كلية العلوم التطبيقية
Faculty of Applied Sciences

قسم الكيمياء
Department of Chemistry

# Aromatic Acids & their derivatives

Chapter 7

**COURSE NAME:** Chemistry of Aromatic Compounds
**COURSE CODE:** 4022142-3

# ***By the end of this chapter, you should understand:***

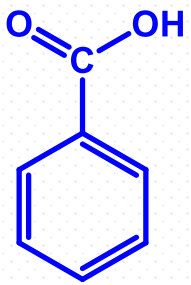
1. How carboxylic and sulfonic acid group are introduced into aromatic molecules.
2. The nature of the acidity of these groups.
3. The effect of the acidic groups on ring reactivity.
4. The reactions of the acidic groups.

# Aromatic acids

## Aromatic carboxylic acids

In these compounds, the carboxylic acid group is attached directly to aromatic ring.

Example:

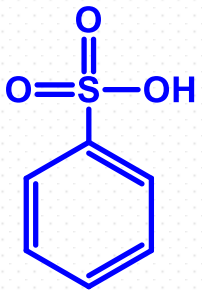



Benzoic acid

## Aromatic sulfonic acids

In these compounds, the sulfonic acid group is attached directly to aromatic ring.

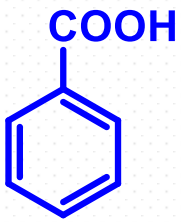
Example:



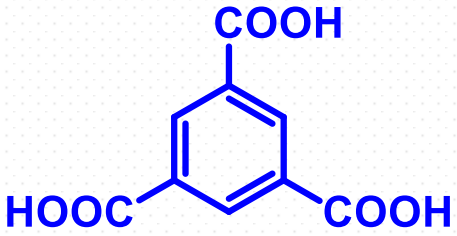

Benzene sulfonic acid

# Aromatic Carboxylic acids

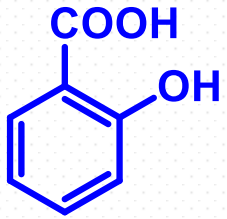
## Nomenclature




Benzoic acid

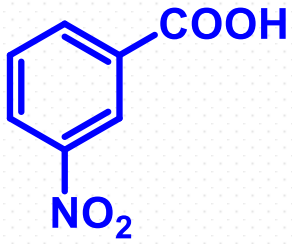



1,3,5-Benzene tricarboxylic acid

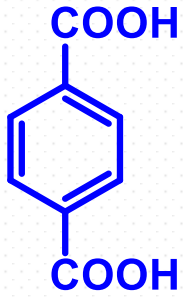



*o*-Hydroxy benzoic acid

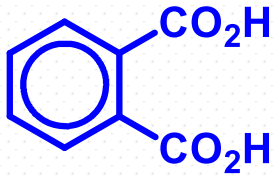
(Salicyclic acid)




*m*-nitrobenzoic acid



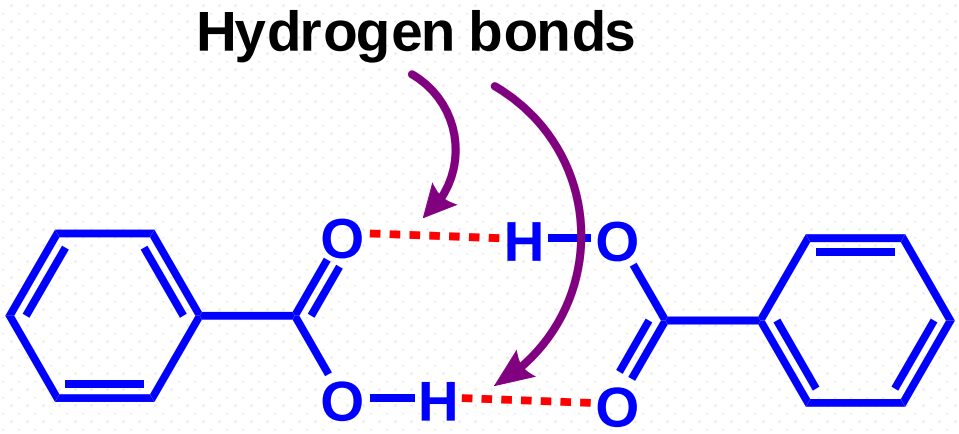

Terphthalic acid




Phthalic acid

# Physical properties

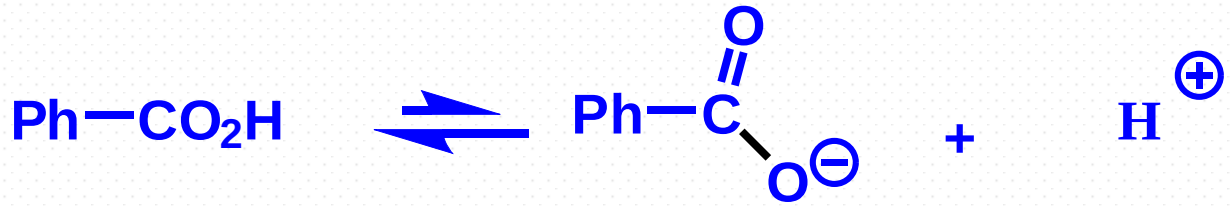
**Q .Why carboxylic acids have high boiling and melting points?**

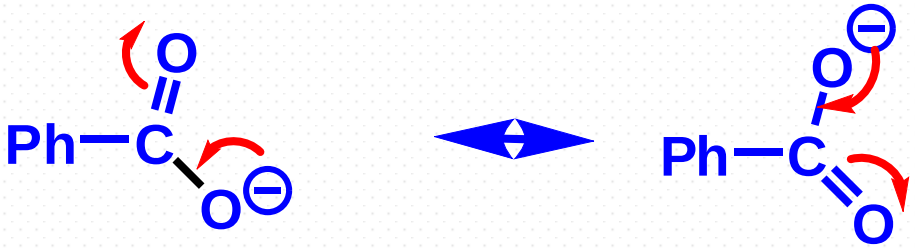



- *Higher boiling and meting points compare to alcohols, ketones and aldehydes due to dimer formation.*

# Acidity

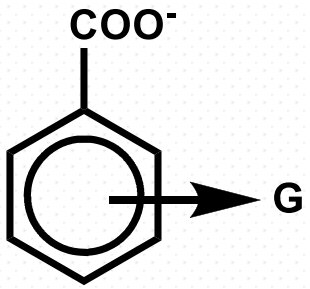
**The acidity of aromatic carboxylic acid is more than phenols because of carbocsalate ion is more sable than phenoxide ion (resonance stabilized)**



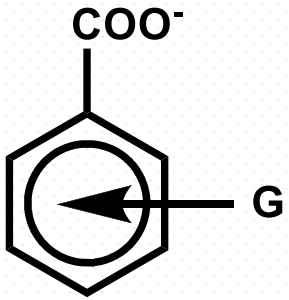




# Effect of substituent groups on acid strength of benzoic acids?

- **Electron withdrawing groups will stabilize the anion, decrease the $\Delta H$, shift the ionization to the right, increasing the $K_a$, increasing acid strength.**




- **Electron donating groups will destabilize the anion, increase the $\Delta H$, shift the ionization in water to the left, decreasing the $K_a$, decreasing acid strength.**



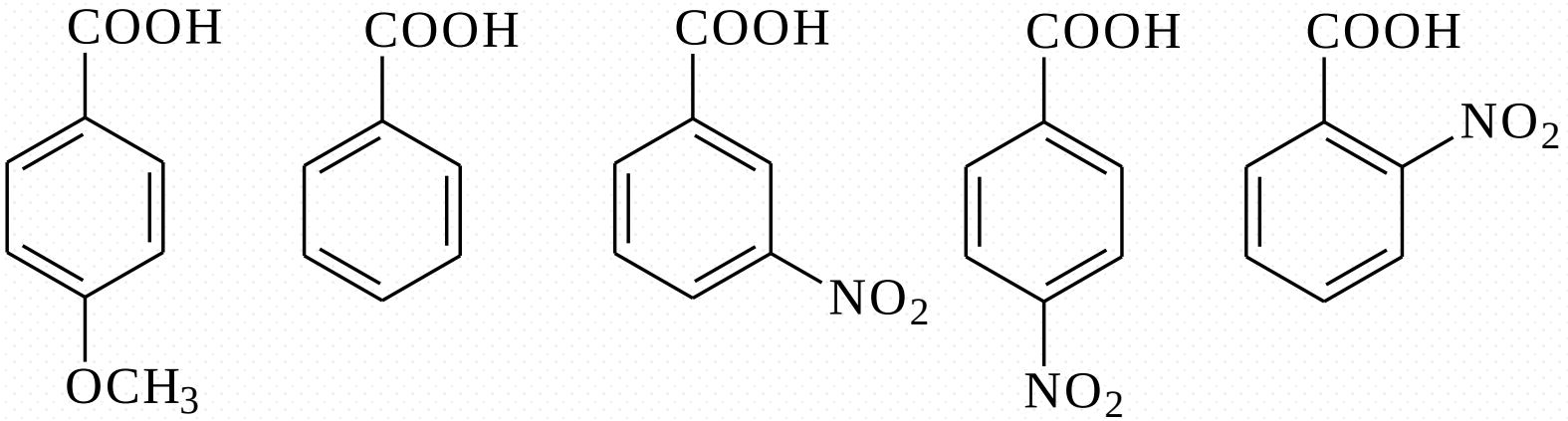
**$-NH_2$, $-NHR$, $-NR_2$**
**-OH**
**-OR**
**$-NHCOCH_3$**
**$-C_6H_5$**
**-R**

