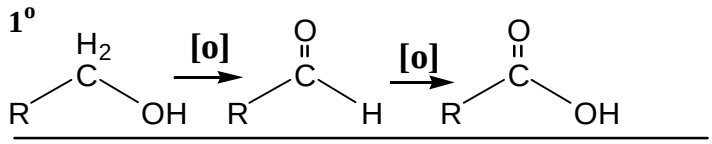
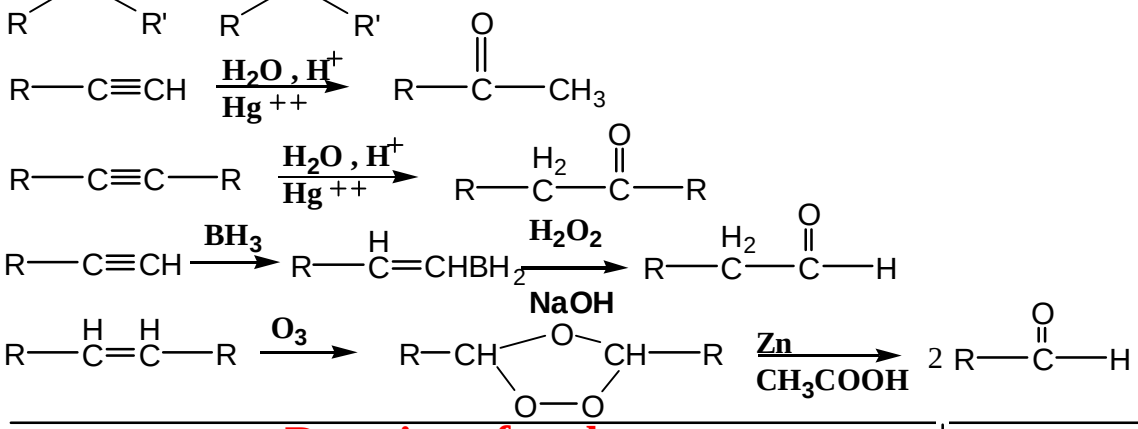
Synthesis of Aldehydes And Ketones

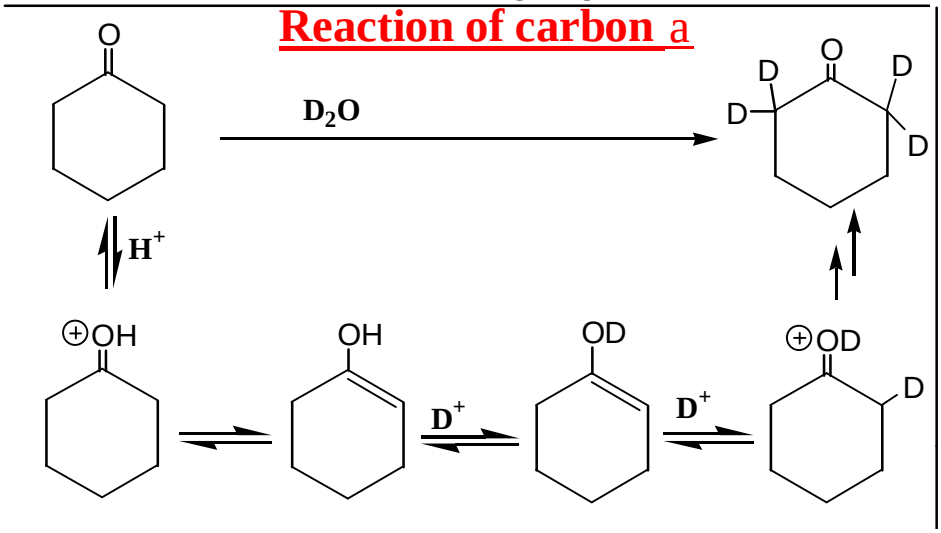


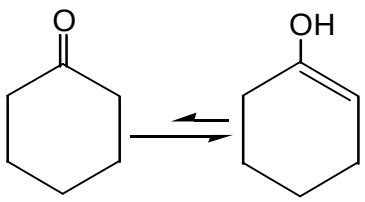
To Oxidate of the **1°alcohol** to **Aldehyde only** , and not to the Carboxylic Acid we should use **PCC** as the oxidating Reagant

