






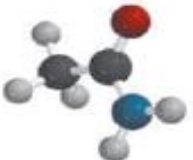
جامعة ذي قار
كلية العلوم
قسم الكيمياء

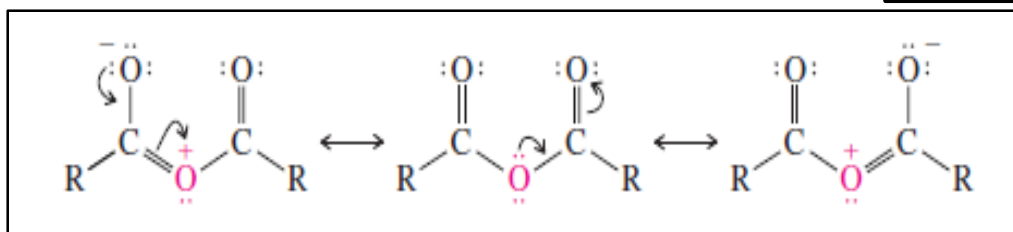
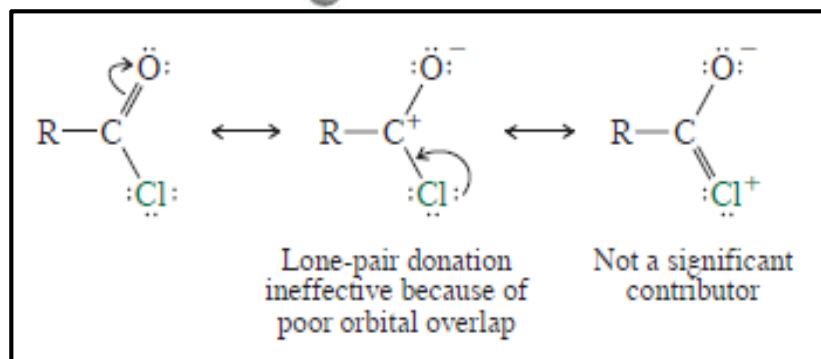
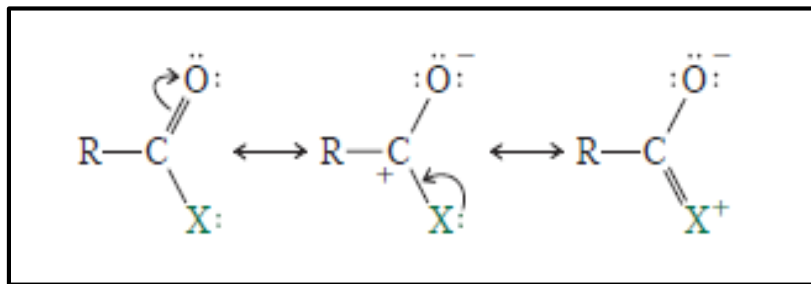


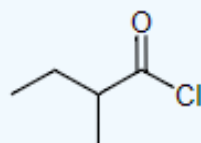
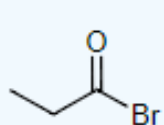
الكيمياء العضوية – المرحلة الثالثة
العام الدراسي 2023-2024

الاحماض الكاربوكسيلية و النتريلات
Carboxylic Acids and Nitriles

أ.م. د. عذراء حامد مكي

Reactivity	Compound	formula	model	carbonyl group
Most reactive	Acetyl chloride	$\text{CH}_3\text{C}(=\text{O})\text{Cl}$		Least stabilized
	Acetic anhydride	$\text{CH}_3\text{C}(=\text{O})\text{OC}(=\text{O})\text{CH}_3$		
	Ethyl acetate	$\text{CH}_3\text{C}(=\text{O})\text{OCH}_2\text{CH}_3$		
Least reactive	Acetamide	$\text{CH}_3\text{C}(=\text{O})\text{NH}_2$		Most stabilized

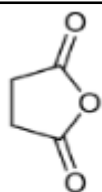




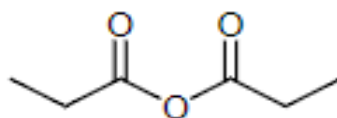
Propanoyl bromide (Propionyl bromide)
2-Methylbutanoyl chloride (2-Methylbutyryl chloride)



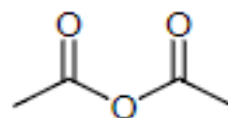
Heptanoyl chloride



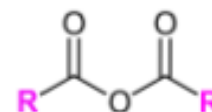
Succinic Anhydride



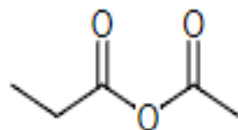
Propanoic anhydride (Propionic anhydride)



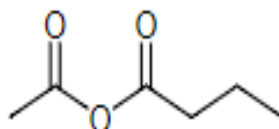
Ethanoic anhydride (Acetic anhydride)



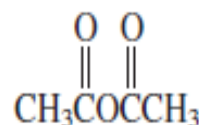
Symmetrical Anhydride



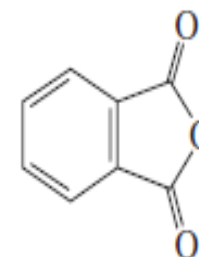
Ethanoic propanoic anhydride (Acetic propionic anhydride)



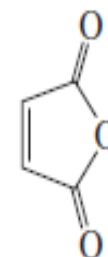
Butanoic ethanoic anhydride (Acetic butyric anhydride)



Acetic anhydride

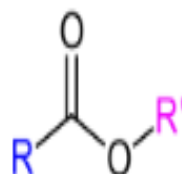


Phthalic anhydride

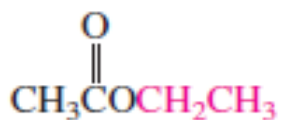


Maleic anhydride

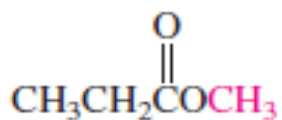
Chain from the Corresponding Carboxylic Acid



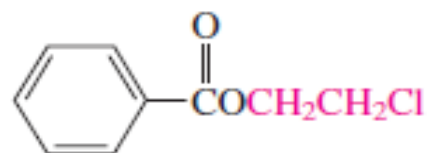
Alkoxy Alkyl Chain



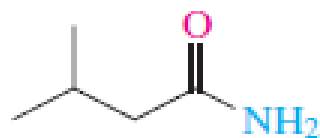
Ethyl acetate



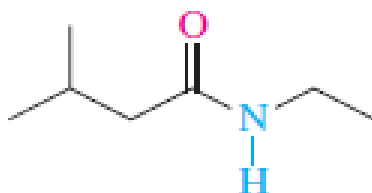
Methyl propanoate



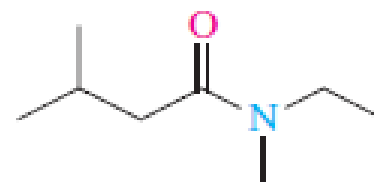
2-Chloroethyl benzoate



3-Methylbutanamide

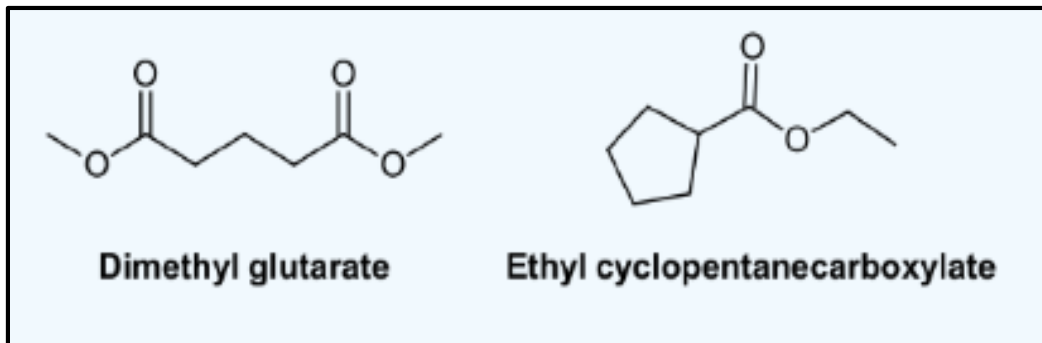
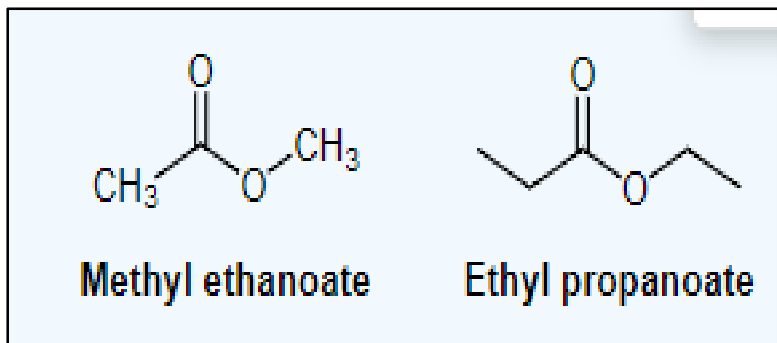


N-Ethyl-3-methylbutanamide

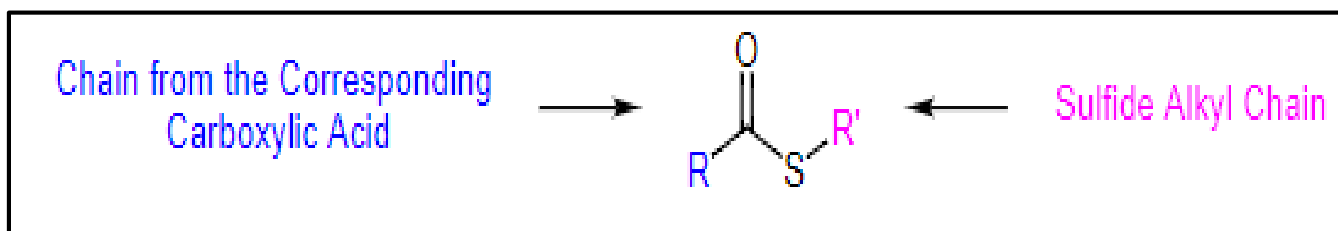


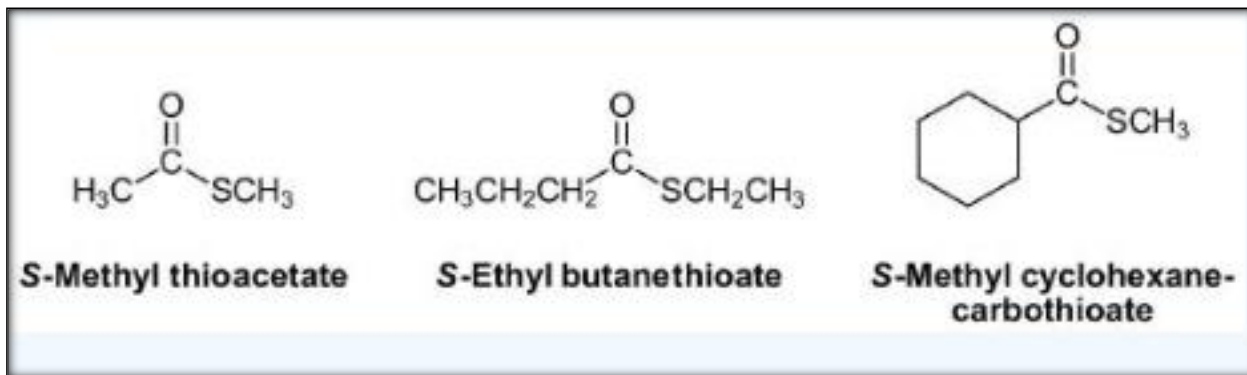
N-Ethyl-*N*,3-dimethylbutanamide

Esters are named as if the alkoxy alkyl chain is a substituent (**Prefix + yl**). This is followed by the name of the corresponding carboxylic acid part of the ester with **-ic acid** or **-oic acid** replaced with the ending **-ate**. The carbonyl carbon is given the location number. The carbonyl functional group is assumed to be on the end of the parent chain, so it is not necessary to include the functional group location number in the name



Thioesters are named as if the sulfide alkyl chain is a substituent with the letter *S* preceding (**S-Prefix + yl**). This is followed by the parent chain of the corresponding carboxylic acid, named as an alkane with the ending **-thioate** added. For thioesters attached to a carbon ring the ending **-carboxylic acid** is replaced with **-carbothioate**. When using the common names of the carboxylic acid the **-ic acid** ending is replaced **-ate** and the prefix **thio-** is added.

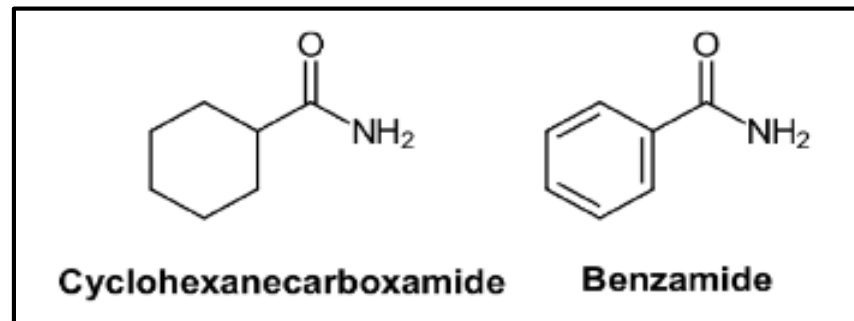
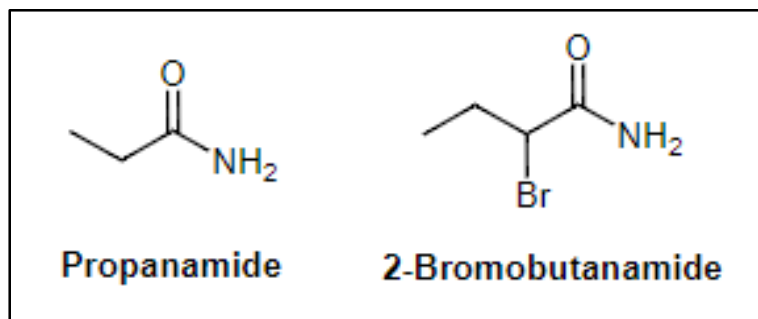




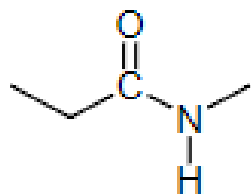
تسمية الاميدات

Nomenclature of Amides, RCONH₂, RCONHR', RCONR'R''

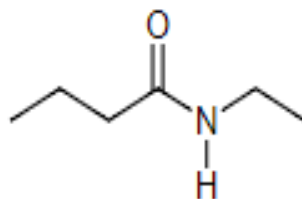
Primary amides (RCONH₂) are named by changing the name of the corresponding acid by removing the **-oic acid** or **-ic acid** endings and adding **-amide**. Amides derived from a cyclic carboxylic acid have the **-carboxylic acid** ending replaced with **-carboxamide**. The carbonyl carbon is given the #1 location number. It is not necessary to include the location number in the name because it is assumed that the functional group will be on the end of the parent chain.



