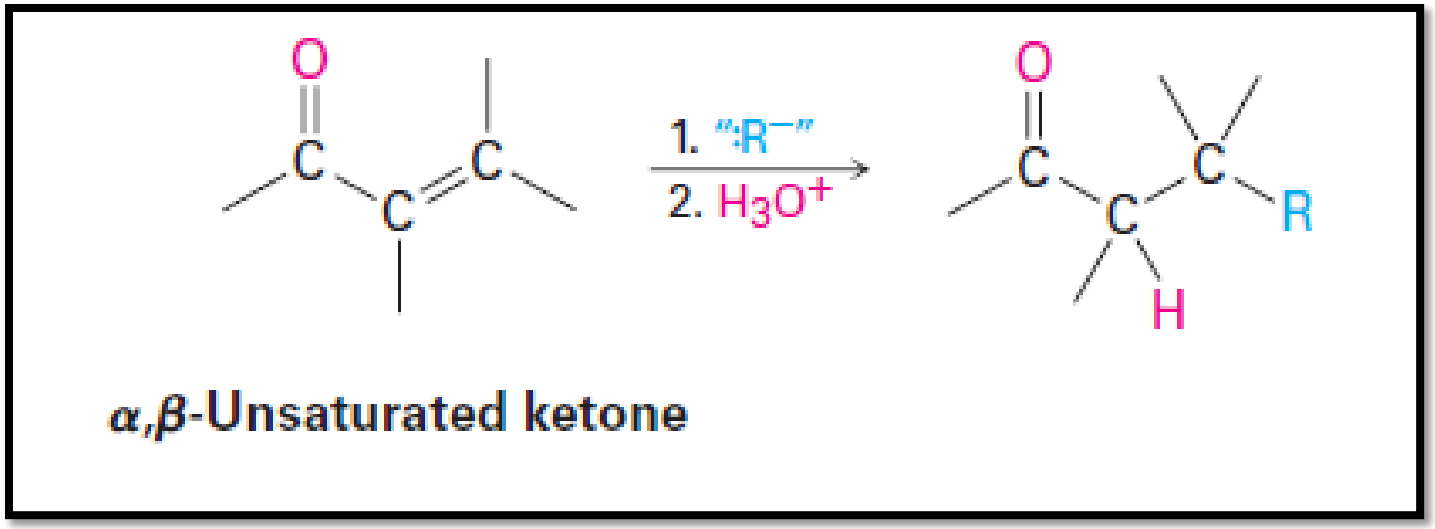
**The Michael Reaction**

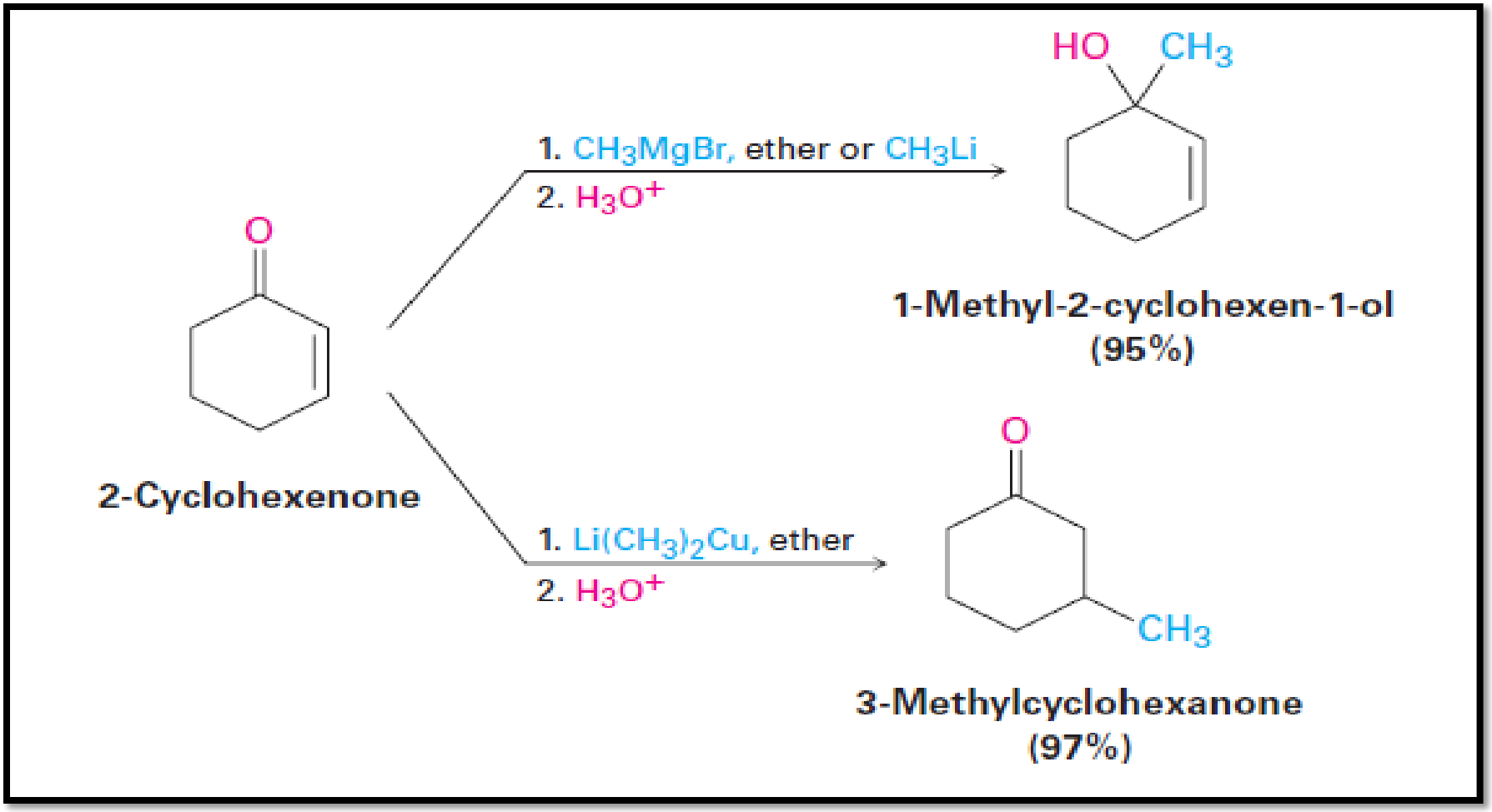
**Saturated aldehyde/ketone**

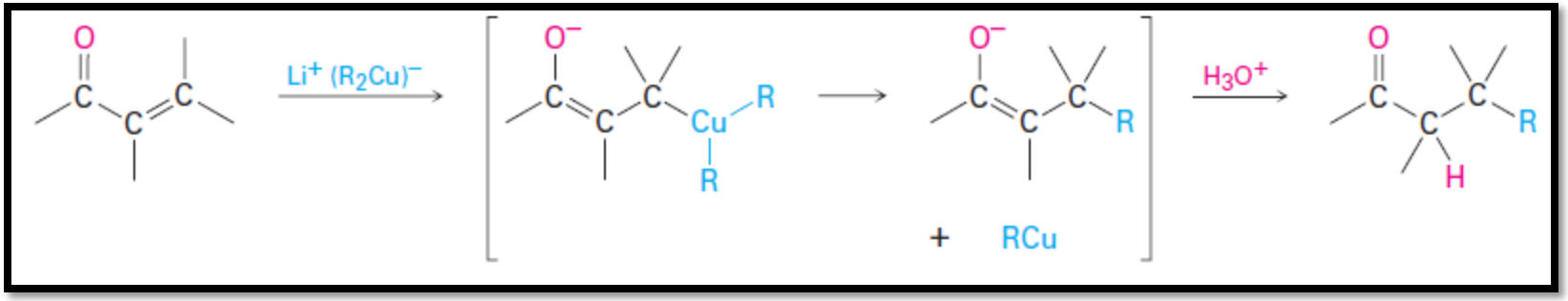

Electrophilic
Electrophilic

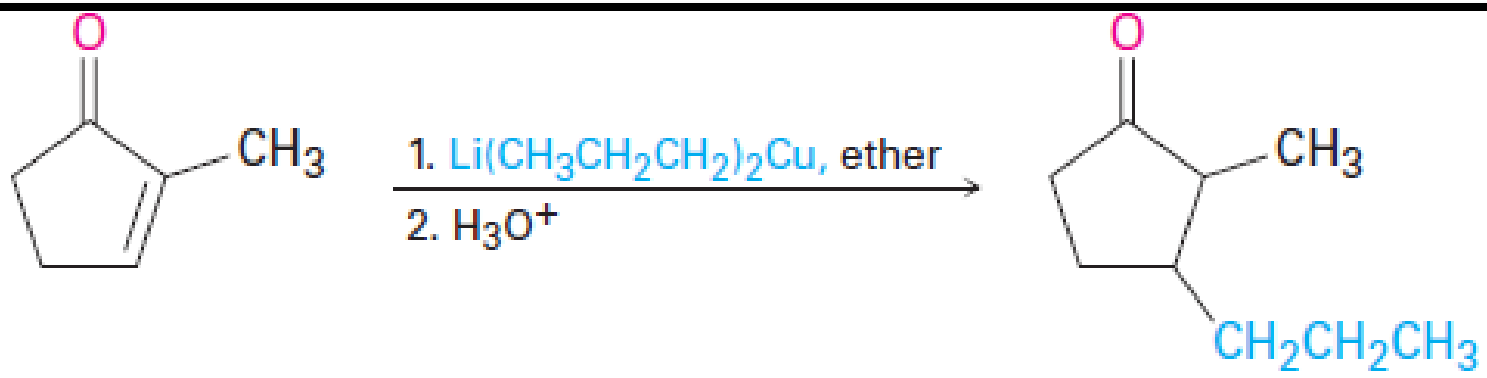

Activated double bond
1. :Nu⁻
2. H3O+
Nu
H
Unactivated double bond
:Nu⁻
No reaction


O
CH3NH2
O−
+NH2CH3
O
NHCH3
Sole product
A β-amino ketone
2-Cyclohexenone
CH3NH2
−O
+NH2CH3
NCH3
+
H2O
Not formed
An unsaturated imine

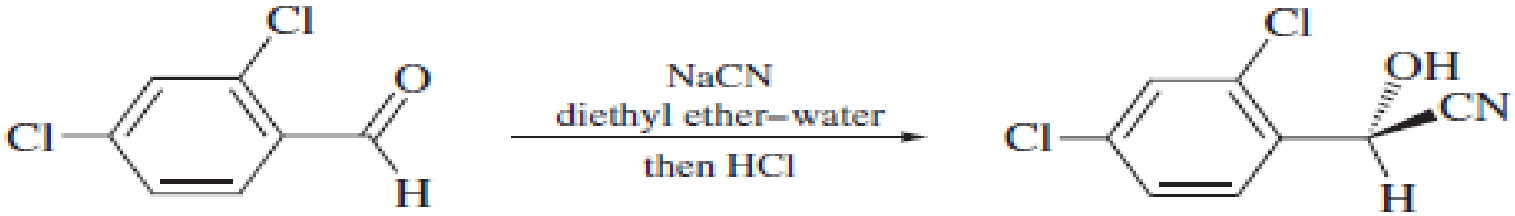

O
C
C
C
1. ":R−"
2. H3O+
O
C
C
C
R
H
α,β-Unsaturated ketone


HO
CH3
1. CH3MgBr, ether or CH3Li
2. H3O+
O
1-Methyl-2-cyclohexen-1-ol
(95%)
2-Cyclohexenone
1. Li(CH3)2Cu, ether
2. H3O+
O
CH3
3-Methylcyclohexanone
(97%)


O