**electron donating groups**

-H
**-X**
**-CHO, -COR**
**$-SO_3H$**
**-COOH, -COOR**
**-CN**
**$-NR_3^+$**
**$-NO_2$**

**electron withdrawing groups**

# Substituent Effects on Acidity

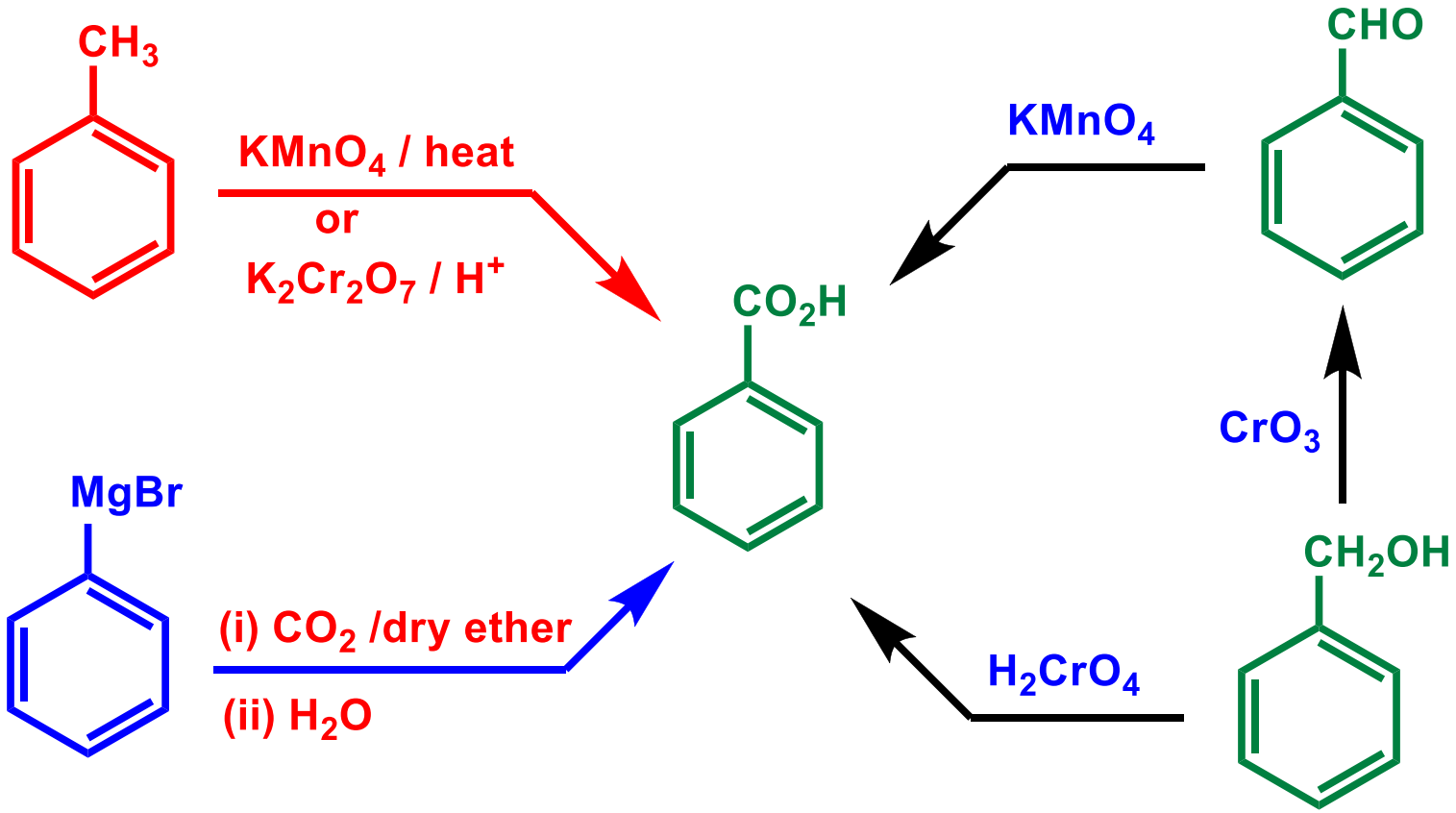

*p*-methoxy benzoic acid *m*-nitro *p*-nitro *o*-nitro

**p$K_a$ = 4.46** **p$K_a$ = 4.19** **p$K_a$ = 3.47** **p$K_a$ = 3.41** **p$K_a$ = 2.16**

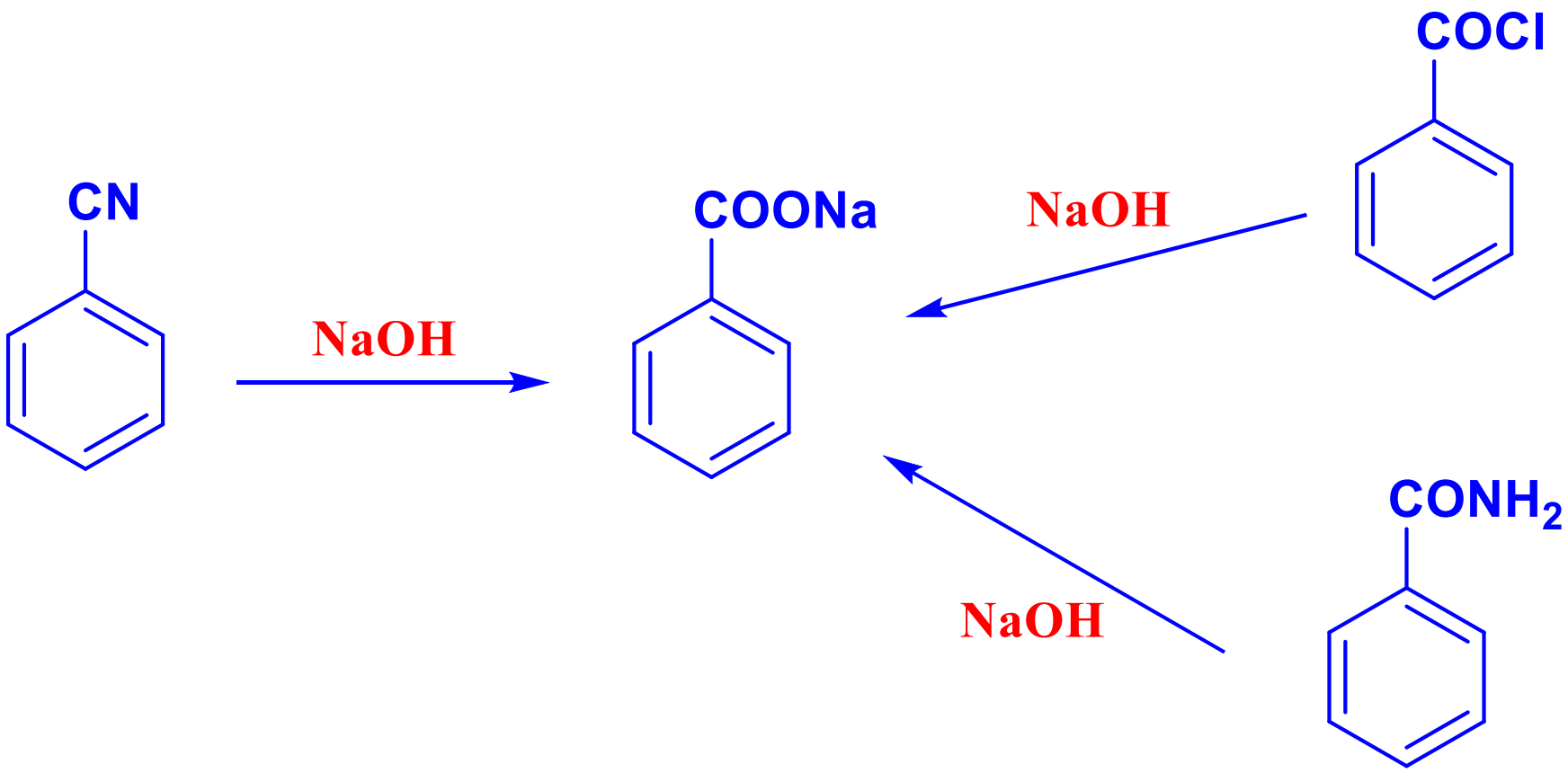
**Worked problem**: explain why *o*-hydroxybenzoic acid is more acidic than *p*-hydroxybenzoic acid

