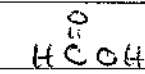


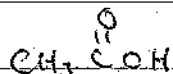
Carboxylic Acids

Nomenclature

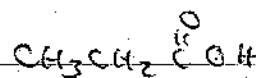
Alkane → Alkanonic Acid



methanoic acid  
(formic Acid)

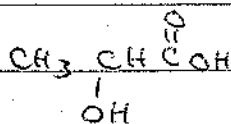


ethanoic acid  
(acetic acid)

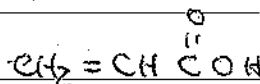


propanoic acid  
propanoic

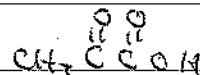
Name other subst. accordingly...



2-hydroxypropanoic acid

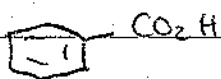


propenoic acid

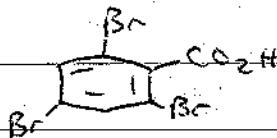


2-oxopropanoic acid

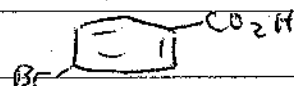
Aromatic Acids



Benzoic acid

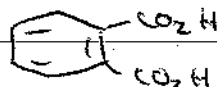


2,4,6-tribromo benzoic acid



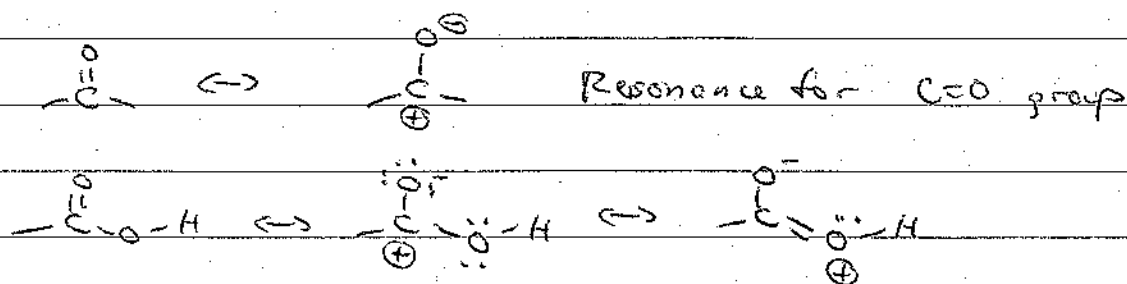
p-bromo benzoic acid

4-bromobenzoic acid

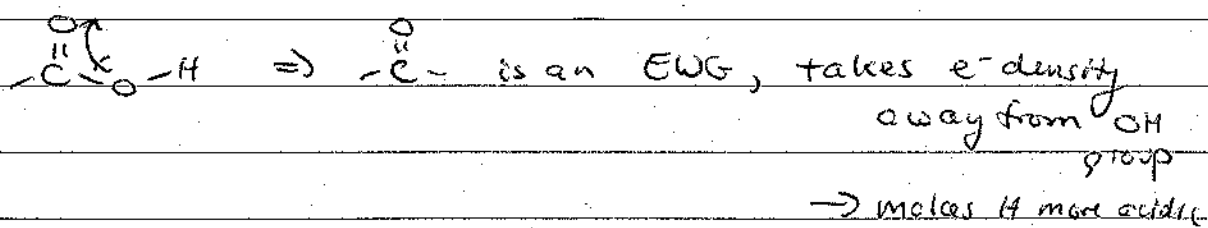


phthalic acid

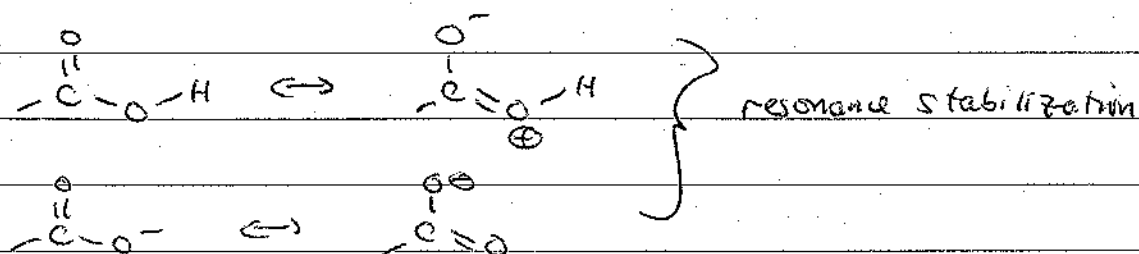
## Properties of acids



H is much more acidic than ROH  
(pKa 0.5-4.5) (pKa 15-20)



Also



Also means  $-\text{CO}_2\text{H}$  is less reactive than  $-\text{C}^{\oplus}-\text{H}$ ,  $-\text{C}^{\ominus}$