Li+ (R2Cu)−
O−
Cu
R
R
+ RCu
H3O+
H

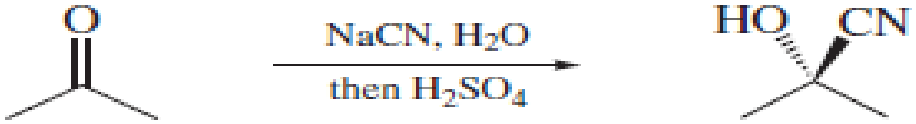



**2-Methyl-2-cyclopentenone** **2-Methyl-3-propylcyclopentanone**




2,4-Dichlorobenzaldehyde

2,4-Dichlorobenzaldehyde cyanohydrin (100%)




Acetone

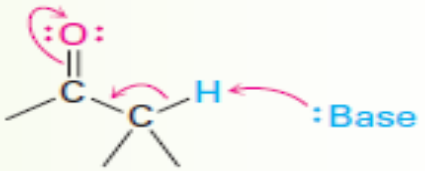
Acetone cyanohydrin (77–78%)

# Carbonyl Condensations: The Aldol Reaction

1. A carbonyl compound with an $\alpha$ hydrogen atom is converted by base into its enolate ion.

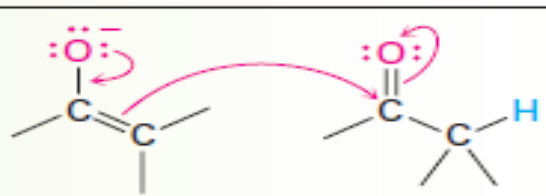
2. The enolate ion acts as a nucleophilic donor and adds to the electrophilic carbonyl group of a second carbonyl compound.

3. Protonation of the tetrahedral alkoxide ion intermediate gives the neutral condensation product and regenerates the base catalyst.