# Synthesis of carboxylic acids

## Oxidation methods



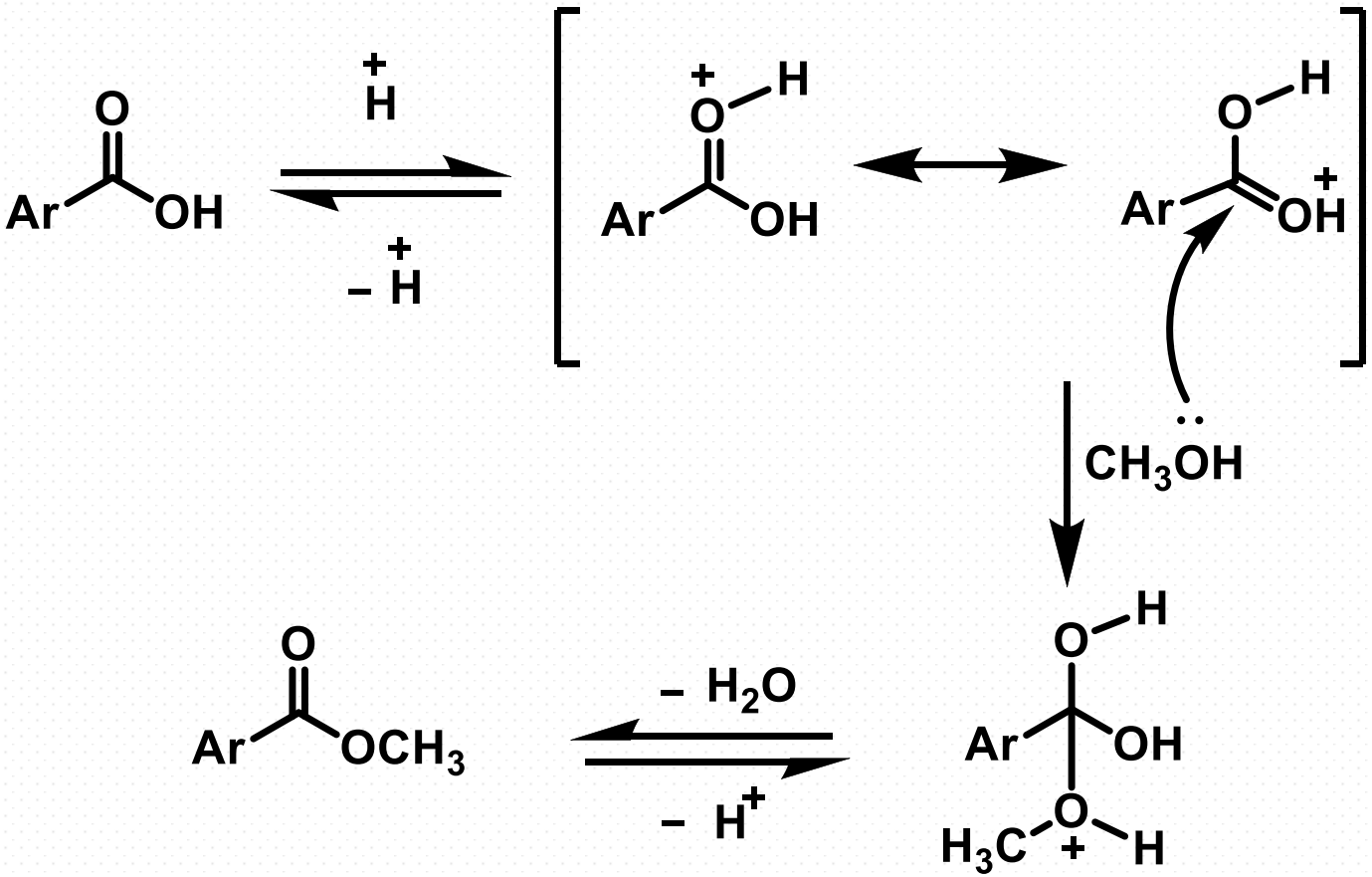
# Hydrolytic Methods



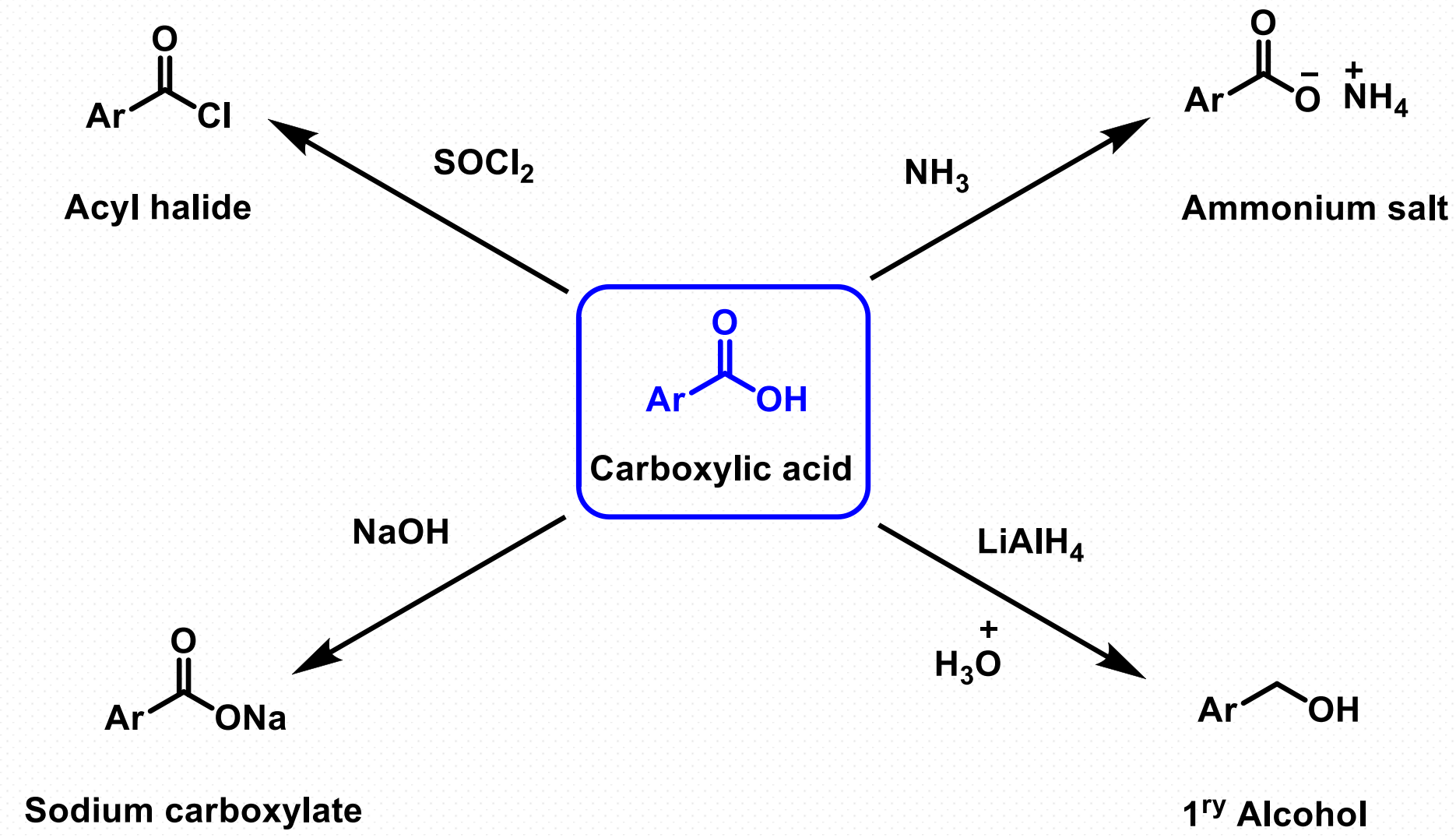
- *Q: Write equations to show how each of the following compounds could be converted into benzoic acid:*
- *a) Toluene*
- *b) Bromobenzene*
- *c) Benzonitrile*
- *d) Benzyl alcohol*
- *e) Acetophenone*

# Reactions of carboxylic acids

## Esterification *(Fisher esterification reaction)*



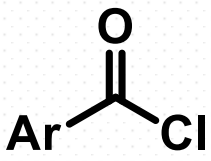
# Other reactions



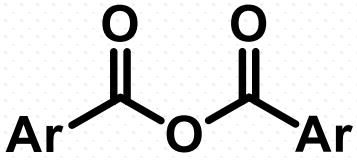
# The carboxylic acid derivatives

## The structure of carboxylic acid derivatives

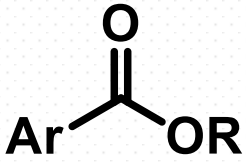
- **Acyl halides, acid anhydrides, esters and amides are called carboxylic acid derivatives.**



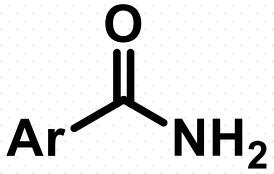

**Acid halide**




**Acid anhydride**

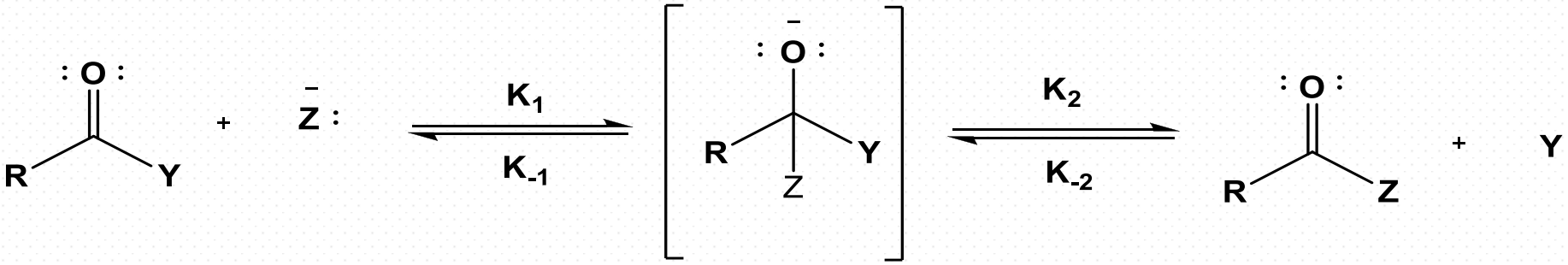



**Ester**

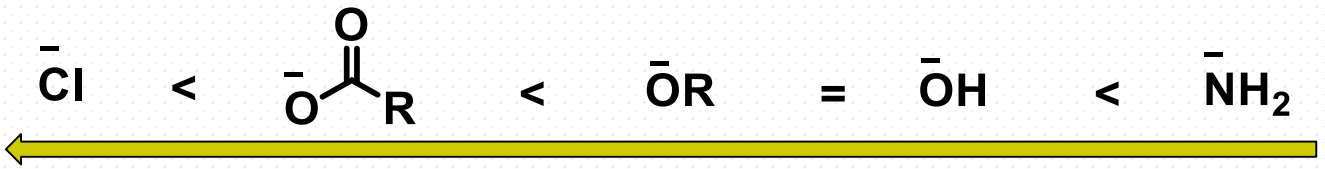



**Amide**

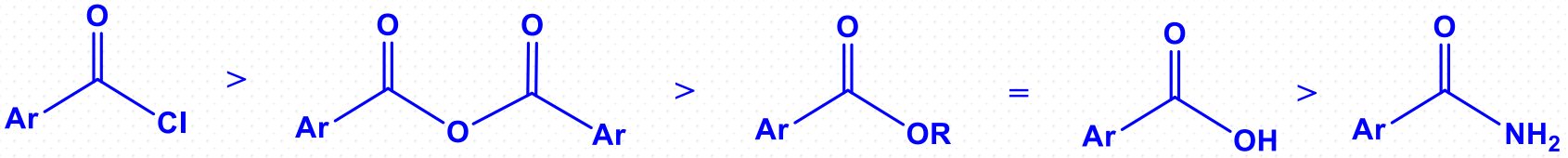
# Reactivity consideration




As the basic character of leaving group (Y) decrease, the reactivity of acid derivatives will increase.