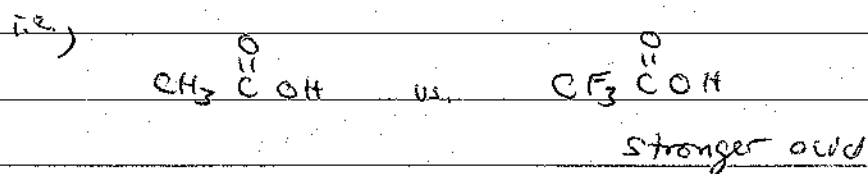
## Acidity of CA's

$pK_a \sim 5$

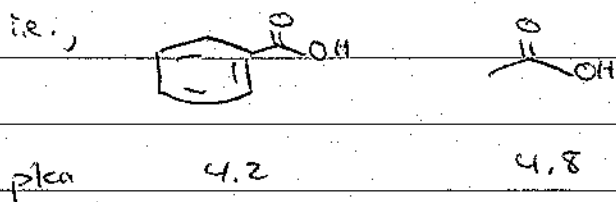
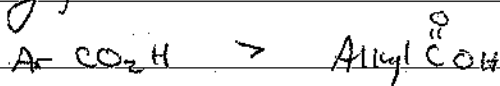
$pK_a \sim -7$  HCl

$pK_a \sim -9$   $H_2SO_4$

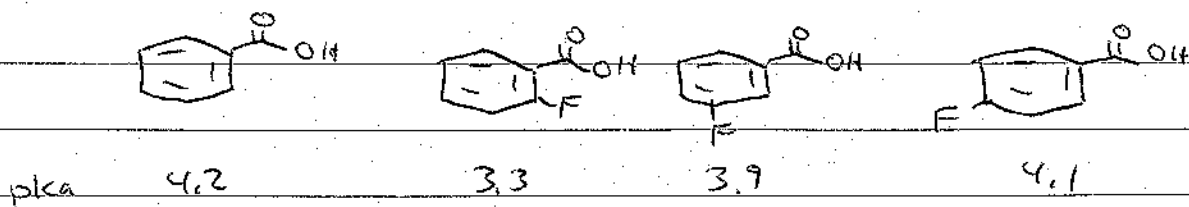
Talked about Alkyl acids  $\rightarrow$  inductive effects (1st semester)



Generally,

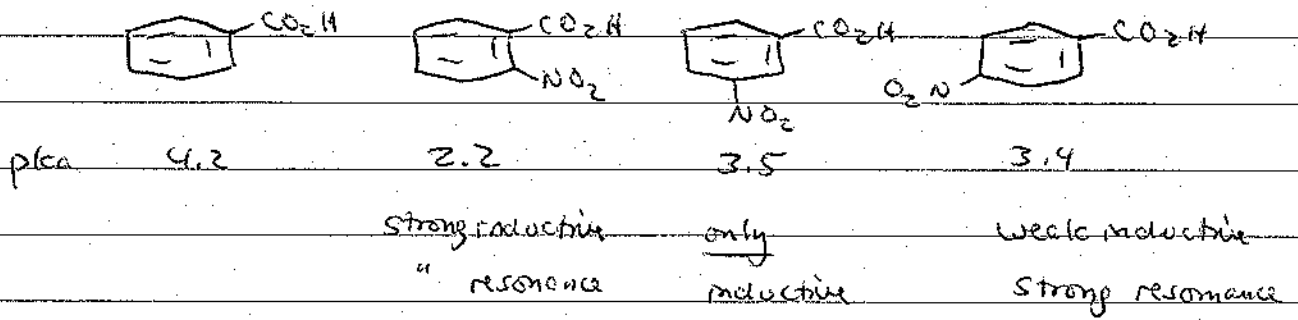


Add subst. on Ph ring  $\rightarrow$  change  $pK_a$ :