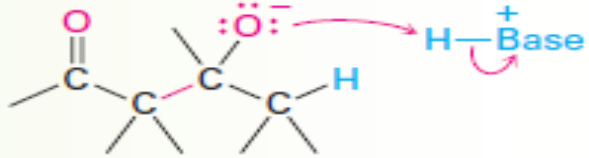



1

An enolate ion

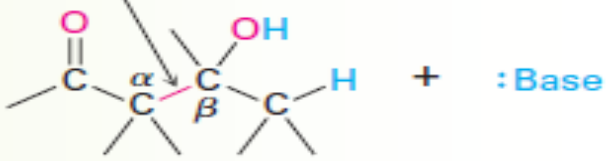


2

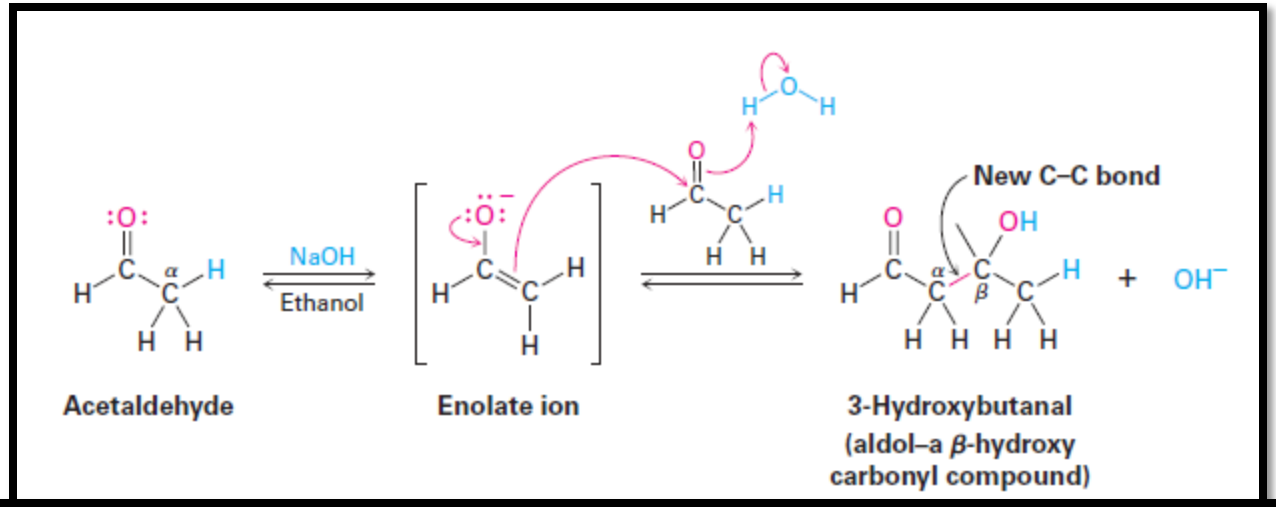



3

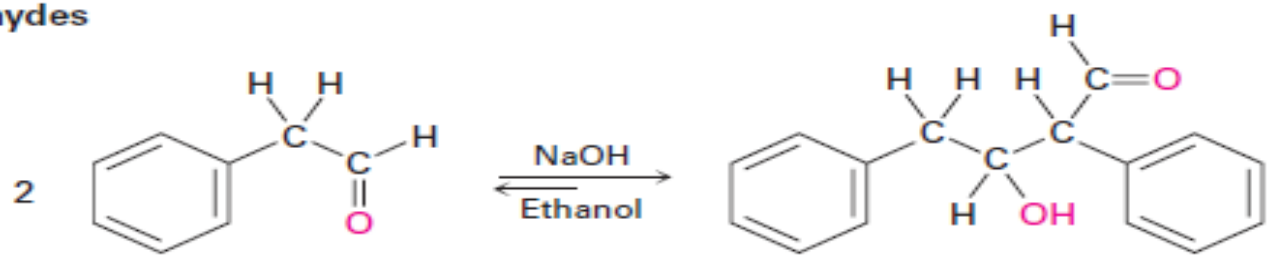
New C–C bond




A $\beta$-hydroxy carbonyl compound



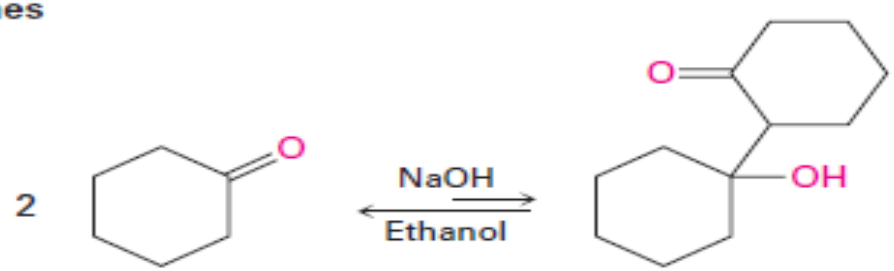

## Aldehydes




Phenylacetaldehyde (10%)

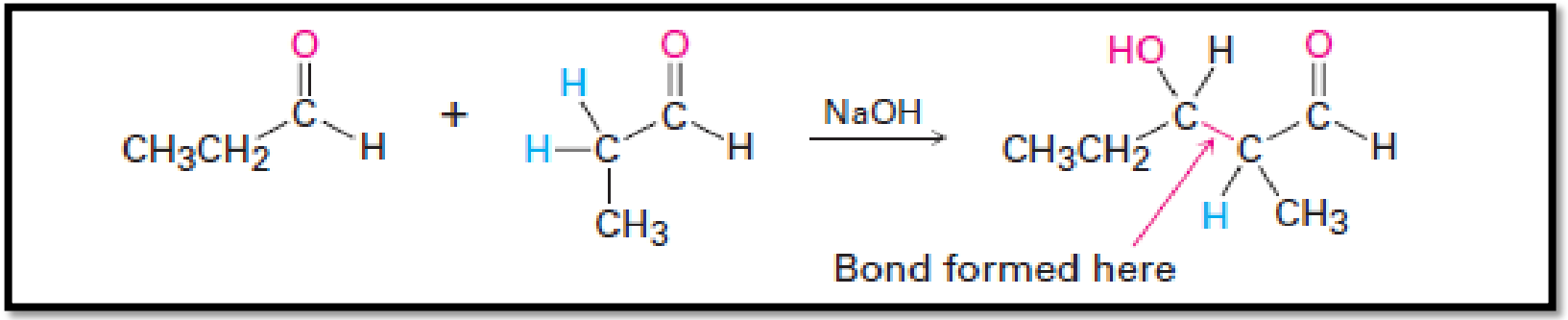
(90%)

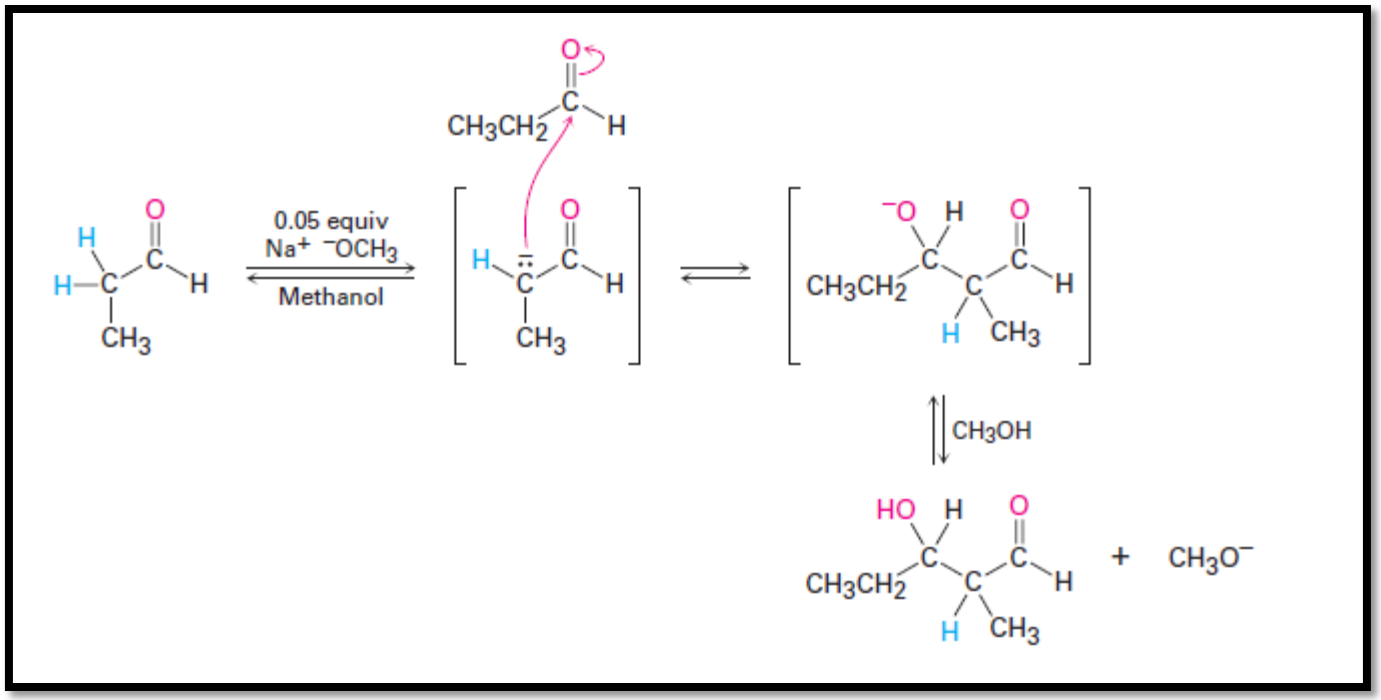
## Ketones



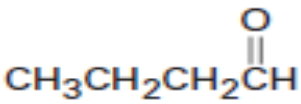

Cyclohexanone (78%)

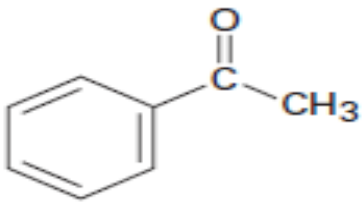
(22%)

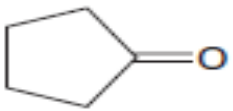


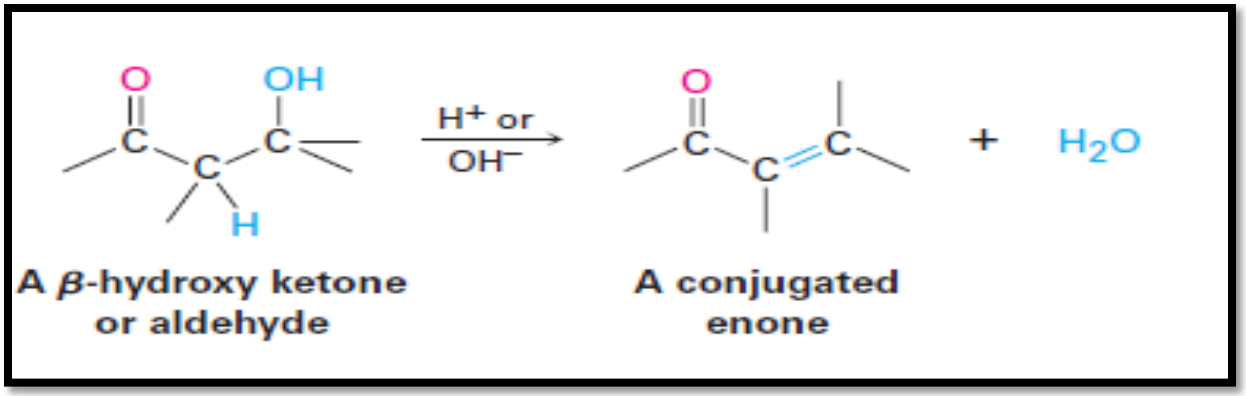

Predict the aldol reaction product of the following compounds:

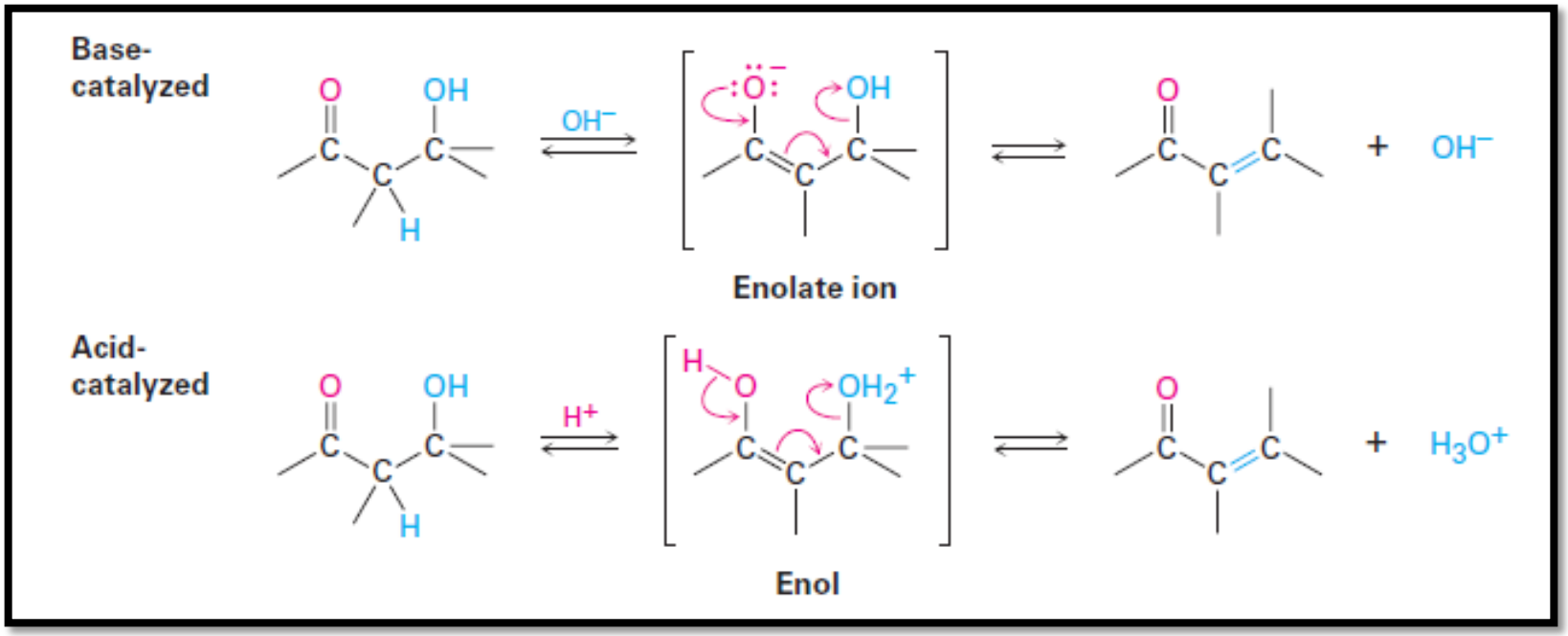
(a) 

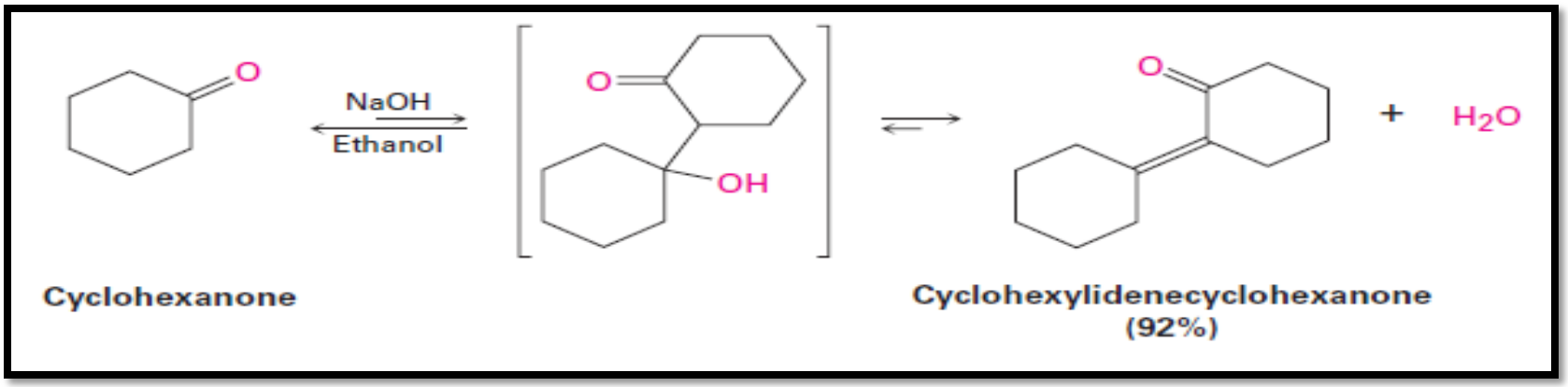
(b) 

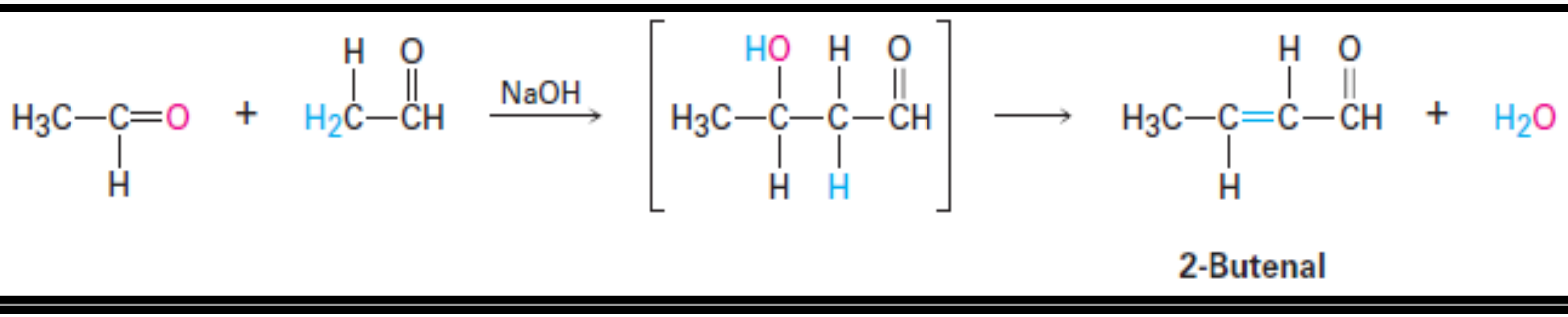
(c) 