[o]= $KCr0_7$, $KCrO_4$, $NaCrO_4$



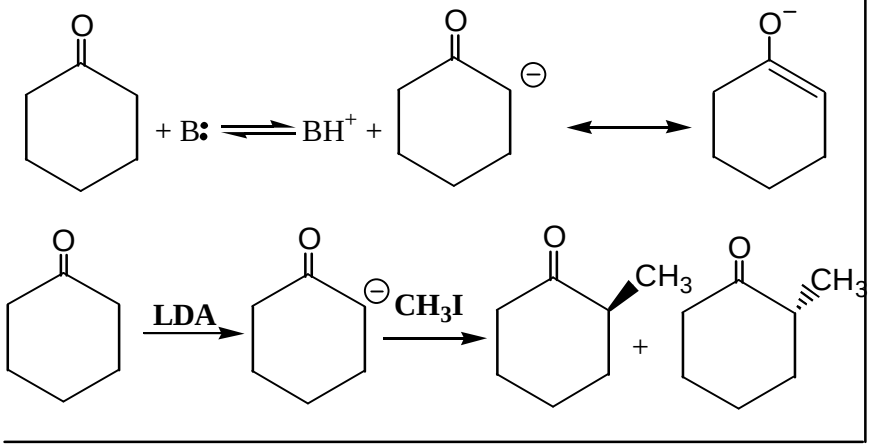
Reaction of carbon a

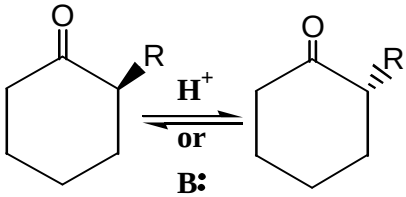


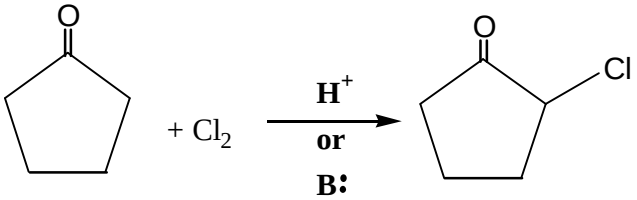


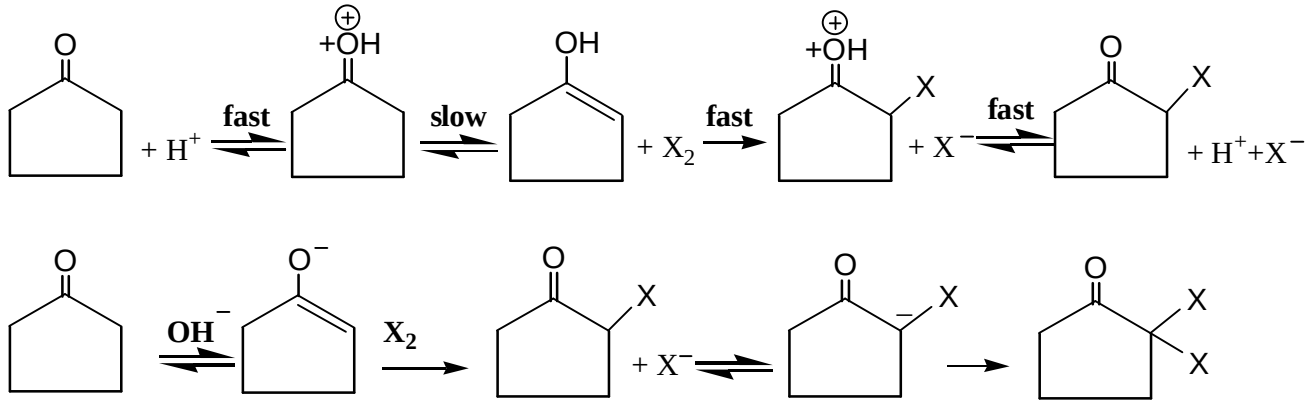
Tautomerisation Keto-Enol

The Ketone form is the favorite form

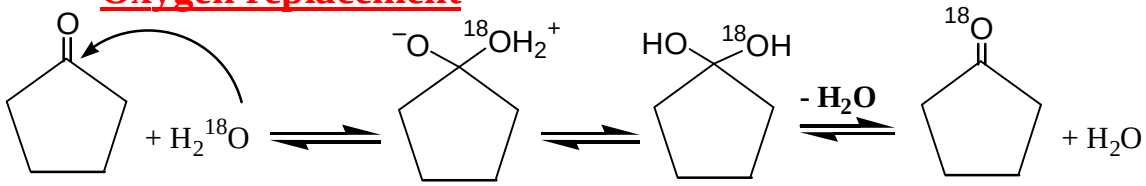




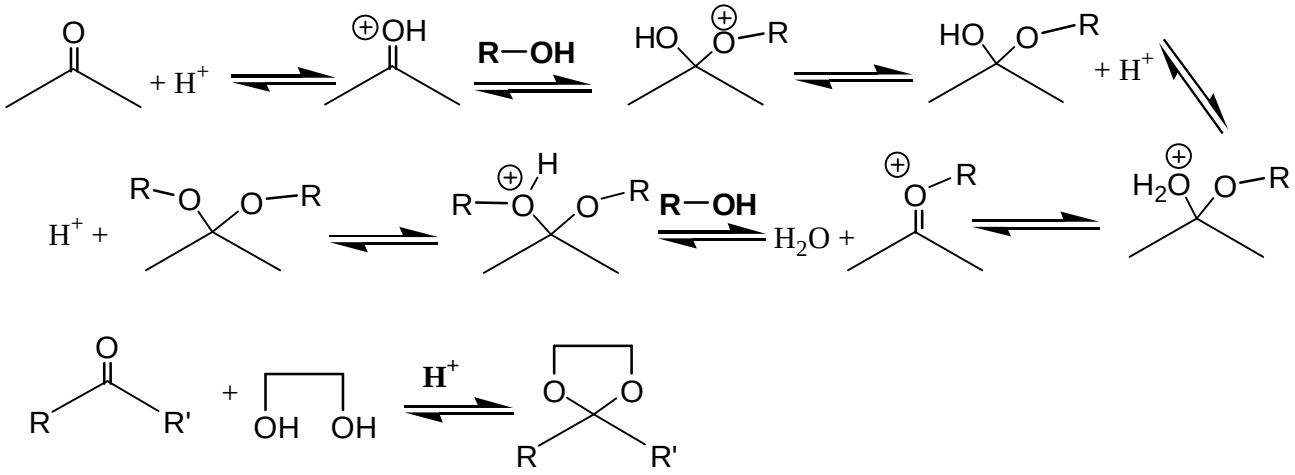




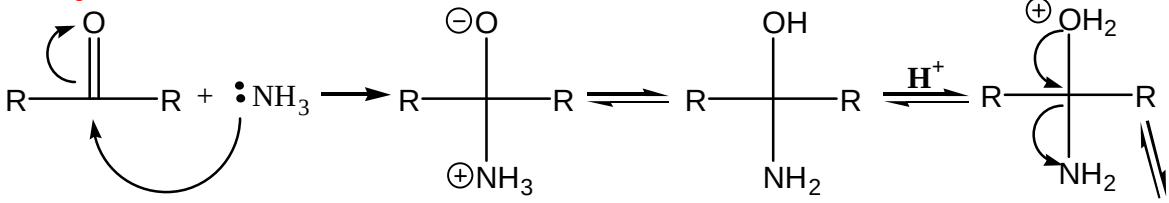
Oxygen replacement



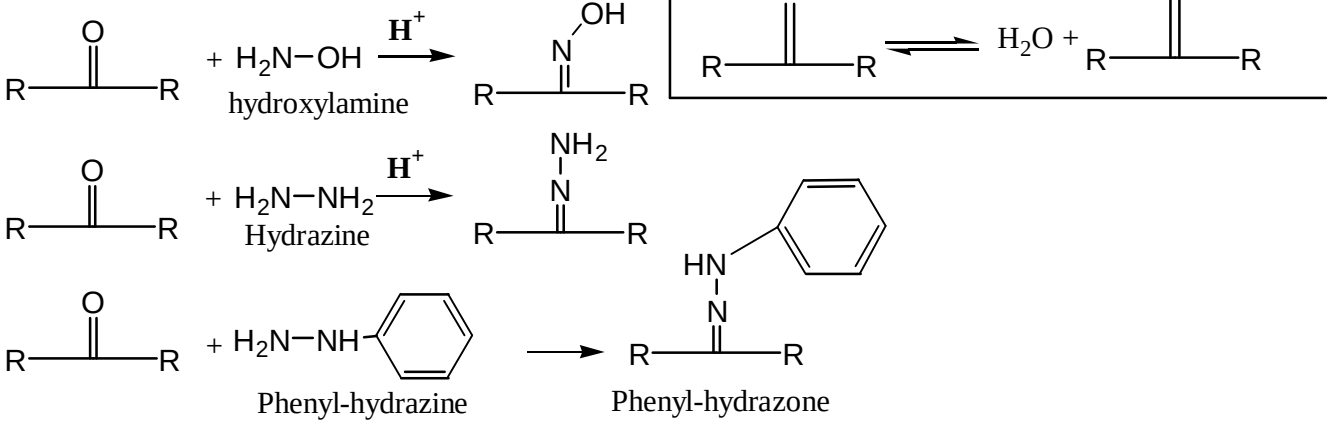
Reactions with Alcohols



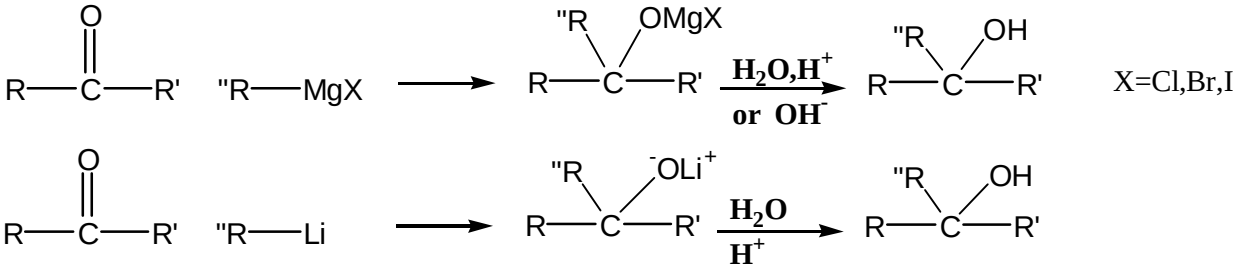
Synthesis of Imine

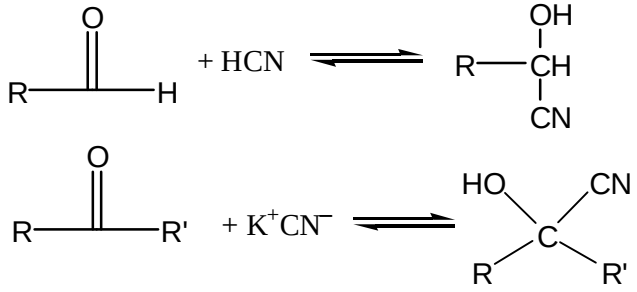


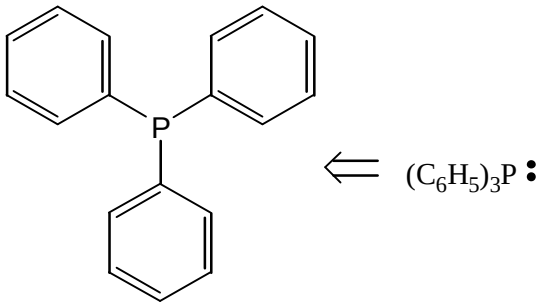
Reactions whit Derivatives of Amonia



Grignard reagnt reaction

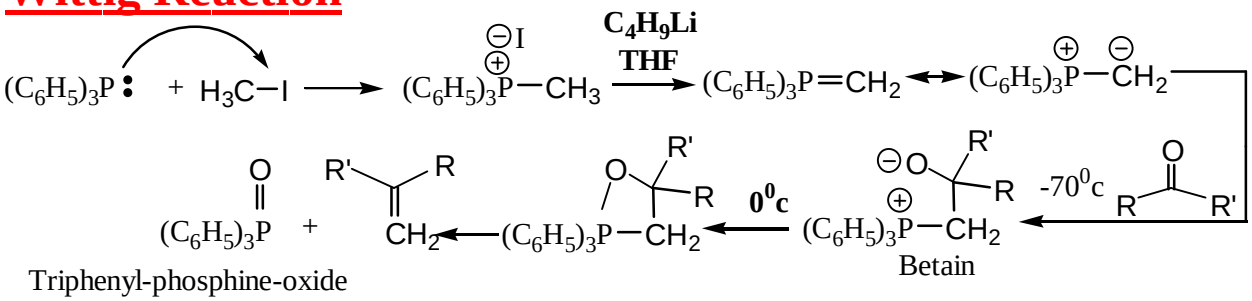






Triphenyl-phosphine

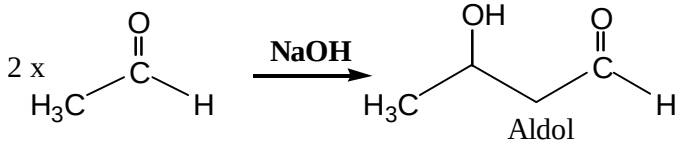
Wittig Reaction



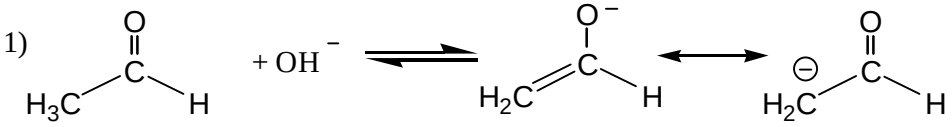
Triphenyl-phosphine-oxide

