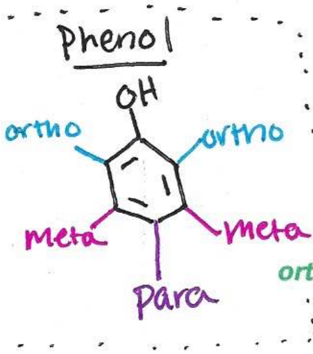
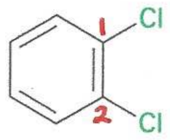
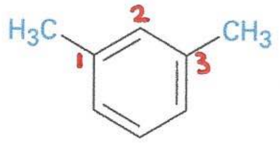
Naming Aromatic Compounds

Disubstituted benzene are named using the prefixes **ortho (o), meta (m) and para (p)**

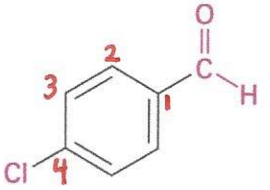




***ortho*-Dichlorobenzene**
1,2 disubstituted

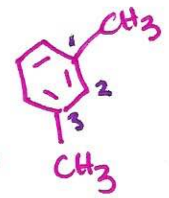


***meta*-Dimethylbenzene**
(*meta*-xylene)
1,3 disubstituted



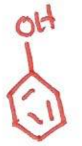
***para*-Chlorobenzaldehyde**
1,4 disubstituted

"meta"



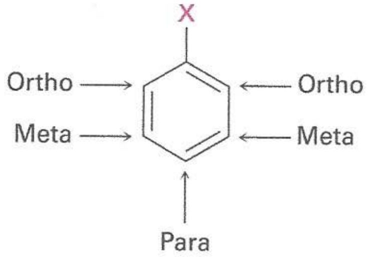
Can spin around & not look exactly like images to the left

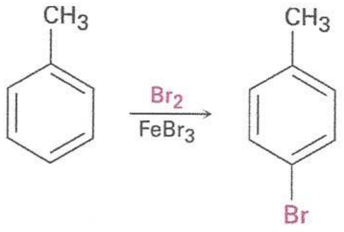
This naming system is useful when discussing reactions:



Phenol

Toluene





Toluene **p-Bromotoluene**

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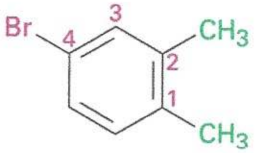
"The reaction occurs at the para position"

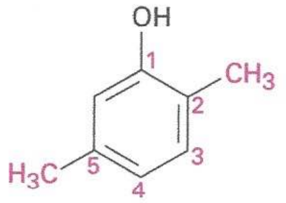
(aka the position para to the methyl)

If there is any ambiguity, number so that the 3rd and 4th are as low as possible until a difference is found.

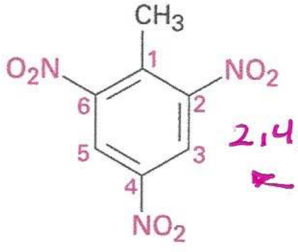


ortho-methyl-para-bromo toluene

ortho-meta-2,5-dimethyl phenol



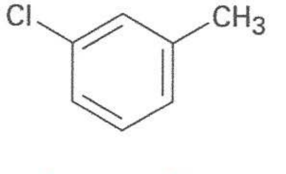
"nitro"



2,4,6-trinitro toluene

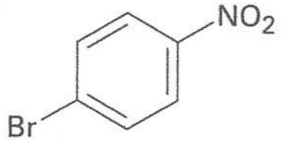
choose carbon as #1 and number so the substituents have the lowest # possible. Write the substituents in alphabetical order

(a)



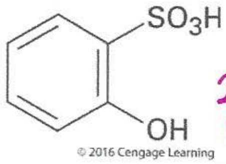
meta-chlorotoluene
OR
1-chloro-3-methylbenzene

(b)



para-bromonitrobenzene
OR
(p) 1-bromo-4-nitrobenzene

(c)



