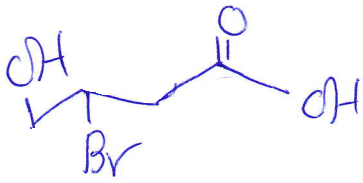
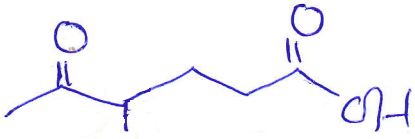
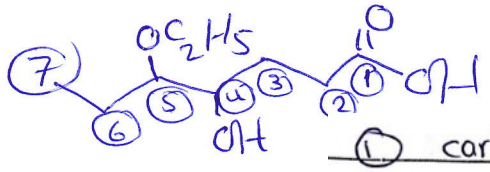
Chapter 10. Carboxylic Acids and their Derivatives

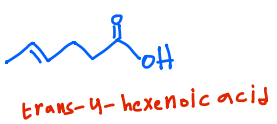
① Carboxylic acids have a general formula $R-\overset{O}{\overset{\|}{C}}-OH$ $(RCO_2H)(RCOOH)$.

② Nomenclature of acids:-

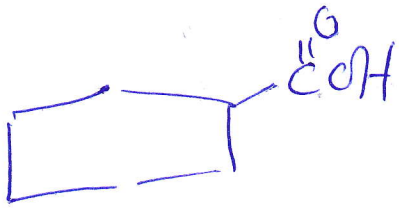
* $H-\overset{O}{\overset{\|}{C}}-OH$ methanoic acid (Formic acid)
* $CH_3-\overset{O}{\overset{\|}{C}}OH$ ethanoic acid (Acetic acid)
*  butanoic acid
*  3-Bromo-4-hydroxy butanoic acid
* $H_2C=\underset{H}{C}-\overset{O}{\overset{\|}{C}}OH$ propenoic acid
*  4-Methyl-5-oxohexanoic acid

($-\overset{O}{\overset{\|}{C}}-$ as substituent is called: oxo).

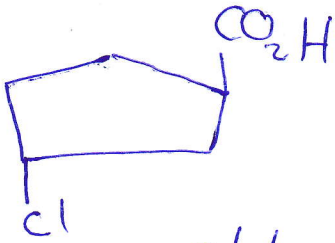
*  5-Ethoxy-4-hydroxy heptanoic acid



① carboxylic acid	تسميات ⟸ الذي يعوز :
② Aldehyde	
③ Ketone	تفرعات : $-\overset{O}{\overset{\|}{C}}H$ formyl
④ Alcohol	$-\overset{O}{\overset{\|}{C}}-CH_3$ acetyl
⑤ الباقي بيساوي	$-\overset{O}{\overset{\|}{C}}-C_6H_5$ Benzoyl
	$-\overset{O}{\overset{\|}{C}}-$ oxo

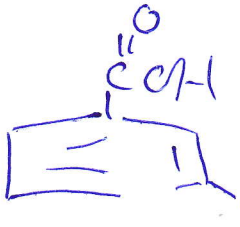


Cyclohexane carboxylic acid.

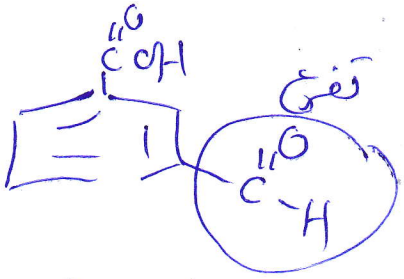


trans-3-Chloro cyclo pentane carboxylic acid

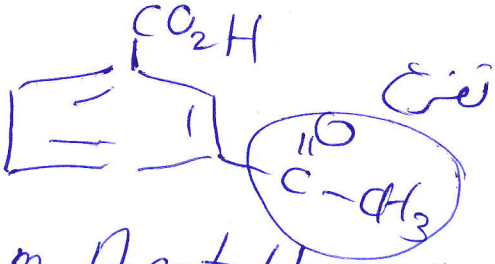
benzoic acid



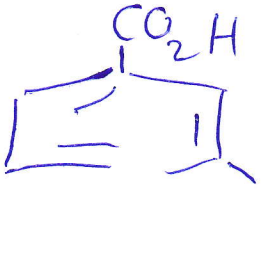
m-hydroxy benzoic acid.



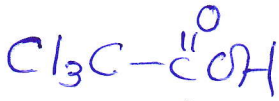
m-Formyl benzoic acid



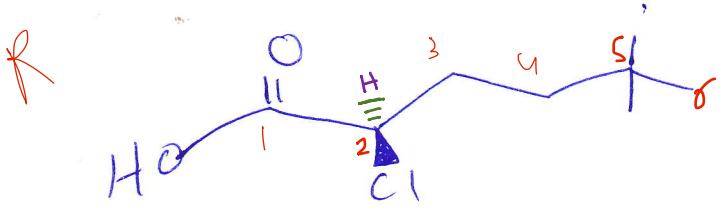
m-Acetyl benzoic acid



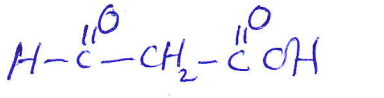
m-toluic acid



Trichloro acetic acid



(R)-2-chloro-5,5-dimethylhexanoic acid



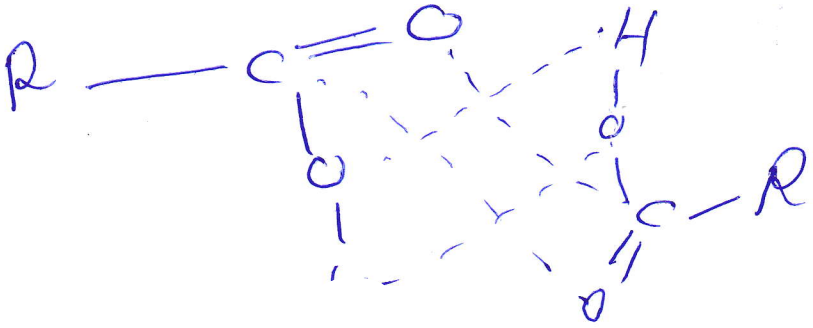
3-oxopropanoic acid

3-benzoylbenzoic acid

* Physical properties of Acids

① Carboxylic acids are polar molecules and among their molecules there are hydrog bonding and dipole-dipole interactions.

Boiling point of RCOOH > ROH > RCHO / RCOR for a given molar mass.



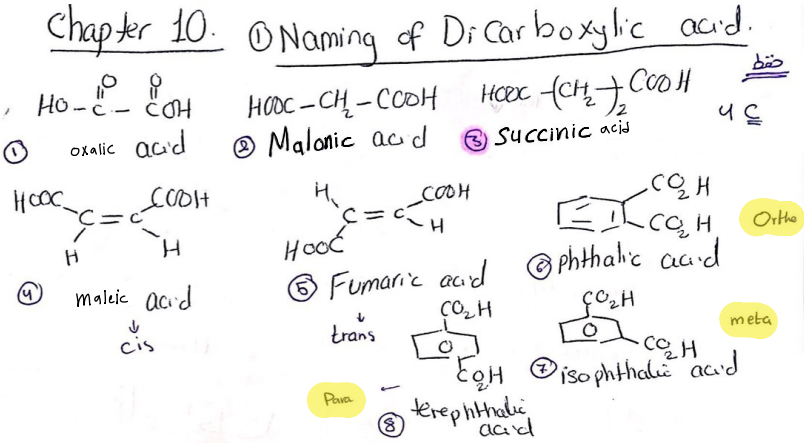
② They have a higher boiling point than alcohols (with closer molar masses).