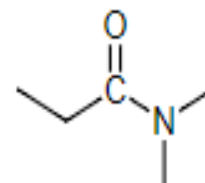
Secondary (RCONHR') and tertiary (RCONR'R'') amides are named by using an upper case N to designate that the alkyl groups are attached to the nitrogen atom. These alkyl groups are named as substituents (**Prefix + yl**).



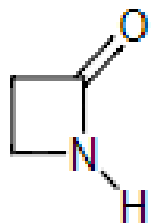
N-Methylpropanamide



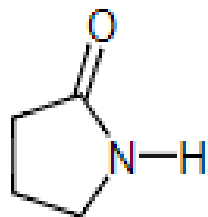
N-Ethylbutanamide



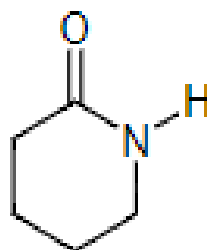
N,N-Dimethylpropanamide



β -Lactam



γ -Lactam

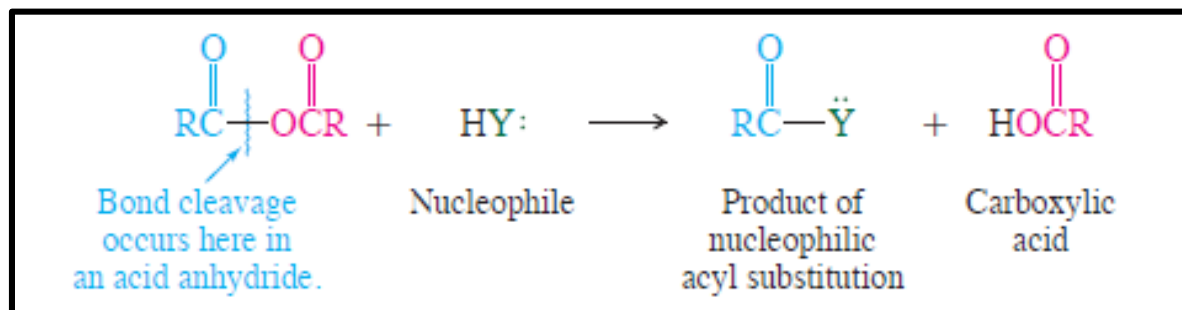


δ -Lactam

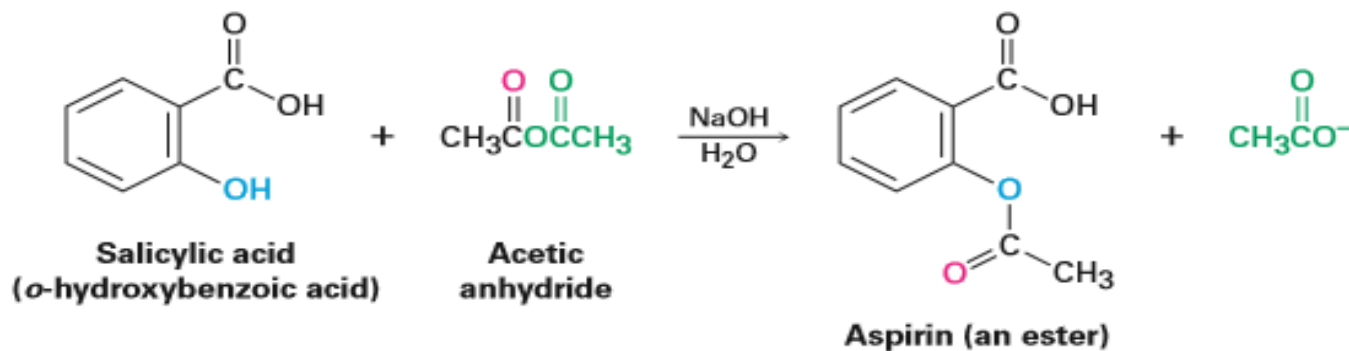
- 1.2-methylpentanoyl chloride .
- 2.2-cyclopentylacetamide .
- 3.propyl 2-methylpropanoate .
- 4.Cyclohexylbutanoate .
- 5.sec-butyl cyclopentanecarboxylate .
- 6.1-methylbutylcyclopentane carboxylate.
- 7.N-methyl-3-butenamide.
8. propyl 2,3-dimethyl-2-butenethioate .

- 1.benzoic anhydride
- 2.phenyl hexanoate
- 3.methyl benzoate
- 4.3-chloro-N-ethylbenzamide
- 5.pentanamide
N-phenylethanamide.1
- 6.Methyl 1-methylcyclohexanecarboxylate
- 7.Ethyl 3-oxopentanoate
- 8.*S*-Methyl *p*-bromothiobenzoate
- 9.Formic propanoic anhydride
- 10.cis-2-Methylcyclopentanecarbonyl
bromide

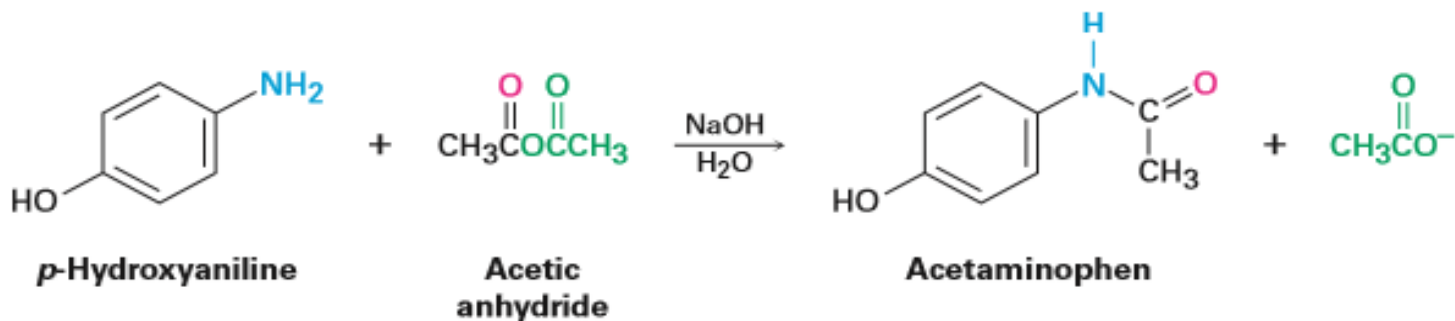
Reaction of acid anhydride

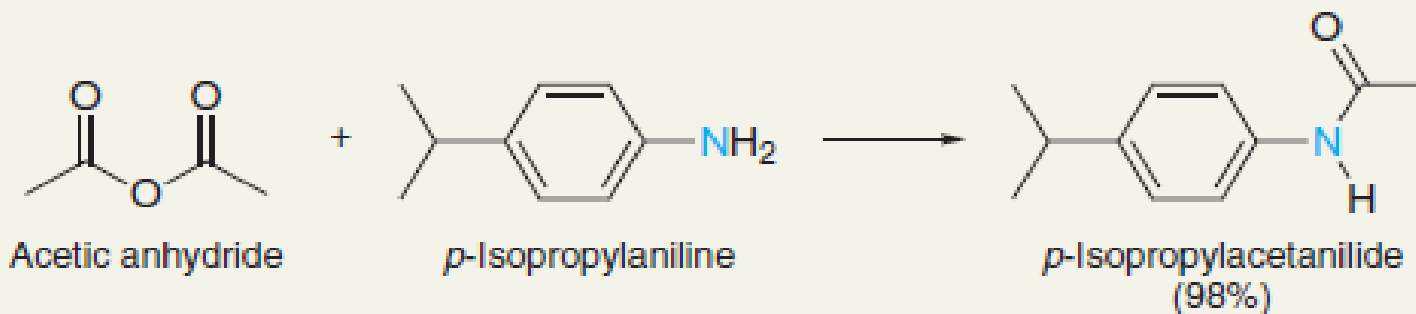
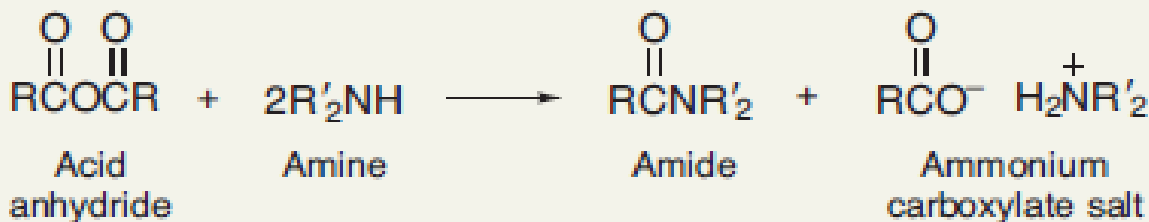
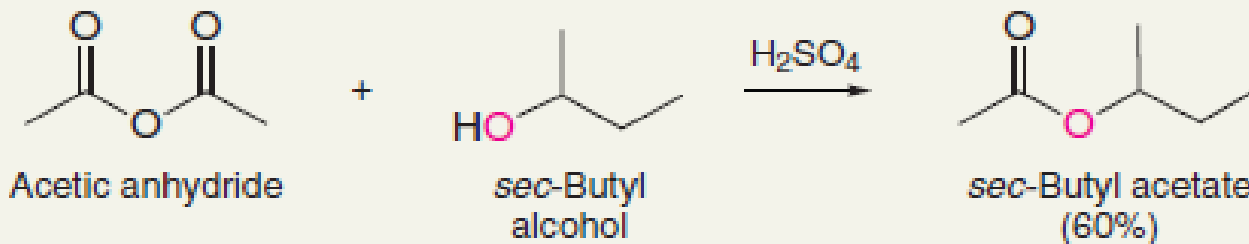
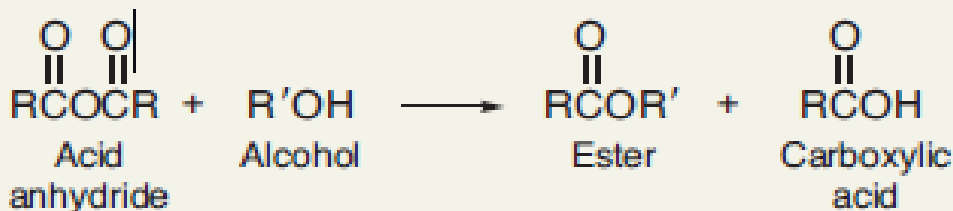


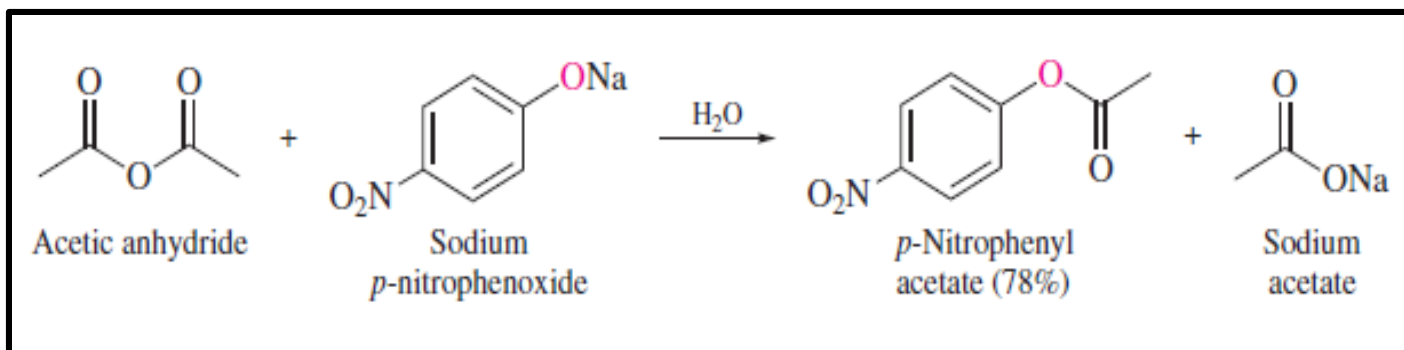
Conversion of Acid Anhydrides into Esters



Conversion of Acid Anhydrides into Amides

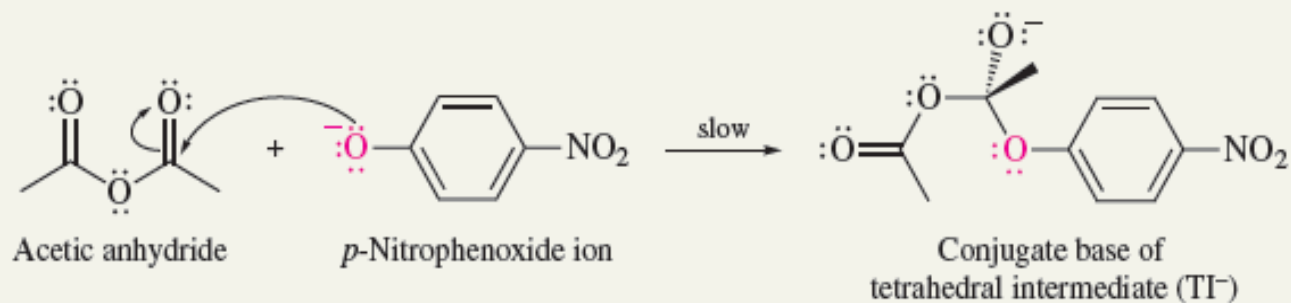




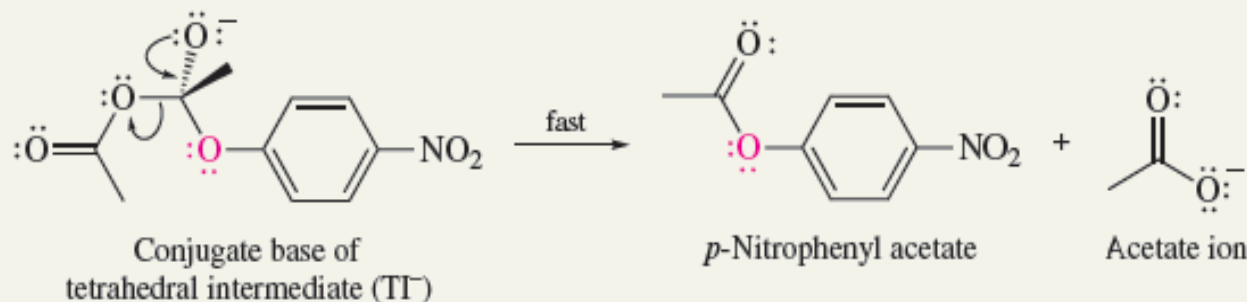


THE MECHANISM:

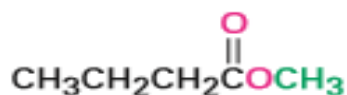
Step 1: Nucleophilic addition of *p*-nitrophenoxide to one of the carbonyl groups of the anhydride gives the conjugate base of the tetrahedral intermediate (TI^-).



Step 2: Expulsion of acetate from TI^- restores the carbonyl group.