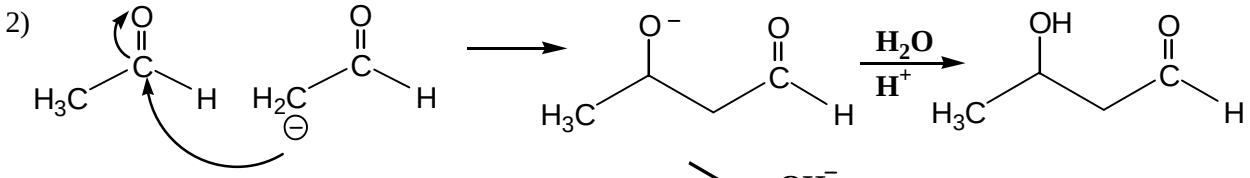
Betain

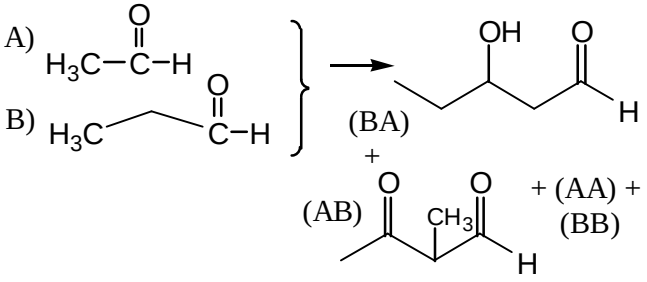
Aldol Condensetion

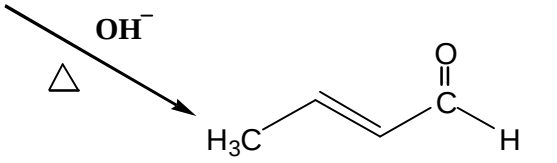


Aldol

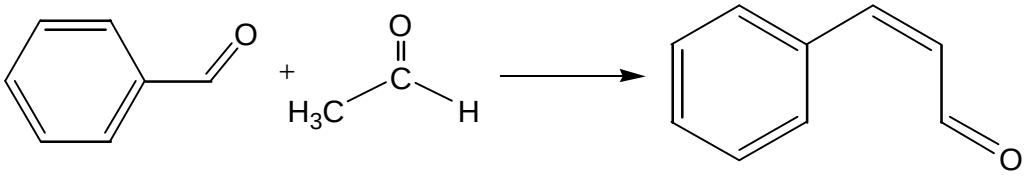








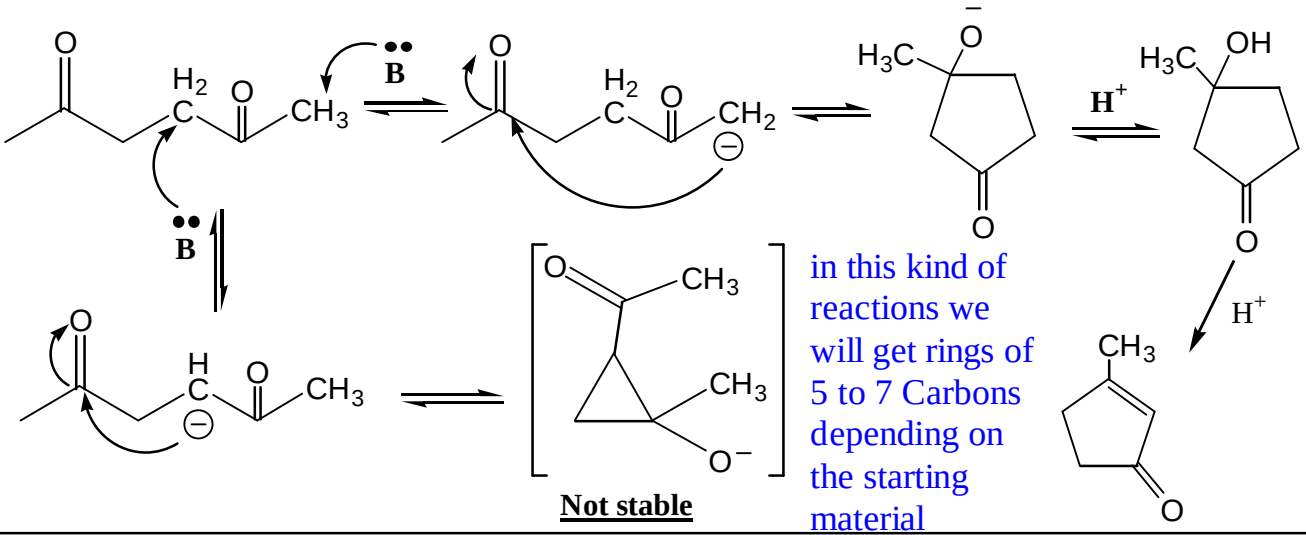
We can get 4 different products:
A & B can react with themselves or with each other- A attacks B or B attacks A.



Benzaldehyde

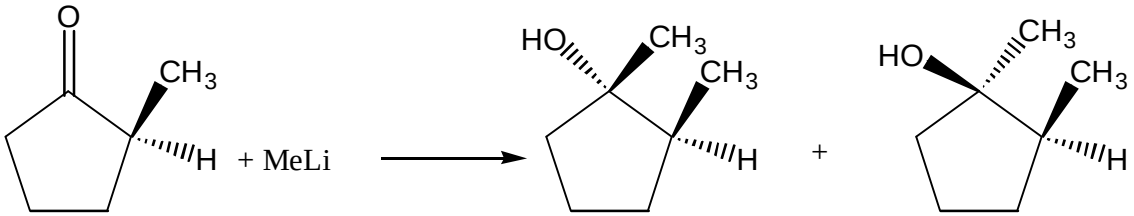
Cinnamaldehyde

Only 1 option because there is no H on C alpha



Not stable

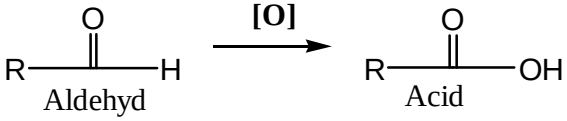
in this kind of reactions we will get rings of 5 to 7 Carbons depending on the starting material



cis 10%

trans 90%

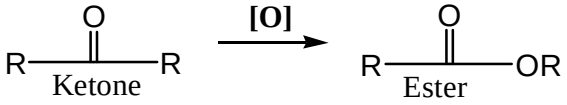
Oxidation



Aldehyd

Acid

[O]= $KMnO_4$,CrO_3,Cr^{VI},H_2O_2,RCOOOH (peroxy acids)



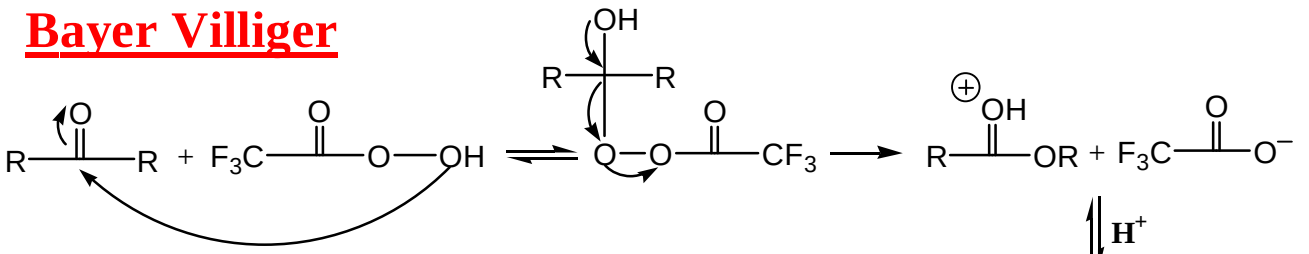
Ketone

Ester

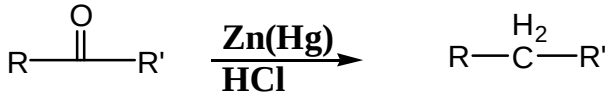
[o] = CF_3COOOH (Peroxide)