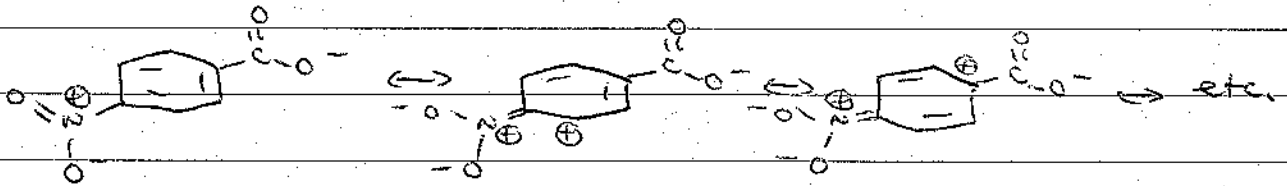


Shows decreasing effects of inductive effect w/  
increasing distance

Also,



Resonance

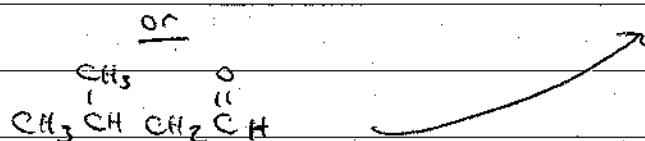
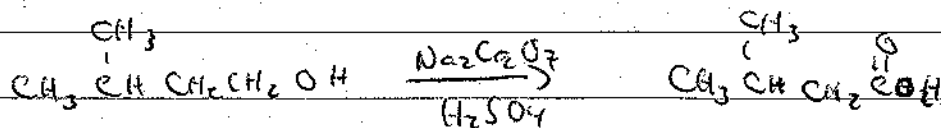


Resonance is more imp't than inductive effects



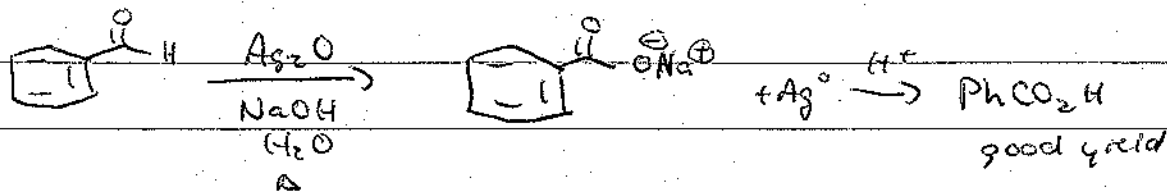
## Synthesis of Carboxylic Acids

a) Ox. Reans



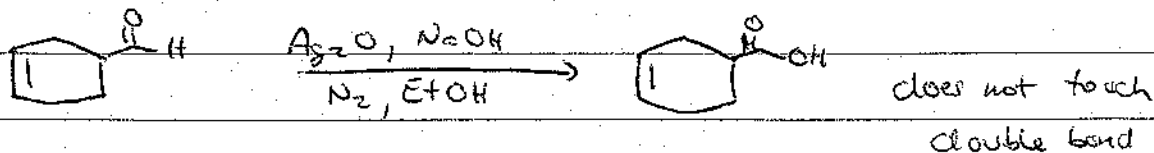
(F acid sensitive compds, can use  $\text{KMnO}_4, \text{OH}^-$ )

### Tollens Reagent



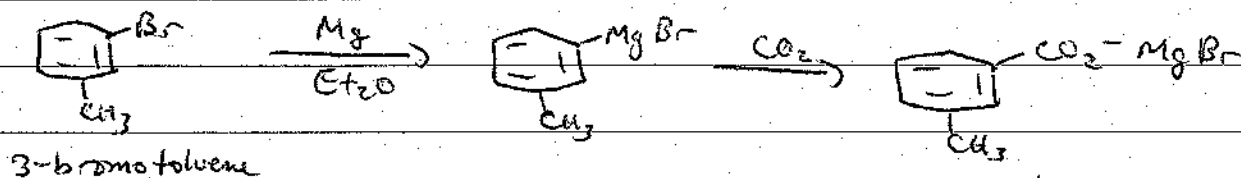
very mild conditions ... also  $\text{Ag}^+ \rightarrow \text{Ag}^0$   
leaves a silver  
deposit on glassware

can be useful:

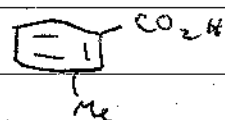


Use  $\text{N}_2$  because many reans are sensitive  
to  $\text{O}_2$  (in the form of Oxidation, etc)

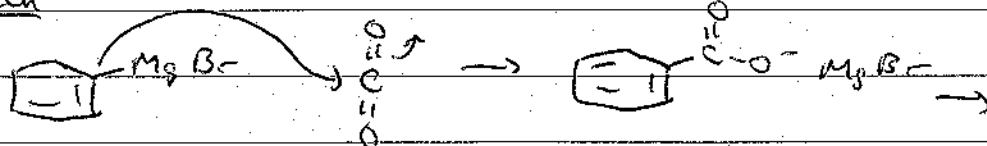
# Organic metallic Reagents $\rightarrow$ $\text{CO}_2$ $\rightarrow$ $\text{CO}_2$