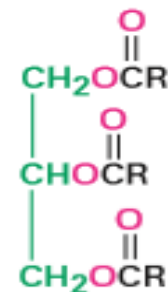
Chemistry of Esters



Methyl butanoate
(from pineapples)

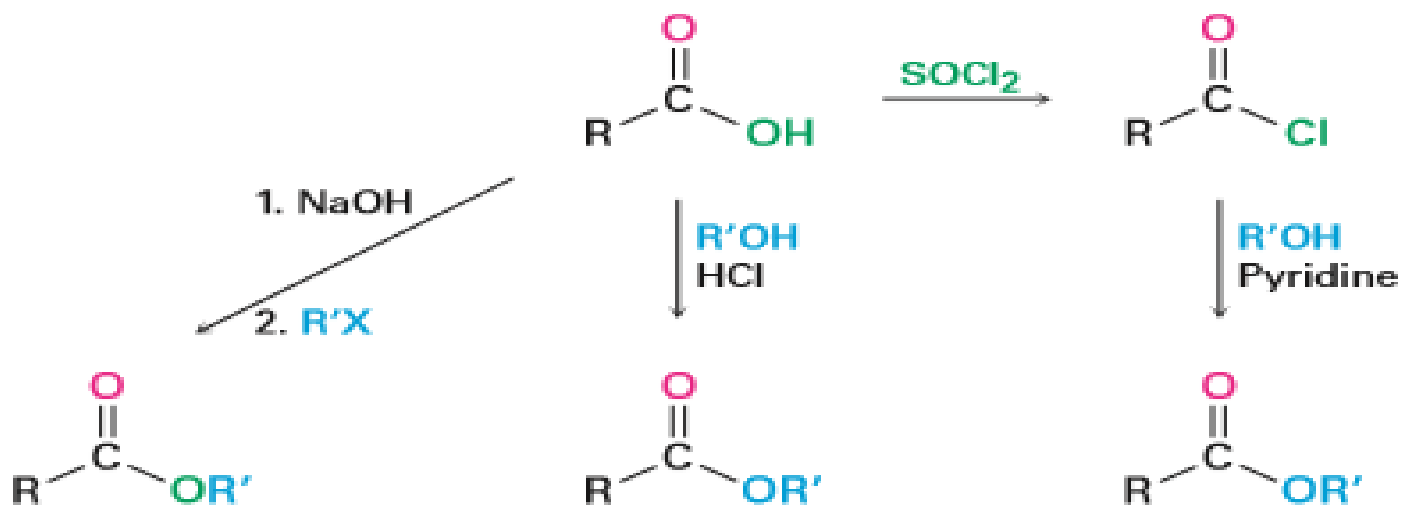


Isopentyl acetate
(from bananas)



A fat
(R = C₁₁₋₁₇ chains)

Preparation of Esters

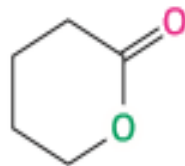


Method limited to primary alkyl halides

Method limited to simple alcohols

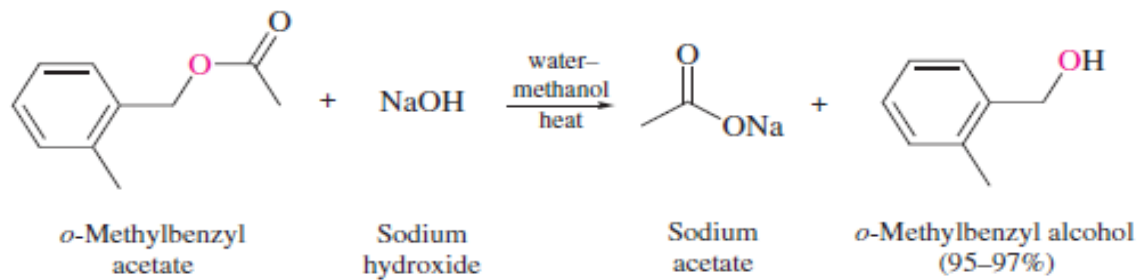
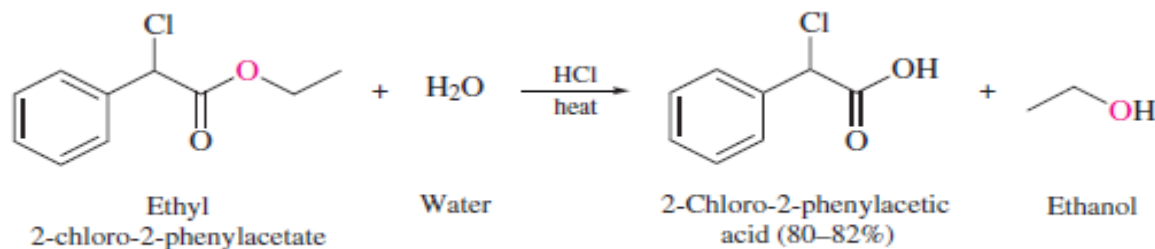
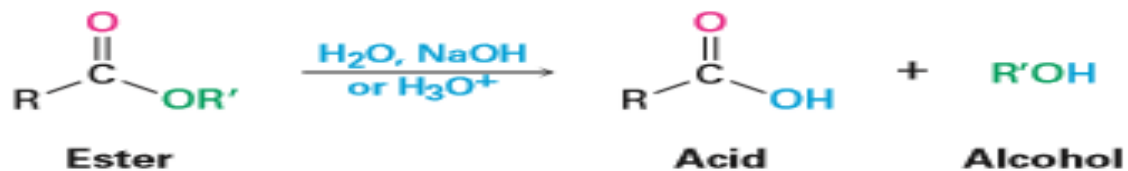
Method is very general

Reactions of Esters



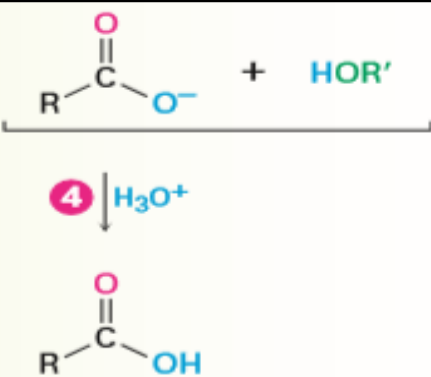
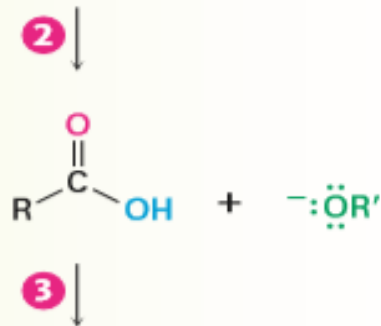
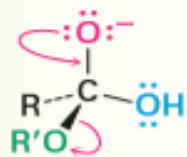
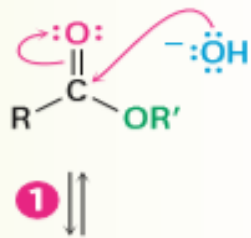
A lactone
(cyclic ester)

Conversion of esters into Carboxylic Acids: Hydrolysis

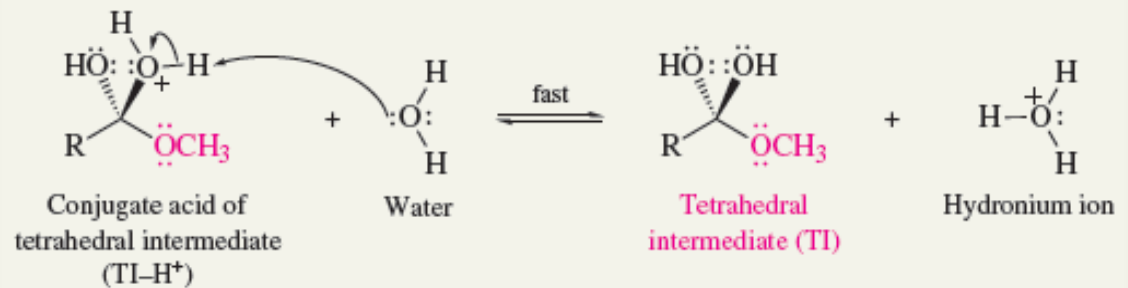
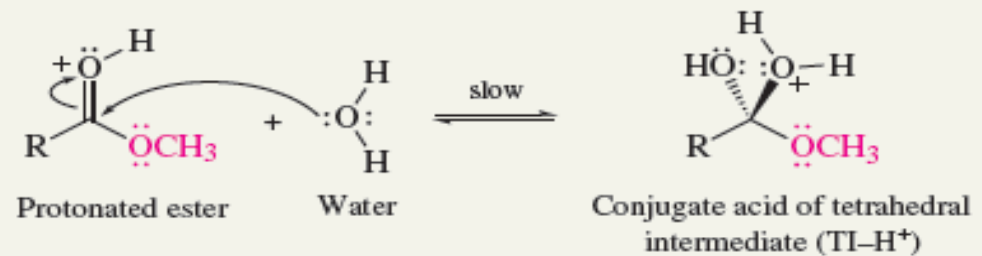
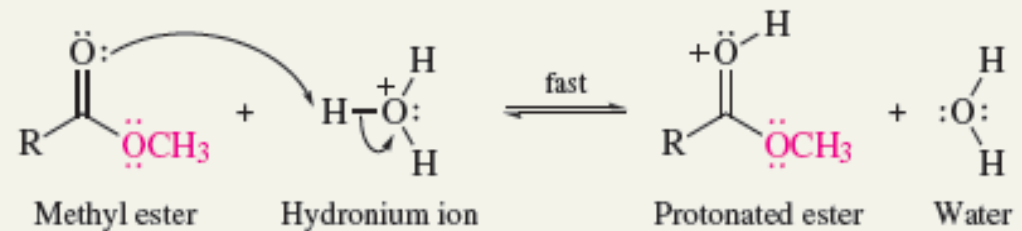
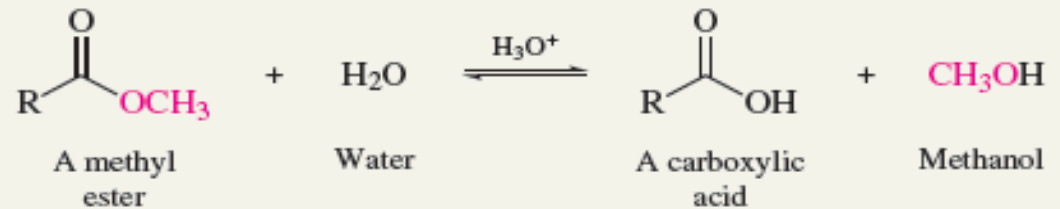


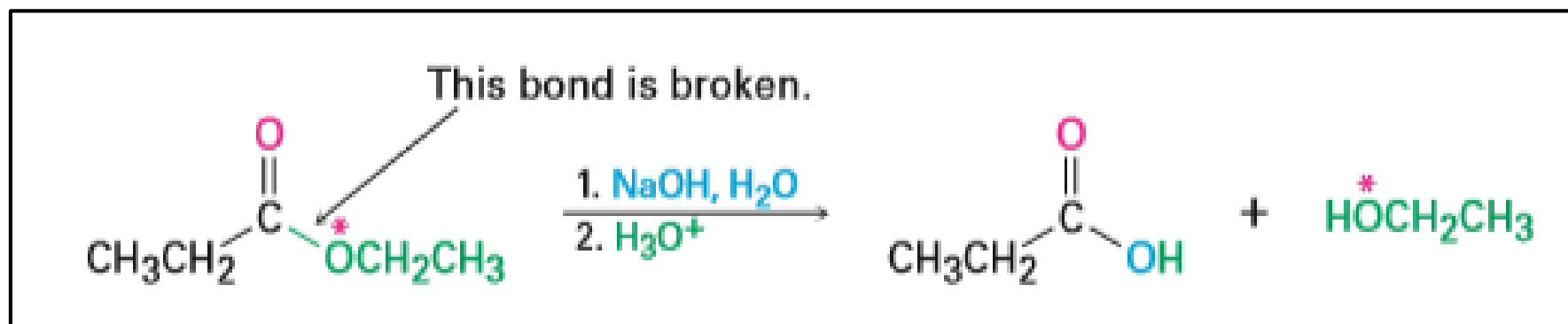
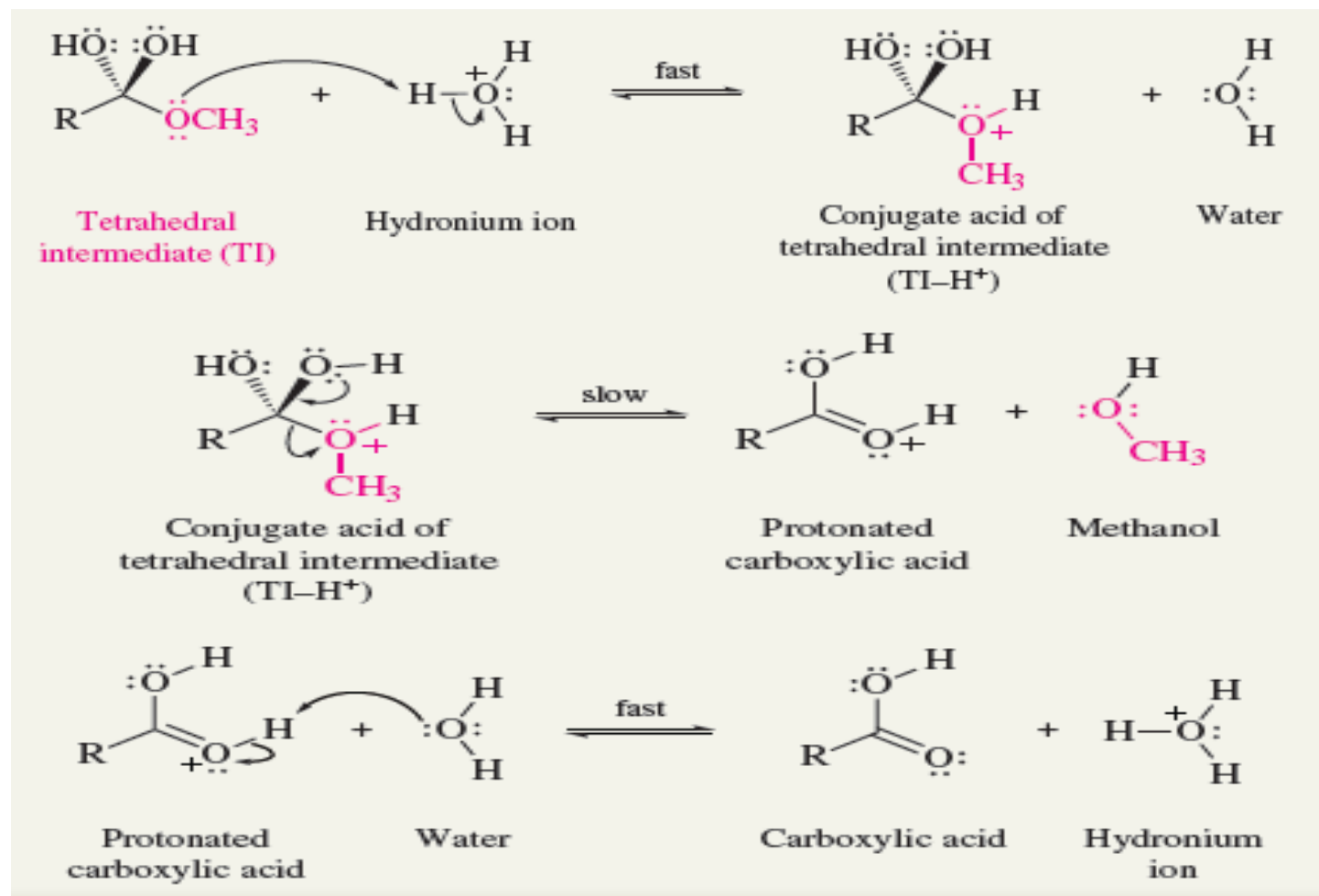
Mechanism of base-induced ester hydrolysis (saponification)