Mechanism is in Bayer Viliger

Bayer Villiger

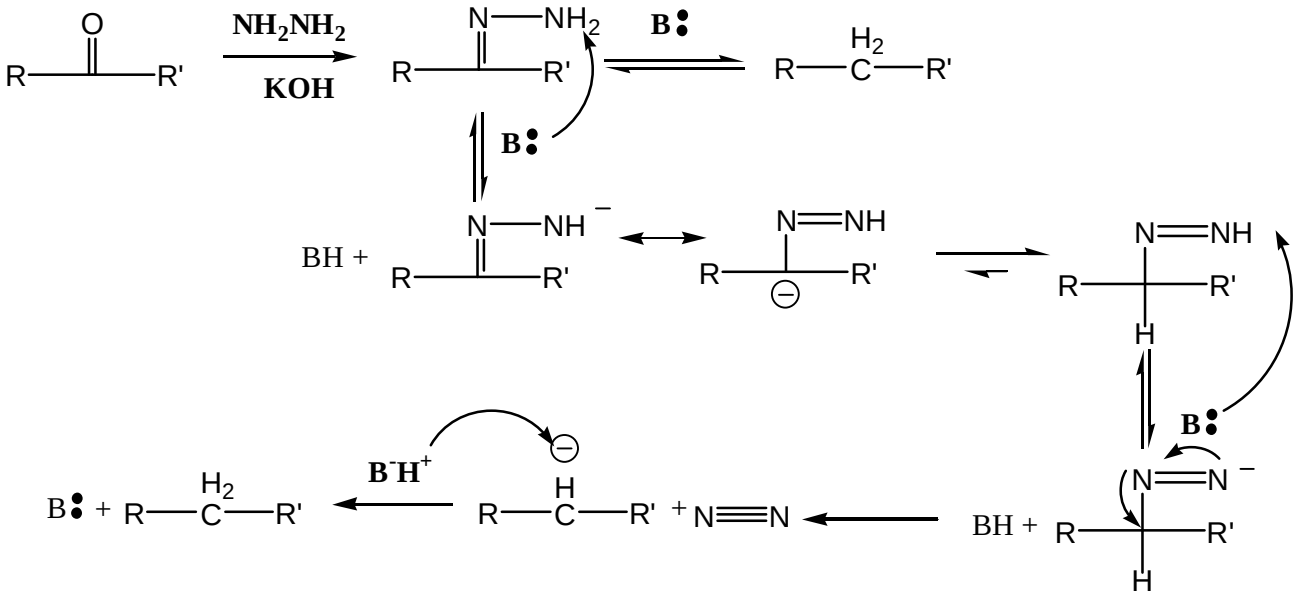


Clemmensen

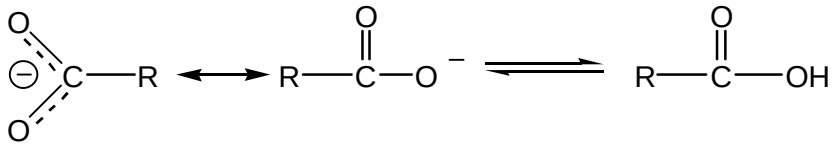


Wolf Kishner

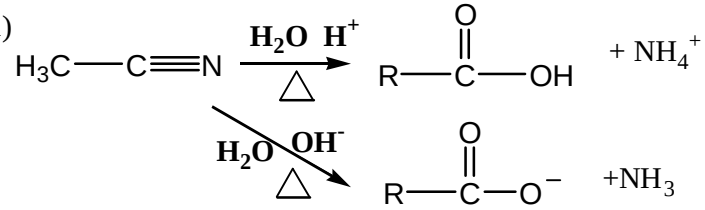
B: =KOH, R-ONa, R-OK



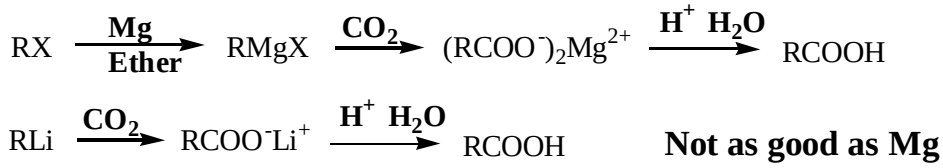
Carboxylic Acid Synthesis



1)

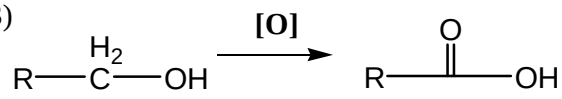


2)

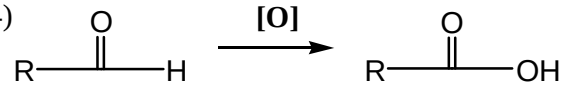


Not as good as Mg

3)

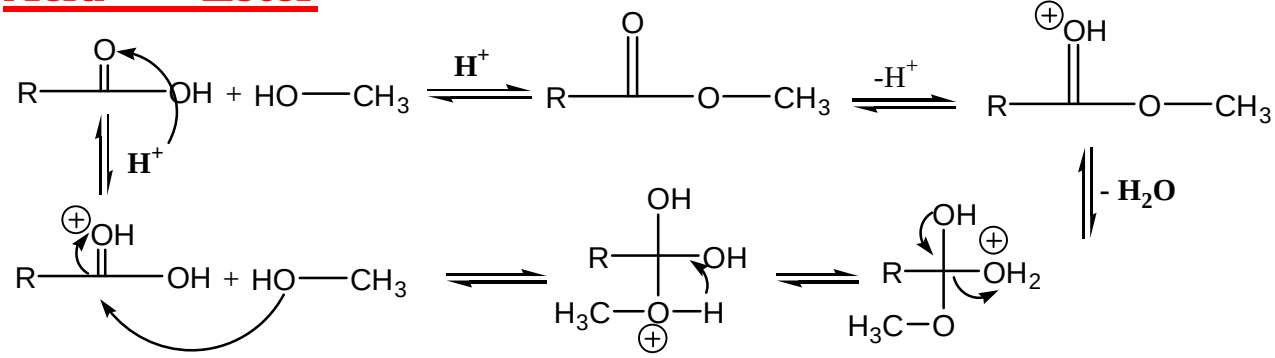


4)

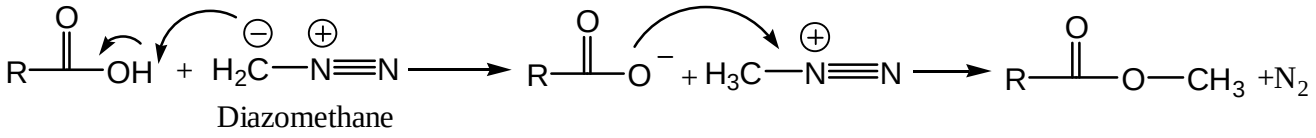


[O]= $KMnO_4$,$KrCrO_4$

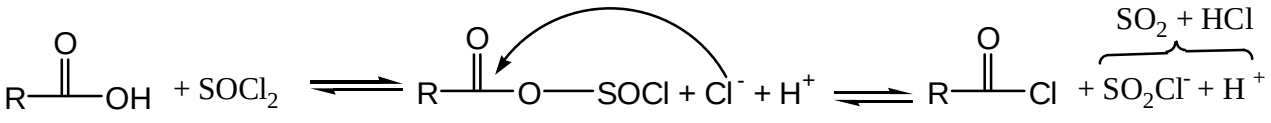
Acid ==>Ester



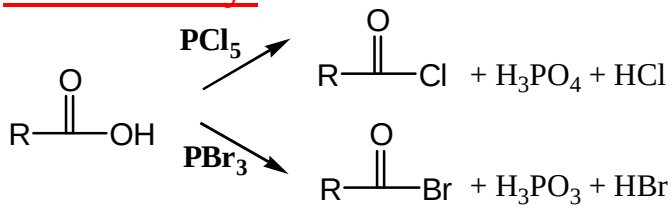
Reaction with Diazomethane



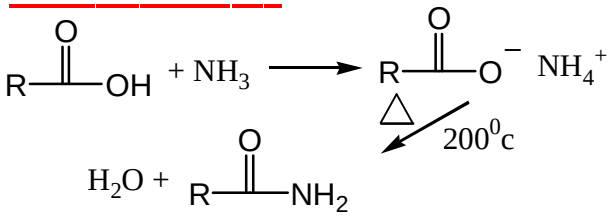
Reaction with Thionylchloride ($SOCl_2$)