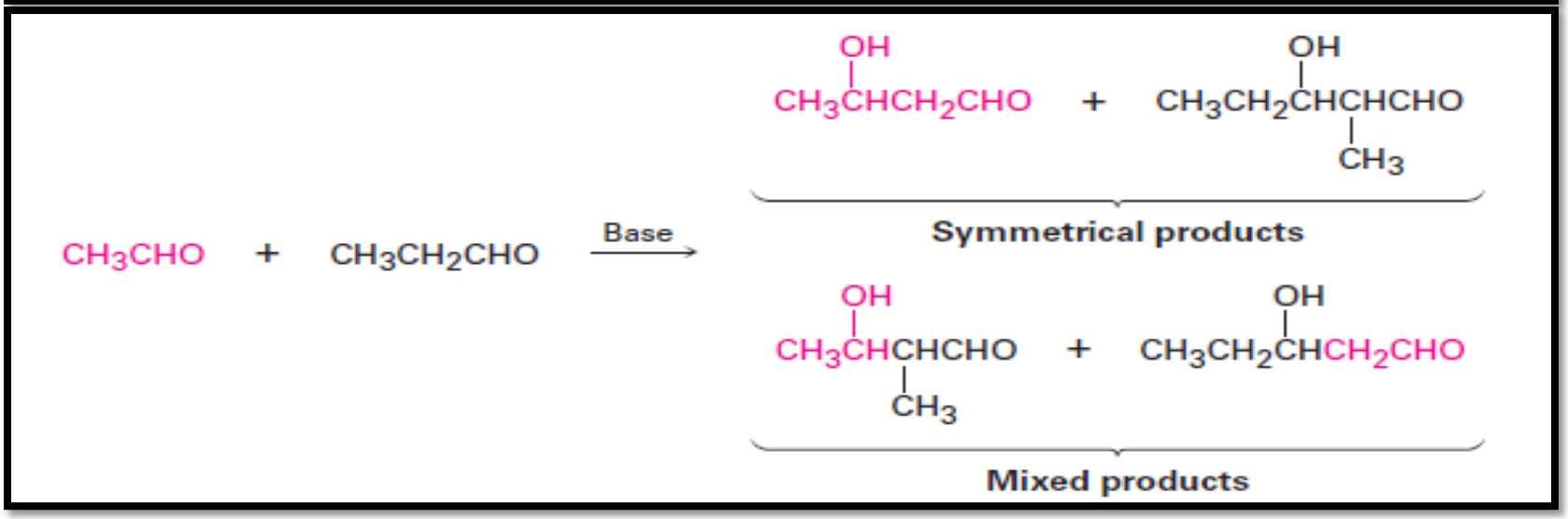
# Dehydration of Aldol Products: Synthesis of Enones

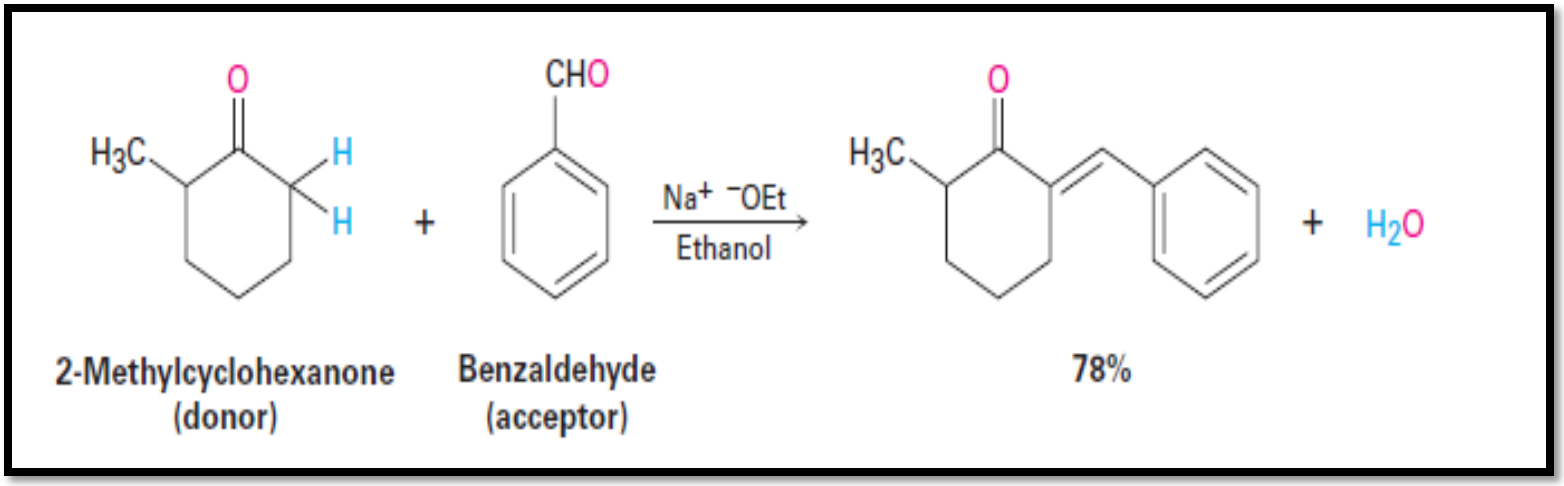


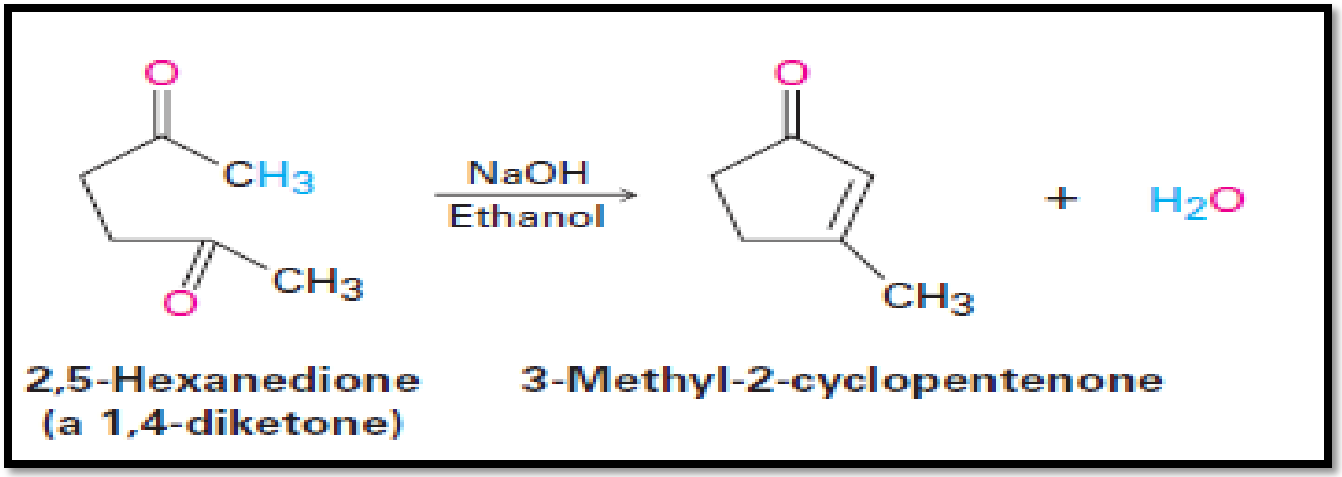

O
NaOH
Ethanol
O
OH
O
+ H2O
Cyclohexanone
Cyclohexylidenecyclohexanone
(92%)

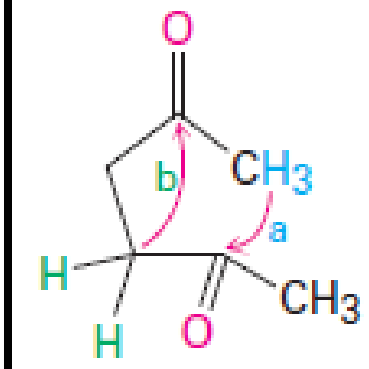

H3C—C=O
H
+
H O
H2C—CH
NaOH
HO H O
H3C—C—C—CH
H H
H O
H3C—C=C—CH
H
+ H2O
2-Butenal


CH3CHO + CH3CH2CHO
Base
OH
CH3CHCH2CHO
+
OH
CH3CH2CHCHCHO
CH3
Symmetrical products
OH
CH3CHCHCHO
CH3
+
OH
CH3CH2CHCH2CHO
Mixed products