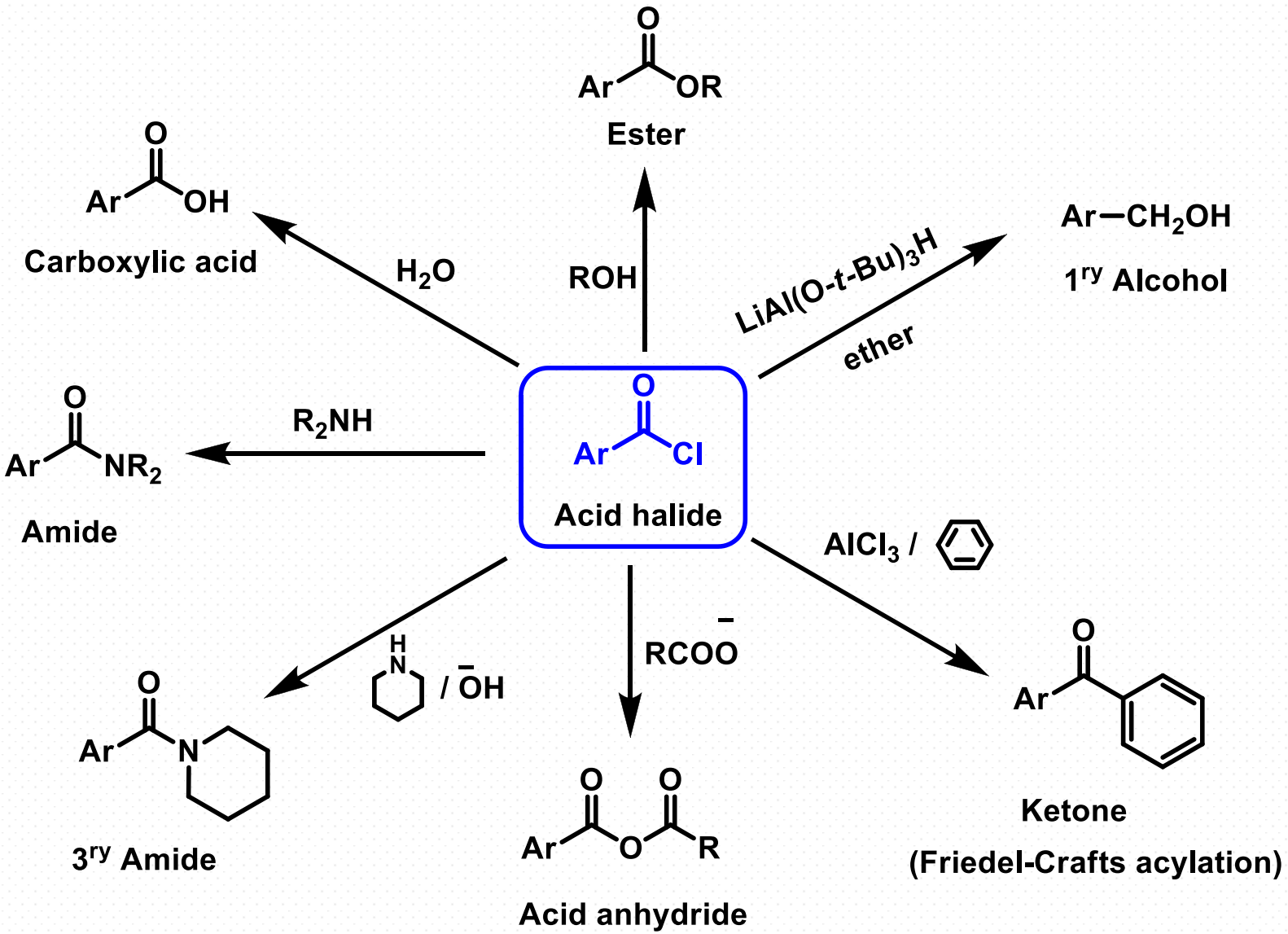



Decrease the basic character of the leaving group




**Increase the reactivity of acid derivatives**

# Reactions of acyl halides

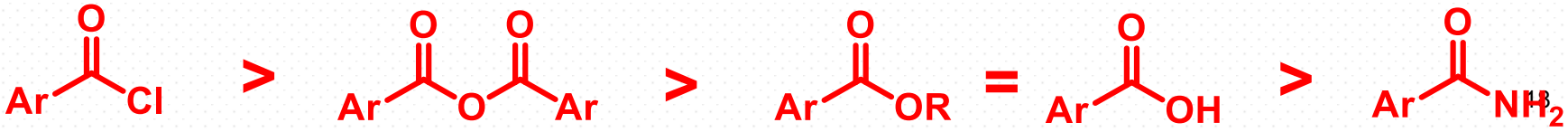


# Acid anhydrides

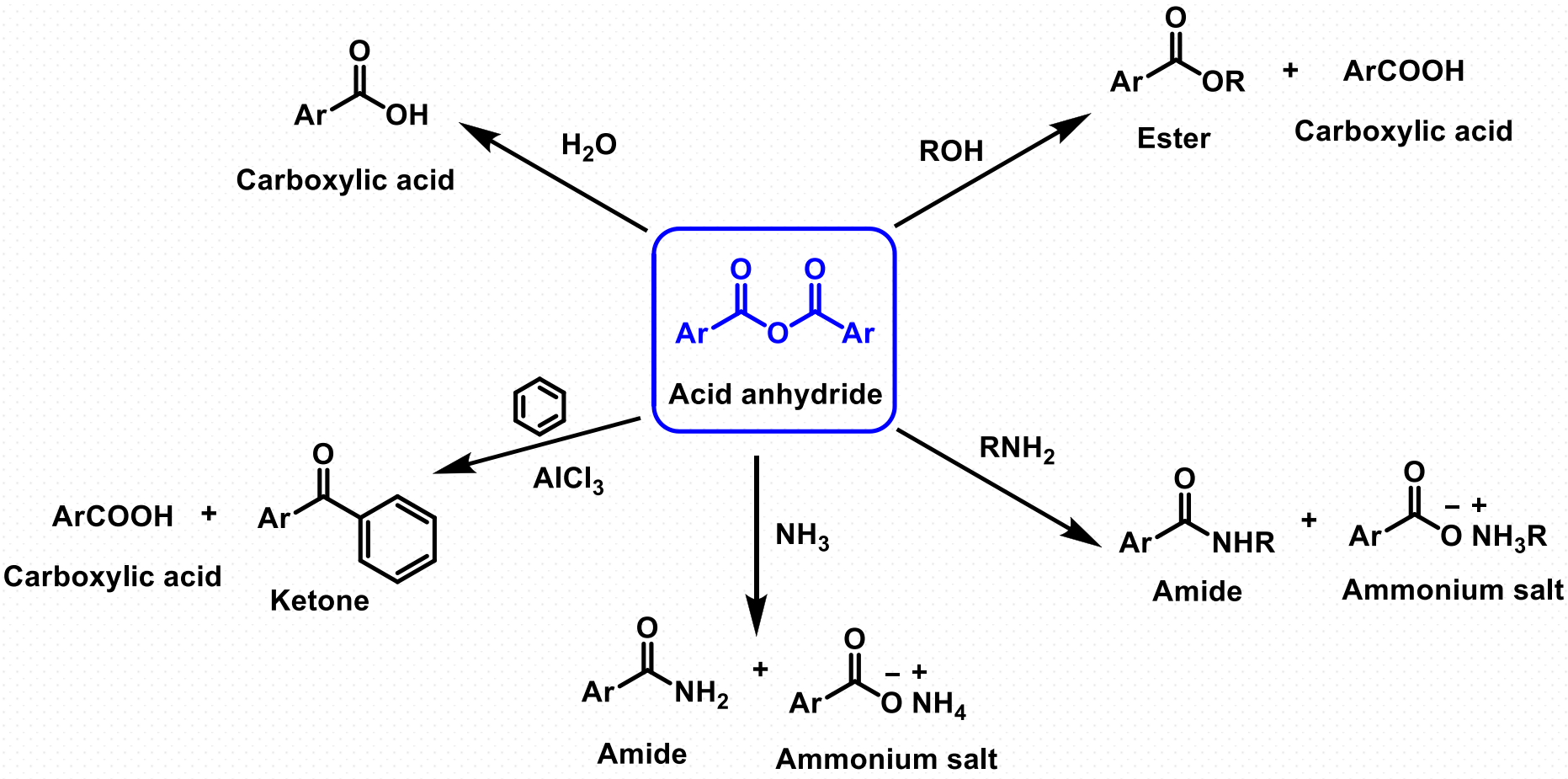
The acid anhydride derivatives can also undergo nucleophilic substitution reactions. But it less reactive than acyl halides. So they can not react with NaCl, this is because the incoming halide ion is a weaker base than the deporting ion.