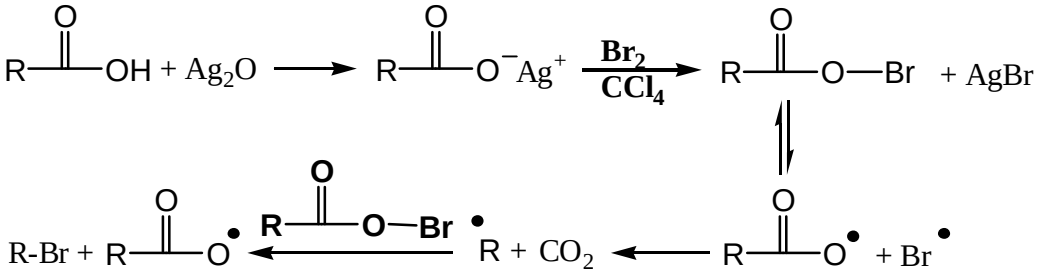
Acid ==> Acyl

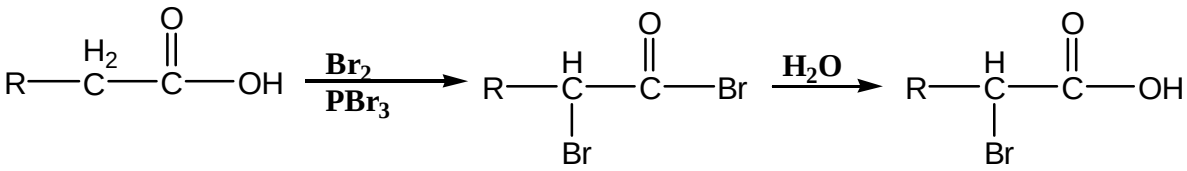


Acid ==> Amide

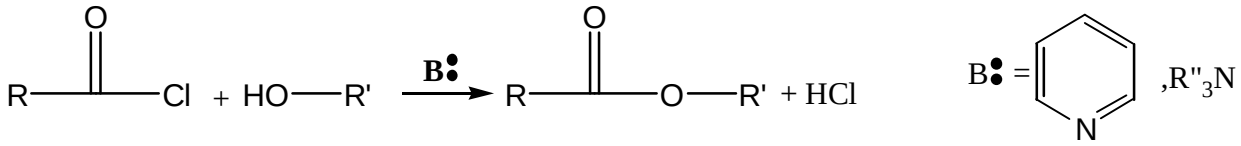


Hunsdiecker Reaction (chain reaction)

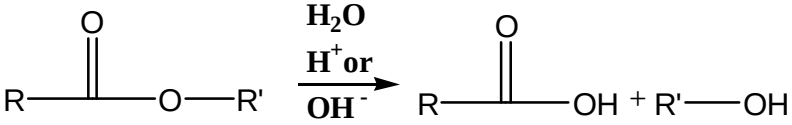




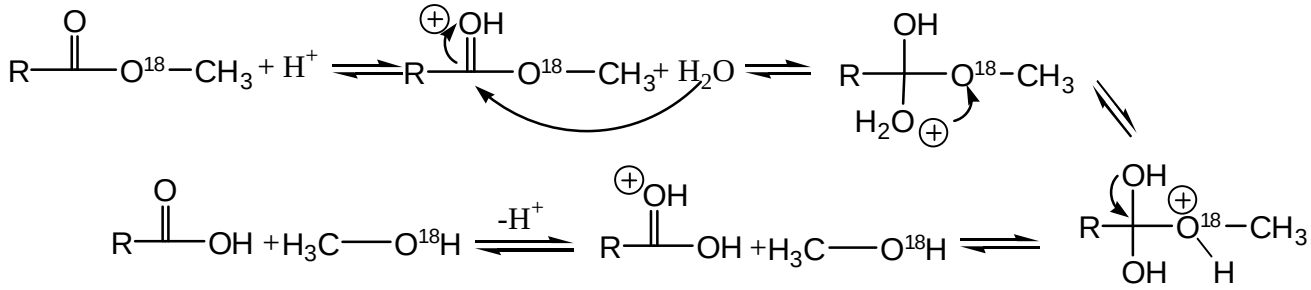
Esters synthesis



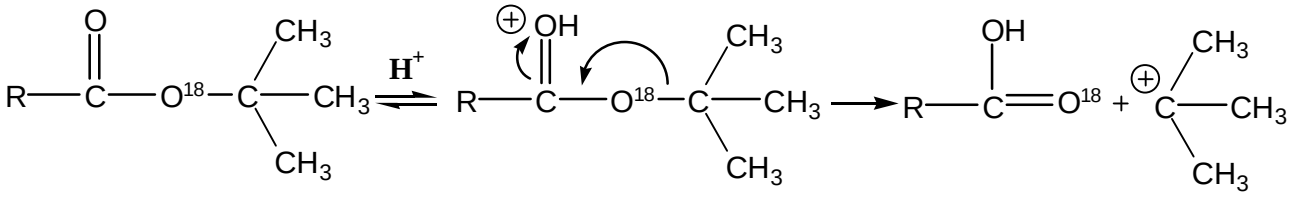
Esters Reactions



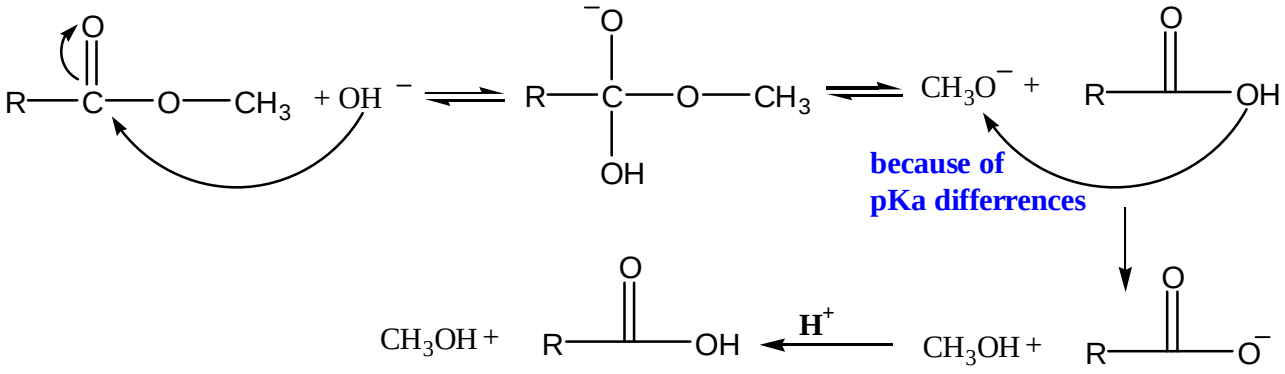
Acid Mechanism



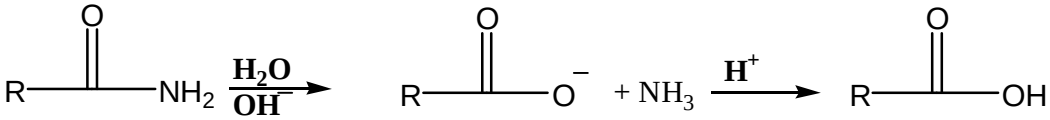
Different mechanisem for 3° Carbon on the Ester



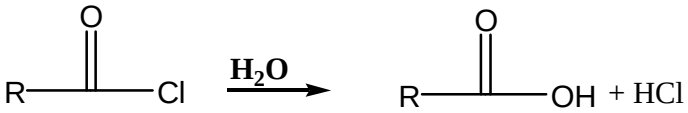
Base mechanisem for the same reaction (better than the Acid mechanisem if there are no halogens)