$CH_3\overset{O}{\overset{\|}{C}}OH$ — 60 g/mol — b.p 118°C

$CH_3CH_2CH_2OH$ — 60 g/mol — 97°C

③ low molar masses of carboxylic acids are soluble in water.

Chapter 10. ① Naming of Di carboxylic acid.



* Acidity of Carboxylic acids:-

$$R-\overset{O}{\overset{\|}{C}}-O-H \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O} + H^{\oplus}$$

$$R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O} \longleftrightarrow R-\overset{\ominus}{\underset{O}{C}}=O$$

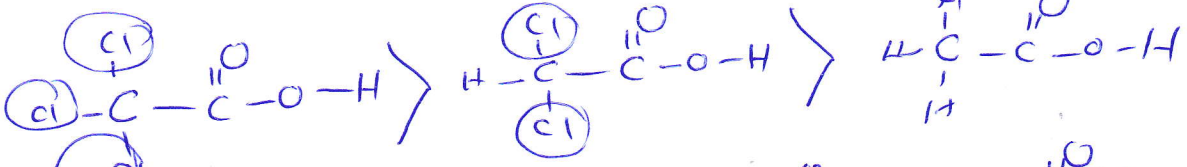
-ve charge is delocalized.

Carboxylic acid (The strongest acid)

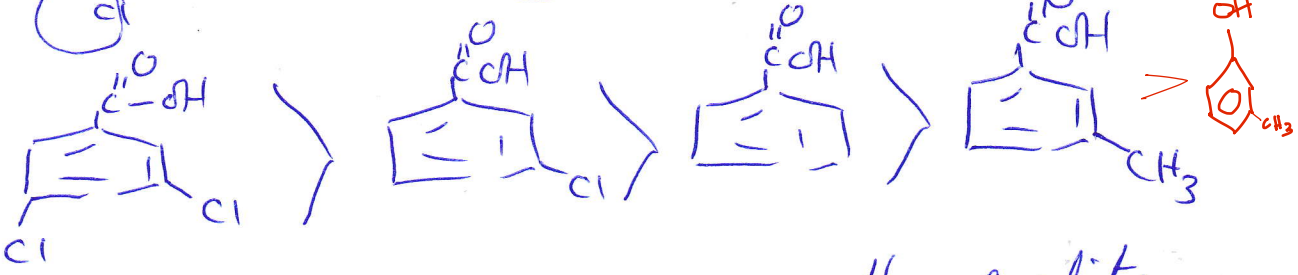
phenol

alcohol (The weakest acid).

ex 1-

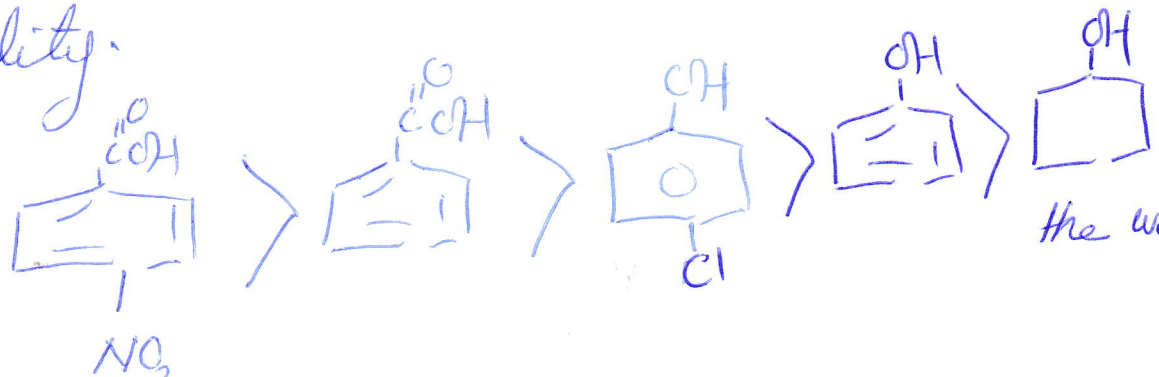


ex 2.



electron-withdrawing groups increase the acidity, while electron-donating groups decrease the acidity.

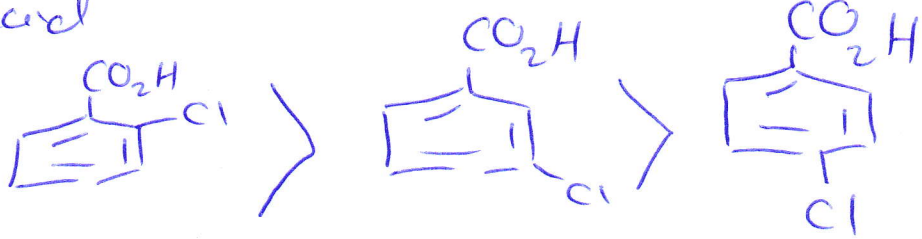
ex 3.



the strongest acid

the weakest.

ex 4.



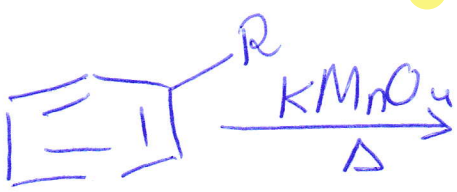
note: As Ka value ↑ PKa ↓ acidity ↑

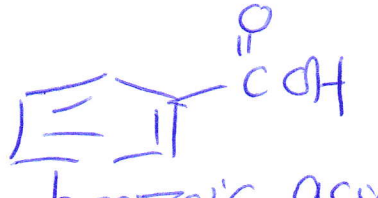
Synthesis of Carboxylic Acids: (4) Methods could be used.

(1) Oxidation of 1° alcohols by Jones' reagent or oxidation of aldehydes.

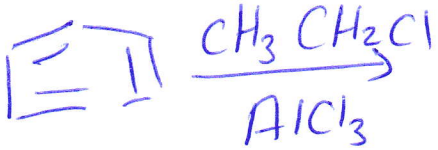
ex: $CH_3CH_2CH_2Br \xrightarrow[\text{② } CrO_3, H^+]{\text{① } NaOH}$ ① → $CH_3CH_2CH_2OH$ ② → $CH_3CH_2\overset{O}{\overset{\|}{C}}OH$

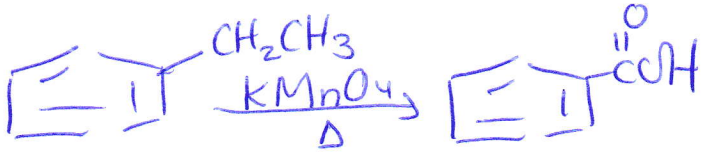
(2) Oxidation of side-chains of benzene occur in the C that has (H)

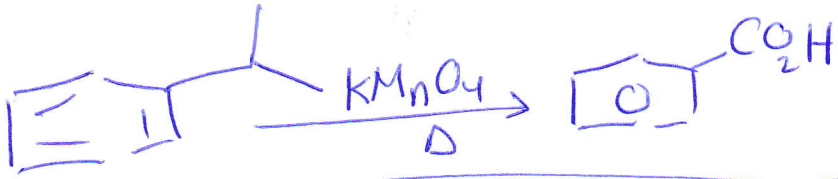




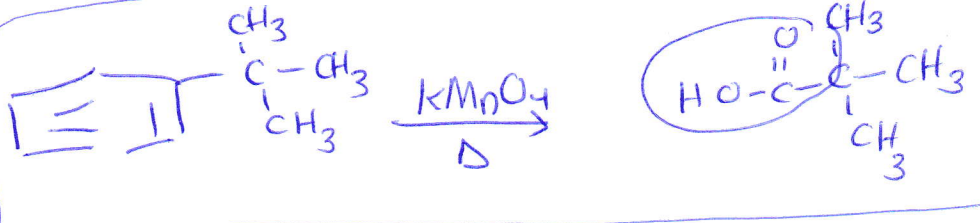
benzoic acid (regardless length of R).