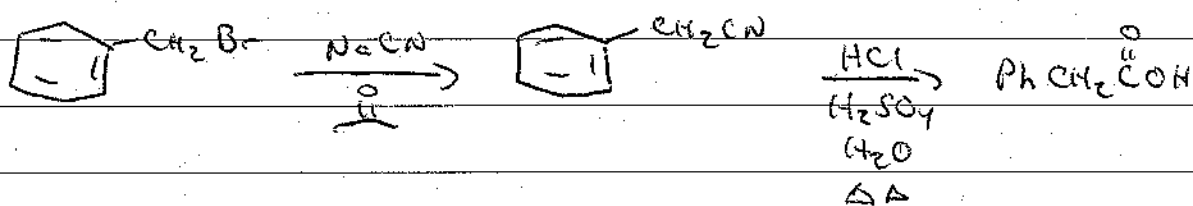
$\downarrow \text{H}^+$



Mech

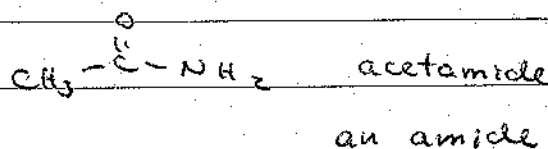
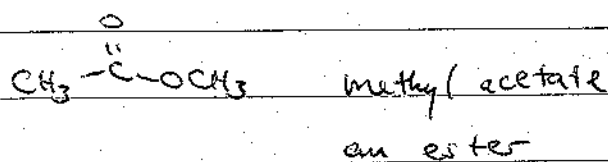
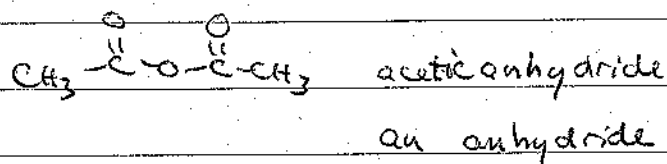
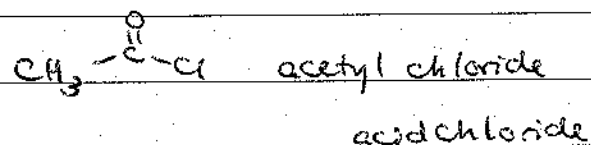
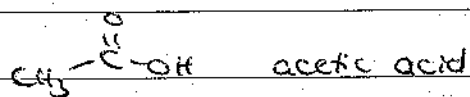


Using Nitriles:

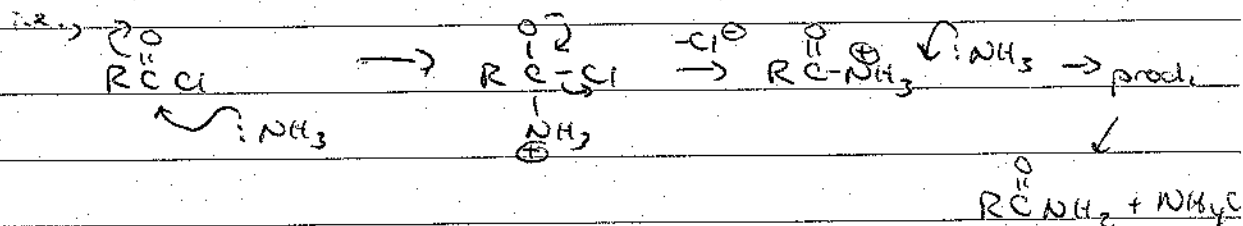


More in Ch. 22

## Reactions of CA & Derivatives



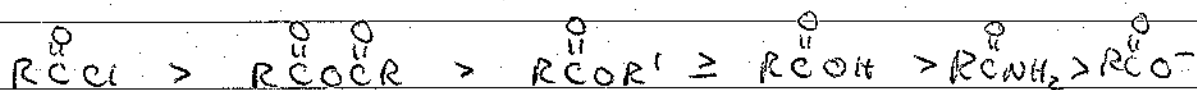
Undergo nucleophilic substitution rxns, NOT addn rxns