## Intramolecular Aldol Reactions

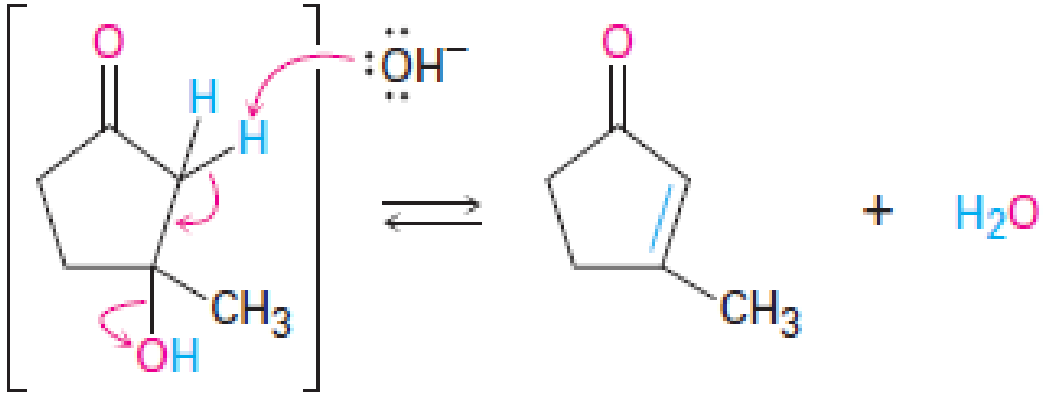




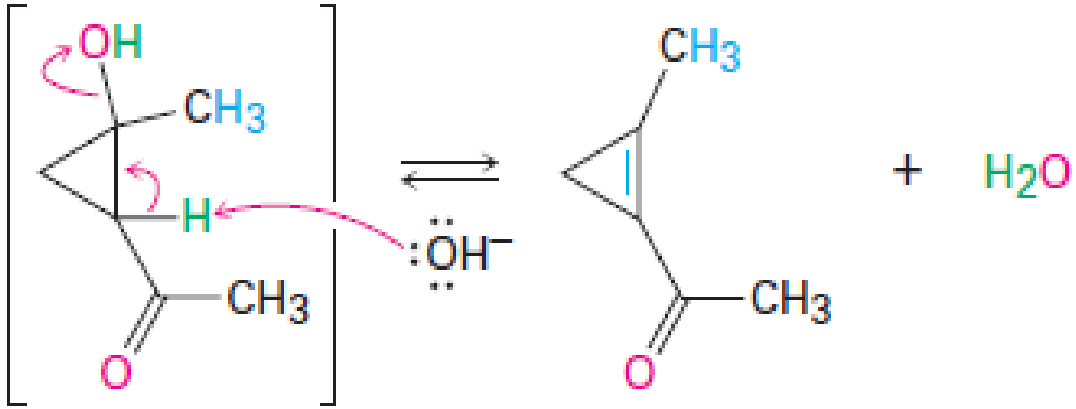

2,5-Hexanedione

Path a
NaOH, $H_2O$

Path b
NaOH, $H_2O$

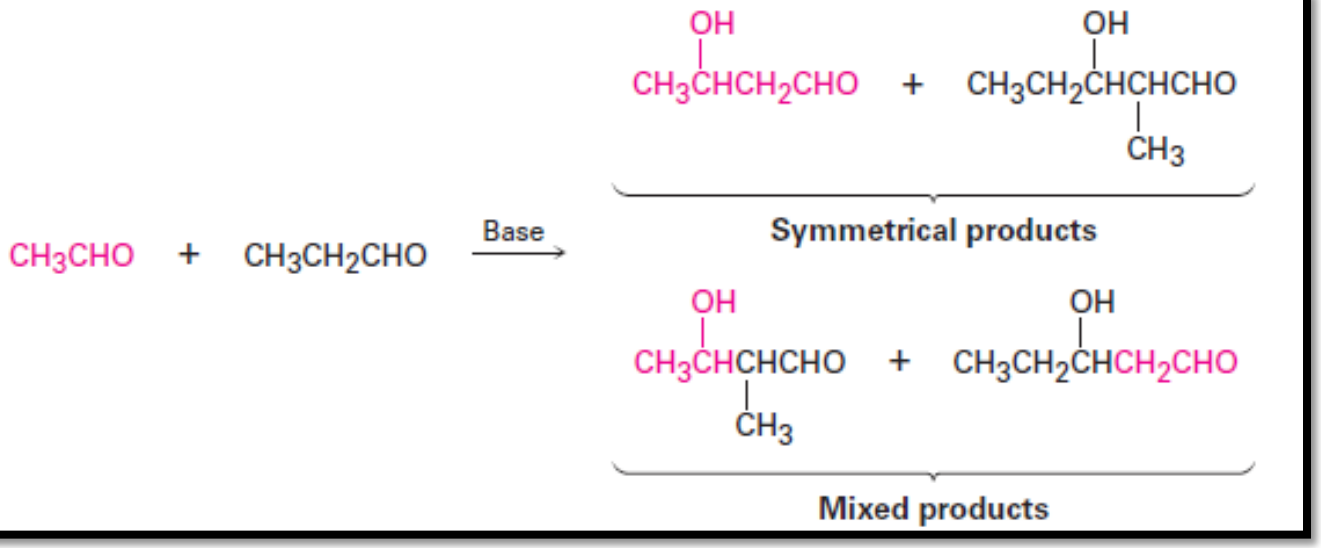


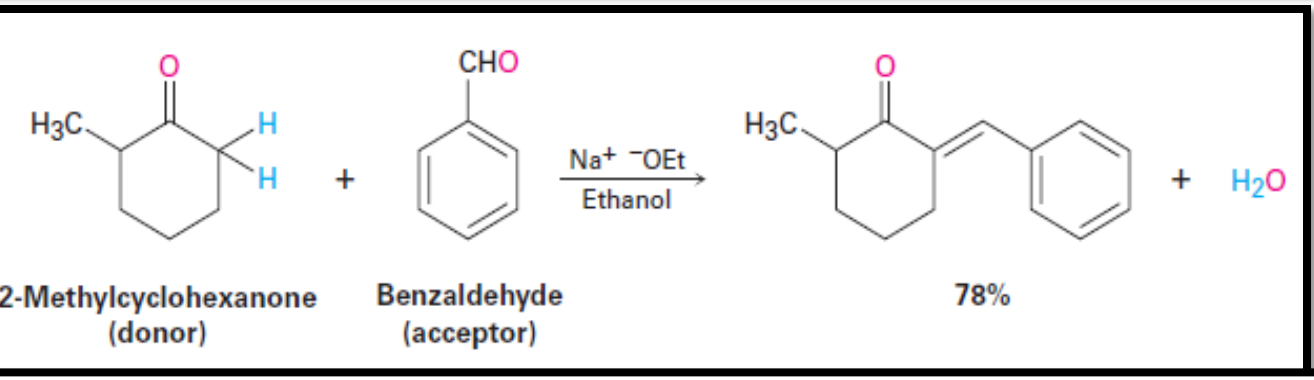

3-Methyl-2-cyclopentenone

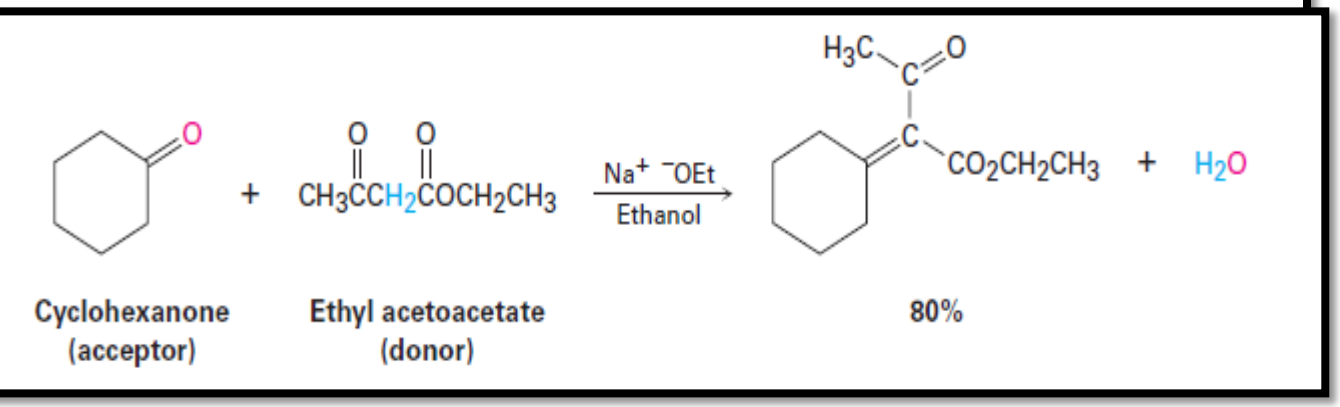



(2-Methylcyclopropenyl)ethanone
*(Not formed)*

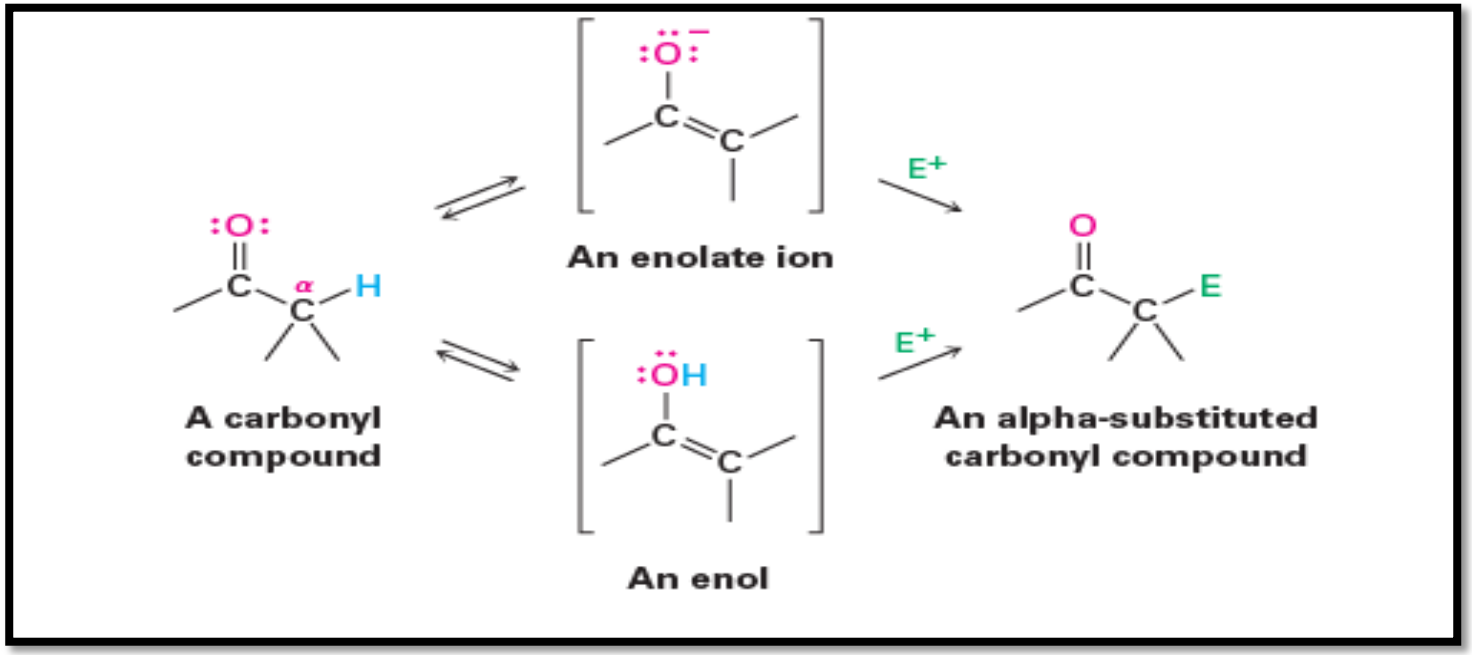
# Mixed Aldol Reactions



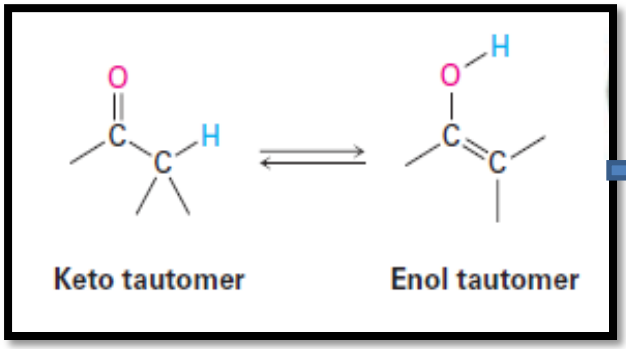



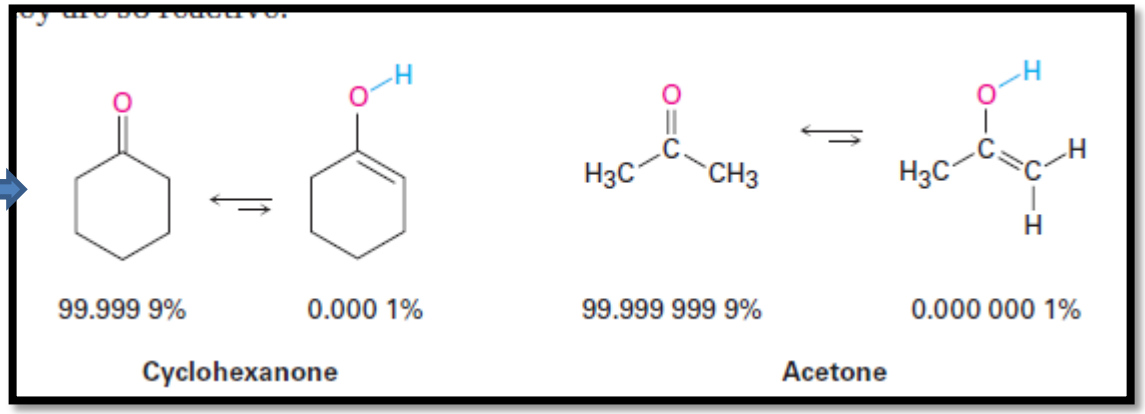