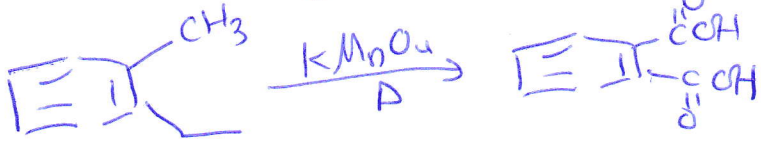




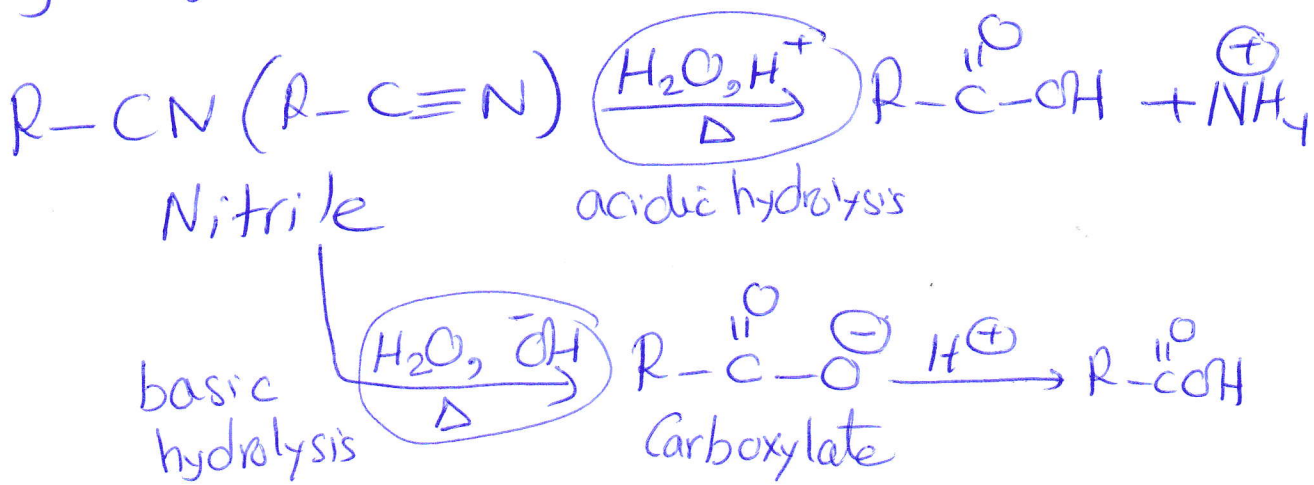


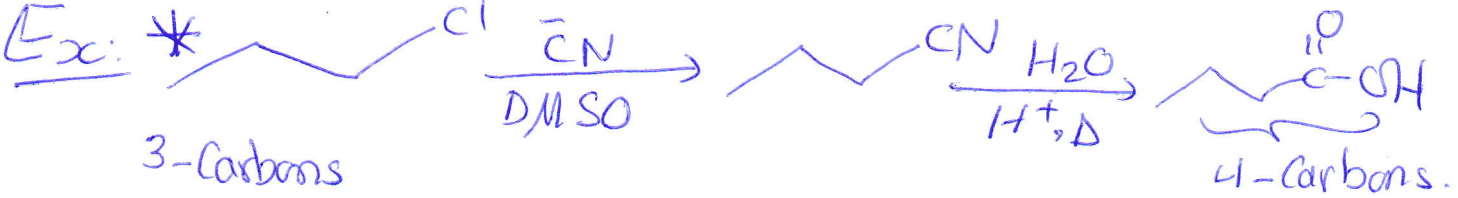
Exception:

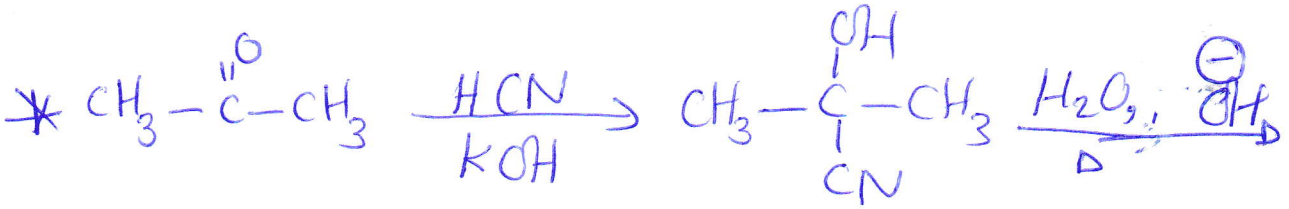


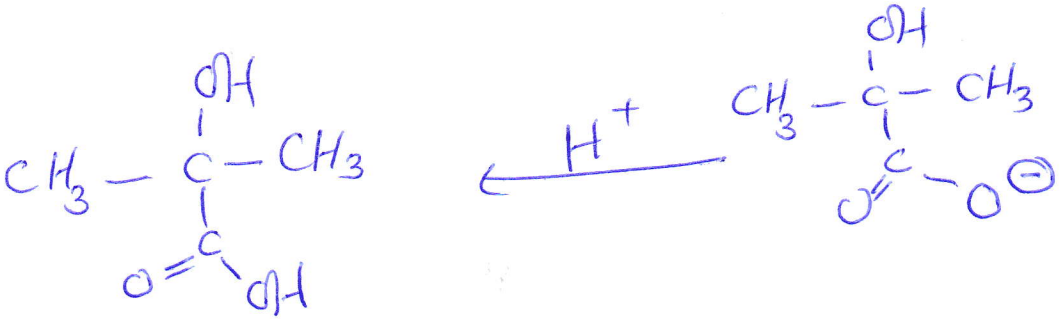


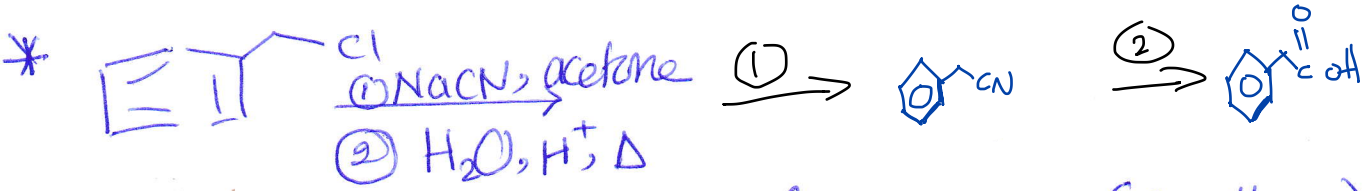
③ Hydrolysis of Nitriles:-



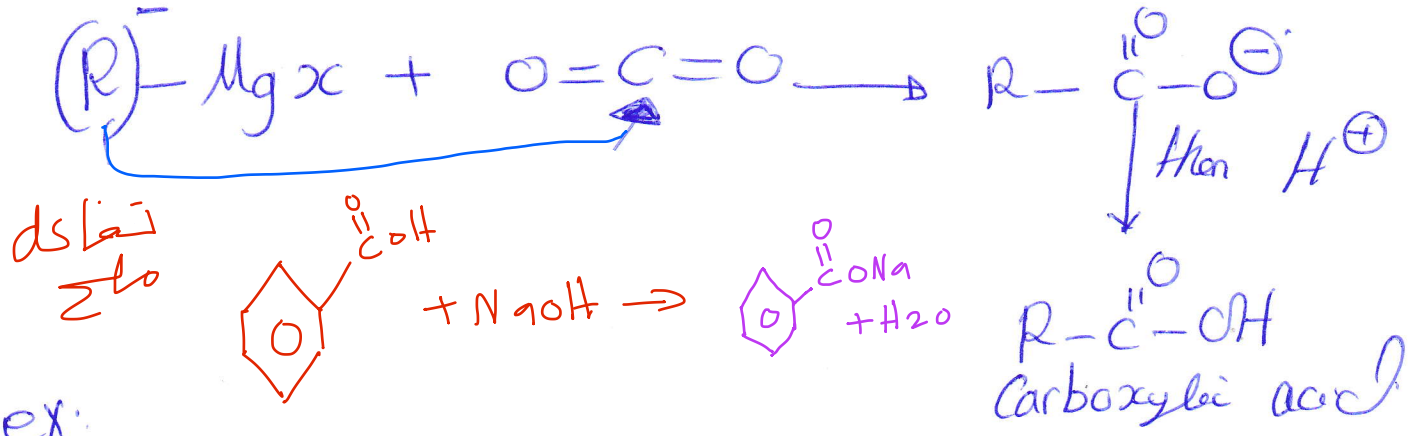




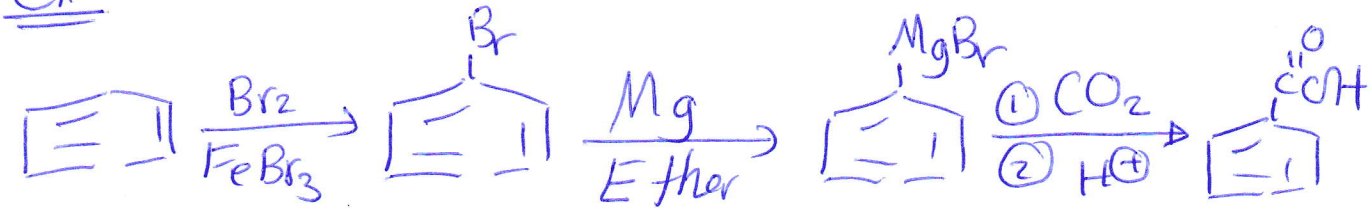


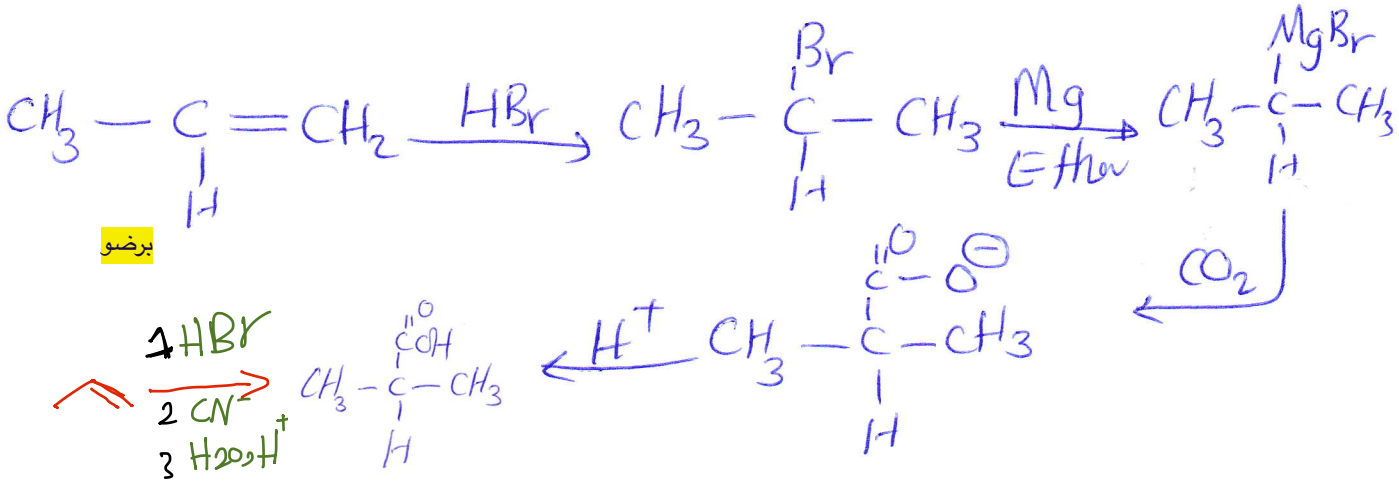


④ Reaction of Grignard reagent (R–Mg–X) with Carbon dioxide (CO_2) then addition of H^+.



ex:





* Carboxylic acid derivatives include:-

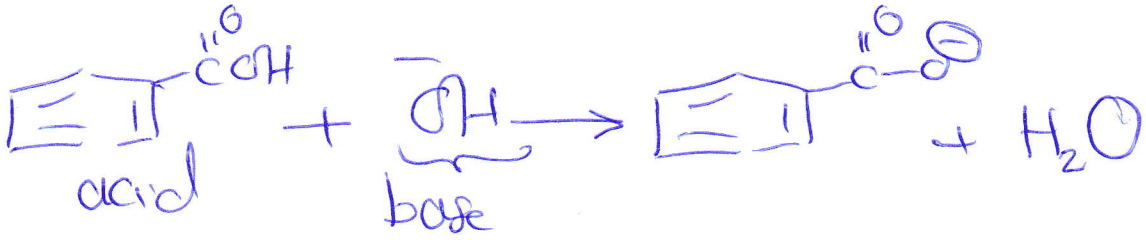
① $R-C(=O)-X$ Acyl halide

② $R-C(=O)-O-C(=O)-R$ Acid anhydride

③ $R-C(=O)-OR$ Ester

④ $R-C(=O)-N$ Amide

These derivatives could be prepared from carboxylic acid.

Note: 

$CH_3COOH + KOH \longrightarrow CH_3COO^{\ominus}K^{\oplus} + H_2O$

First: Acyl halides ($R-\overset{O}{\overset{\|}{C}}-X$)

Synthesis: $R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{SOCl_2} R-\overset{O}{\overset{\|}{C}}-Cl$

$\xrightarrow{PCl_5} R-\overset{O}{\overset{\|}{C}}-Cl$

Reactions: $R-\overset{O}{\overset{\|}{C}}-Cl$

① Hydrolysis → $R-\overset{O}{\overset{\|}{C}}-OH$ (carboxylic acid)

② $R-\overset{O}{\overset{\|}{C}}-O^{\ominus}$ → $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ anhydride

③ $R-O-H$ → $R-\overset{O}{\overset{\|}{C}}-OR$ Ester

④ $\sim\!\!N-H$ → $R-\overset{O}{\overset{\|}{C}}-N\sim$ Amide

Remember: $R-\overset{O}{\overset{\|}{C}}-Cl + \bigcirc \xrightarrow{AlCl_3} \bigcirc-\overset{O}{\overset{\|}{C}}-R$

Aromatic ketone.

