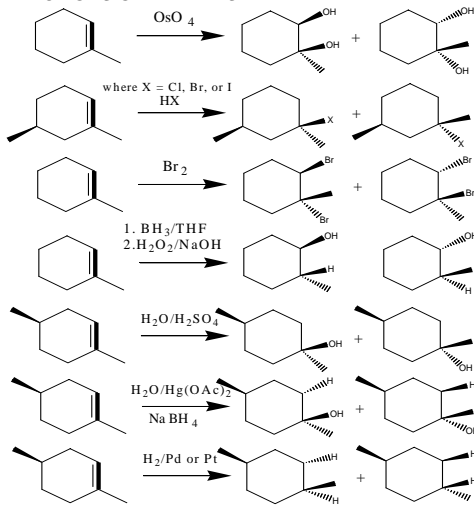
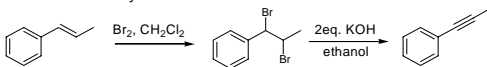


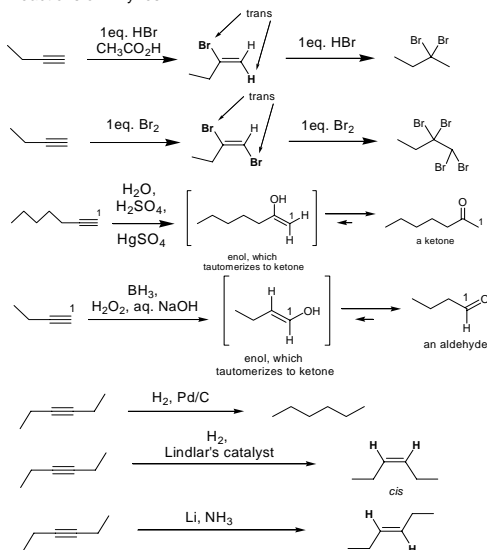
REACTIONS OF ALKENES



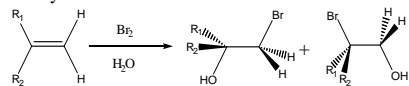
Formation of Alkynes



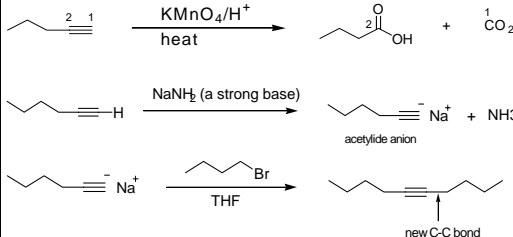
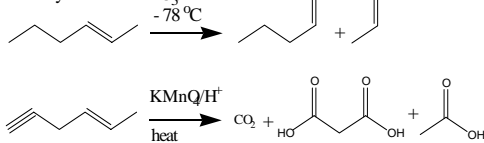
Reactions of Alkynes



Halohydrin formation

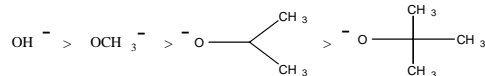


Ozonolysis

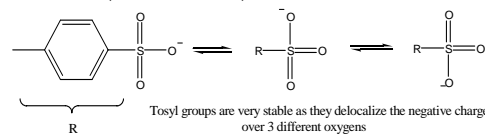


SUBSTITUTION/ELIMINATION SUMMARY

- Nucleophiles:** are atoms with a lone pair of electrons. In nucleophilic substitution they donate the pair of electrons to form a new covalent bond. (factors listed from most important to least important)
 - I⁻ > Br⁻ > Cl⁻ > F⁻
 - CN⁻ > OH⁻ > F⁻
 - H₂S > H₂O
- the best nucleophiles are **negatively charged** (ie. OH⁻ > H₂O)
- the **larger the atom** the better the nucleophile (ie. I⁻ > Br⁻ > Cl⁻ > F⁻)
- smaller molecules** are better nucleophiles than larger ones