التحلل في الوسط القاعدي

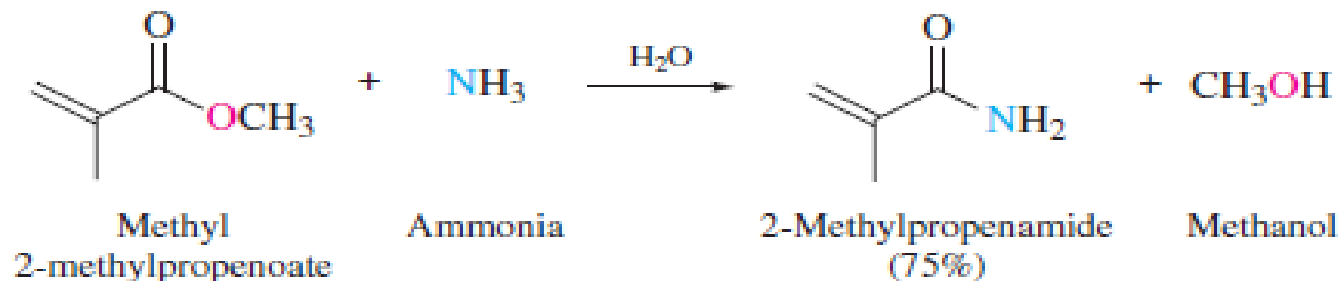
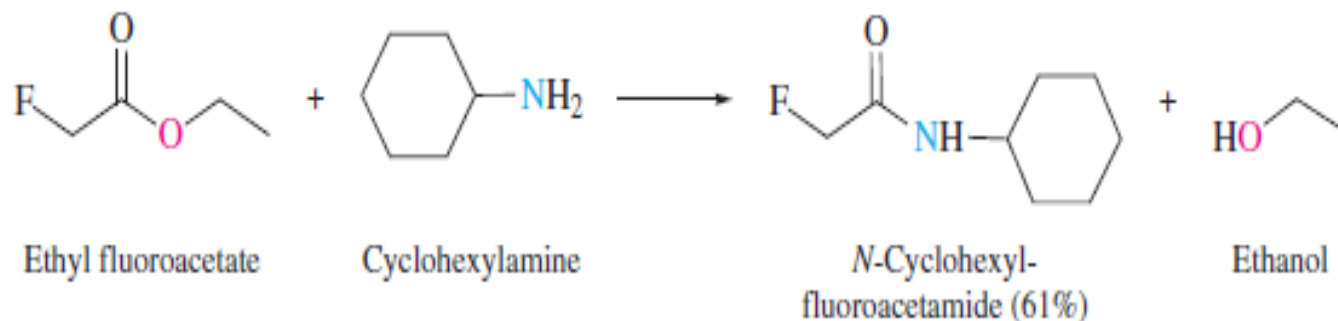
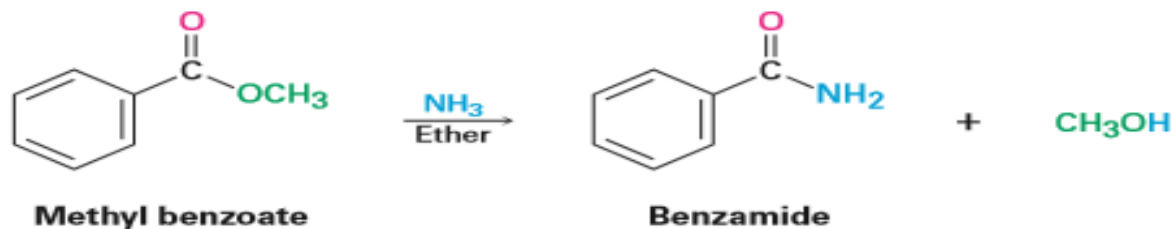
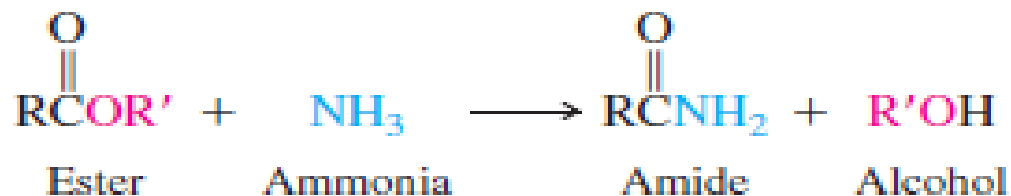


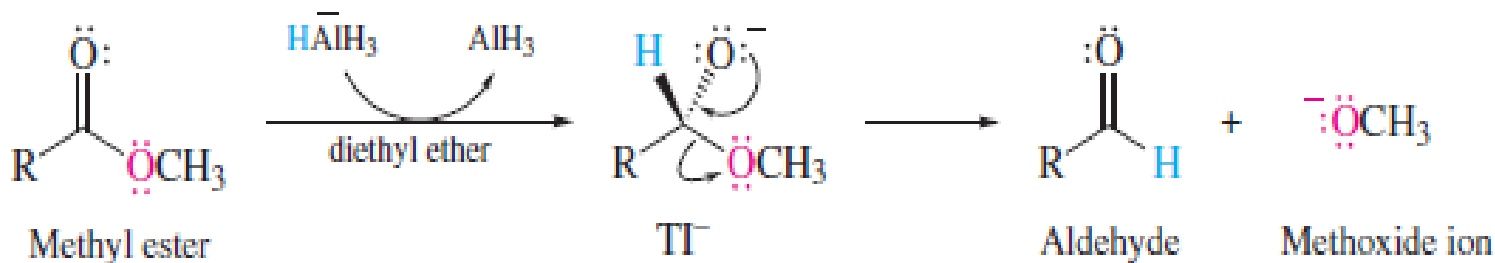
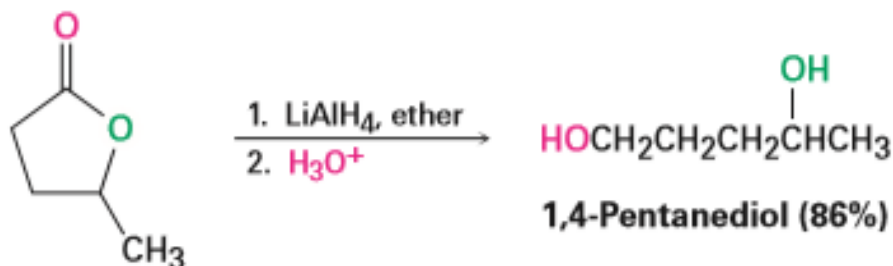
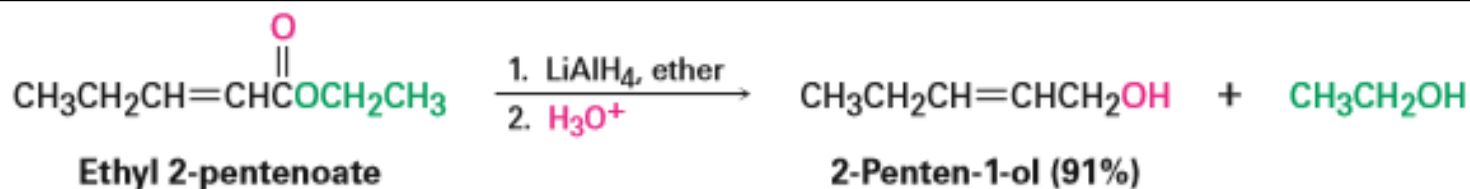
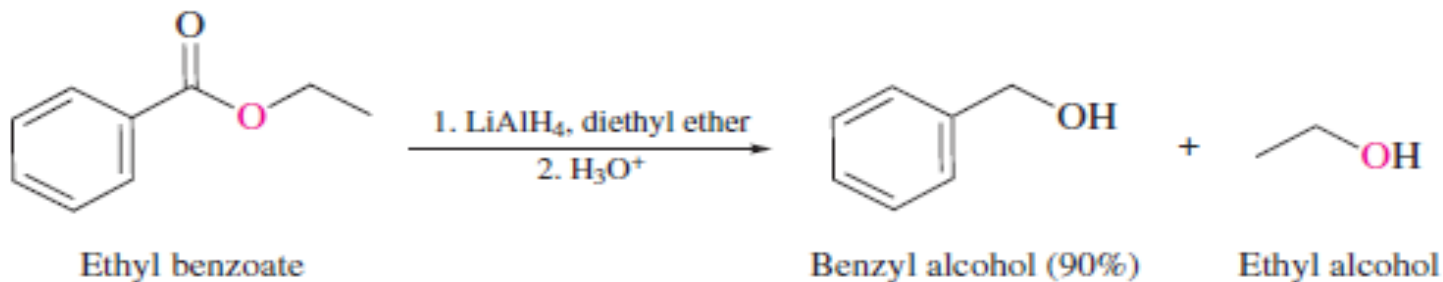
التحلل في الوسط الحامضي



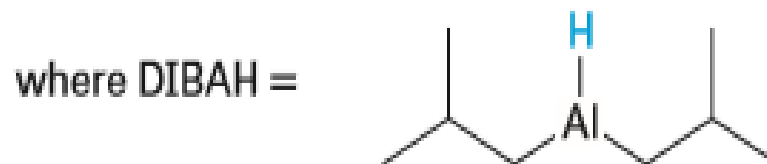
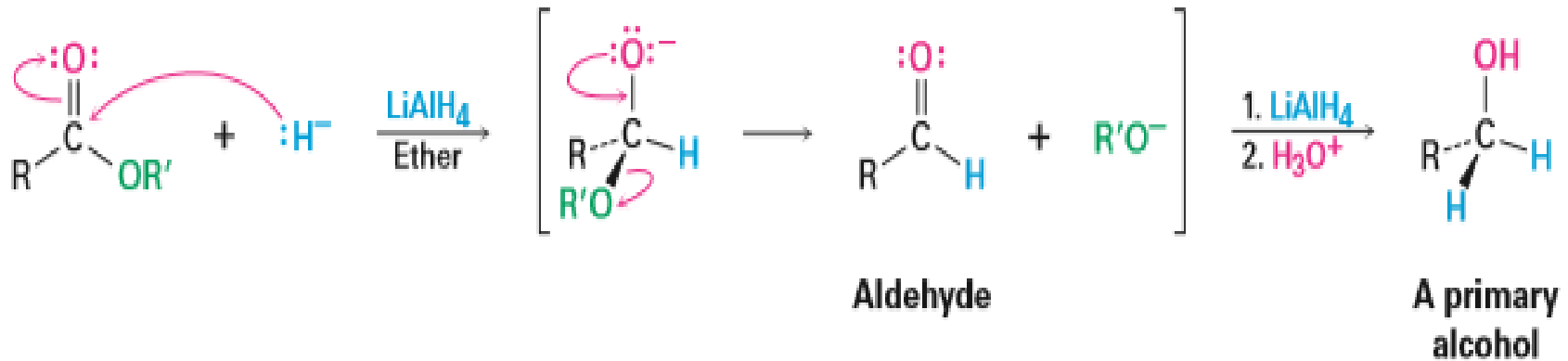


Conversion of Esters into Amides: Amino lysis



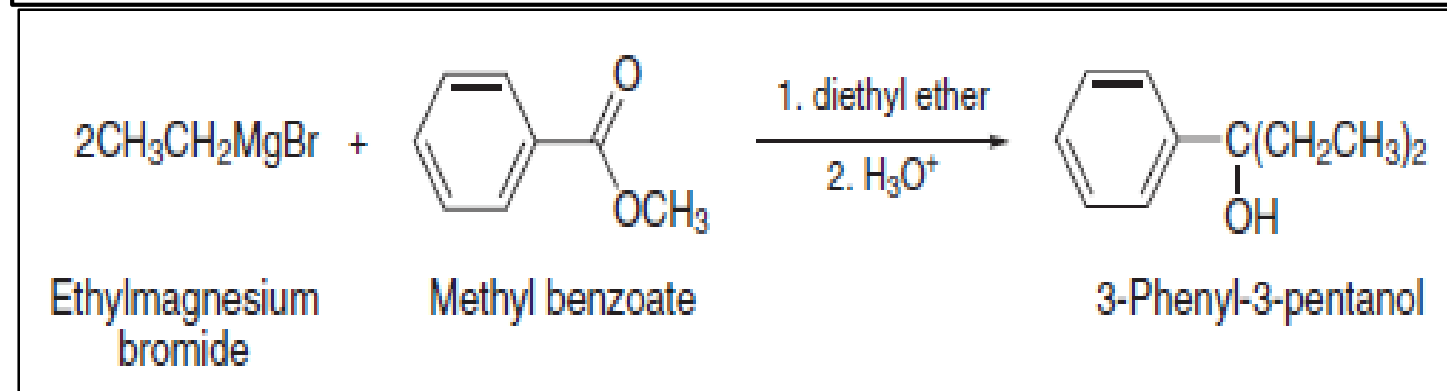
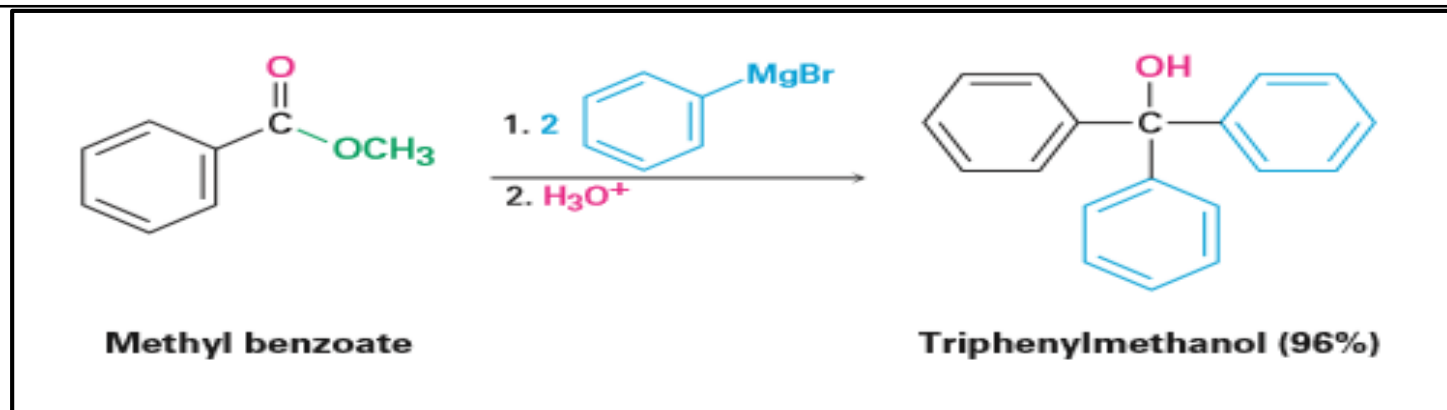
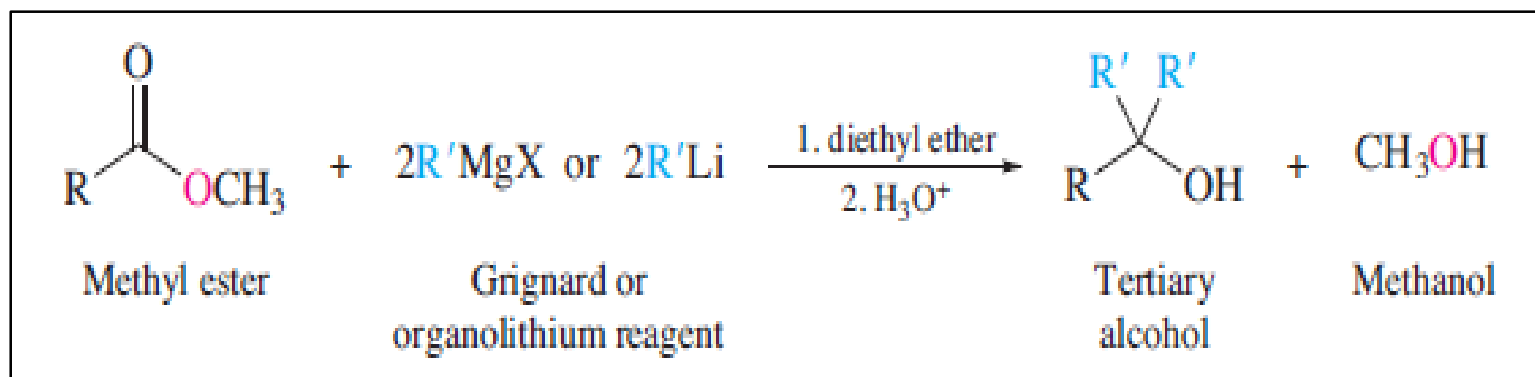