∴ 2 steps

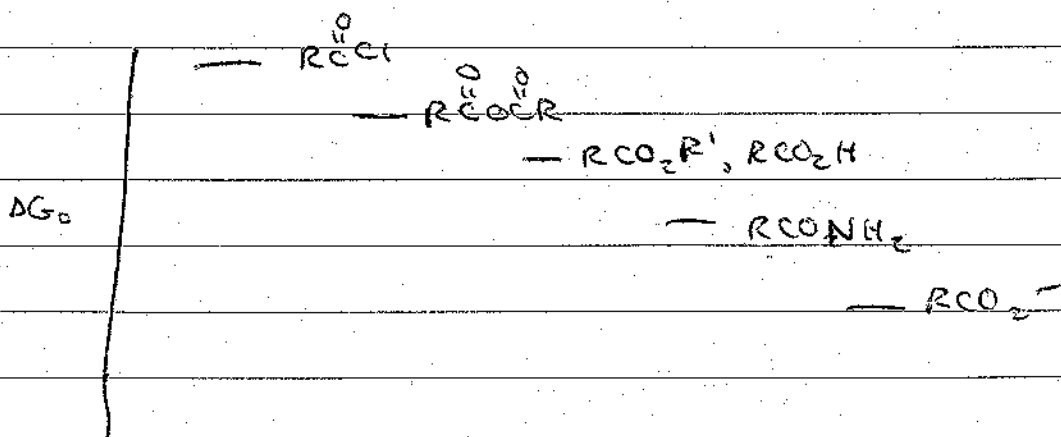
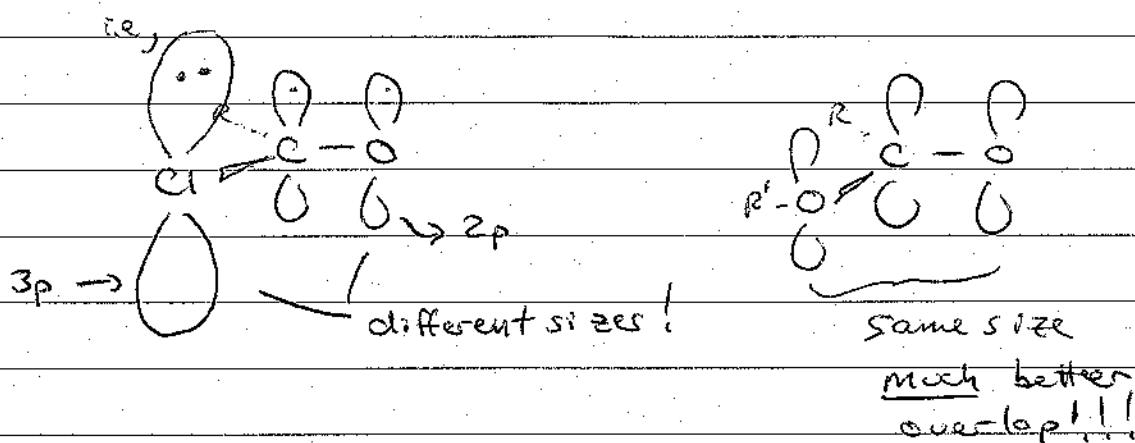
- 1) Nucleophilic attack → forms a tetrahedral intermediate
- 2) loss of LG to re-form C=O group

Reactivity order:



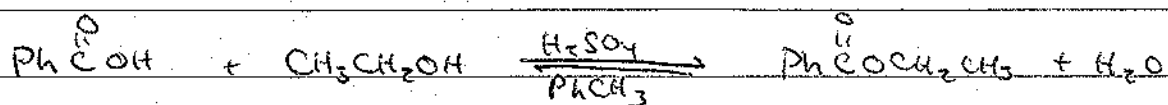
Reactivity ↓ as Resonance ↑

∴ One of reasons  $R\overset{\overset{O}{\parallel}}{C}Cl$  is very reactive is poor orbital overlap of  $-Cl$  w/  $C=O$



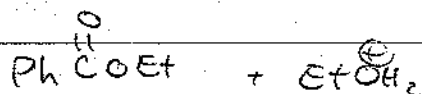
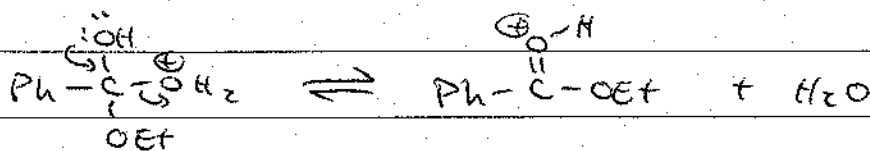
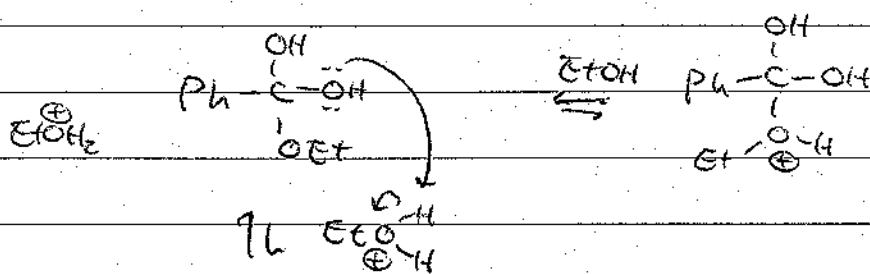
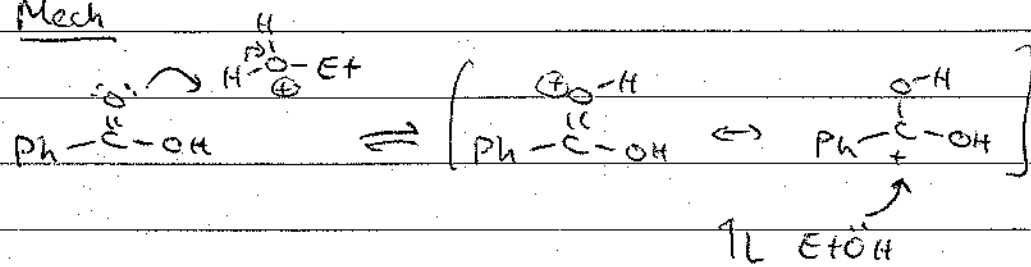
In terms of energy, acid chloride is highest energy species (∴ least stable), so you can cascade downhill (ie, convert to cups of lower energy  $\Rightarrow R\overset{\overset{O}{\parallel}}{C}Cl \rightarrow R\overset{\overset{O}{\parallel}}{C}ONH_2$ ) but its VERY difficult to go uphill a energy! (ie,  $R\overset{\overset{O}{\parallel}}{C}ONH_2 \leftarrow R\overset{\overset{O}{\parallel}}{C}Cl$ )