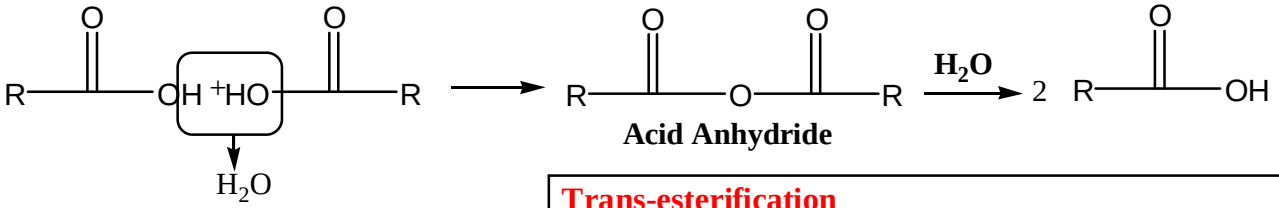
Amide ==>Acid

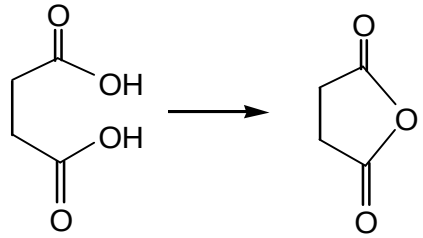


Acylhalide ==>Acid

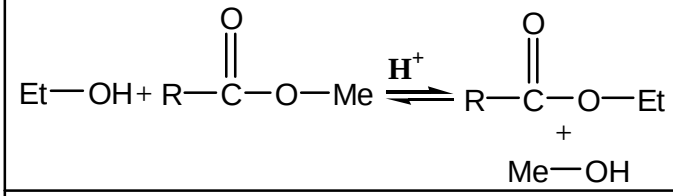


Acid <==>Acid Anhydride

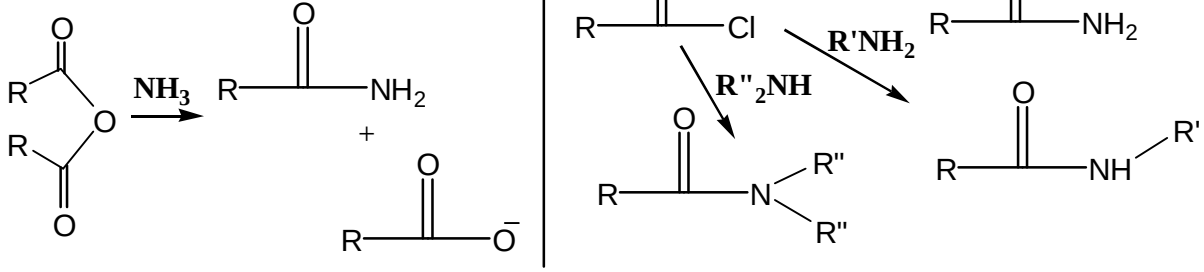




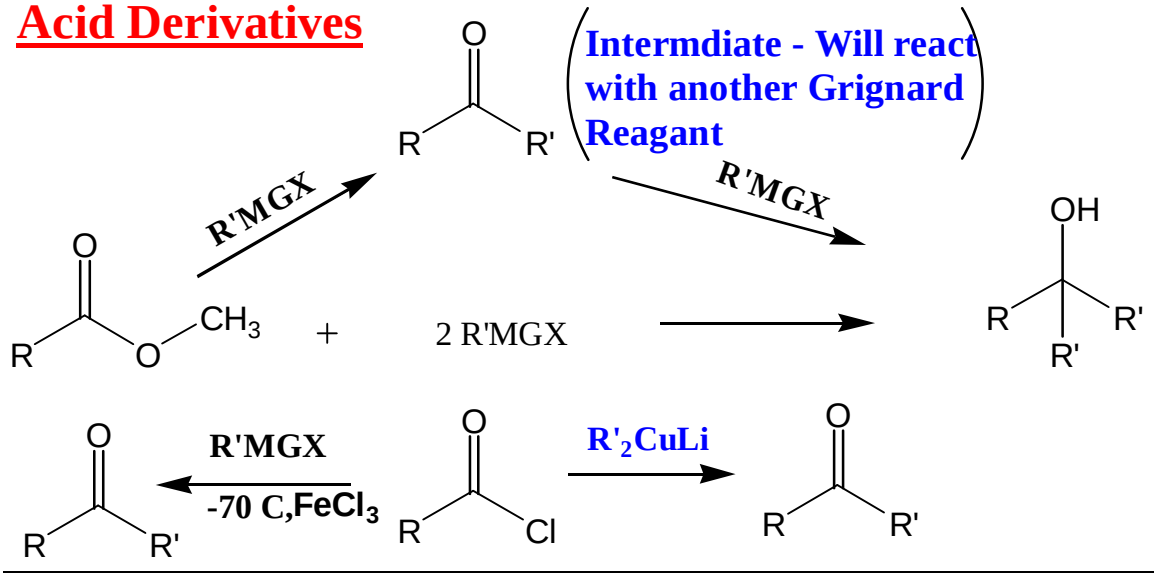
Trans-esterification



Acylhalide ==> Amides

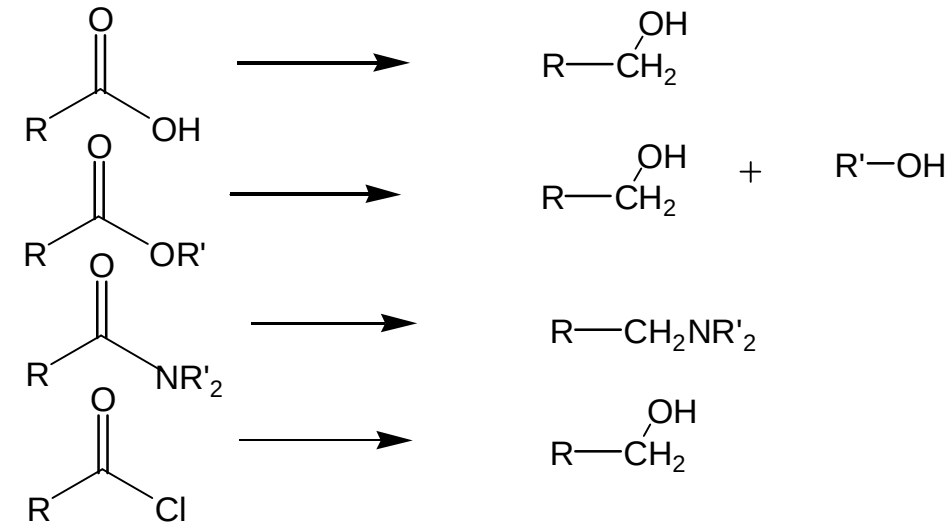


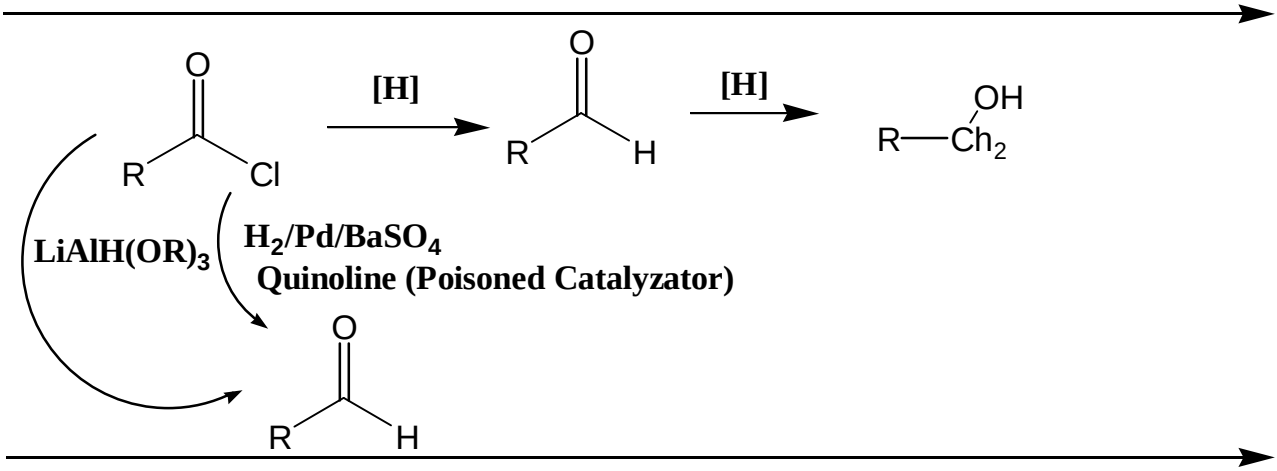
Acid Derivatives

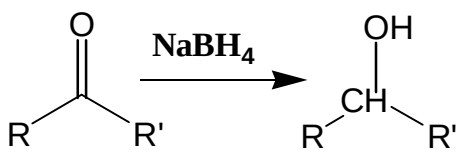


Reduction of Acid Derivatives

LAH



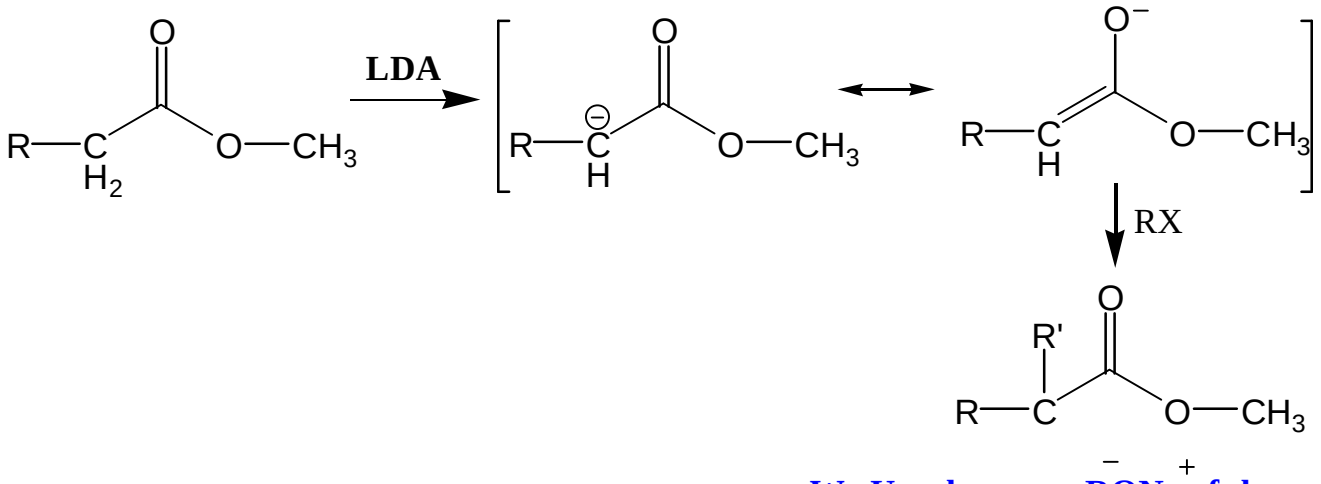




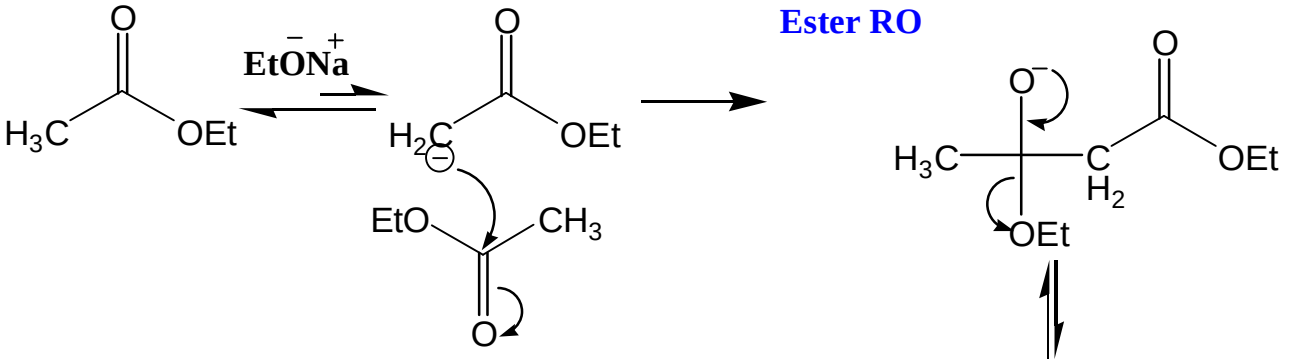
$LiAlH_4$ > $LiBH_4$ > $NaBH_4$ > $LiAlH(OR)_3$

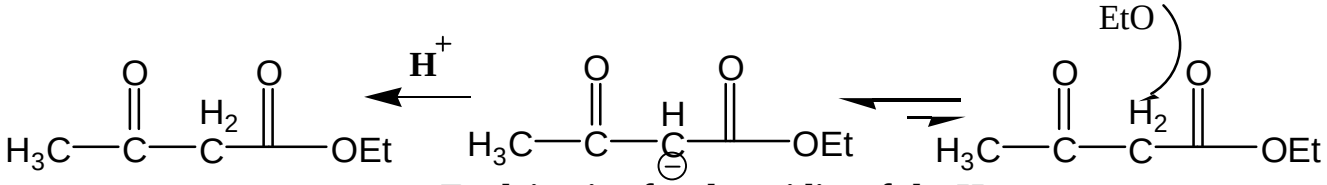
All N=C → HN-CH | Esters, Ketones, Aldehydes | Ketones, Aldehydes, Not Acids | Acyl Halides