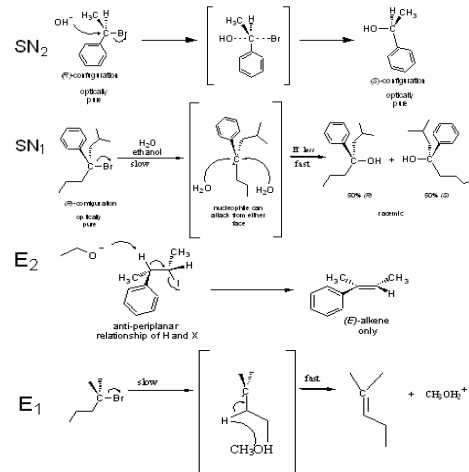


- the lower electronegativity of the atom with the lone pair, the stronger the Nu (ie. CN⁻ > OH⁻ > F⁻)
- Leaving Groups:** groups that best stabilize a negative charge (tosylate, iodide, bromide, chloride, acetate) (factors listed from most important to least important)
 - good leaving groups leave **neutral**
 - good leaving groups are **stable anions** (resonance stabilized)
 - larger** the atom bearing the negative charge the better the Lv group (I⁻ > Br⁻ > Cl⁻ > F⁻)
 - more **electronegative** the atom bearing the negative charge the better the leaving group (F⁻ > O⁻ > N⁻ > C⁻)



Note: halogens are good leaving groups too as they are very electronegative, but they don't have resonance stabilization like tosyl groups

- Bases:** Are atoms with a lone pair of electrons. An atom with a lone pair of electrons can be a base or a nucleophile. By definition if an atom with a lone pair attacks at the carbon it is a nucleophile. If it pulls a proton it is a base.
 - good bases are **negatively charged**
 - the **bigger** the molecule with the lone pair the better the base and poorer the Nu

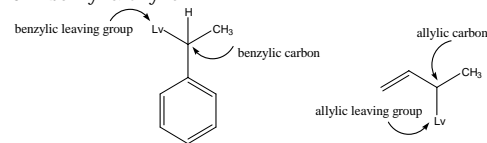


MECHANISM DETERMINATION

- SN²**
- 1° > benzylic/allylic > 2° > (3° does not work)
 - Needs a strong nucleophile
- SN¹**
- 3° > benzylic/allylic > 2° > (1° does not work)
 - Weak nucleophiles will do since any nucleophile will attack a carbocation
- E²**
- Doesn't matter what the carbon with the leaving group is, since you're pulling an H
 - Need a strong base
- E¹**
- 3° > benzylic/allylic > 2° > (1° does not work)
 - Weak bases will do since any base will attack a carbocation

CARBOCATION STABILITY

3° > benzylic/allylic > 2° > 1°



BASE OR NUCLEOPHILE?

small → Nu
 large → base
 negative → strong
 neutral → weak

WHEN THE ATOM WITH THE LONE PAIR CAN ACT AS A BASE OR NUCLEOPHILE:

- SN² and E² will compete and SN¹ and E¹ will compete. To determine the mechanism:
- Look at degree of substitution of the halide, the more substituted, the greater the chance that it will undergo an SN¹ or an E¹
 - Look at what the halide is reacting with → a Nucleophile (SN² or SN¹) → a Base (E² or E¹)



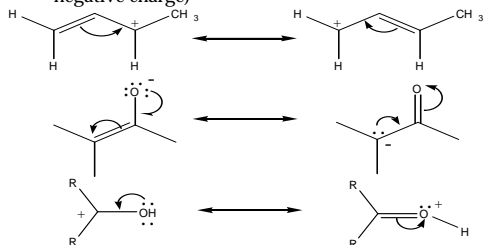
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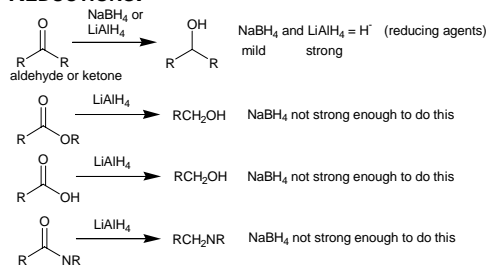
- If you have a molecule which can act as a base or a nucleophile look at the double bond that would be formed in the elimination mechanism. If it is conjugated or highly substituted elimination will be favoured over substitution.