## *Relative Basisities of the leaving group*

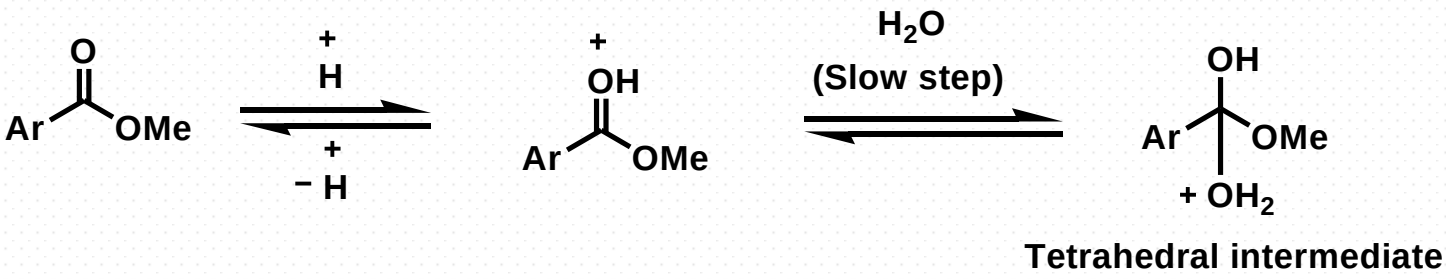

## *Relative reactivities of the Acid derivatives*

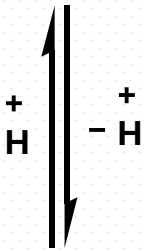


# Reactions of Acid anhydrides

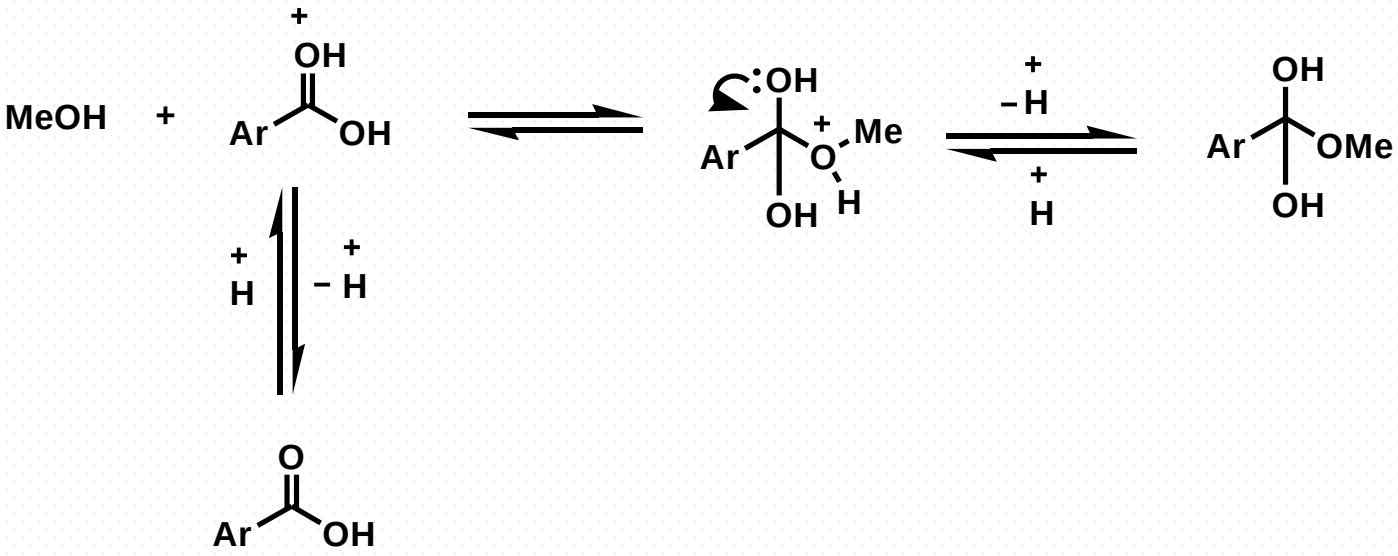


# Reactions of esters

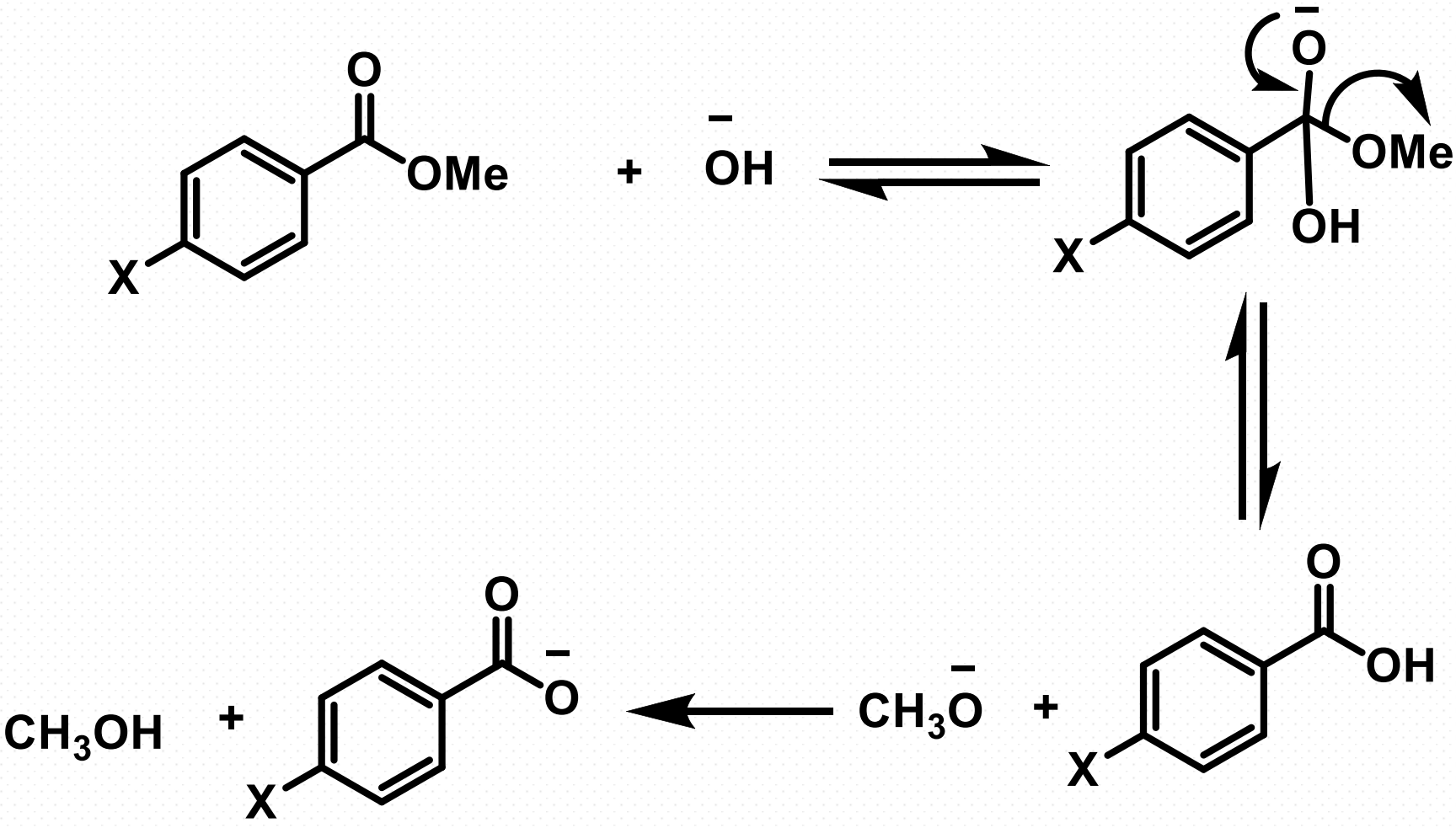


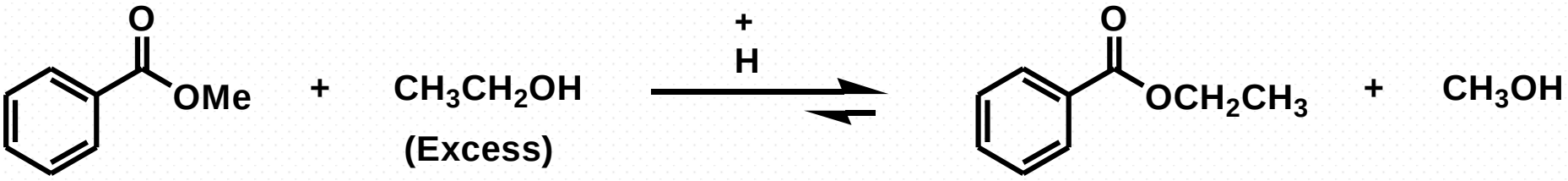

## *Acid catalyzed hydrolysis:*



# Base-catalyzed hydrolysis of esters



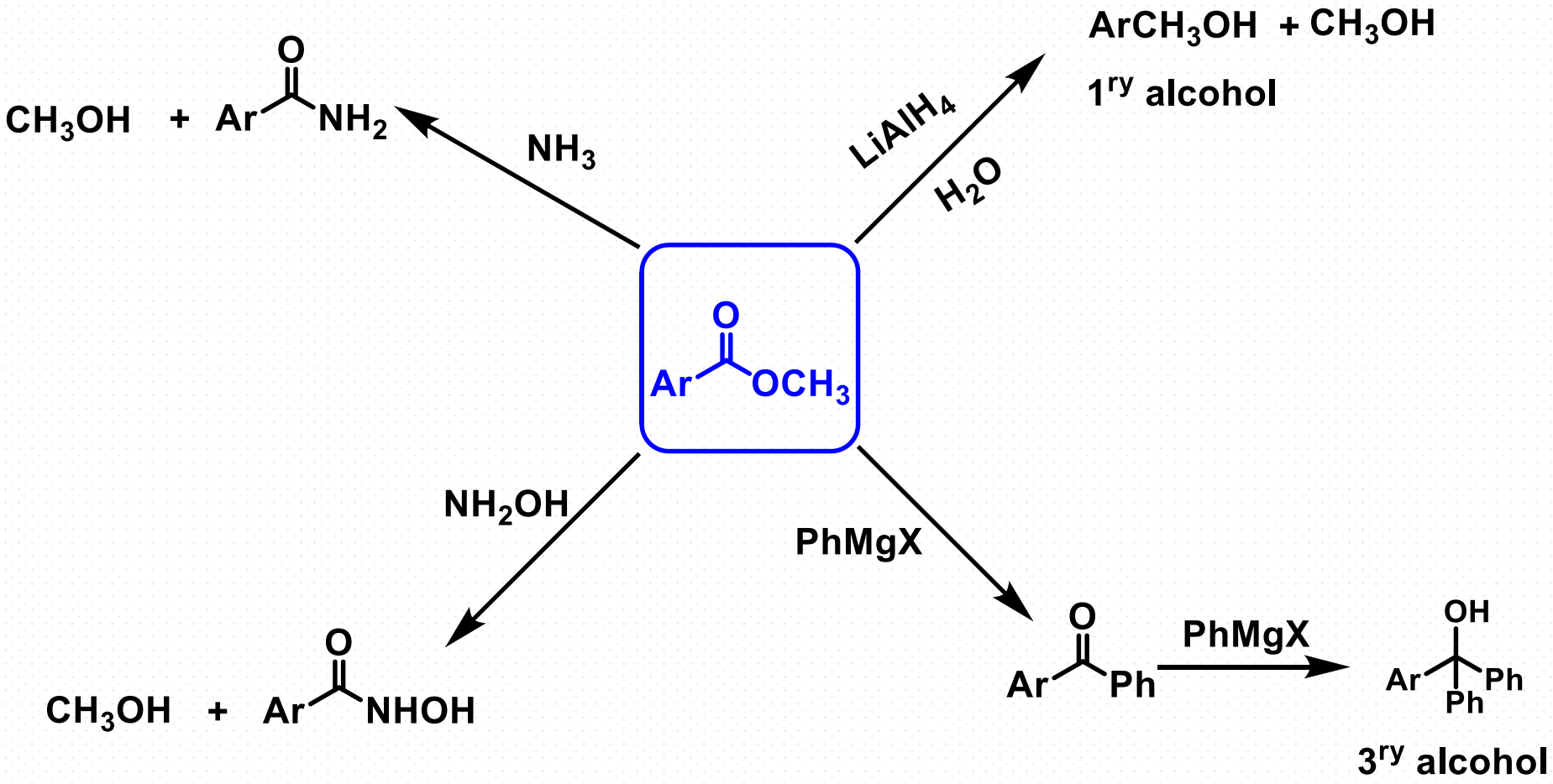
# Transesterfication




**Methyl benzoate** **Ethyl benzoate**

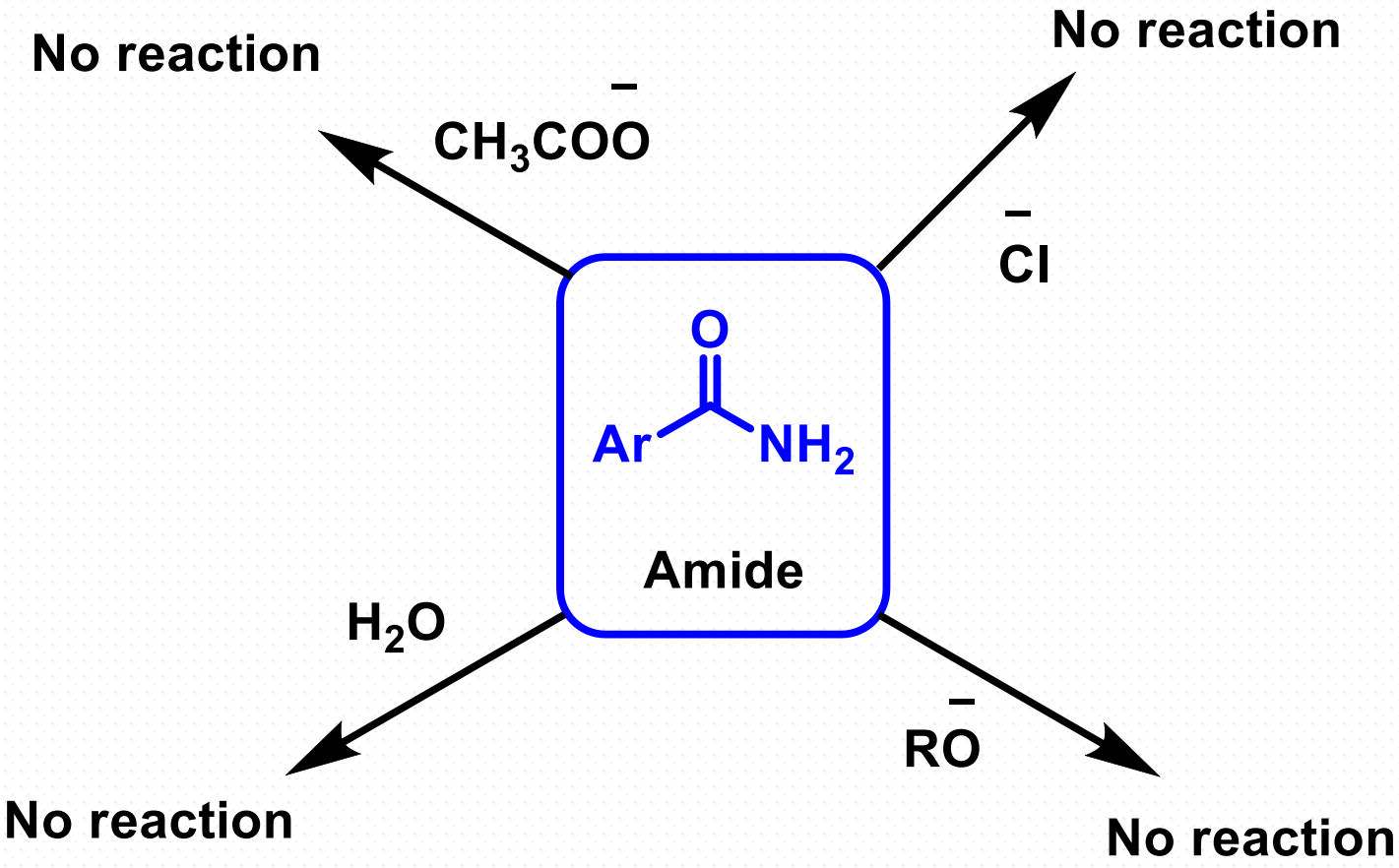
*Worked problem*: *Write the mechanism for the transesterification*