* Principle of reactions:

$R-\overset{O}{\overset{\|}{C}}-X$ (or $-O-\overset{O}{\overset{\|}{C}}-R$, $-OR$, $-N\sim$)

Step 1: $\xrightarrow{Nu}$

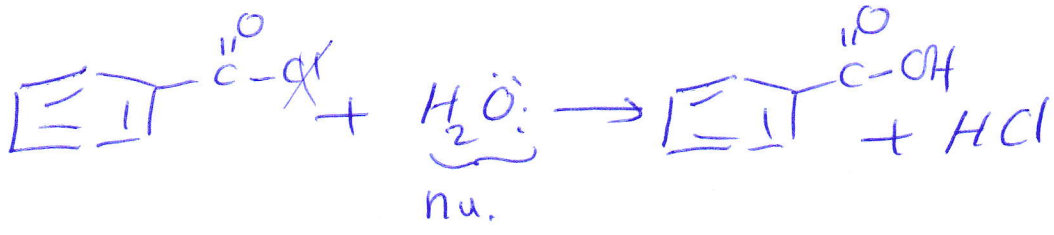
$R-\overset{O^{\ominus}}{\underset{Nu}{\overset{|}{C}}}-X$ (or $-O-\overset{O}{\overset{\|}{C}}-R$, $-OR$, $-N\sim$)

Step 2:

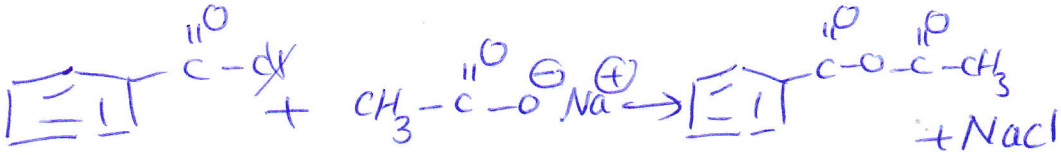
$R-\overset{O}{\overset{\|}{C}}-Nu$ + ...

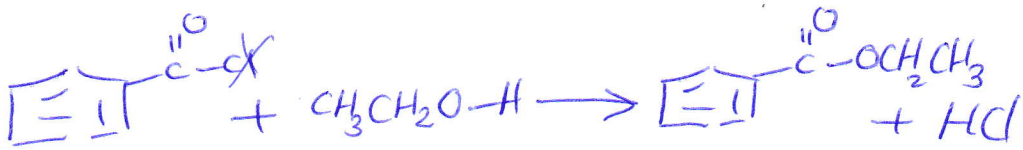
Mechanism is nucleophilic Acyl substitution

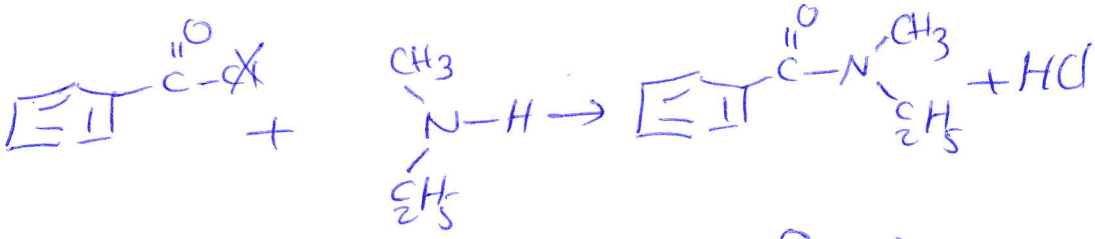
Examples:



nu.





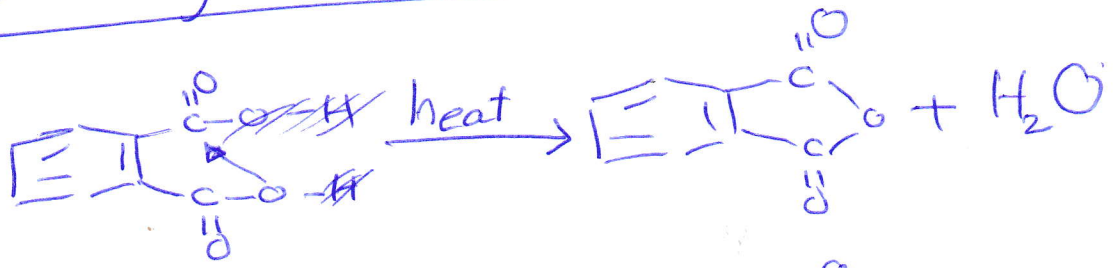


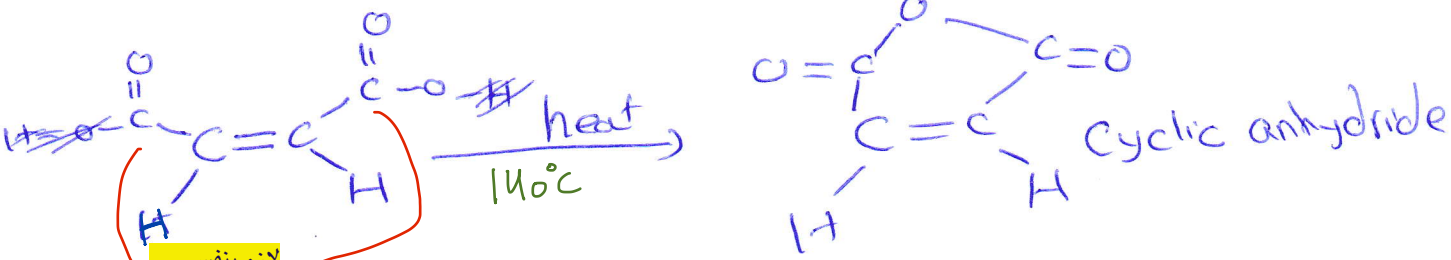
Second: Acid anhydride ($R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$)

synthesis:

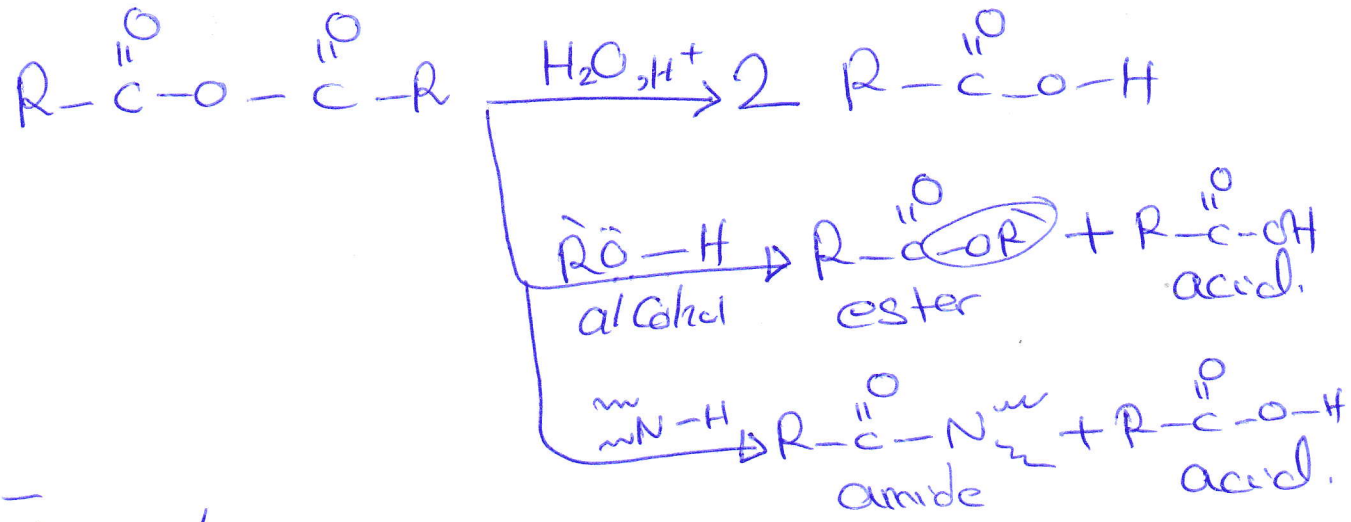
a) From $R-\overset{O}{\overset{\|}{C}}-Cl$: $R-\overset{O}{\overset{\|}{C}}-Cl + R-\overset{O}{\overset{\|}{C}}-O^{-}Na^{+} \rightarrow R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}R$