RESONANCE:

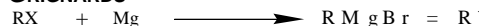
- occurs when there's α, β -unsaturation next to an atom with a charge or an atom with a lone pair next to a carbocation
- to draw the resonance contributor always move electrons (ie. Either the double bond in the case of a cation and lone pair of electrons in the case of a negative charge)



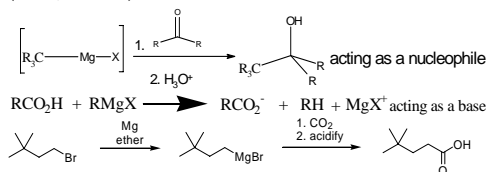
REDUCTIONS:



GRIGNARDS

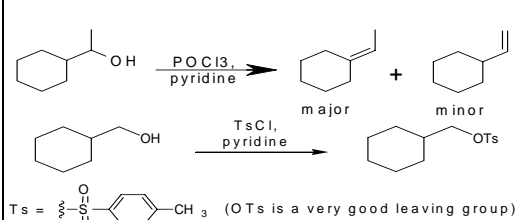
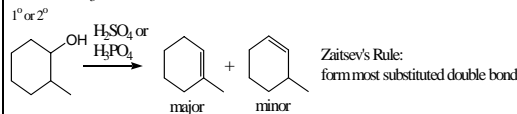
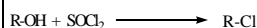
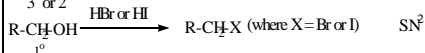
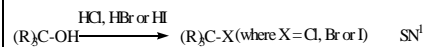
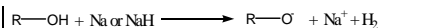


Grignard acts as a base 1st if there's an acidic proton (ROH, RCO₂H) otherwise it acts as a Nu.

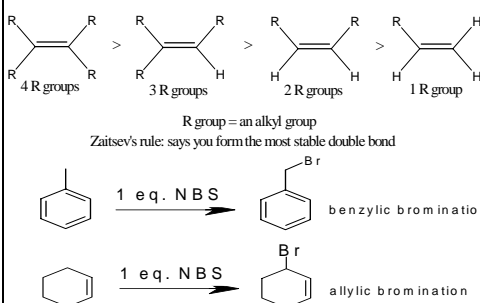


REACTIONS OF ALCOHOLS:

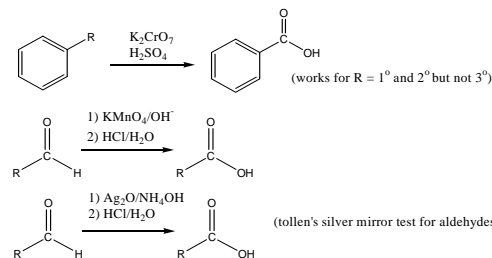
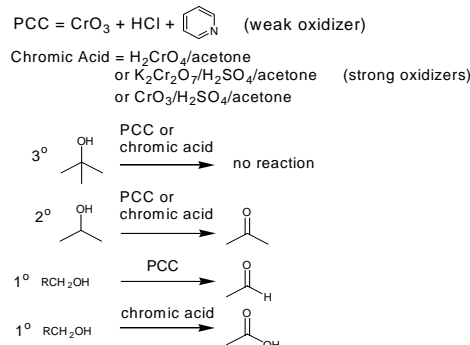
Alcohols: are amphoteric (can act as an acid or a base)



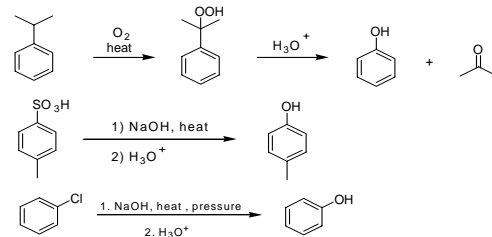
ALKENE STABILITY



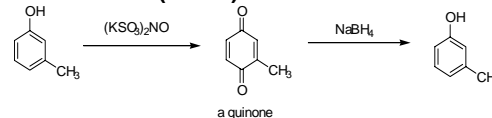
OXIDATIONS



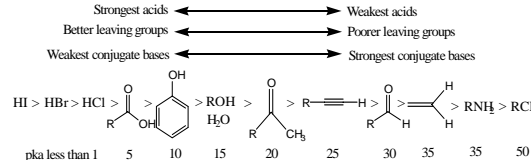
PREPARATION OF PHENOLS:



OXIDATION OF PHENOLS TO QUINONES USING FREY'S SALT (KSO₃NO)



ACIDITY SUMMARY



IONIC BOND

- an atom from the left side of the periodic table bonding with an atom on the right side (ex. NaCl)

POLAR COVALENT BOND

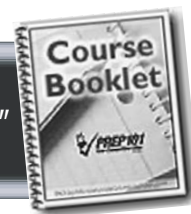
- two atoms from the right side of the periodic table bonding with one another (ex. C-O)

NON-POLAR COVALENT BOND

- 2 of the same atoms bonding to one another or a C-H bond, since they have very similar electronegativity
 - ***NOTE*** a polar molecule has at least one polar bond non-polar molecules have only non-polar bonds
 - an atom is **SP³** hybridized if it contains only single bonds (tetrahedral geometry)
 - an atom is **SP²** hybridized if it contains 1 double bond (trigonal geometry)
 - an atom is **SP** hybridized if it contains 2 double bonds or 1 triple bond (linear geometry)
- determining formal charge: # of electrons an atom wants (4 for C, 5 for N, 6 for O) - (# of bonds and each electron in a lone pair)



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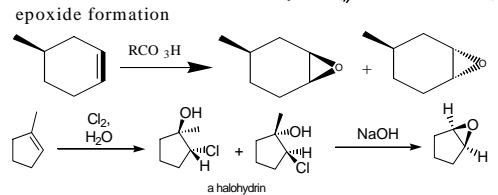
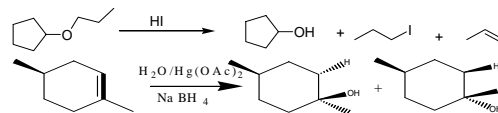
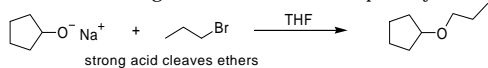
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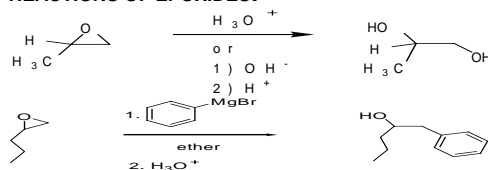
- a single bond has 1 σ bond
- a double bond has 1 σ bond and 1 π bond
- a triple bond has 1 σ bond and 2 π bonds

WILLIAM ETHER SYNTHESIS: (Follows S_N2)

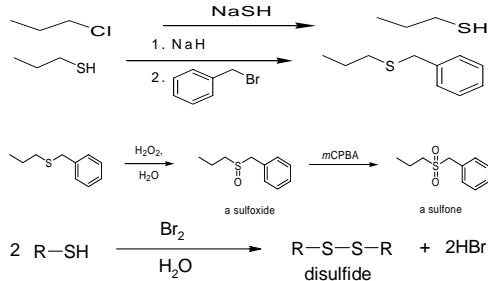
Mechanism strong Nu and C-Lv should be primary



REACTIONS OF EPOXIDES:

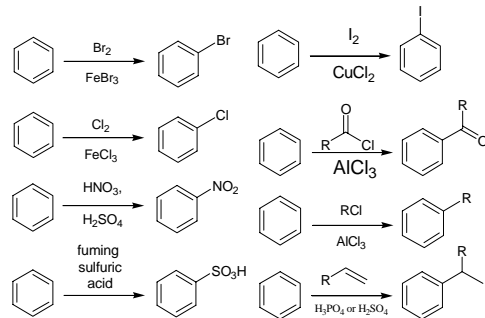


THIOLS AND SULFIDES:



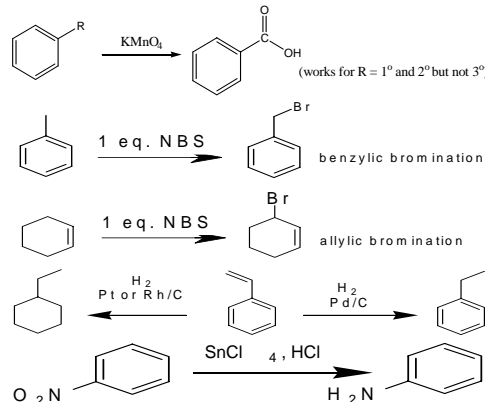
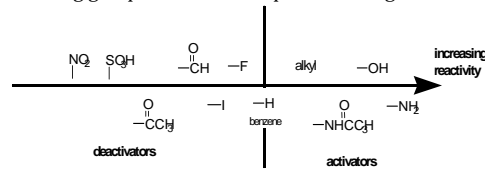
This reaction can be reversed (generating 2 sulfides) by adding Zn/HCl.