Alkyl Insert to Ester Alfa Carbon - Claisen Condensation

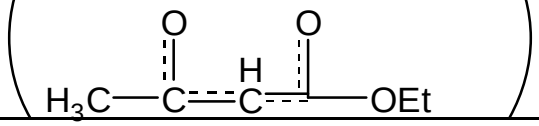


We Use the same RONa of the Ester RO

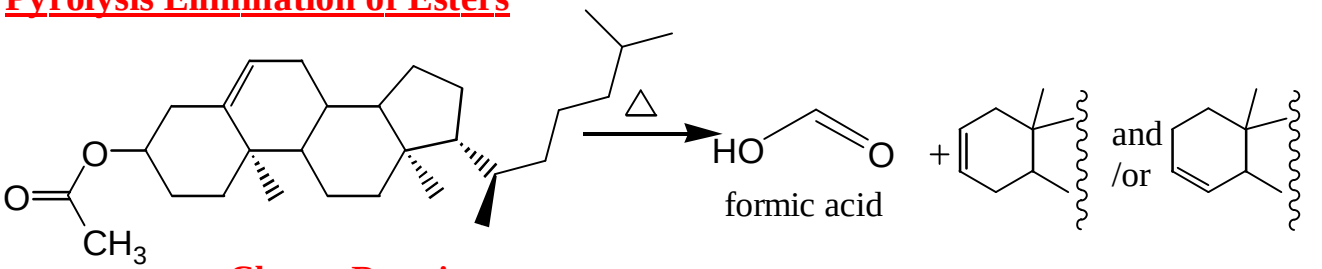




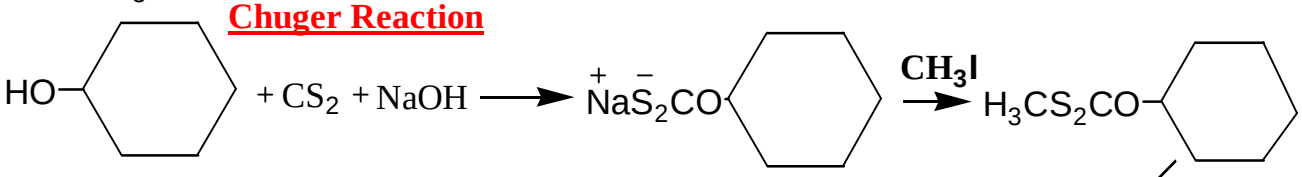
Explanation for the acidity of the H



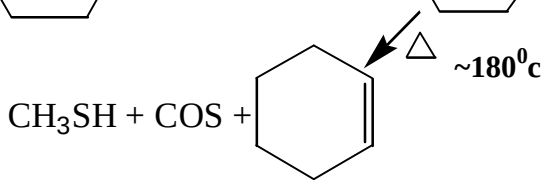
Pyrolysis Elimination of Esters



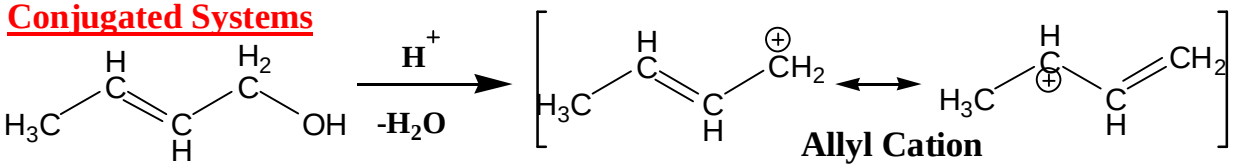
Chuger Reaction

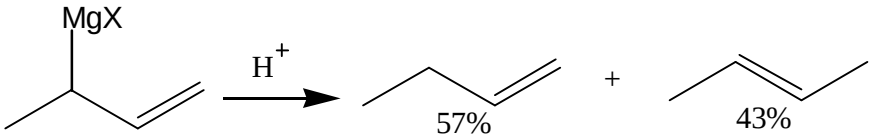


cyclohexanol



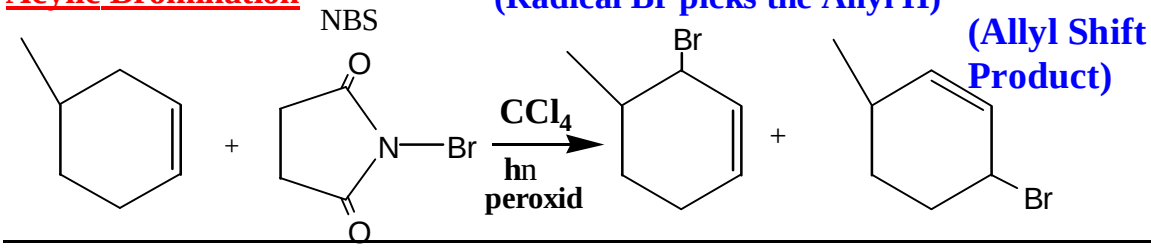
Conjugated Systems





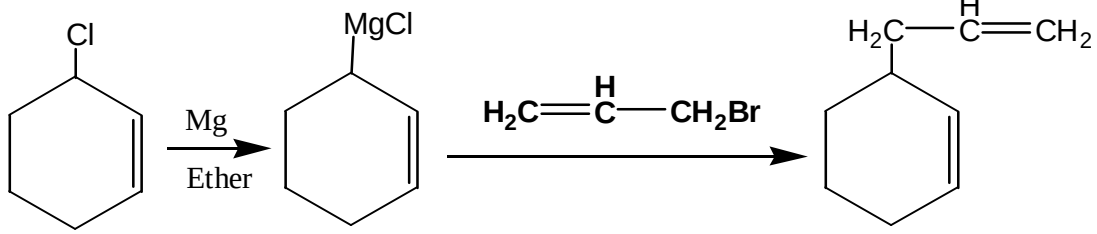
Acylic Bromination

(Radical Br picks the Allyl H)

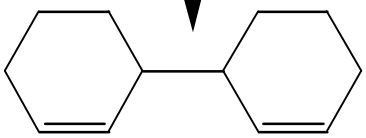


Grignard Reagent + Conjugated

1)