b) For cyclic anhydride: Heating of dicarboxylic acids

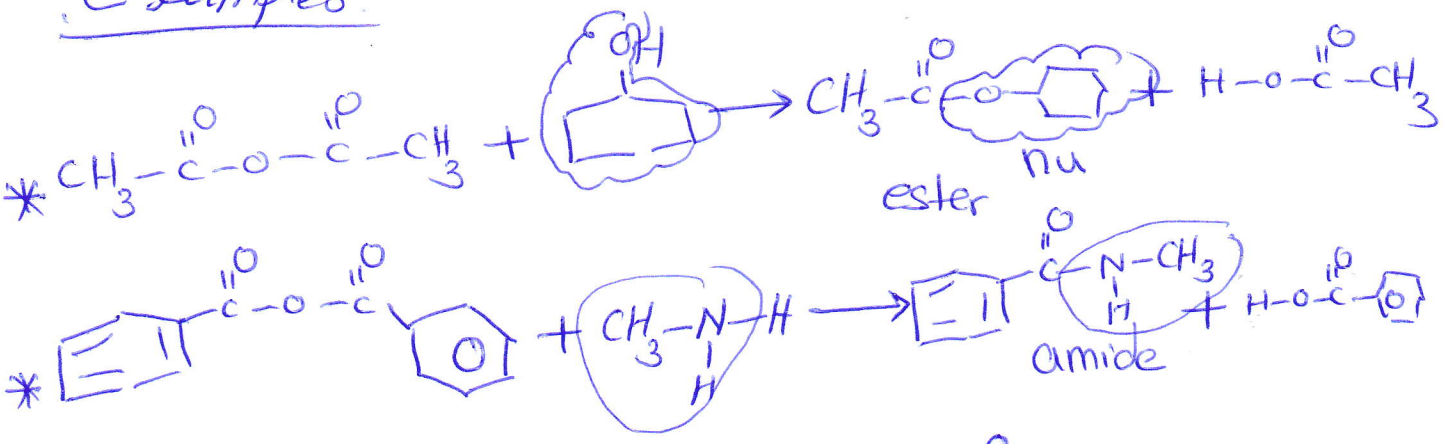


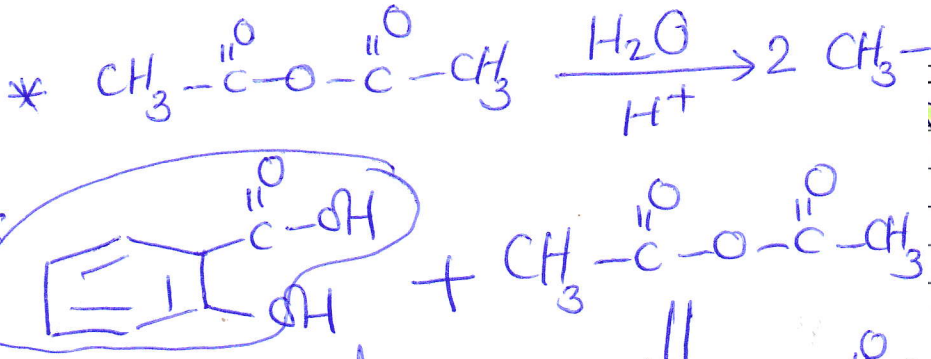


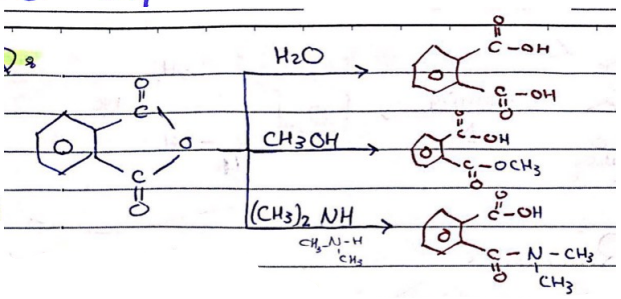
لازم بنفس الاتجاه للأعلى

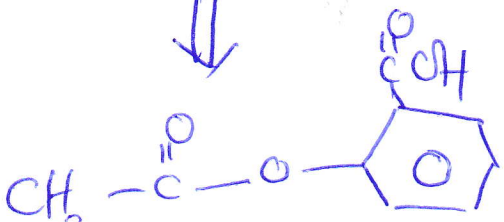

H2O, H+
2
ROH
alcohol
ester
acid
amide

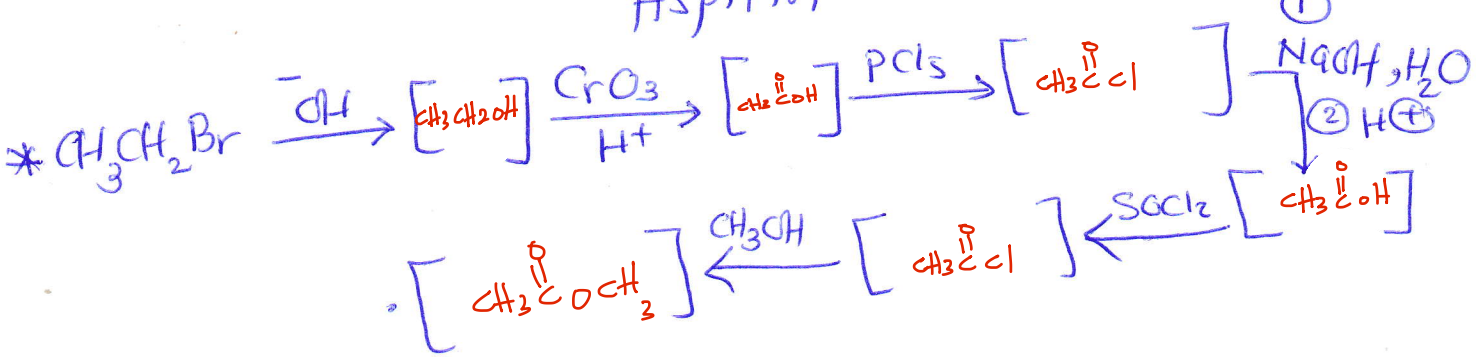
Examples:


ester
nu
amide


H2O
H+
Salicylic acid


H2O
CH3OH
(CH3)2 NH


Aspirin


CH3CH2Br
OH-
CH3CH2OH
CrO3
H+
PCl5
1 NaOH, H2O
2 H+
SOCl2
CH3OH

Third.

Esters: have a general formula $R-\overset{O}{\overset{\|}{C}}-OR$.

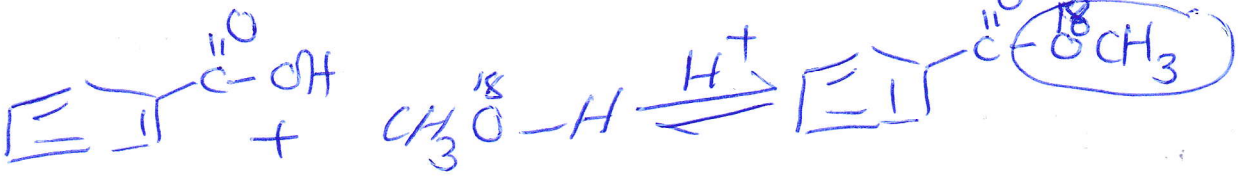
Synthesis: ① From $R-\overset{O}{\overset{\|}{C}}-X$ (acyl halide) + $R\grave{O}-H$ (alcohol) → $R-\overset{O}{\overset{\|}{C}}-O\grave{R}$