ELECTROPHILIC AROMATIC SUBSTITUTION:

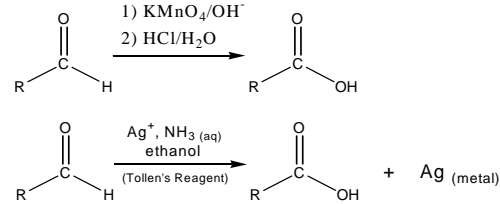
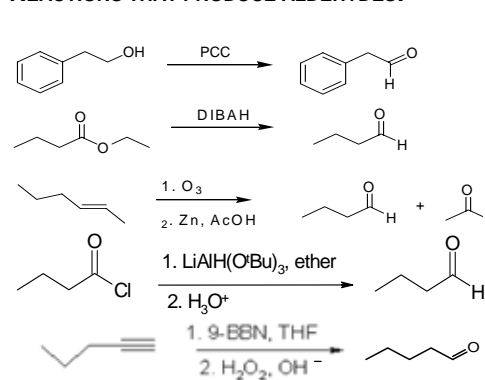


When adding a 2nd substituent to a mono substituted benzene ring:

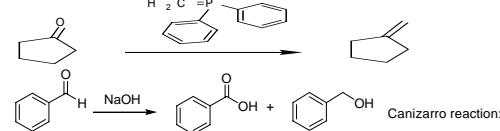
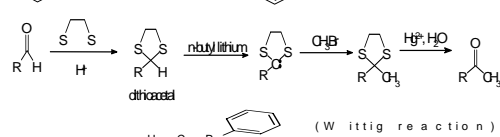
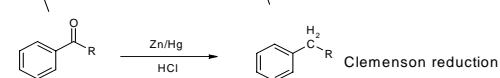
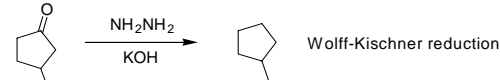
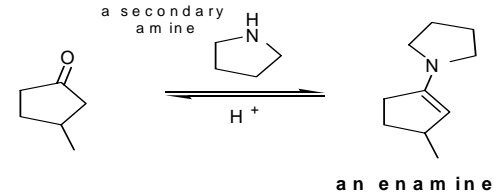
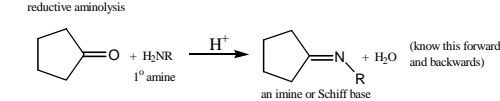
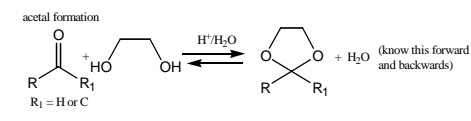
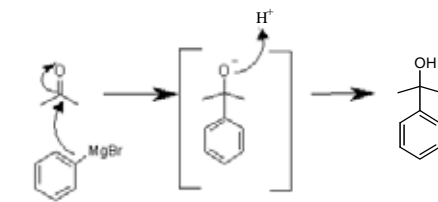
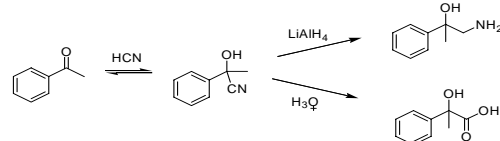
With the exception of the halides, all electron withdrawing groups are meta-directing and all electron donating groups are ortho- and para-directing.