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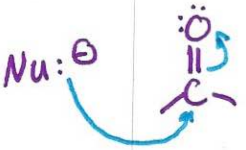
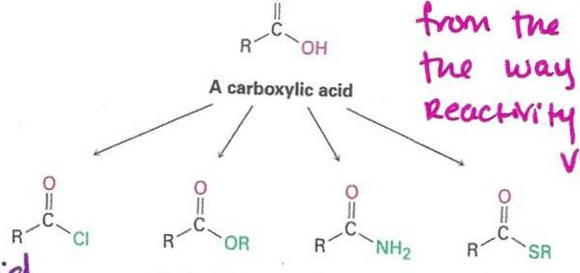
ortho-hydroxy benzene sulfonic acid
OR
2-hydroxy benzene sulfonic acid

Carboxylic Acid Derivatives



like ketones, carboxylic acids undergo addition of nucleophile to carbonyl group



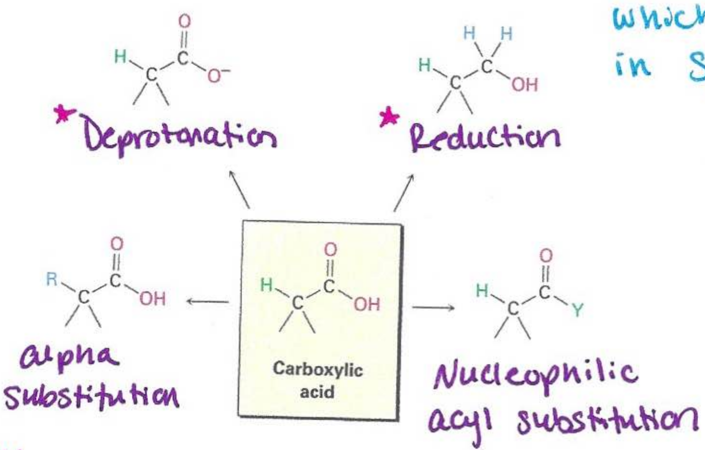
* acid chlorides are the most reactive because the electronegative chlorine atom withdraws electrons from the carbonyl carbon - similar to the way substituents affect the reactivity of aromatic rings w/ EWD vs. ED - page 686 in book

Reactions of Carboxylic Acids

Remember - like alcohols, carboxylic acids can be deprotonated to give anions which act as good Nu:⊖ in S_N2 Reactions

Reactions of Carboxylic acids can be graped in 4 catagories:

* of the 4 catagories we have already discussed the acidic behavior of carboxylic acids (Deprotonation) as well a Reduction w/ $LiAlH_4$

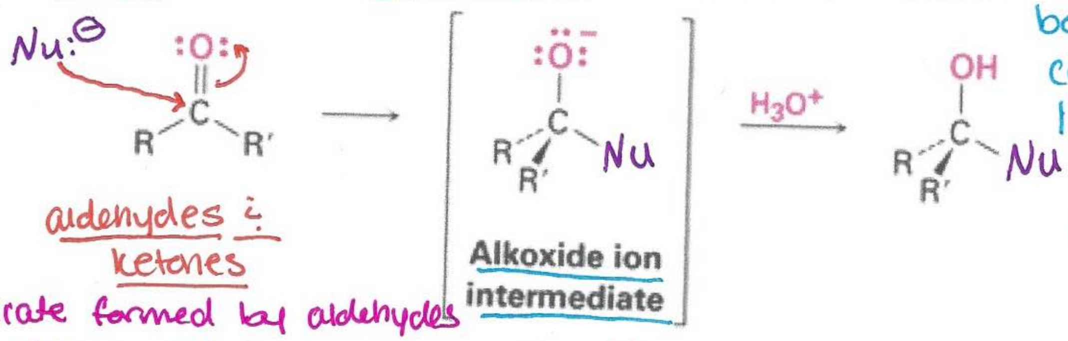


Nucleophilic Acyl Substitution

we initially looked at substitution Rxns w/ aldehydes and ketones...

etones & Aldehydes = Addition Rxns

The initially formed tetrahedral intermediate eliminates one of the two substituents organally bonded to the carbonyl carbon leading to nucleophilic acyl substitution