# other reactions of esters

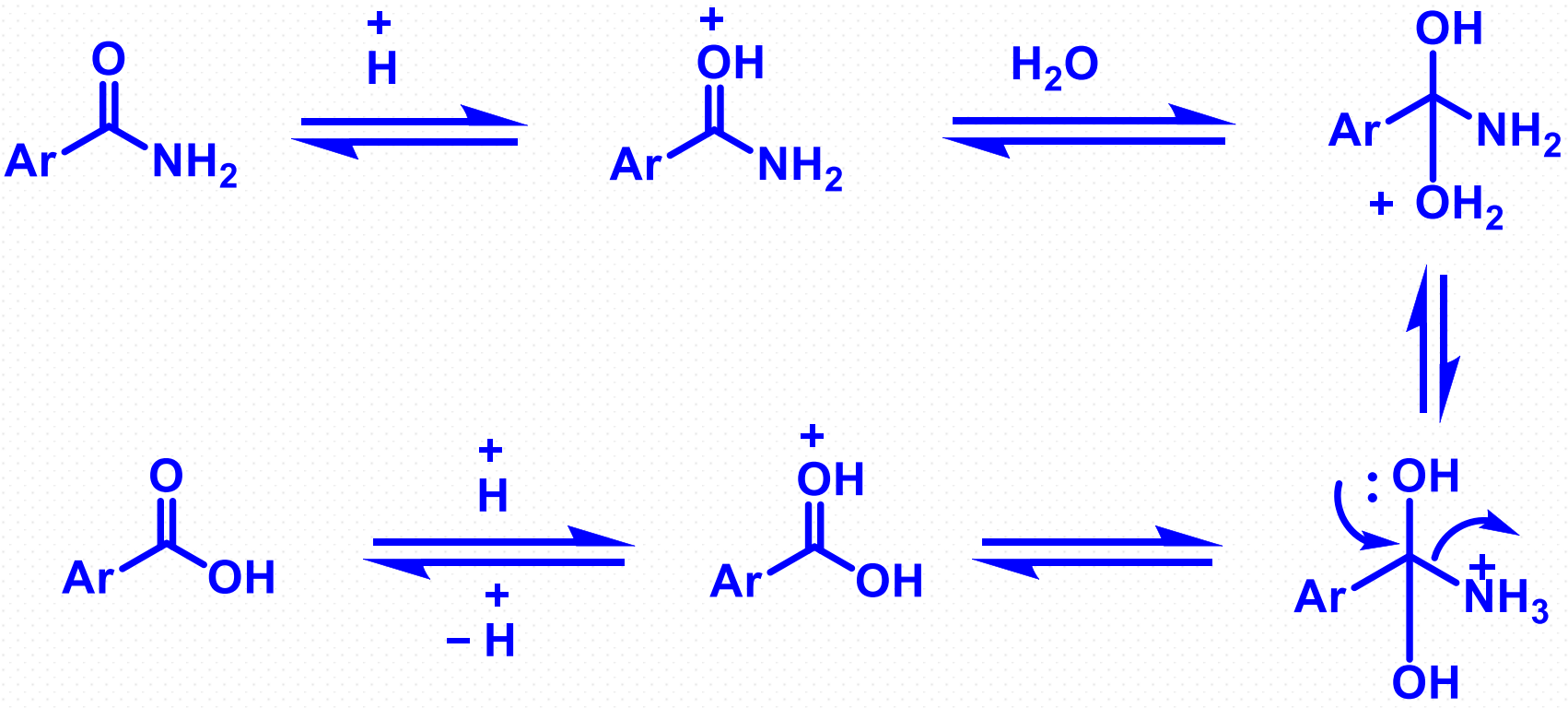


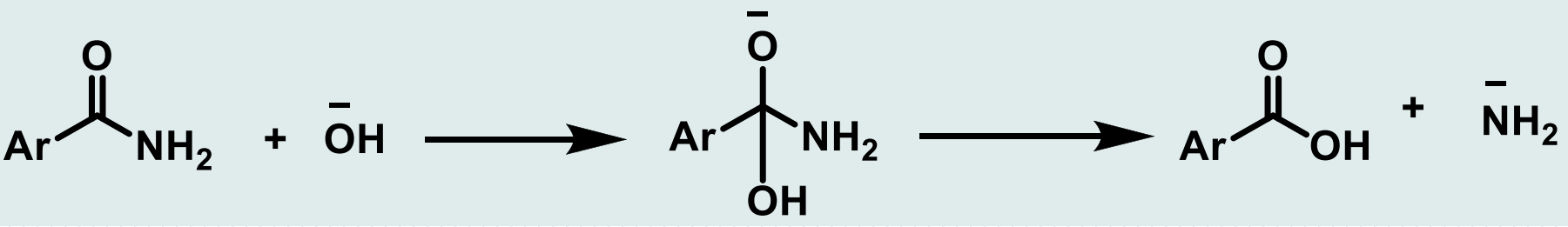
# Reactions of amides

*Amides don't react with halide ions, alcohols or water because, in each case the incoming nucleophile is weaker base than the leaving group ($NH_2$) of the amide.*