REACTIONS THAT PRODUCE ALDEHYDES:



REACTIONS OF KETONES AND ALDEHYDES:



CONJUGATE ADDITION REACTIONS:



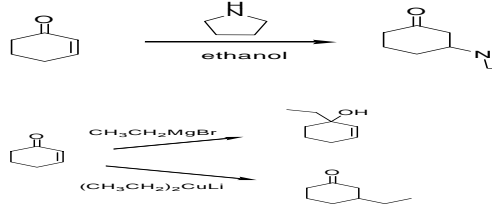
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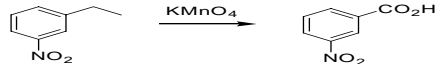


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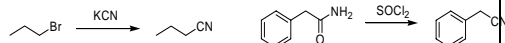
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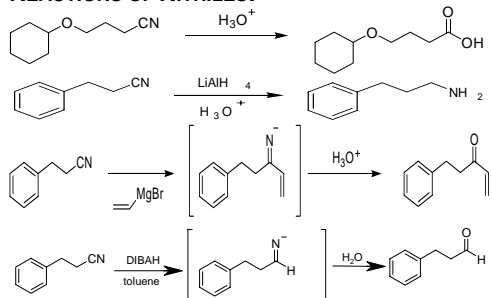
CARBOXYLIC ACID SYNTHESIS:



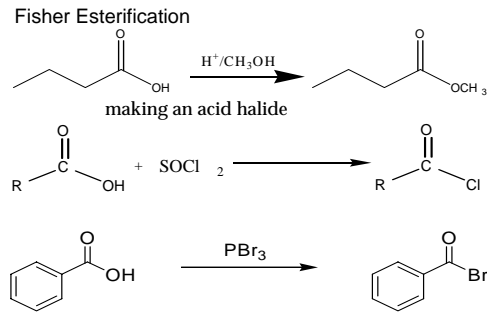
SYNTHESIS OF NITRILES:



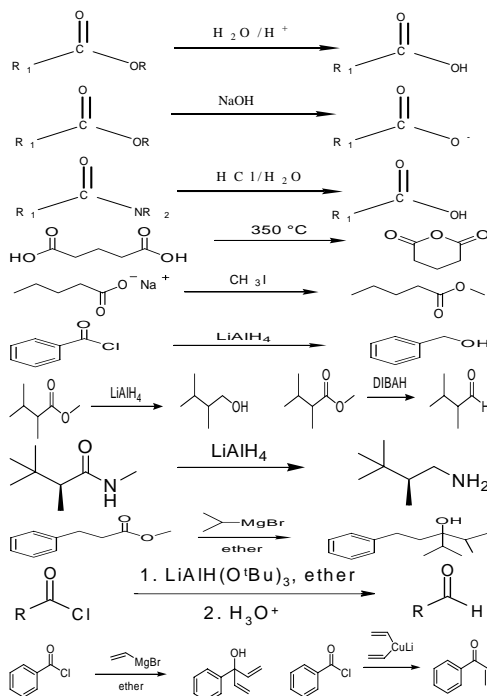
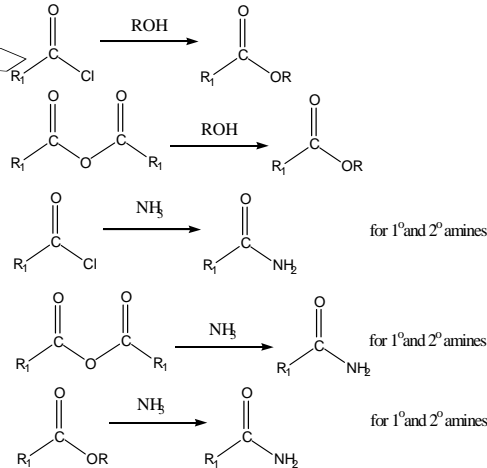
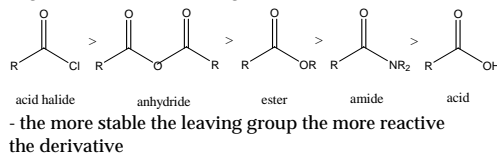
REACTIONS OF NITRILES:



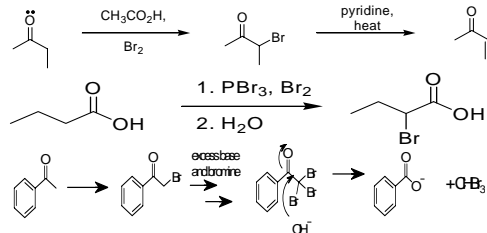
ACID DERIVATIVE REACTIONS:



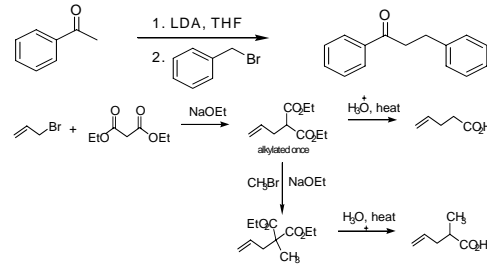
ACID DERIVATIVE REACTIVITY:



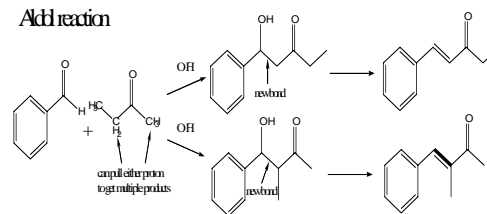
ALPHA SUBSTITUTION REACTIONS OF ENOLS



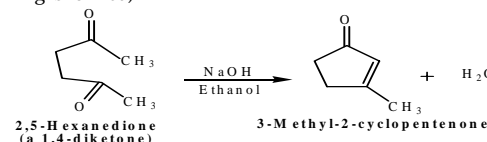
REACTIONS OF ENOLATES:



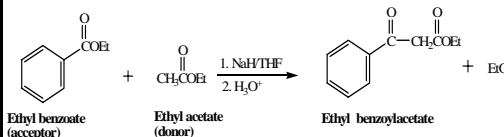
CARBONYL CONDENSATION REACTIONS:



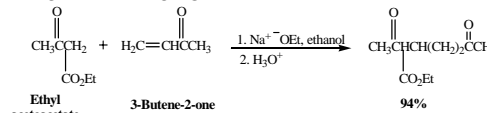
Intramolecular Aldol: (only works if a 5 or 6 membered ring is formed)



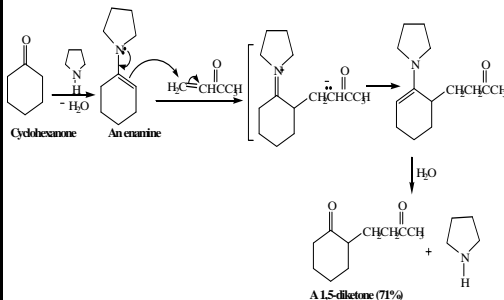
CLAISEN CONDENSATION:



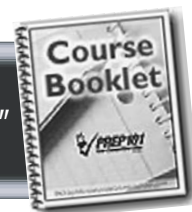
MICHAEL REACTION:



STORK-ENAMINE REACTION:



MICHAEL ANNULATION:

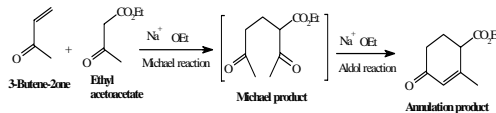


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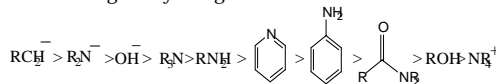
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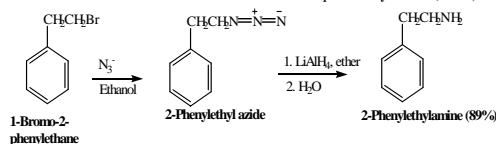
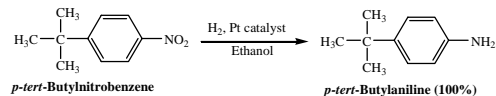
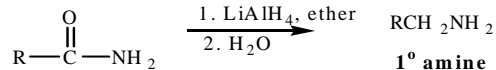
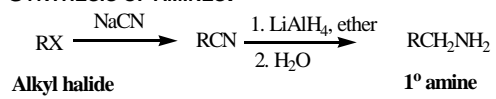
AMINES:

Basicity Review

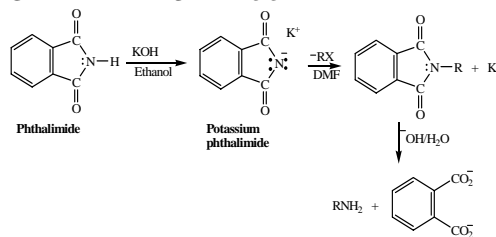
A base is an atom with a lone pair of electrons. The best bases are negatively charged.