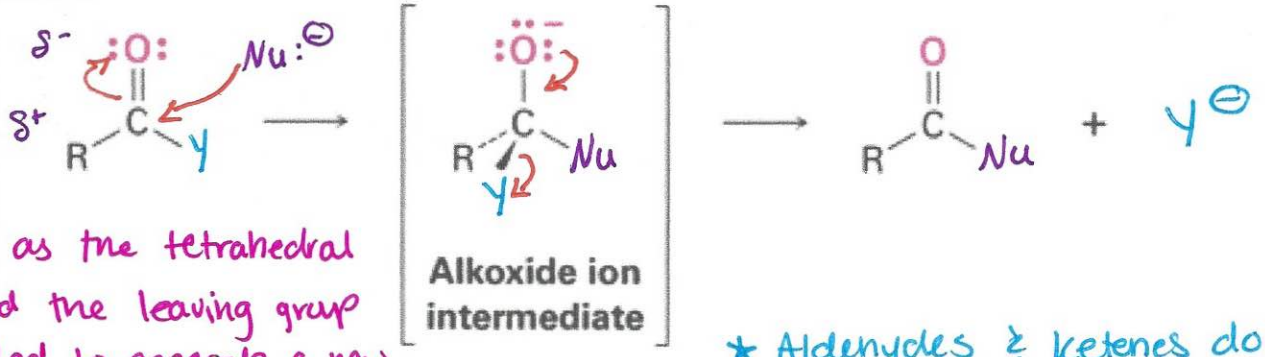


he intermediate formed by aldehydes & ketones is protonated to create an alcohol

... when a nucleophile adds to a carboxylic acid a different Rxn takes place...

Nucleophilic acyl substitution continued...

carboxylic acids have an acyl carbon bonded to group "y" that can act as a leaving group, often as a stable anion

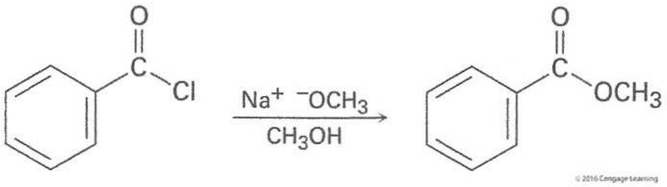


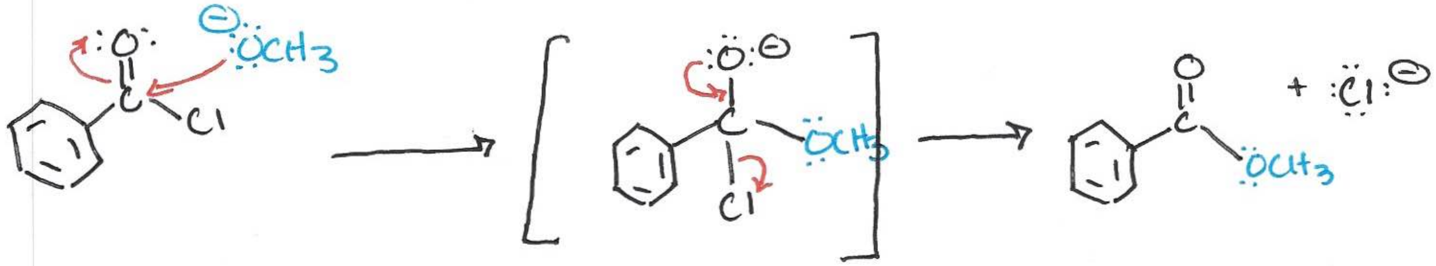
As soon as the tetrahedral is formed the leaving group is expelled to generate a new carbonyl compound

* Aldehydes & ketenes do not have a leaving group so the undergo Addition Rxns not substitution Rxns

Both Rxns begin w/ a Nu:⊖ attacking the polar C=O bond to give a tetrahedral alkoxide ion intermediate

Draw the mechanism of the nucleophilic acyl substitution reaction:

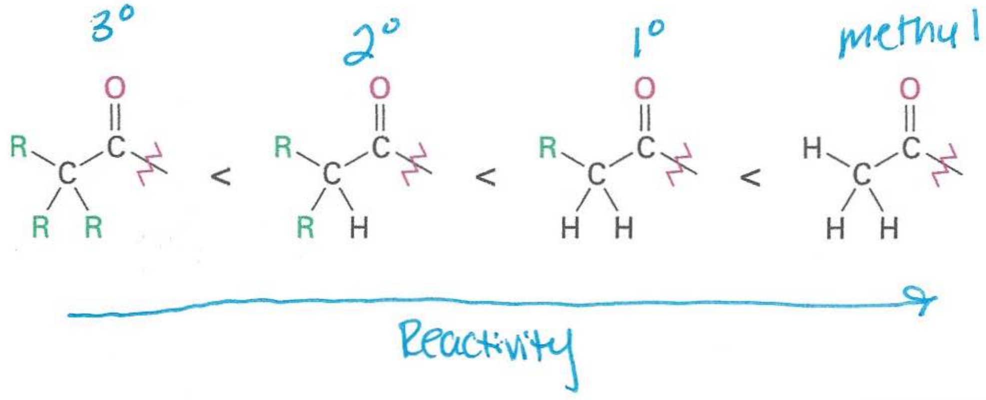




* acid chlorides are the most reactive because of the electronegative chlorine atoms withdraws electrons from the carbonyl carbon - it is similar to the way substituents affect the reactivity of aromatic rings, electron withdrawing vs. electron donating (page 686 in text book)

Factors that affect carboxylic acid reactivity towards nucleophile acyl substitution

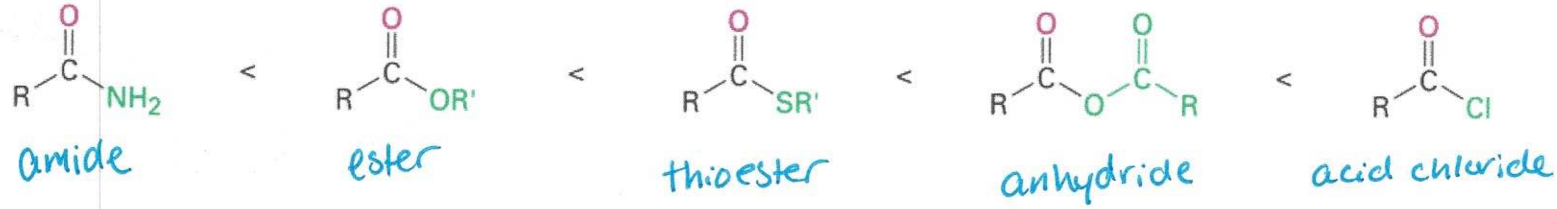
Steric factors: unhindered, accessible carbonyl groups react with nucleophiles more readily than steric hindered groups.



Electronic factors: strongly polarized acyl compounds react more readily than less polar ones

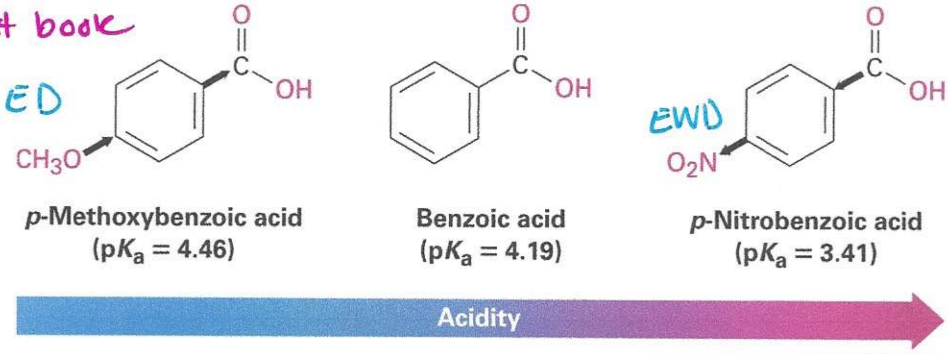
(ED)
Electron Donating

(EWD)
Electron withdrawing



Reactivity →

Substituents affect the orientation of the reaction... page 494 in text book



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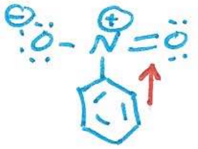
NO_2 = EWD



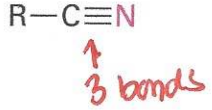
substituents affect the reactivity of the aromatic ring:

activate = make it more reactive than benzene alone

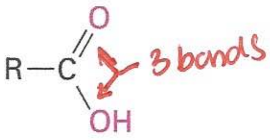
deactivate = make it less reactive then benzene alone

Chemistry of Nitriles

Nitriles are similar to carboxylic acids in that they have a carbon atom with 3 bonds to an electronegative atom