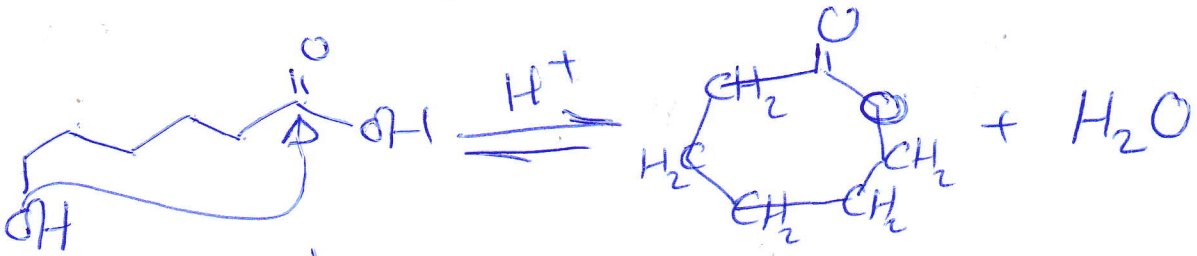
② From $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ (anhydride) + $R\grave{O}-H$ (alcohol) → $R-\overset{O}{\overset{\|}{C}}-O\grave{R}$

③ From $R-\overset{O}{\overset{\|}{C}}-OH$ (carboxylic acid) + $R\grave{O}-H$ (alcohol) $\overset{H^+}{\rightleftharpoons}$ $R-\overset{O}{\overset{\|}{C}}-O\grave{R}$

This method is called: Fischer Esterification

ex1. $CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3CH_2O-H \overset{H^+}{\rightleftharpoons} CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$

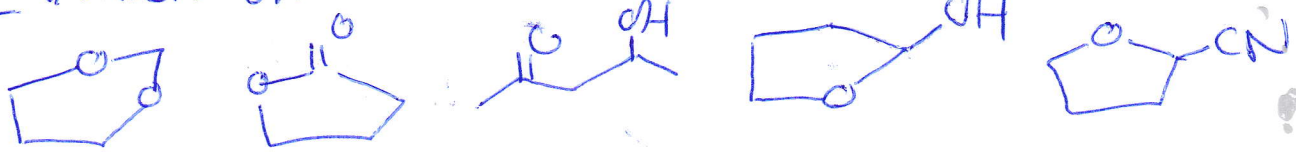
ex2. 

ex3. 

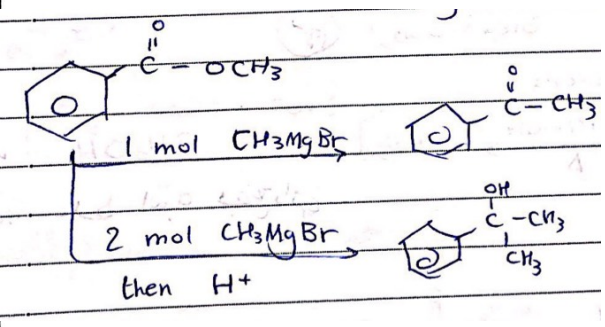
alcohol and acid in the same molecule.

Cyclic ester. "lactone".

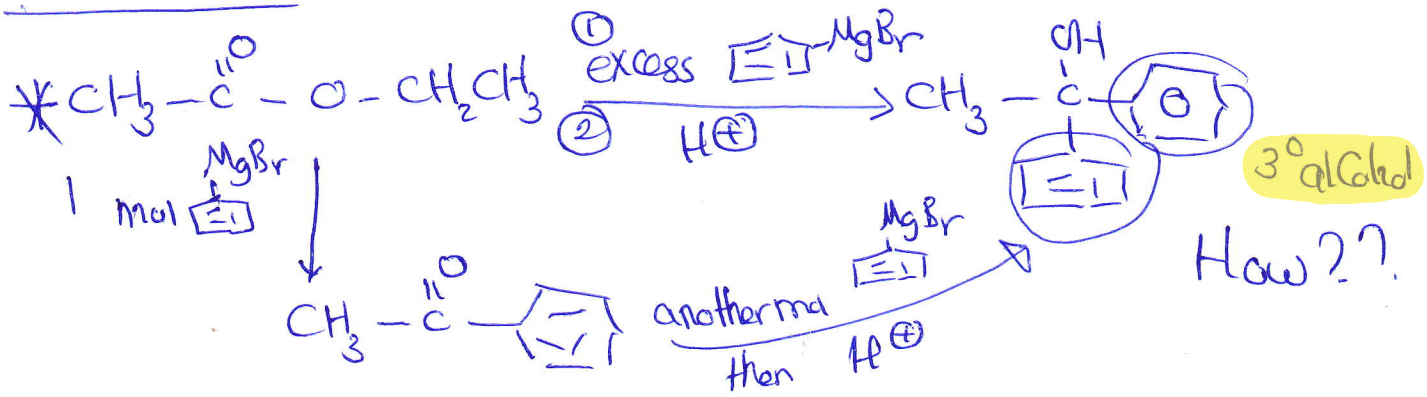
ex4. Which one is a lactone?

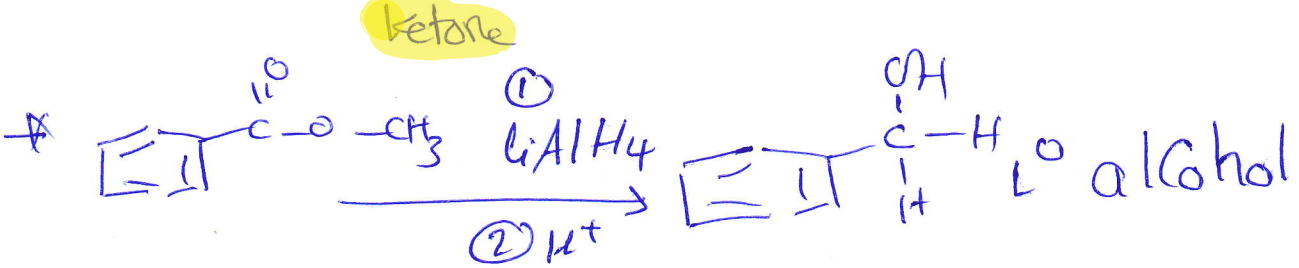


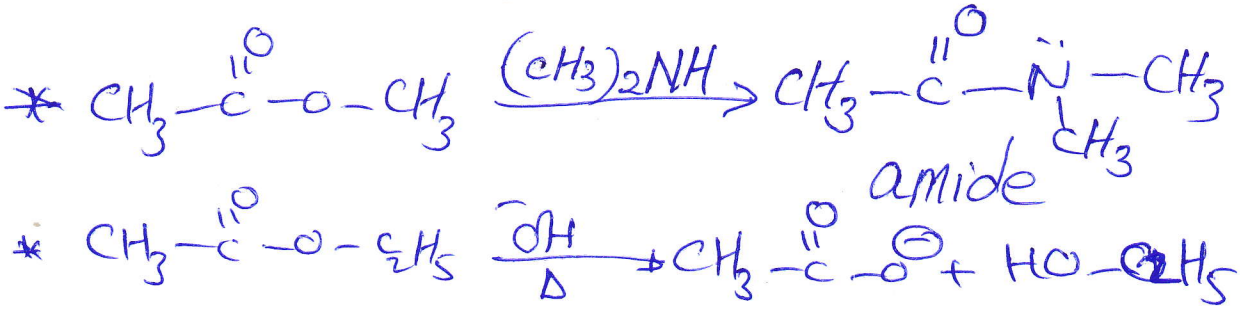
Reactions of Esters:



Examples:



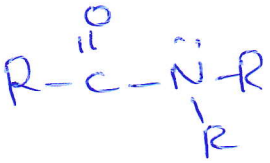




Fourth:- Amide 

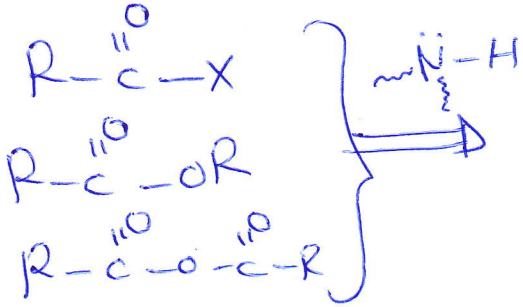

1° amide

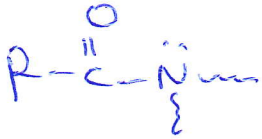

2° amide


3° amide

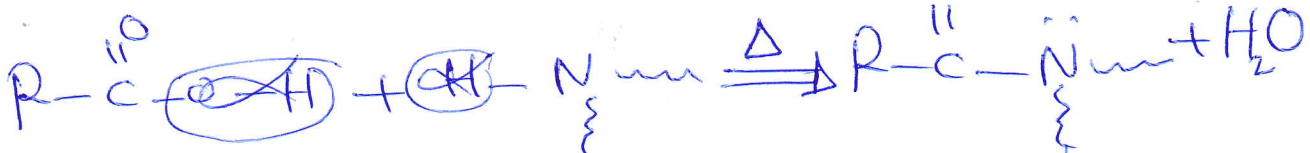
* 1° and 2° amides can form hydrogen bonding among their molecules, while 3° amides can't.