ميكانيكية التفاعل

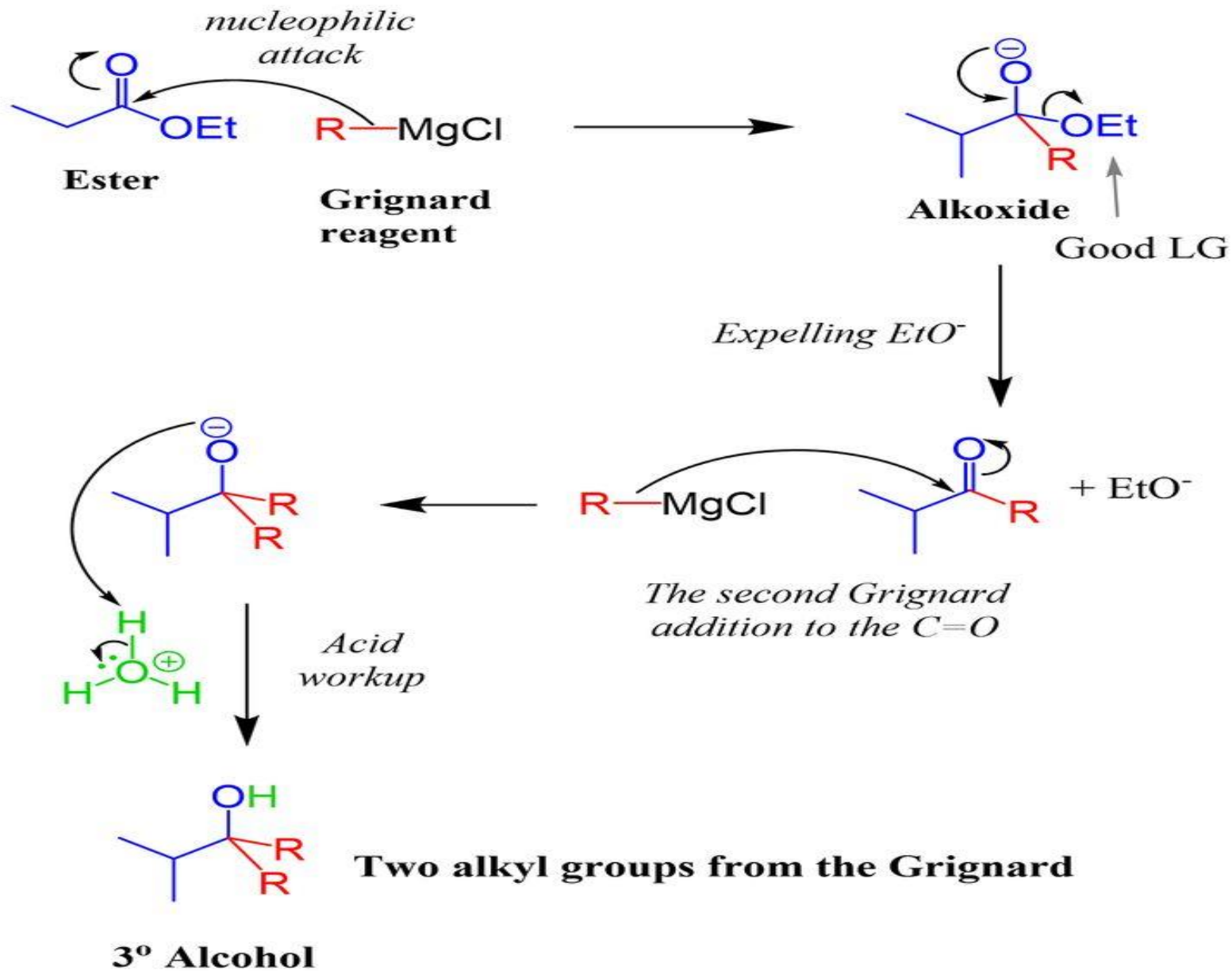


Reaction of Esters with Grignard and Organolithium Reagents and Lithium Aluminum Hydride

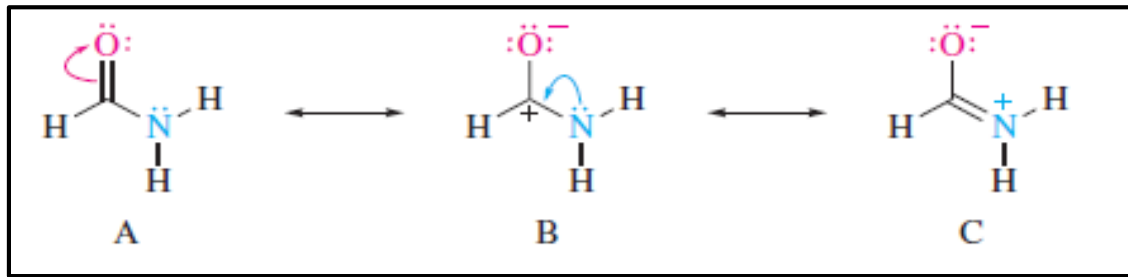
التفاعل مع كاشف كرينارد



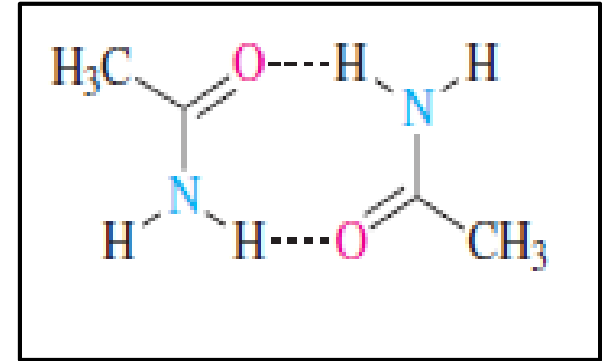
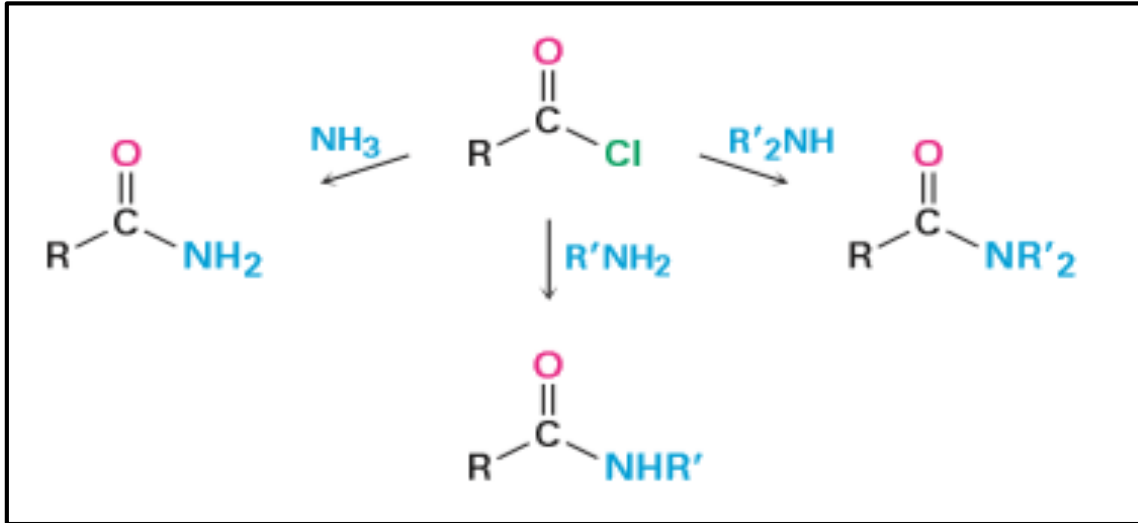
The Mechanism of Grignard reaction with Esters



Chemistry of Amides



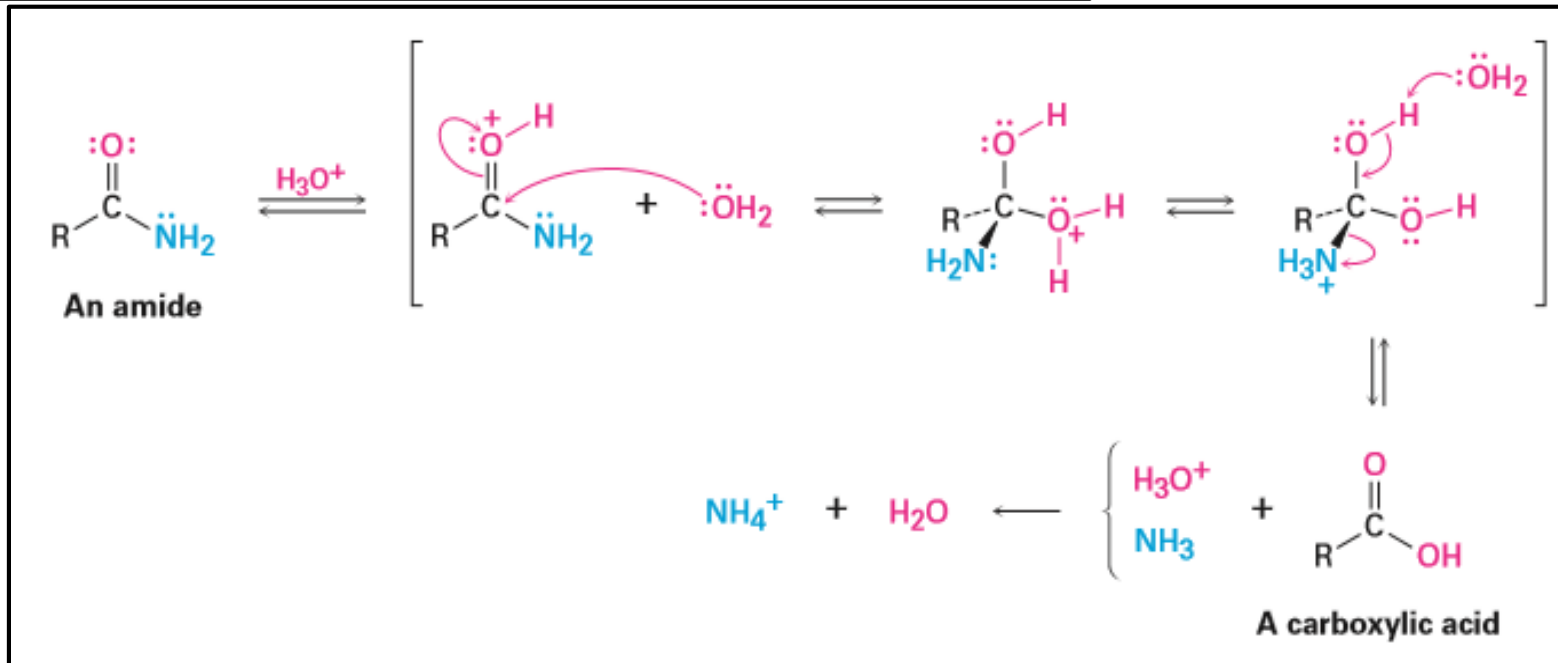
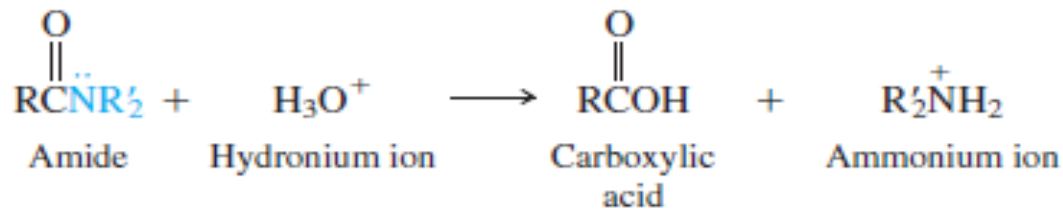
Preparation of Amides



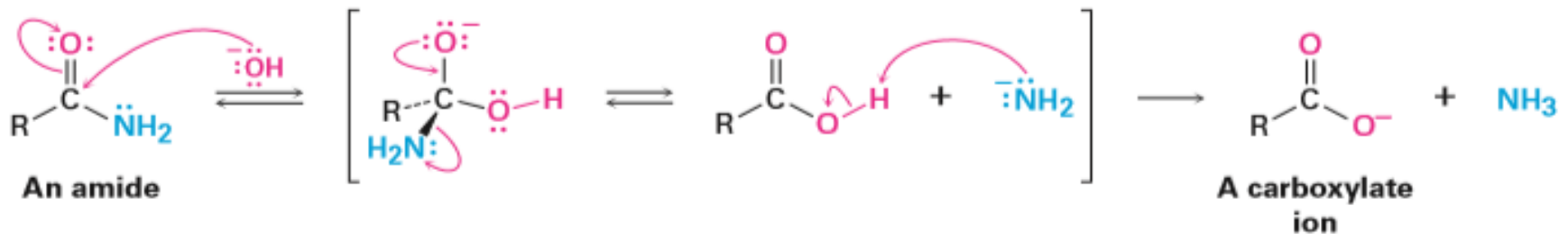
Reactions of Amides Conversion of Amides into Carboxylic Acids: Hydrolysis

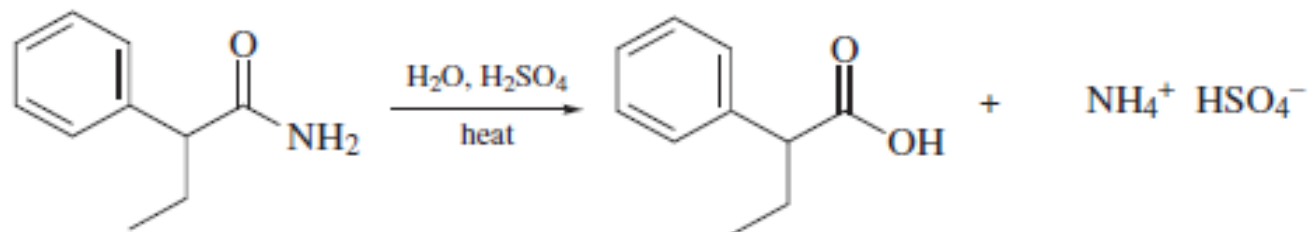
تتحلل الأميدات بالماء ببطء شديد، إلا أن التحلل بالماء يتسارع بحضور الأحماض القوية (معطياً الحامض وملح الأمونيوم للحامض القوي)، كما تتحلل بحضور الأسس القوية (لتعطي الملح المعدني للحامض وتطلق النشادر أو الأمين). ويطلق على هذا التحلل بالماء تعبير «تصبن الأميد». أما تحلل الأميدات بالكحول إلى إستر وأمين فتفاعل صعب ومحدود.