A nitrile—three bonds to nitrogen



An acid—three bonds to two oxygens

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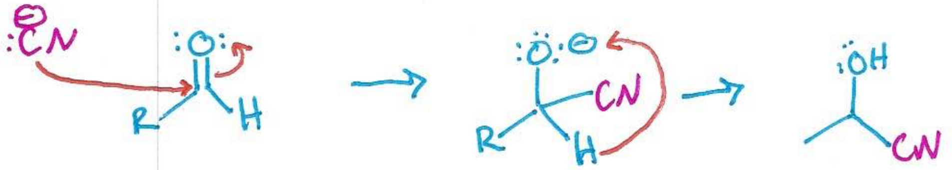
Preparation of Nitriles

* Both of these Rxns are useful but the synthesis from amides is more general and not limited by steric hindrance

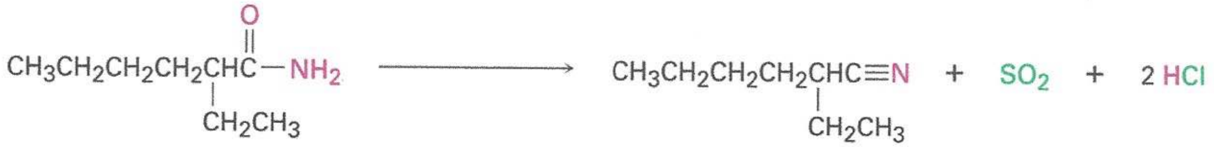
1. SN2 reaction of CN- that we discussed Thursday



2. Dehydration of primary amide. * more general Rxn, not limited by steric hindrance

Thionyl chloride is commonly used in this reaction

↳ $POCl_3$ also works



$$\mathrm{CH_3CH_2CH_2CH_2}\underset{\mathrm{CH_2CH_3}}{\mathrm{CH}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH_2} \longrightarrow \mathrm{CH_3CH_2CH_2CH_2}\underset{\mathrm{CH_2CH_3}}{\mathrm{CH}}\mathrm{C{\equiv}N} + \mathrm{SO_2} + 2\,\mathrm{HCl}$$

2-Ethylhexanamide **2-Ethylhexanenitrile (94%)**

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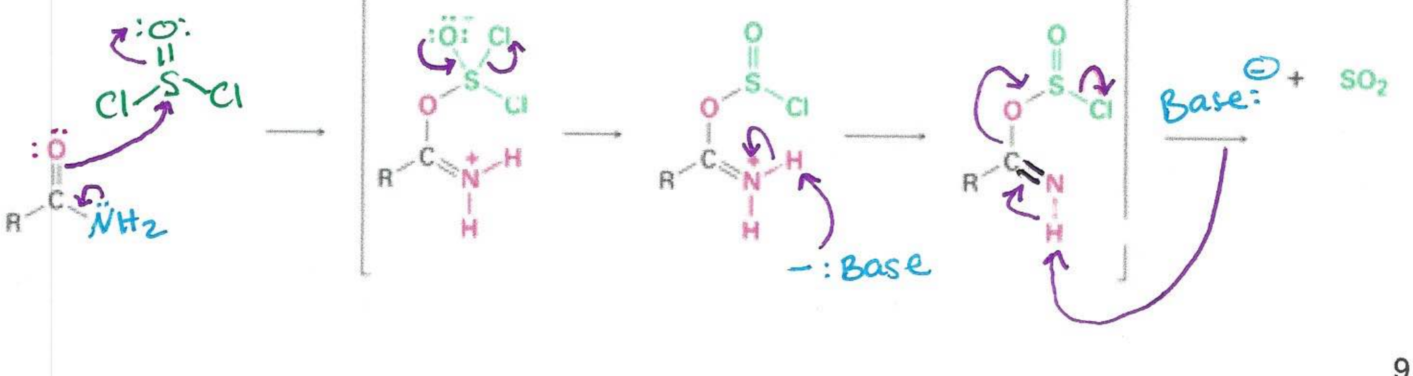
Dehydration occurs by an initial reaction of $SOCl_2$ on the nucleophile amide oxygen atom followed by deprotonation and a subsequent E2-like elimination Rxn.



R-C≡N = "nitrile"