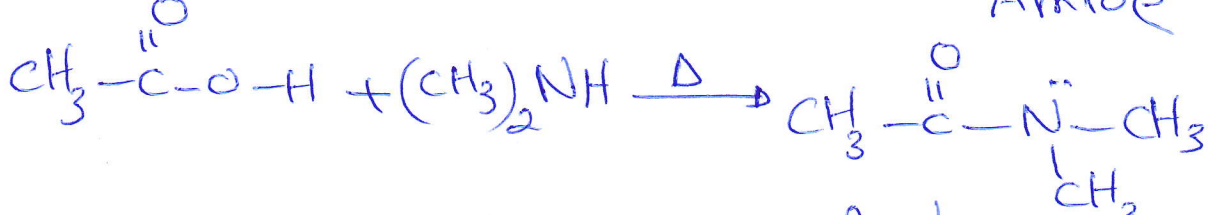
b.p (1° and 2° amides) > b.p (3° amide).

* <u>Synthesis:</u> From 

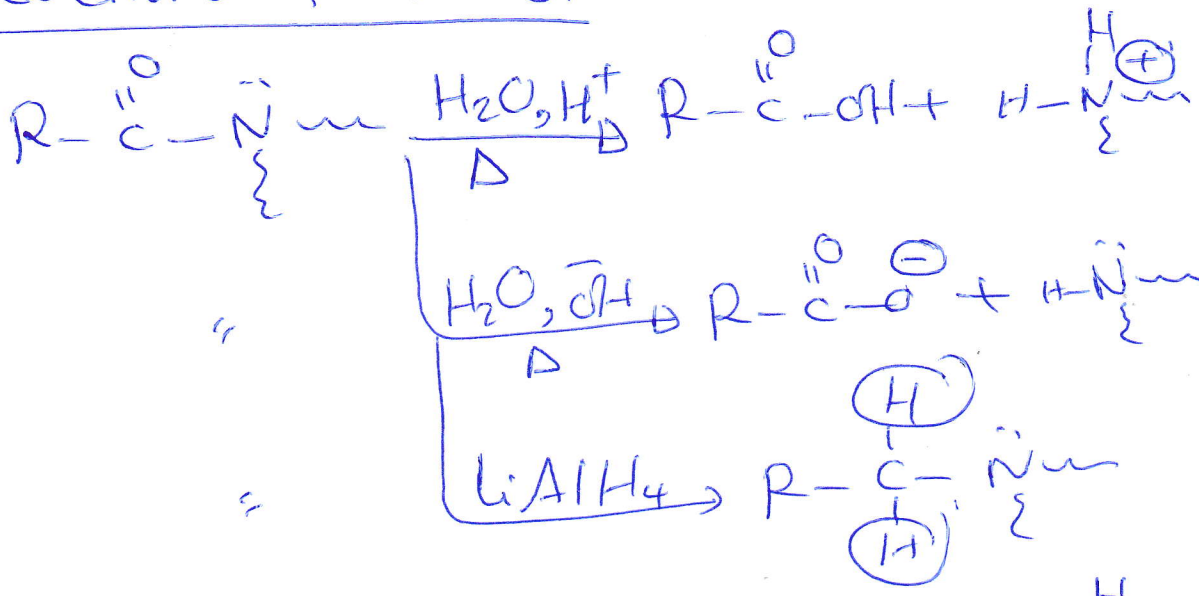

amide.

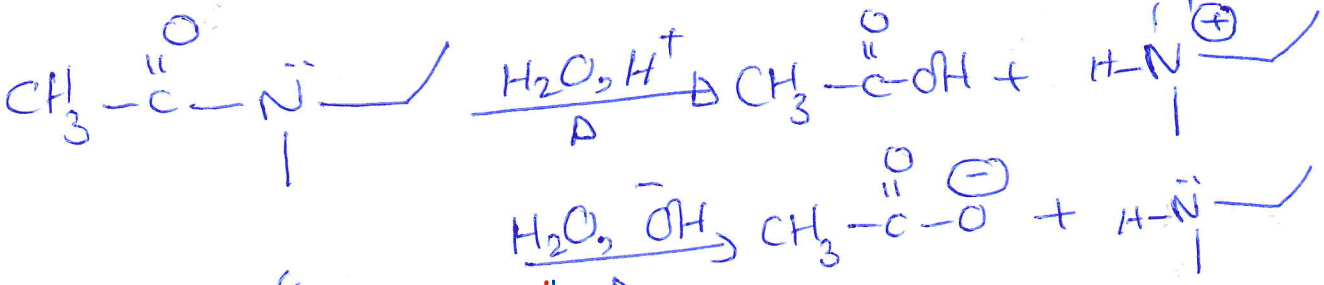
Also, from Carboxylic acid,





* Reactions of amides:



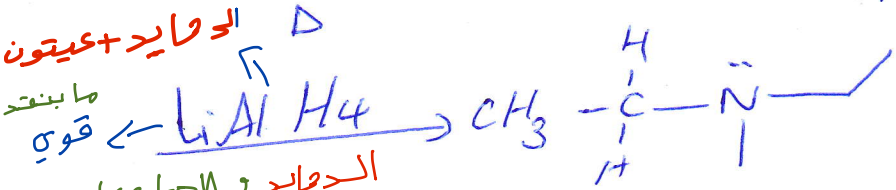


الحوايد + كيتون + ايثر + الأمين

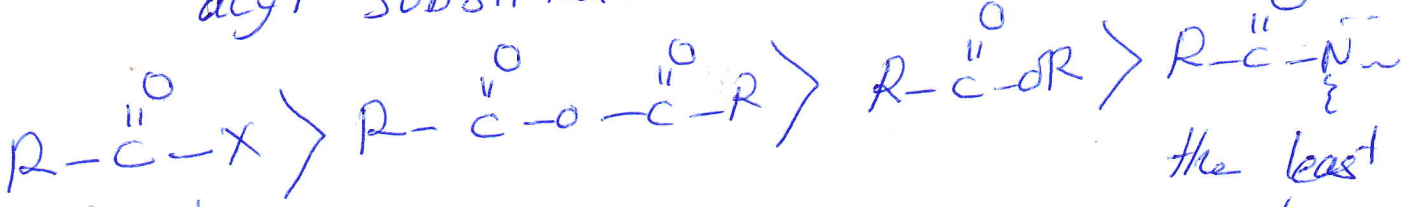
ما بتقدر تستعمل NaAlH4 ← ضعيف

LiAlH4 ← قوي

الحوايد و Ketone ← بستعملوا كلاوا



Note: The order of reactivity at nucleophilic acyl substitution



the most reactive

the least reactive

لإجبار طريقة تحضير الـ amine

ex: ①