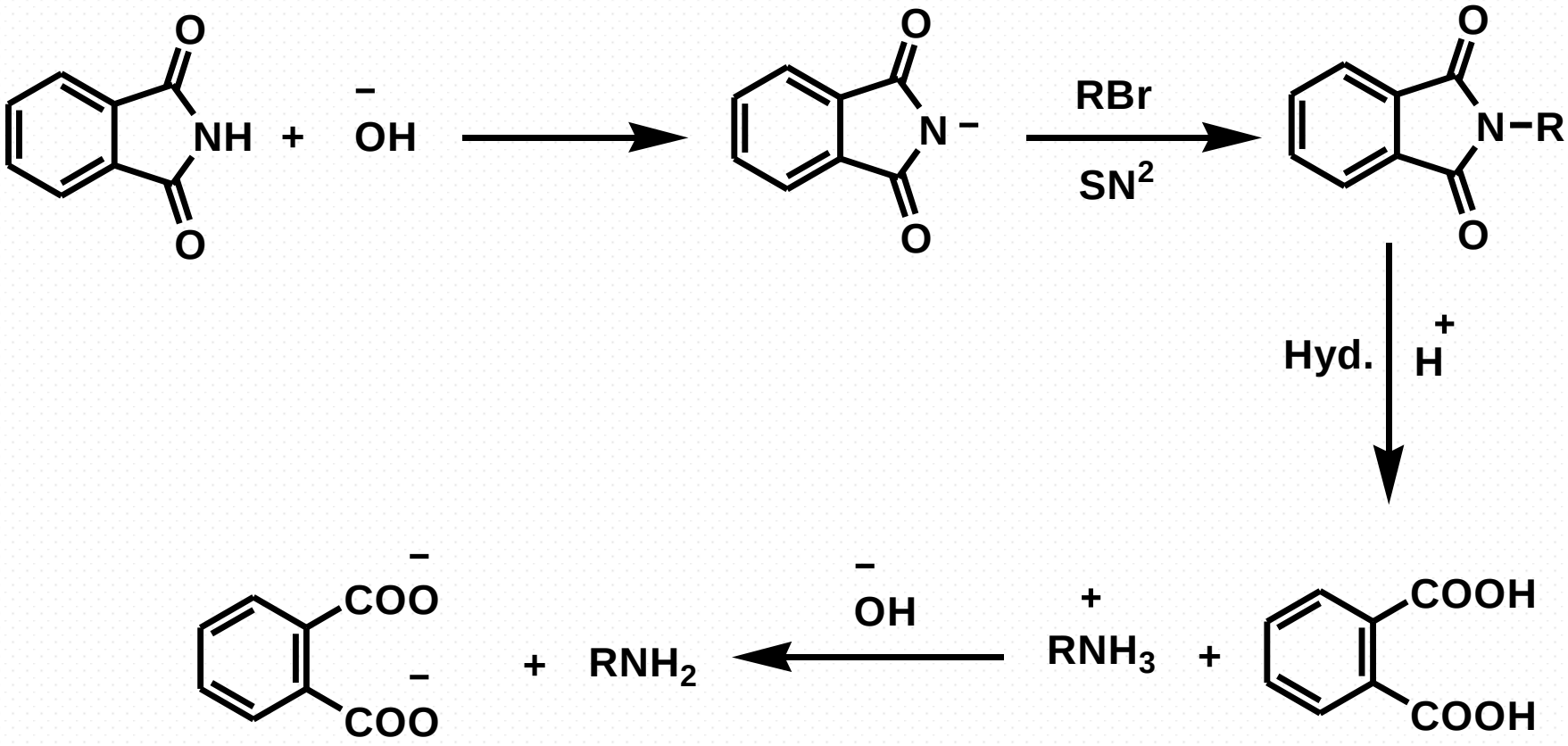


# Hydrolysis of amides



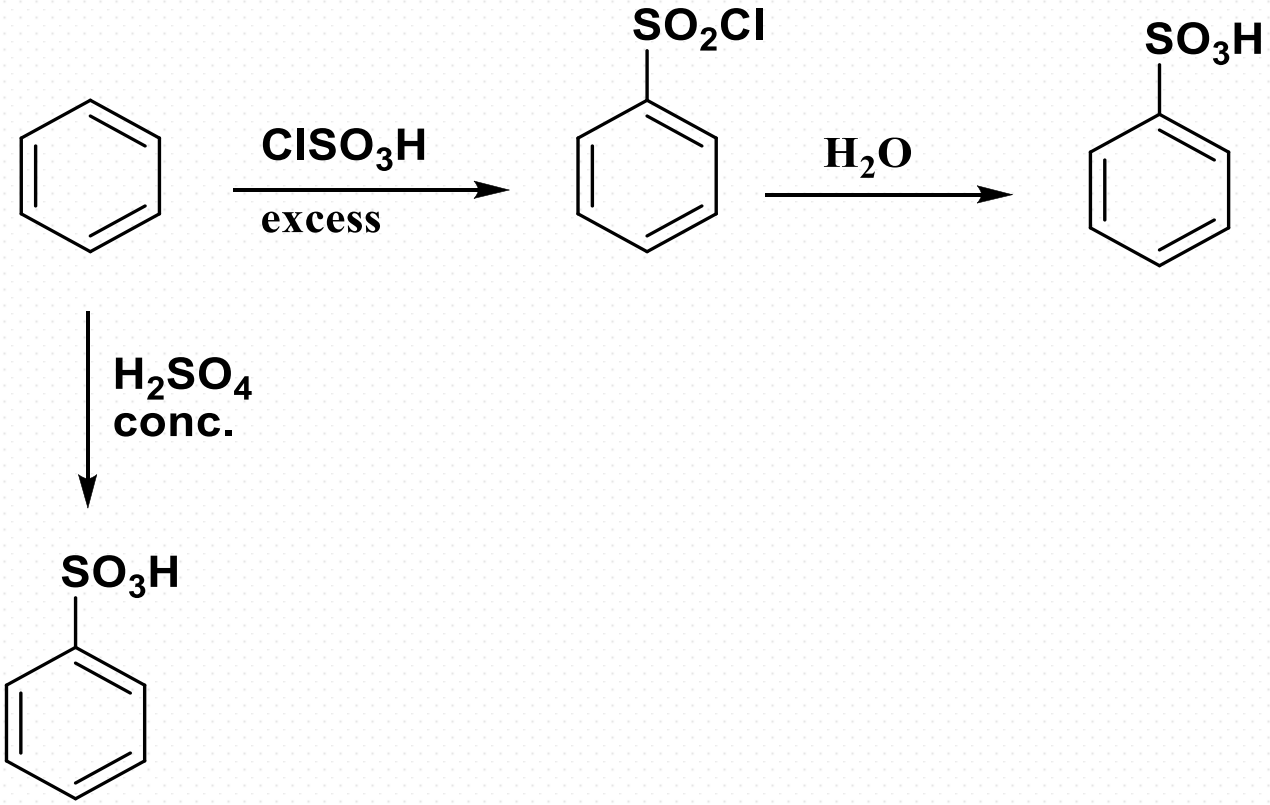



# Gabriel synthesis of primary amines



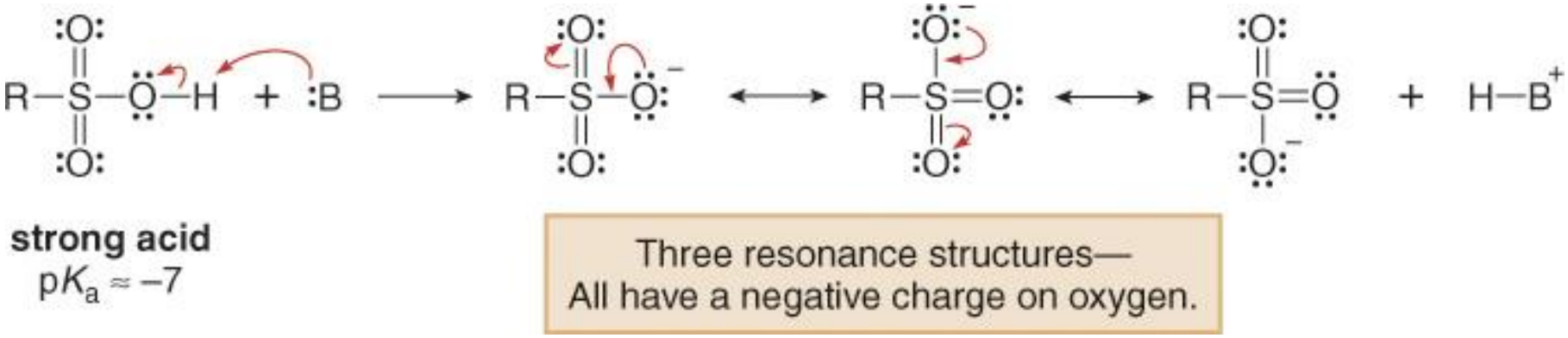
# Aromatic sulfonic acids

## Preparations



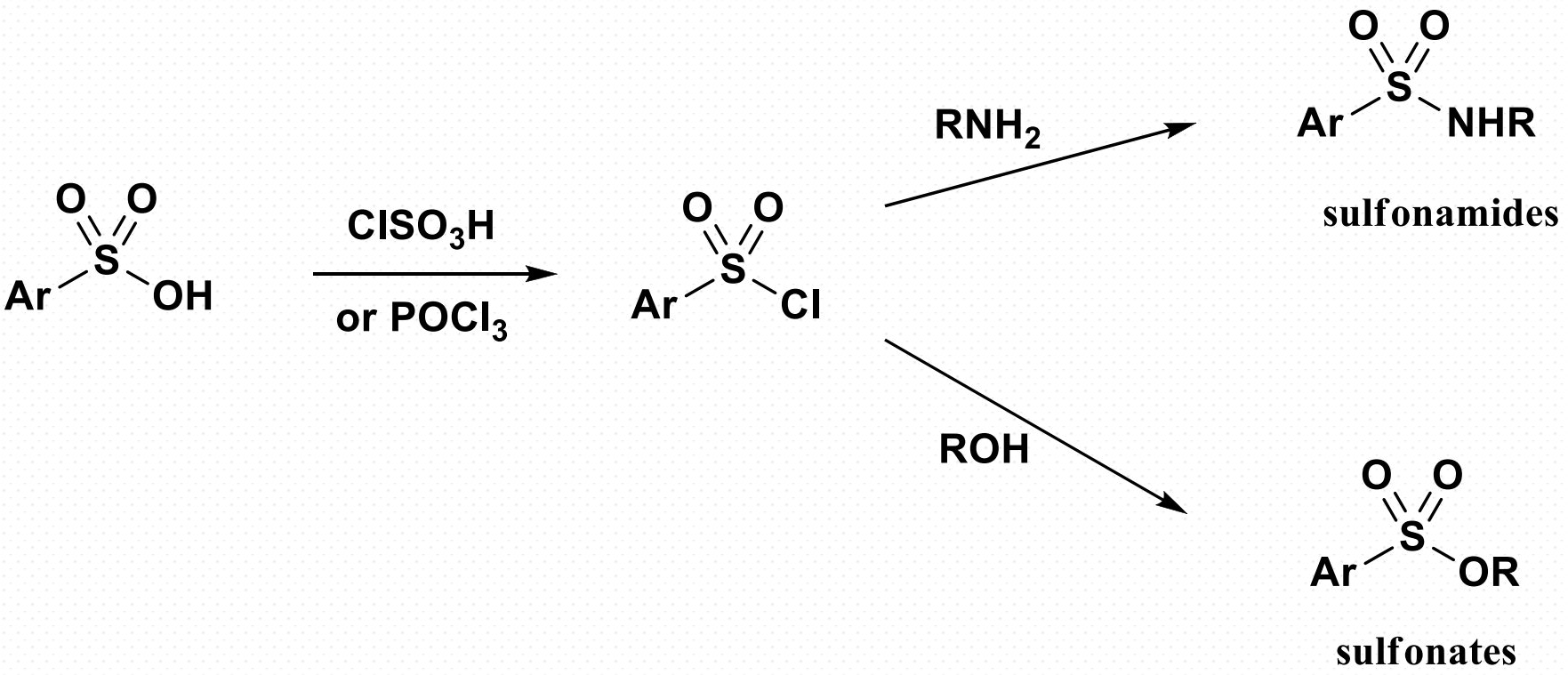
# Acidity of Sulfonic acids

- **Sulfonic acids are strong acids because their conjugate bases (sulfonate anions) are resonance stabilized, and all the resonance structures delocalize negative charge on oxygen.