## Esterification of CA's



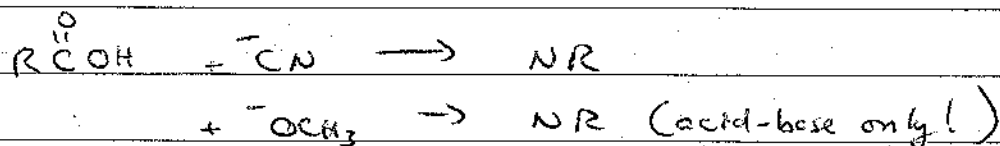
can ↑ yield of product by removing H<sub>2</sub>O (Le Chatliers Principle)

Mech



KNOW & UNDERSTANDS THIS MECHANISM!

## Synthesis + Rxns of Acid Chlorides

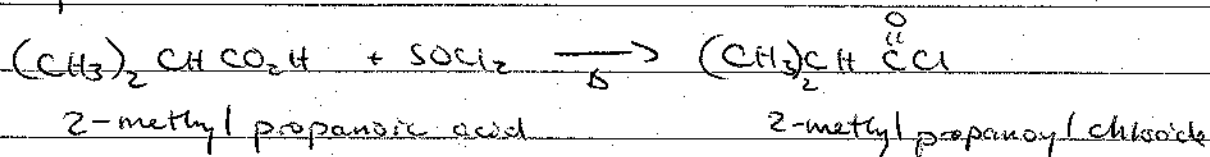


Need to activate  $-\text{CO}_2\text{H}$  somehow  $\Rightarrow$  convert to  $\text{COCl}$

Use  $\text{SOCl}_2$  or  $\text{PCl}_3$

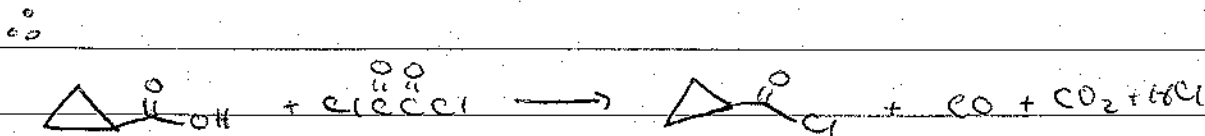
$\hookrightarrow$  thionyl chloride  $\hookrightarrow$  phosphorous trichloride

Thus,



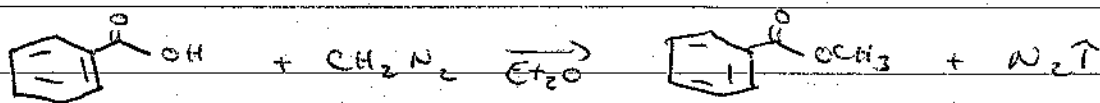
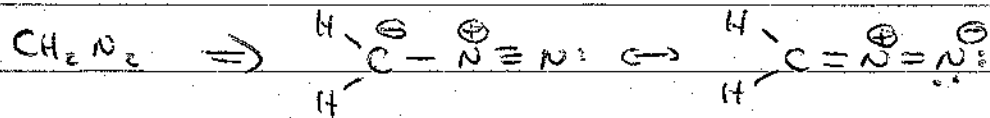
$\text{SOCl}_2 \rightarrow$  kinda nice  $\rightarrow$  byproducts  
are  $\text{SO}_2, \text{HCl(g)}$   
so remove by  
boiling away!