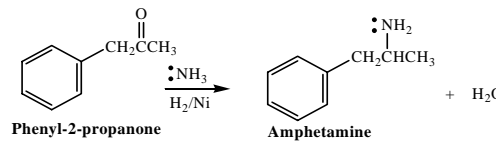
SYNTHESIS OF AMINES:



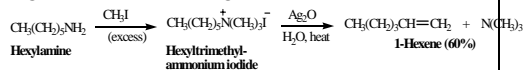
GABRIEL AMINE SYNTHESIS:



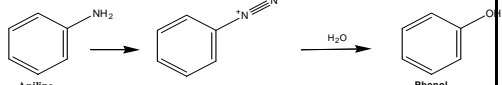
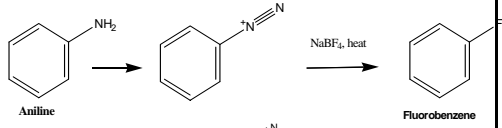
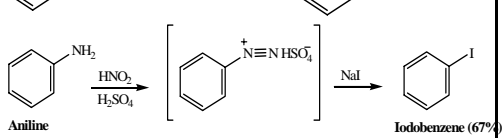
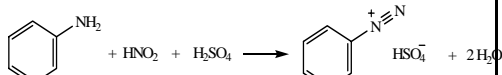
REDUCTIVE AMINATION:



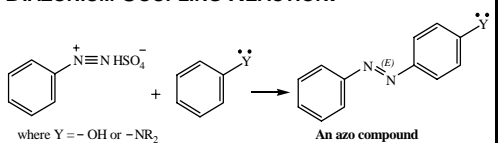
HOFFMANN ELIMINATION:



DIAZOTIZATION REACTION:



DIAZONIUM COUPLING REACTION:



DEGREES OF UNSATURATION:

- A molecule's *degree of unsaturation (D.O.U.)* is simply the number of multiple bonds or rings present in the molecule.

- each ring or double bond is one degree of unsaturation
- each triple bond is 2 degrees of unsaturation

To calculate a molecule's degree of unsaturation

- calculate the saturated number of H's = (2n + 2) where n = # of carbons
- for each halogen (F, Cl, Br, I) subtract 1 from the saturated number of H's
- ignore the number of oxygens - they do not affect the molecule's D.O.U.
- for each nitrogen add 1 to the saturated number of H's
- take the new number you calculated for the saturated number of H's, subtract the actual number you have in the molecular formula and divide by 2 to give the degree of unsaturation.

AN APPROACH TO STRUCTURE DETERMINATION:

1. Determine the units of unsaturation
2. Gather information from the IR spectrum
 From an IR spectrum you should be able to tell if there is a C=O, O-H, CO₂H, N-H, nitrile, C=C or alkyne
 - an IR is good for determining functional groups present when there are heteroatoms in the molecular formula

- ex. If there is an O in the molecular formula the IR can tell you if it is a ketone or aldehyde, carboxylic acid or alcohol. If none of these peaks are observed then it is probably an ether
 ex. If there is an N in the molecular formula the IR can tell you if it is an N-H or nitrile. If neither of these peaks are observed the N may be a tertiary amine or amide. If it was an amide you would observe a C=O peak in the IR.

3. Gather information from the NMR spectrum
 - Easy things to spot in the NMR are aromatic ring, aldehyde, carboxylic acid and alkene.
 - If there is 4 or more units of unsaturation immediately look to see if there is an aromatic ring in the structure (peak in the NMR spectrum between 6.8-8 ppm)
 - Then look for the number of CH₃ peaks there are (integrate for 3 protons)
 - Then use all the data you've learned from the molecular formula, IR and NMR to draw possible structures. Then look at each structure and compare them to the number of chemical shifts in the NMR and the splitting and integration observed in the NMR. The structure should match the observed NMR data perfectly. If it doesn't it is not the correct structure. Eliminate it and look at the next possible structure.



Our Course Booklets - free at prep sessions - are the "Perfect Study Guides."