**

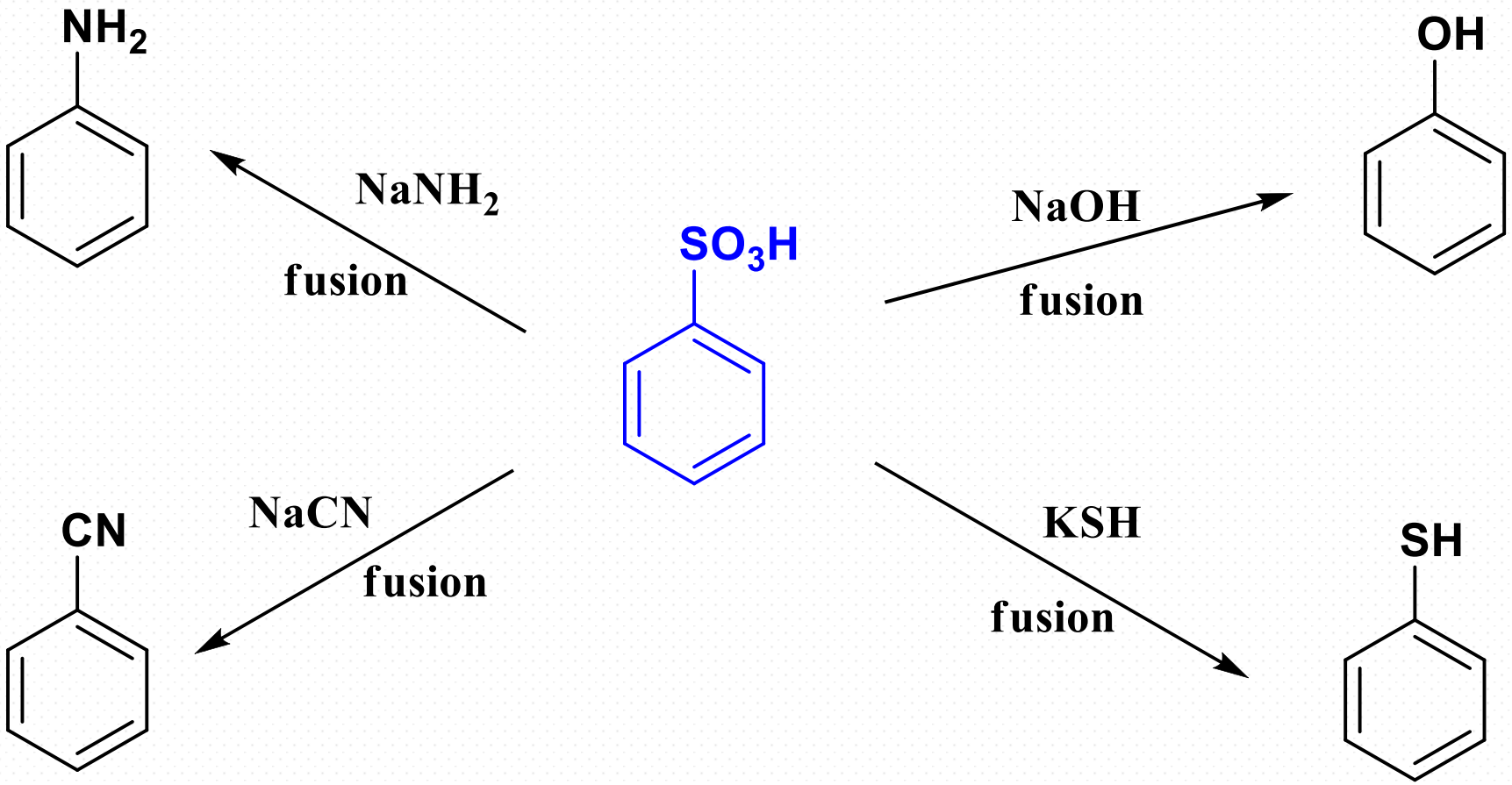


# Reactions of aromatic sulfonic acids

## 1- Reactions with amines and alcohols



# 2- Displacement of sulfonic acid group



# REFERENCES


1. J. D. Hepworth, D. R. Waring and M. J. Waring. "*Aromatic Chemistry*", RSC 2002, ISBN: 0-85404-662-3.
2. J. McMurry. "*Organic Chemistry*", 9th Edition, Cengage Learning, 2015