# Carbonyl Alpha-Substitution Reactions

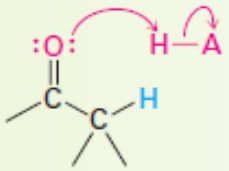



## Keto–Enol Tautomerism



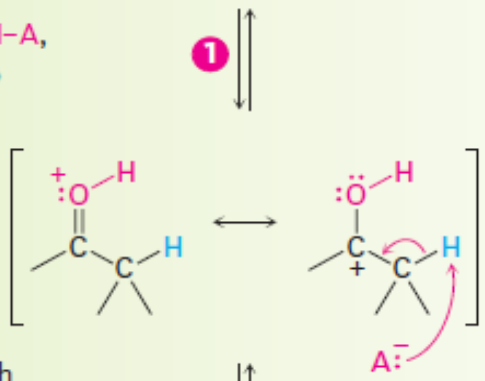



## (a) Acidic conditions

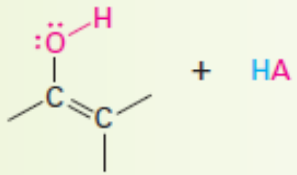


**Keto tautomer**

1. The carbonyl oxygen is protonated by an acid H–A, giving a cation with two resonance structures.

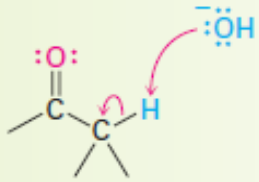


2. Loss of $H^+$ from the $\alpha$ position by reaction with a base $A^-$ gives the enol tautomer and regenerates HA catalyst.