التحلل في الوسط الحامضي



التحلل في الوسط القاعدي

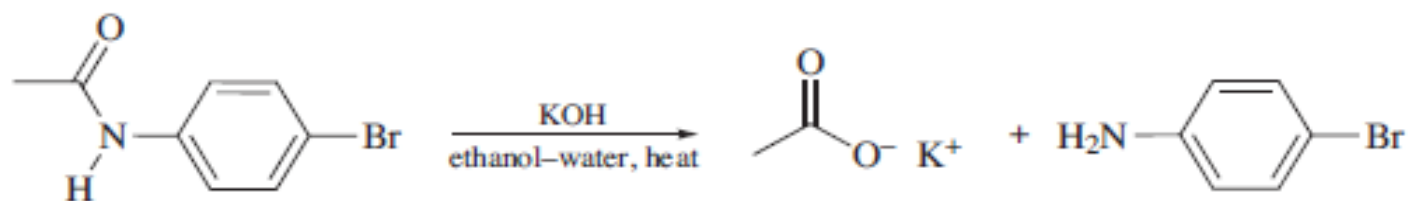




2-Phenylbutanamide

2-Phenylbutanoic acid
(88–90%)

Ammonium hydrogen
sulfate

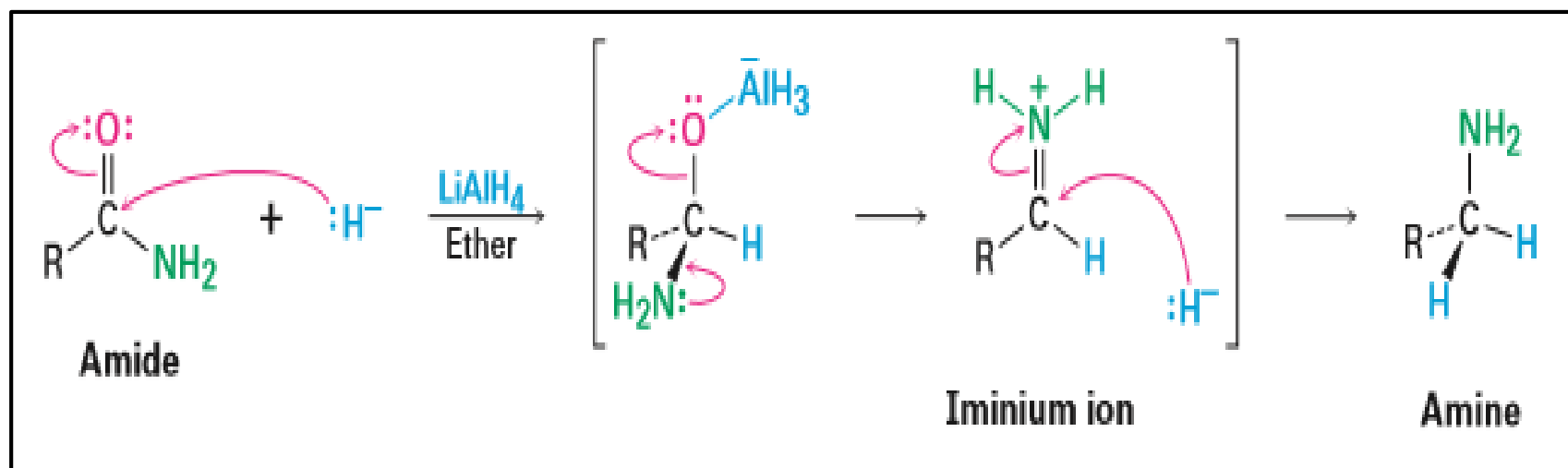
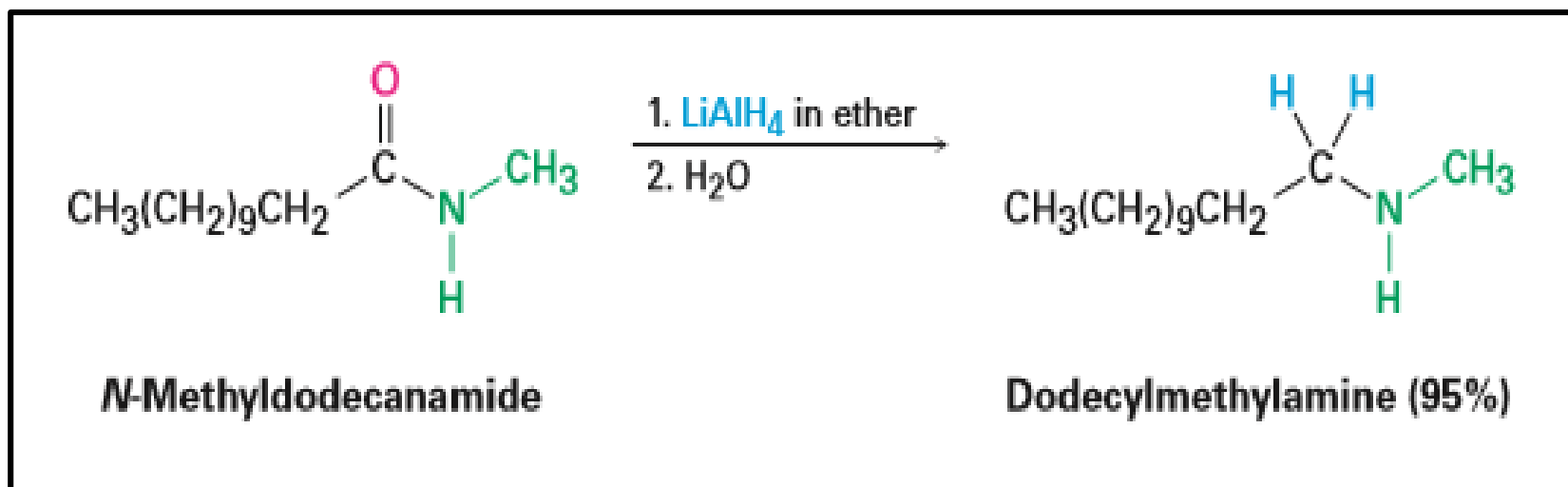


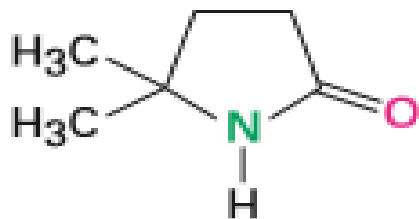
N-(4-Bromophenyl)acetamide

Potassium acetate

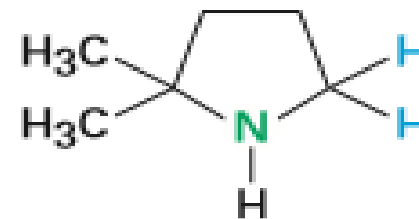
p-Bromoaniline (95%)

Conversion of Amides into Amines: reduction

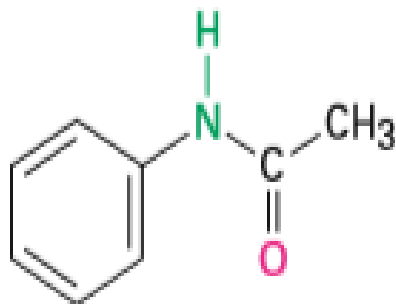




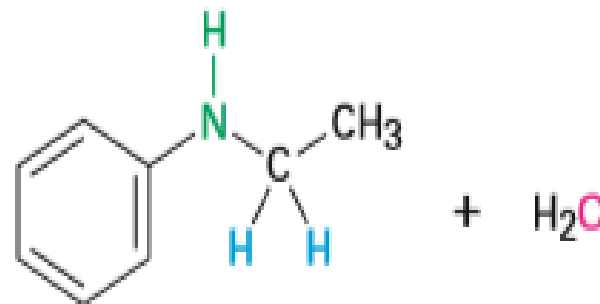
A lactam



A cyclic amine (80%)



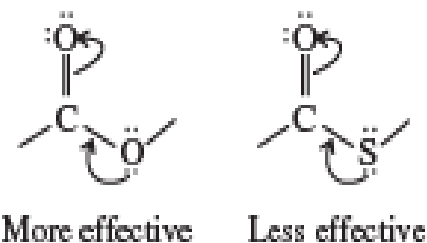
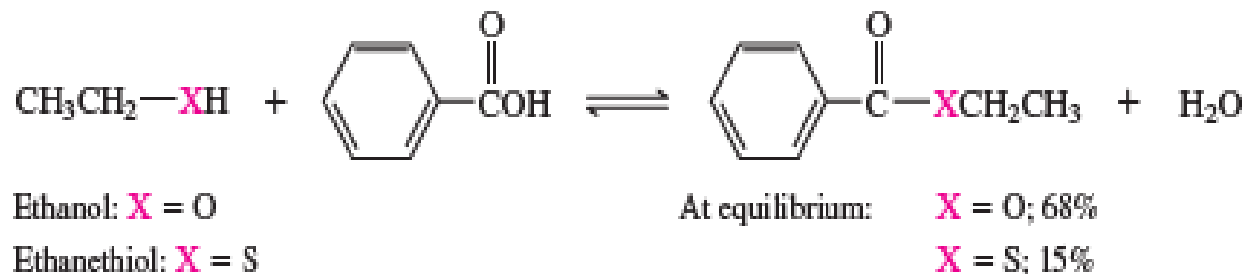
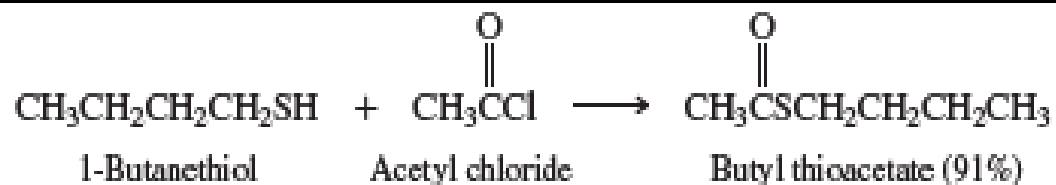
N-Phenylacetamide