$\text{PCl}_3$  reacts similarly  
as does  $\text{Cl}\overset{\overset{\text{O}}{\parallel}}{\text{C}}\overset{\overset{\text{O}}{\parallel}}{\text{C}}\text{Cl}$  (oxalyl chloride)

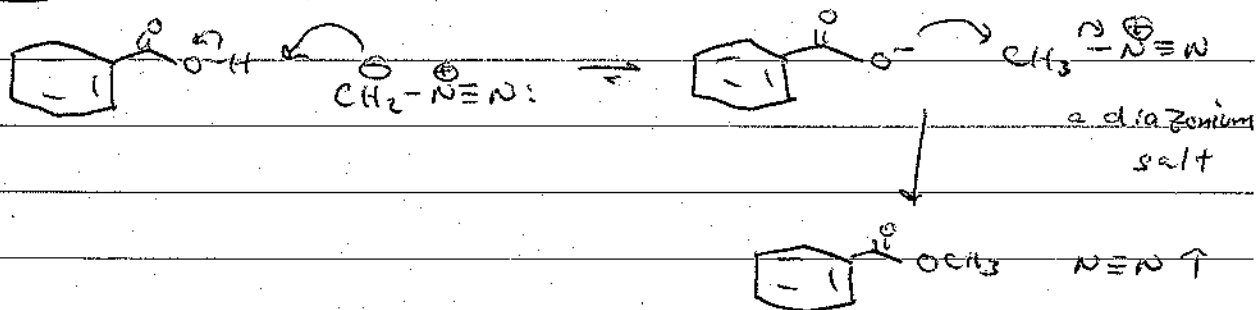




## Esterification of CA's w/ diazomethane

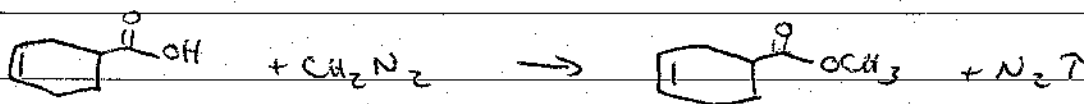


Mech



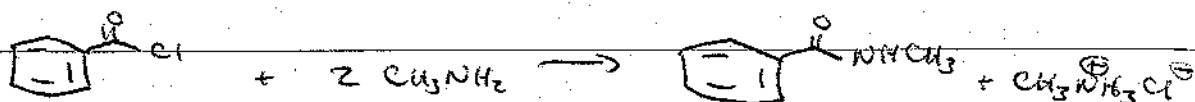
Very easy, very "clean"

↳ only byproduct is  $\text{N}_2 \uparrow$ !  
Nice...

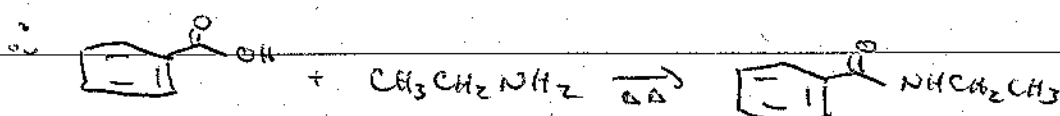


## Direct Synthesis of Amides from amines & CA's

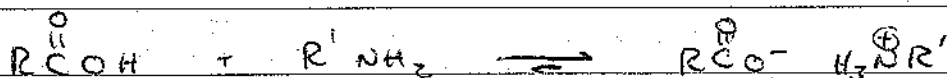
Recall,



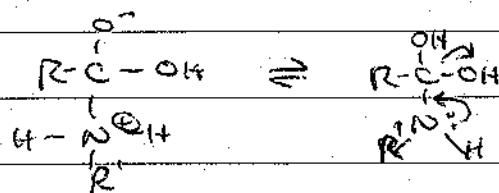
Not always convenient to make  $\text{RCOCl}$



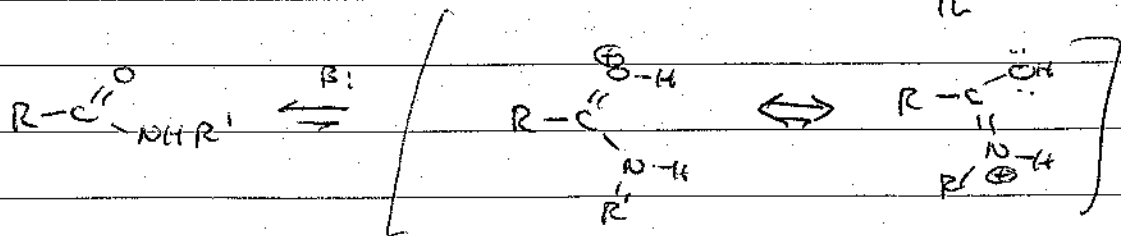
Mech



$\updownarrow$

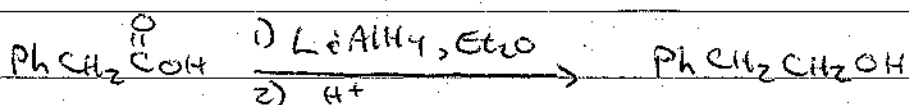
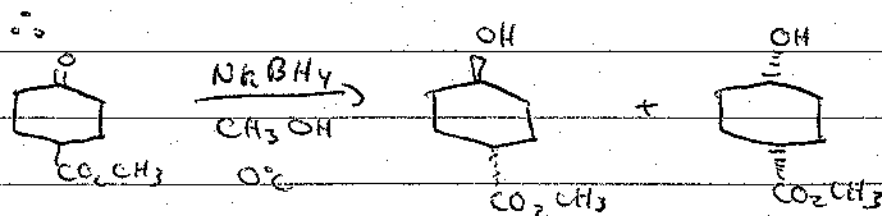