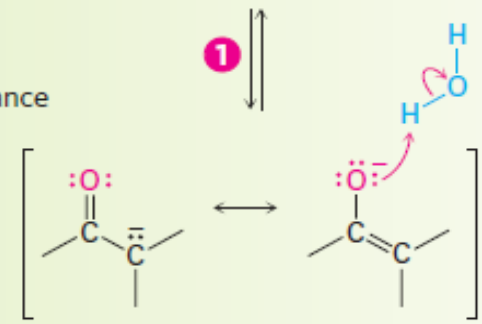
**Enol tautomer**

## (b) Basic conditions



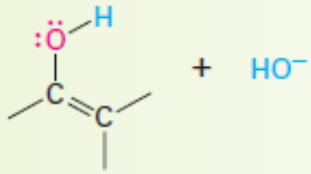
**Keto tautomer**

1. Base removes the acidic $\alpha$ hydrogen, yielding an enolate ion with two resonance structures.



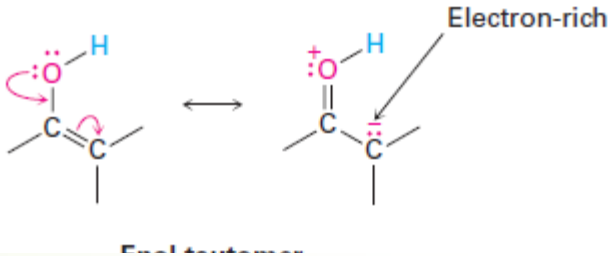
**Enolate ion**

2. Protonation of the enolate ion on oxygen gives the enol and regenerates base catalyst.

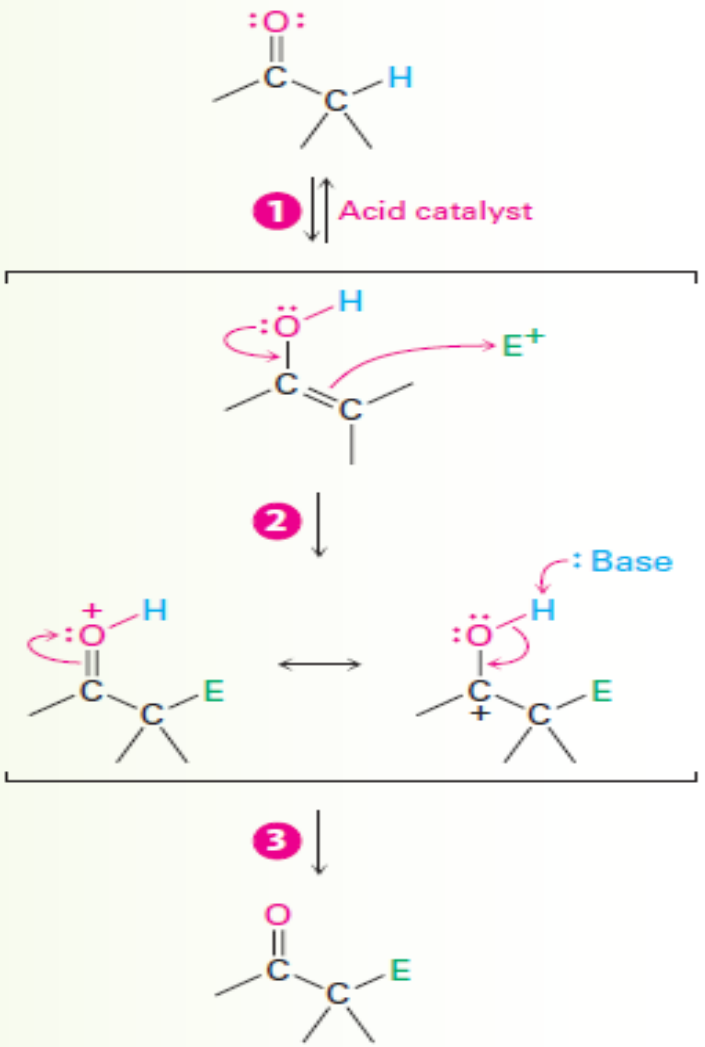


**Enol tautomer**

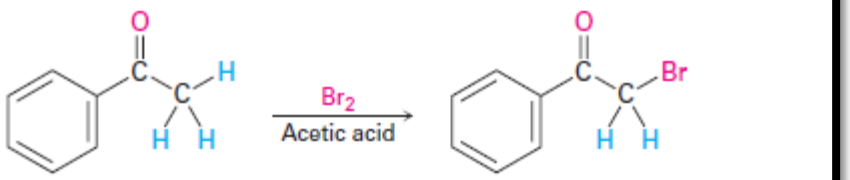
# Reactivity of Enols: *α*-Substitution Reactions



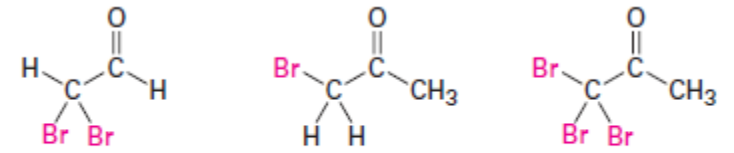

1. Acid-catalyzed enol formation occurs by the usual mechanism.
2. An electron pair from the enol oxygen attacks an electrophile ($E^+$), forming a new bond and leaving a cation intermediate that is stabilized by resonance between two forms.
3. Loss of a proton from oxygen yields the neutral alpha-substitution product as a new C=O bond is formed.



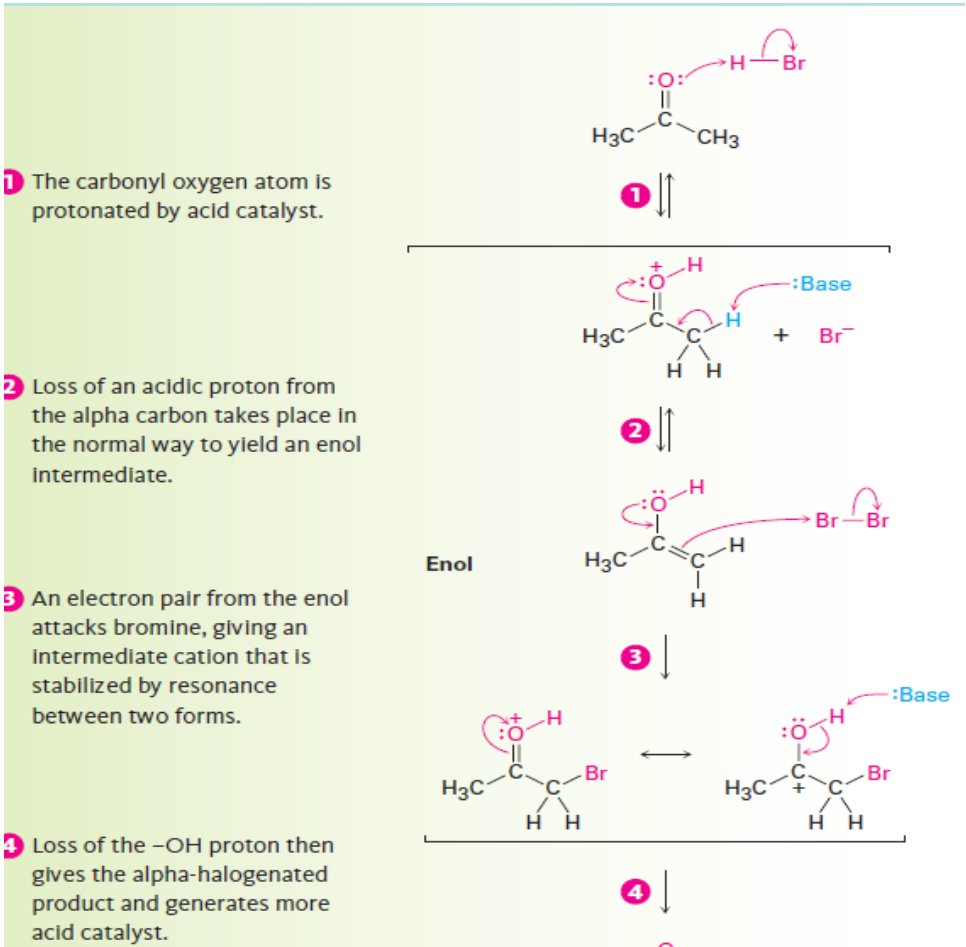
# Alpha Halogenation of Aldehydes and Ketones

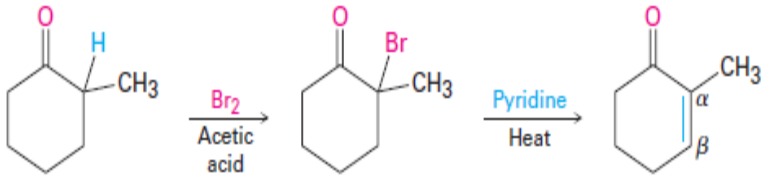



Acetophenone — α-Bromoacetophenone (72%)



From the Hawaiian alga *Asparagopsis taxiformis*




2-Methylcyclohexanone — 2-Bromo-2-methylcyclohexanone — 2-Methyl-2-cyclohexenone (63%)