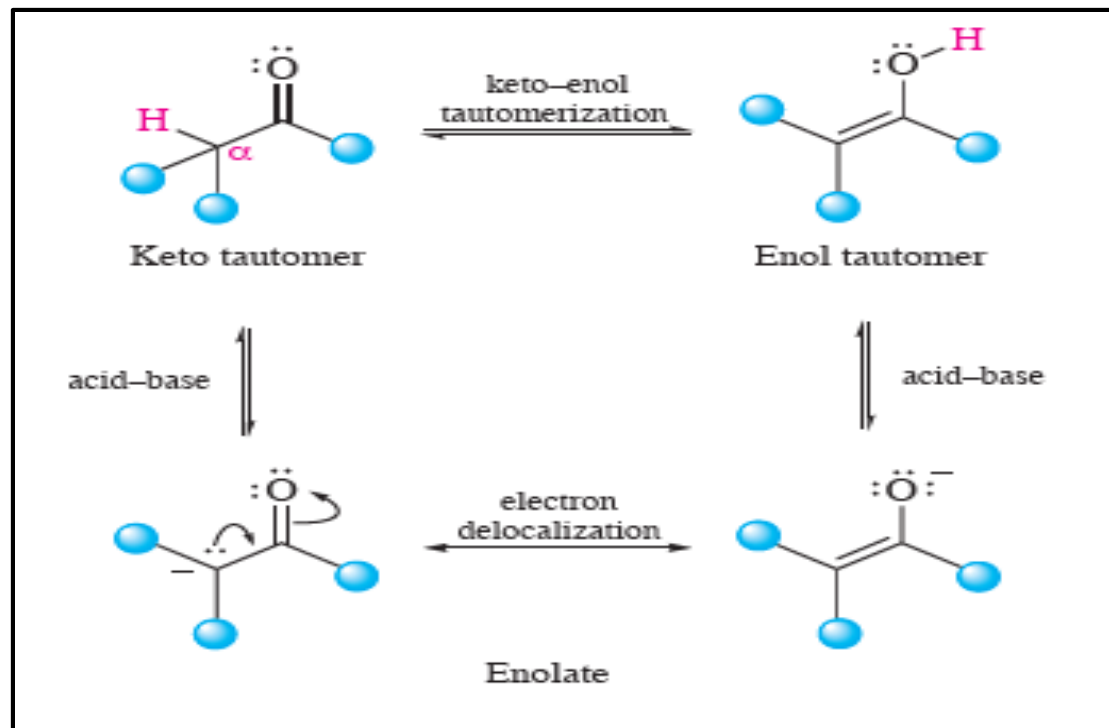
N-Ethylaniline

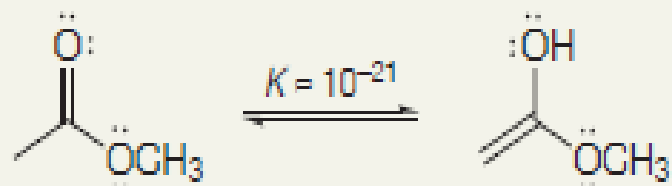


Thioesters

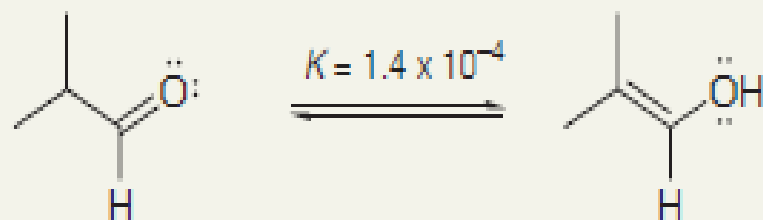


Enols and Enolates

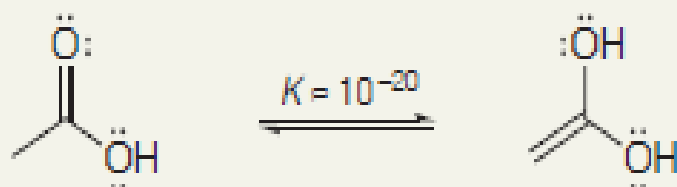




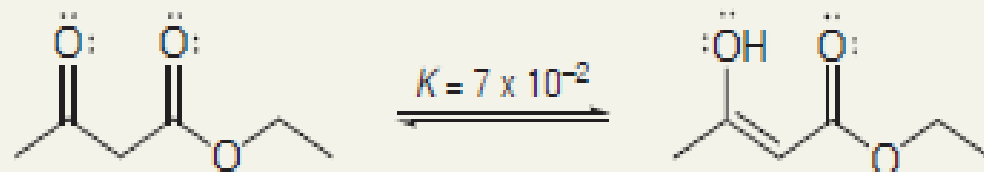
Methyl acetate



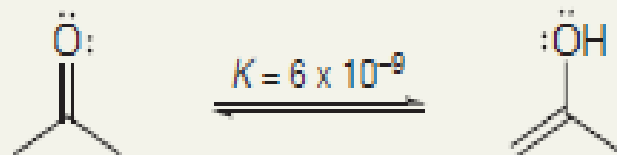
2-Methylpropanal



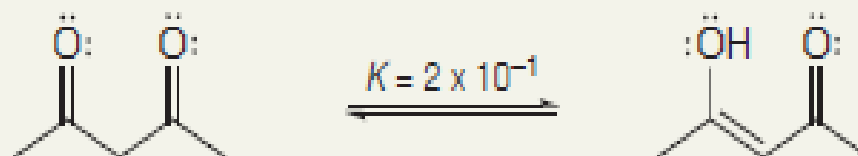
Acetic acid



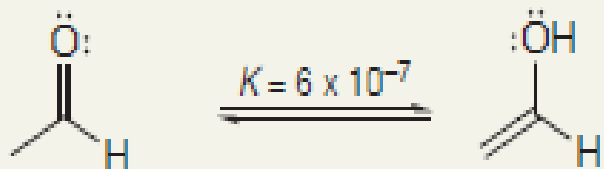
Ethyl acetoacetate



Acetone



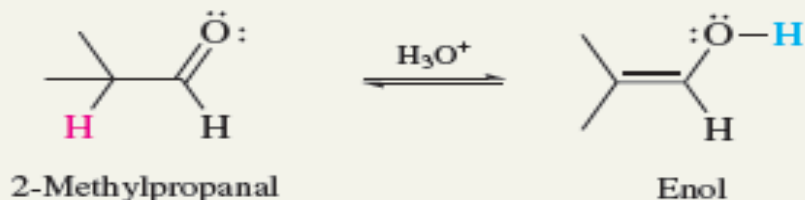
2,4-Pentanedione



Acetaldehyde

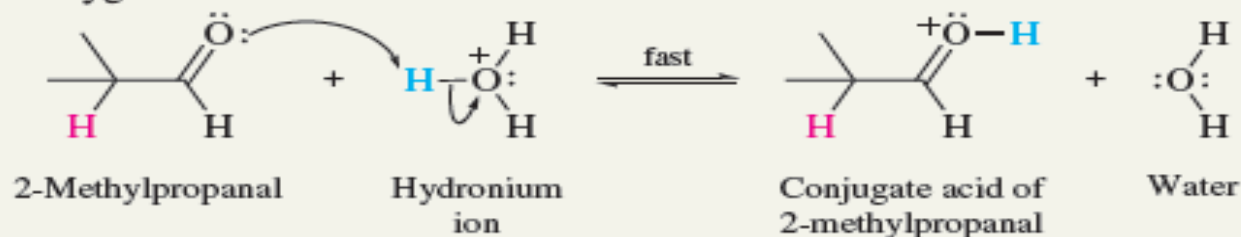
Acid-Catalyzed Enolization of 2-Methylpropanal

THE OVERALL REACTION:

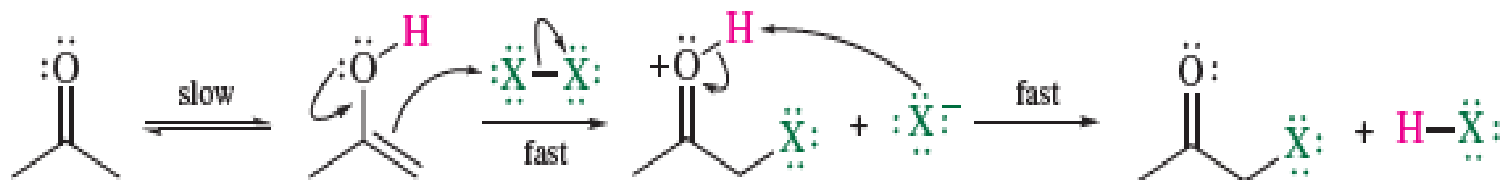
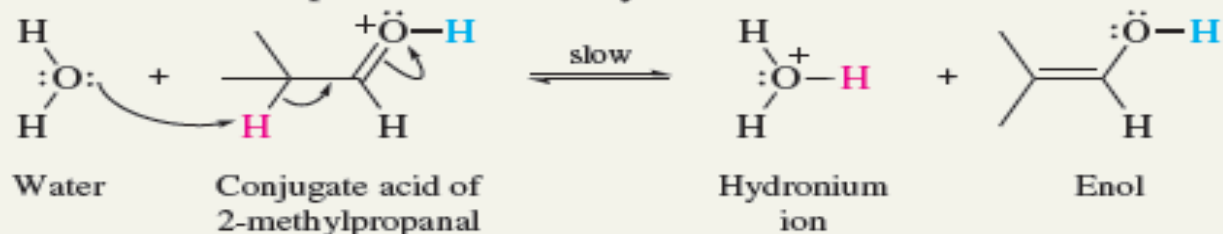


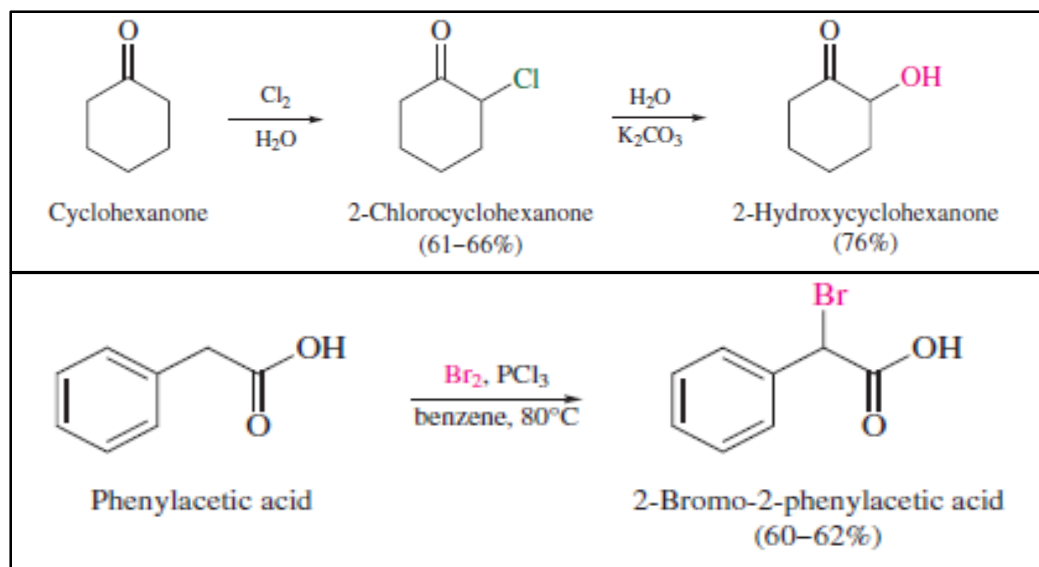
THE MECHANISM:

Step 1: In aqueous solution, hydronium ion transfers a proton to the carbonyl oxygen.

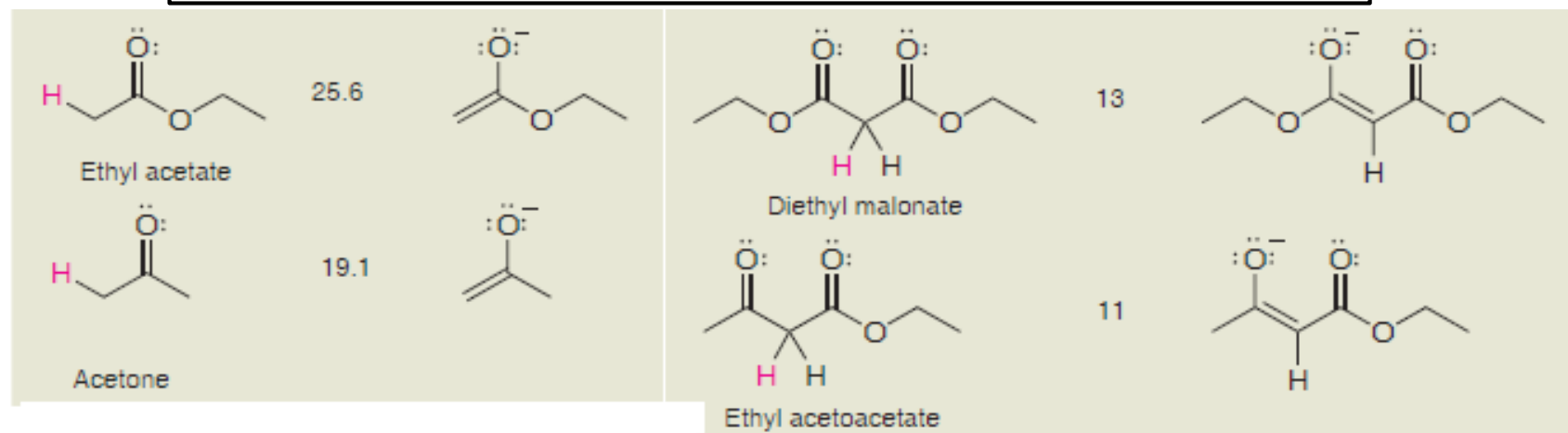
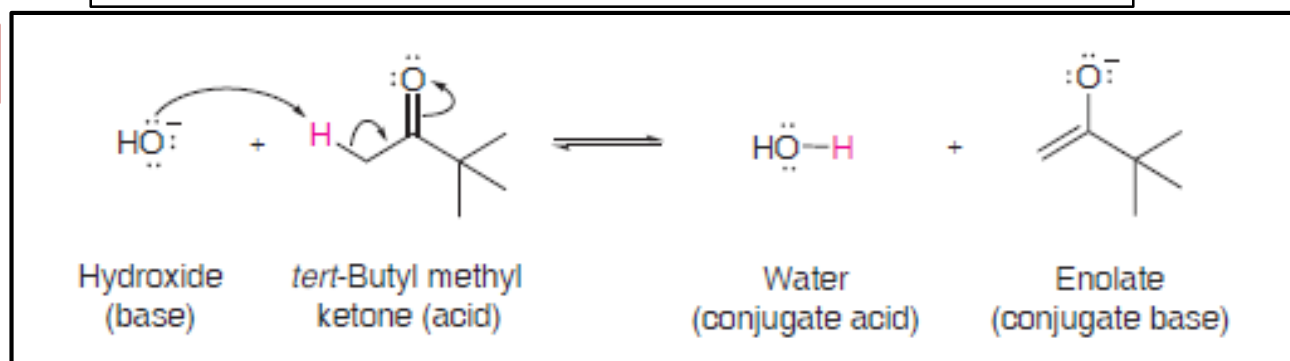


Step 2: A water molecule acts as a Brønsted base to remove a proton from the α carbon of the protonated carbonyl.

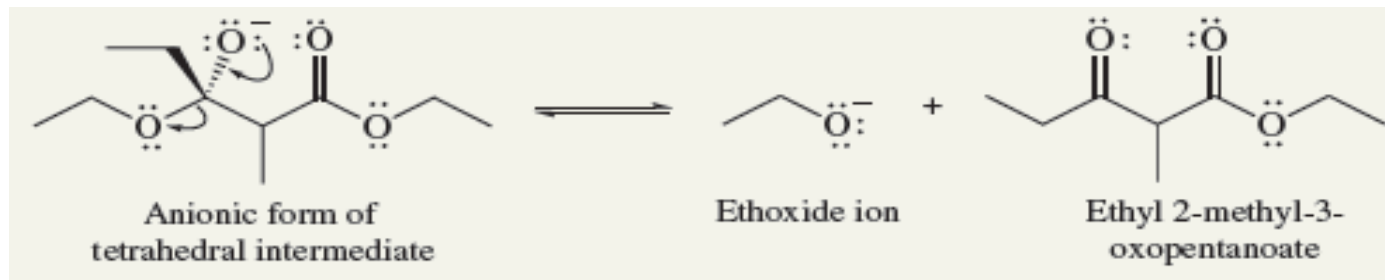




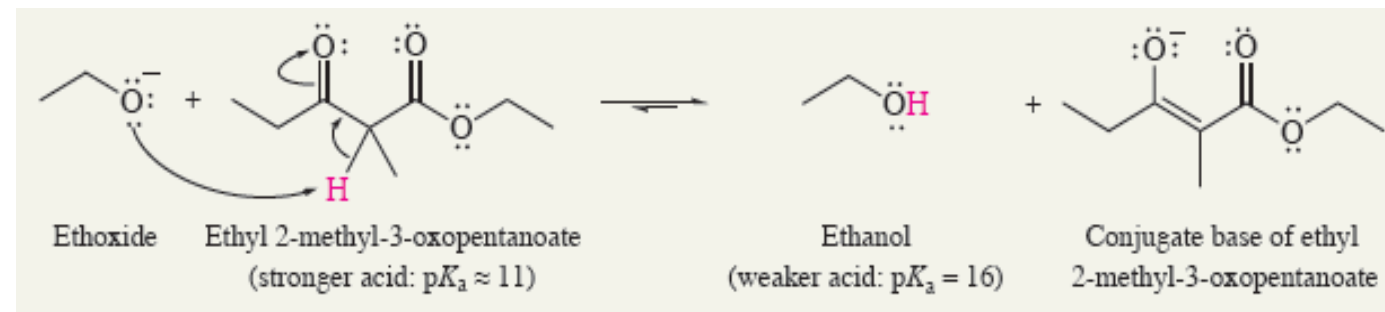
Enolates



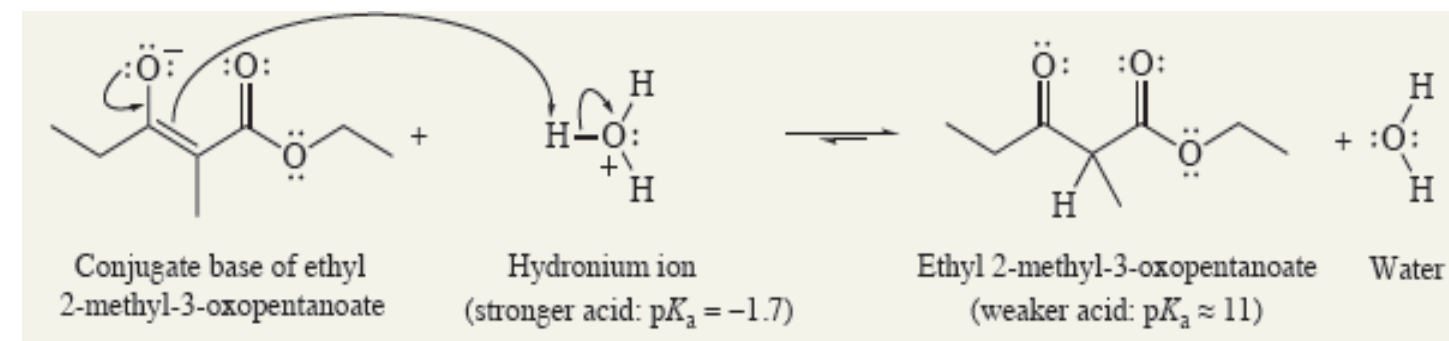
Step 3:



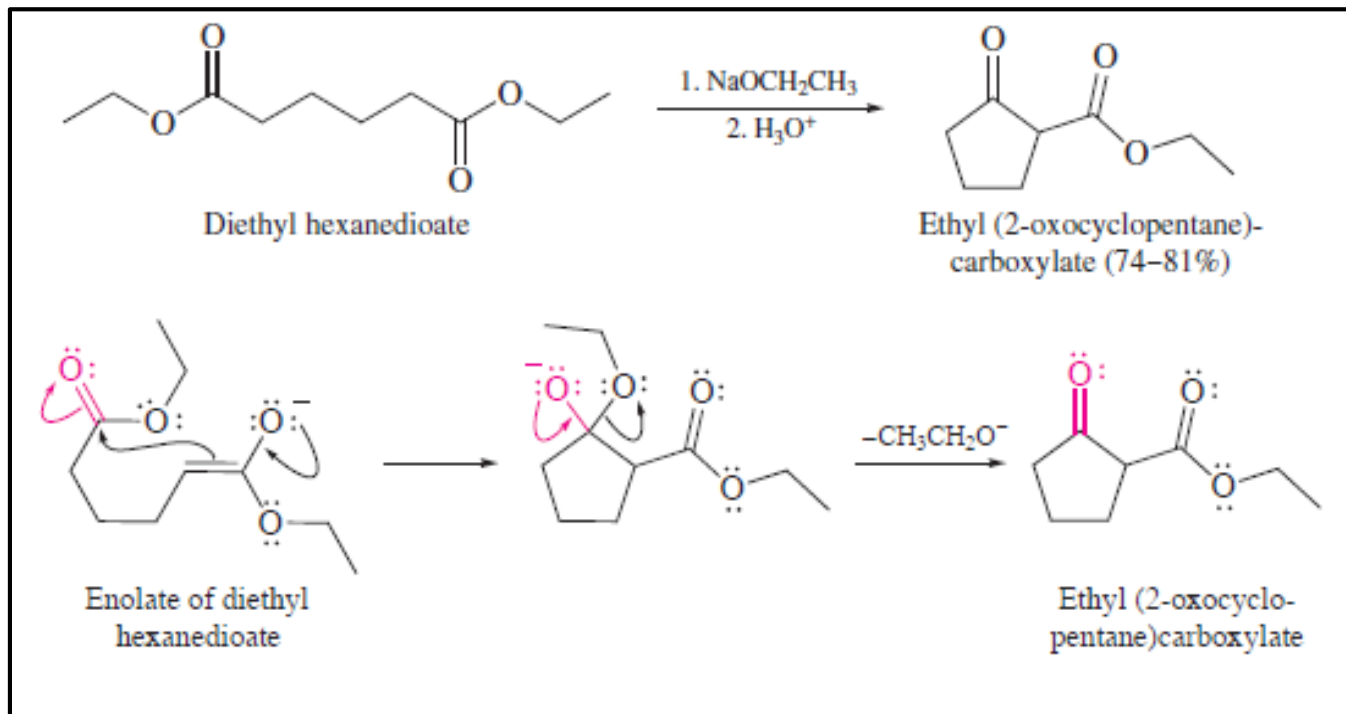
Step 4:



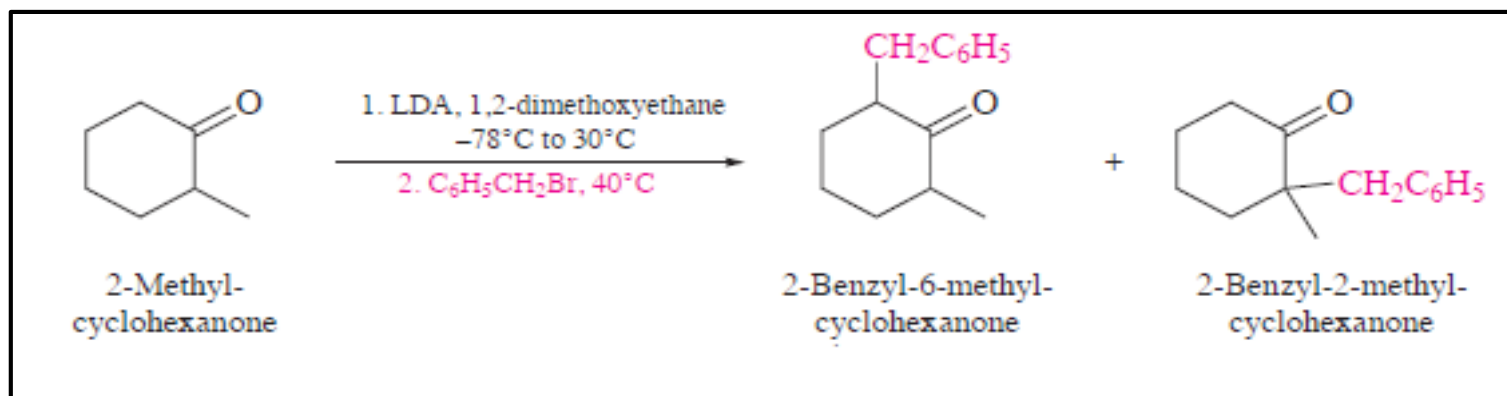
Step 5:

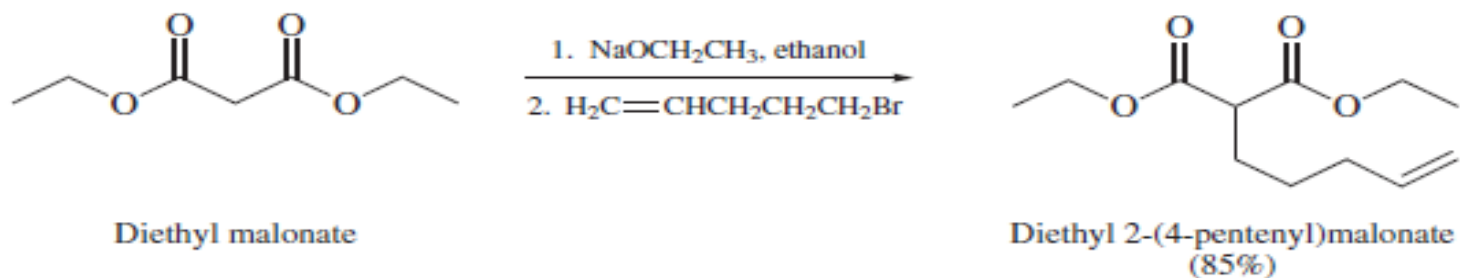
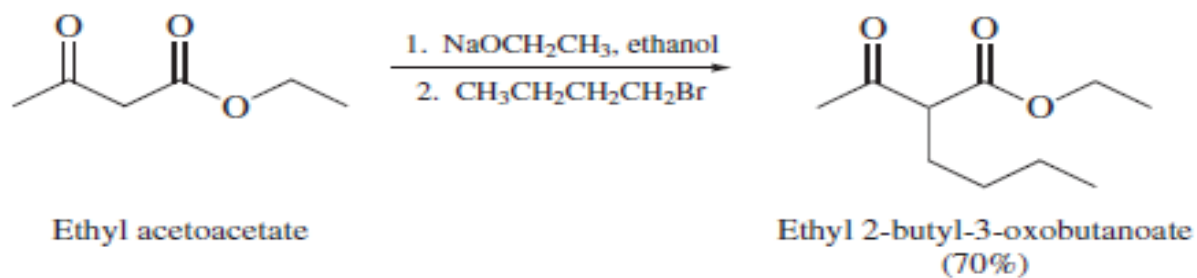
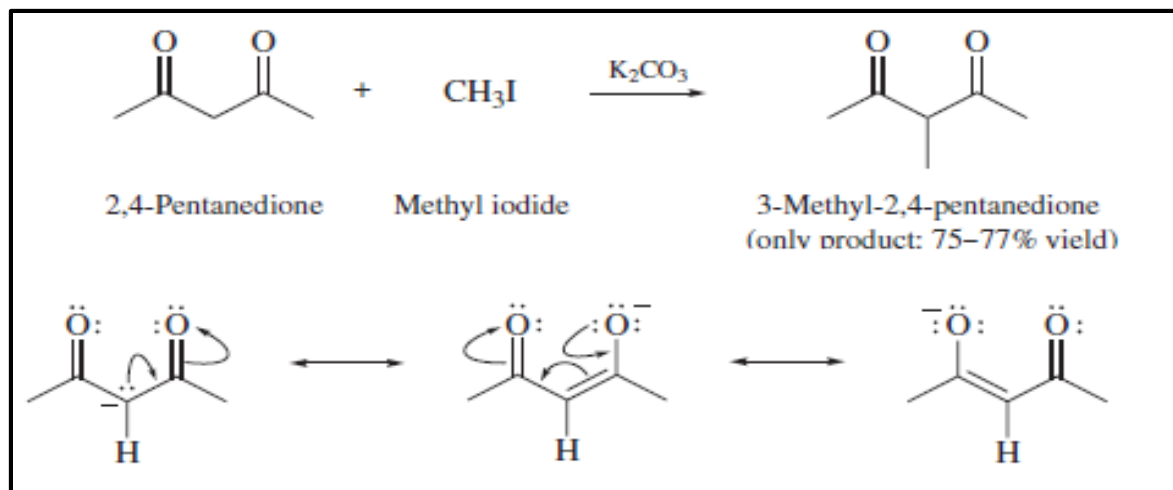


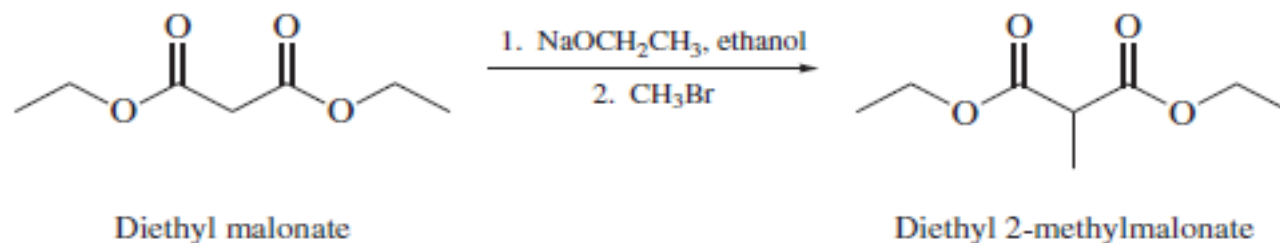
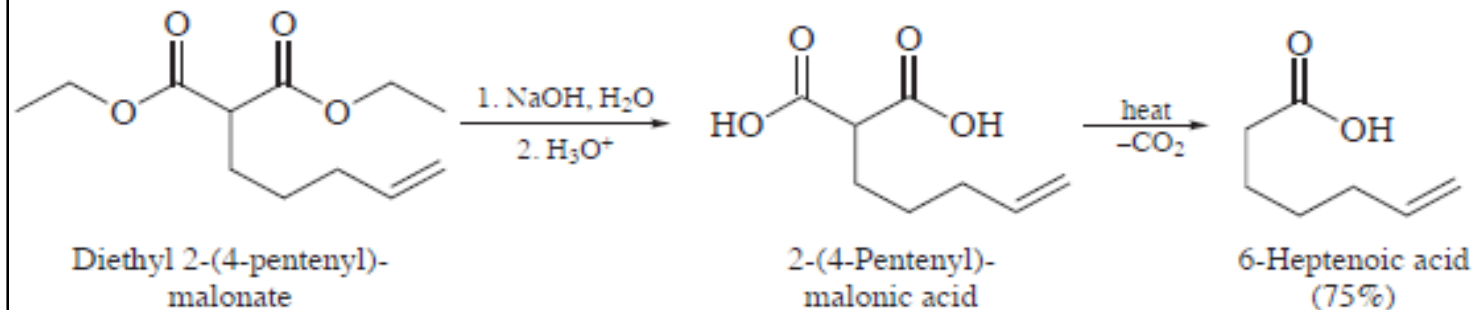
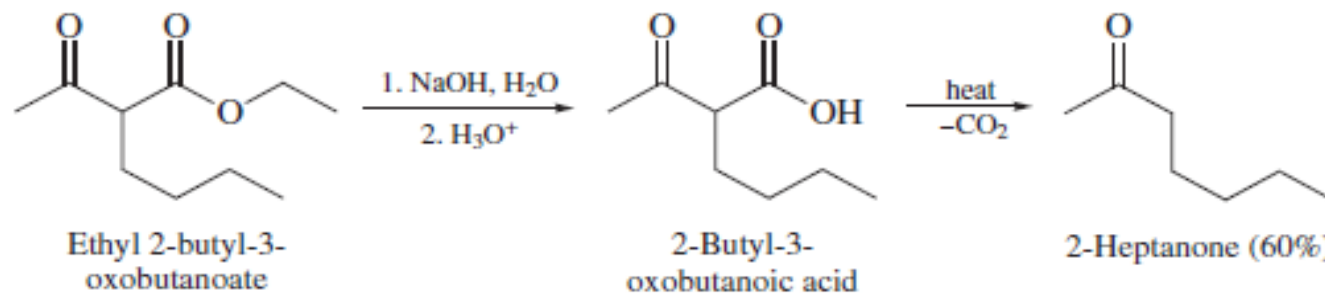
Dieckmann cyclization



Alkylation of Enolates: The Acetoacetic Ester and Malonic Ester Syntheses







then