$\updownarrow$



## Reduction of CA w/ LAH

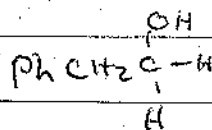
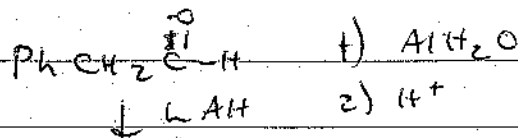
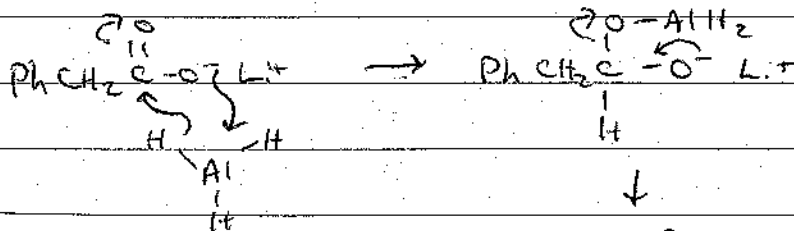
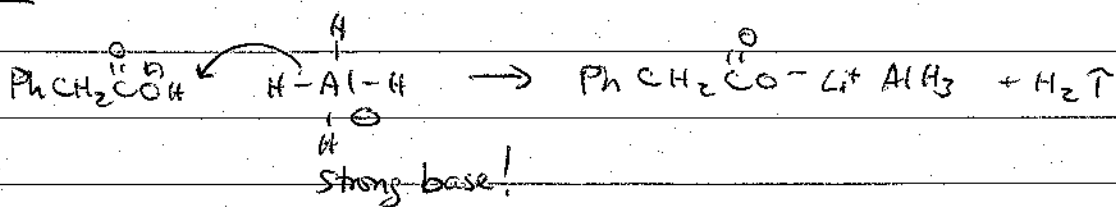
NaBH<sub>4</sub> does not react well w/ CA's or their derivatives  
(Recall it's not as reactive as LAH)



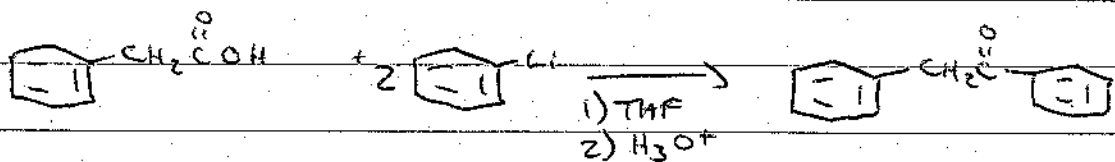
phenylacetic acid

2-phenyl-1-ethanol

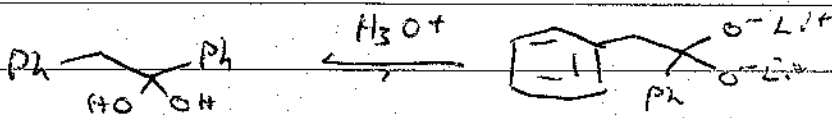
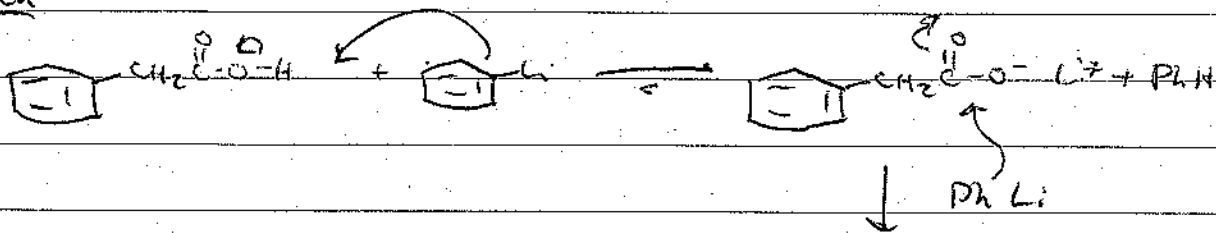
## Mech



# Rxns of CA's w/ organolithium Reagents



Mech



↑ L