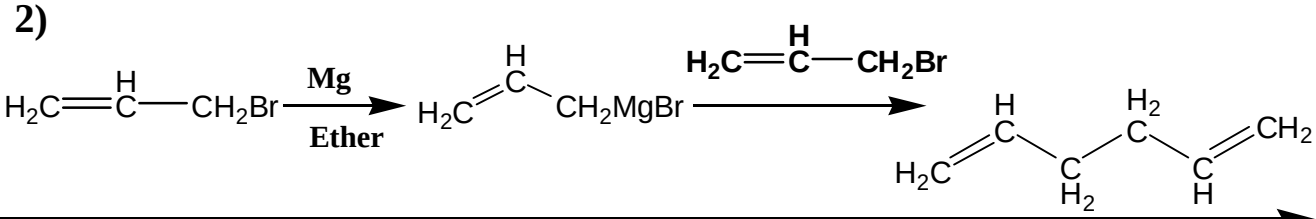


Attacks Itself

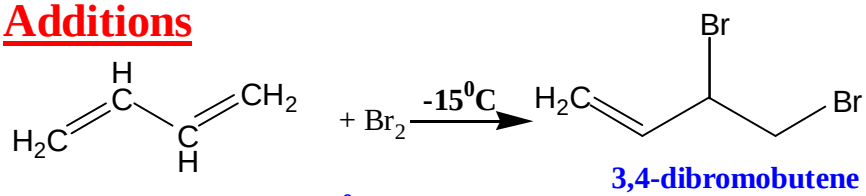


In Order to prevent this - Take low Concentration Of the Allyl

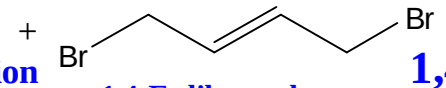
2)



Additions

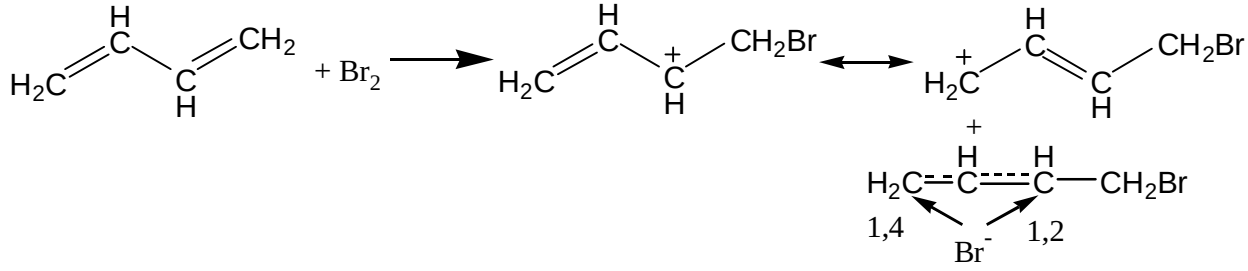


If the reaction is in 60⁰c there are 10% 1,2 addition and 90% 1,4 addition

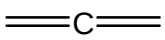


1,4 Addition 54%

1,4-E-dibromobutene



Allenes

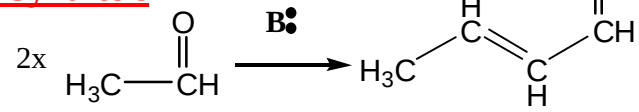


N - No. Of C atoms
Even - A-Chiral (2N)
Odd - Chiral (2N+1)

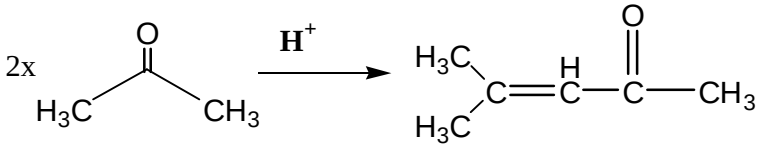
(Just A Possibility)

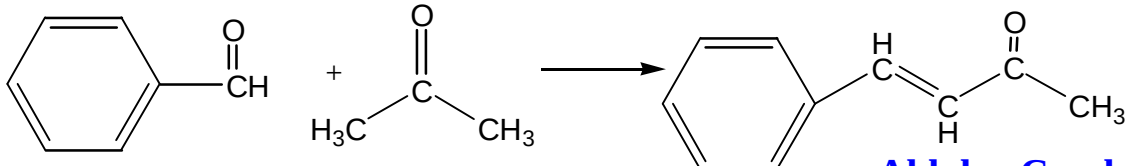
Conjugated sytems with Carbonyls

A) Synthesis

1) 

Aldolyc Condensation

2) 

3) 

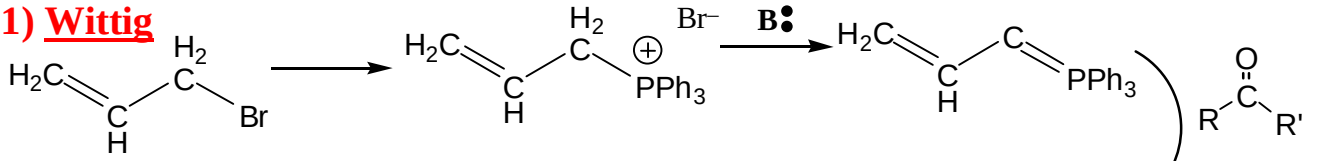
Aldolyc Condensation

4) 

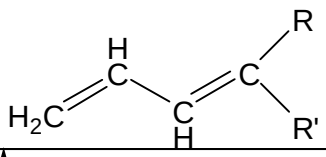
MnO_2 Only Oxydates Allyl Alcohols

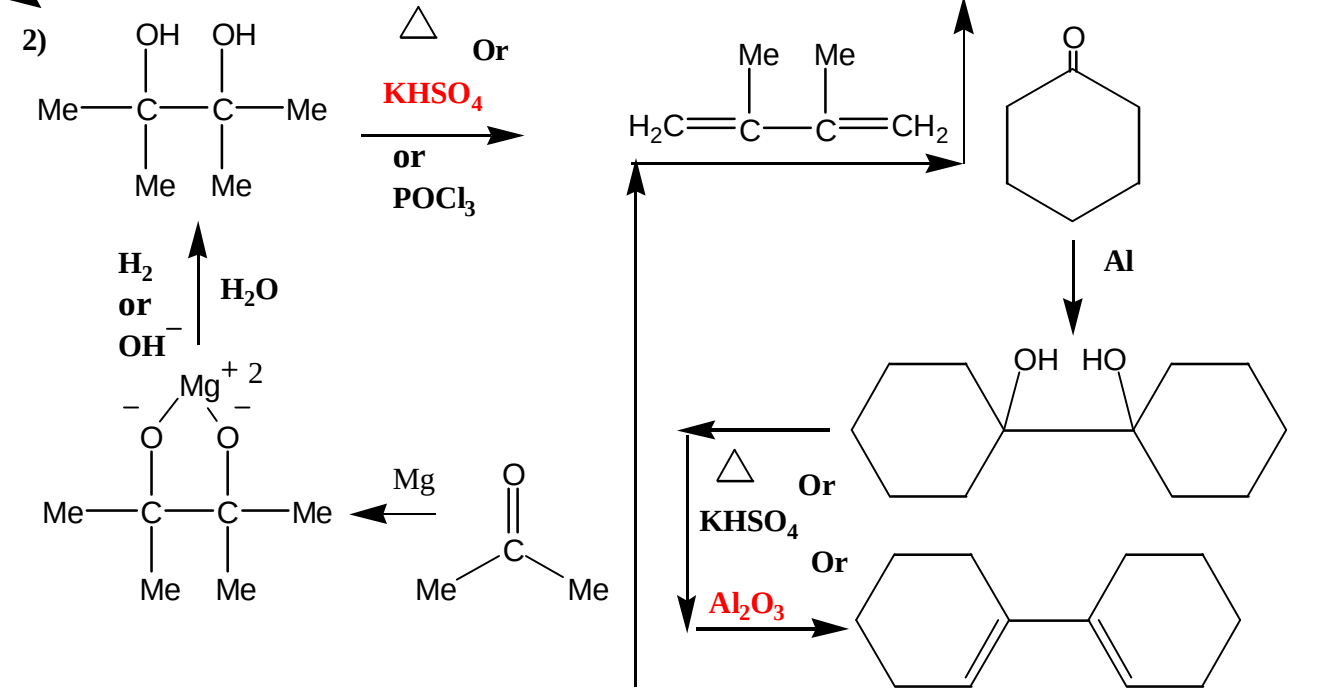
Synthesis Of Dienes

1) Wittig



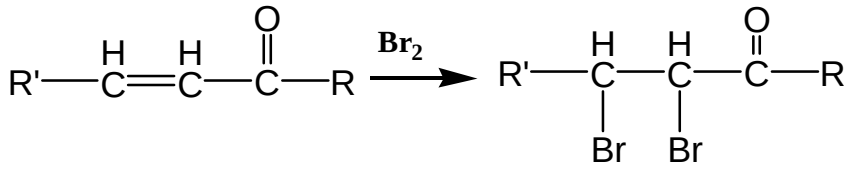
Synthesis from Alekne with Halide



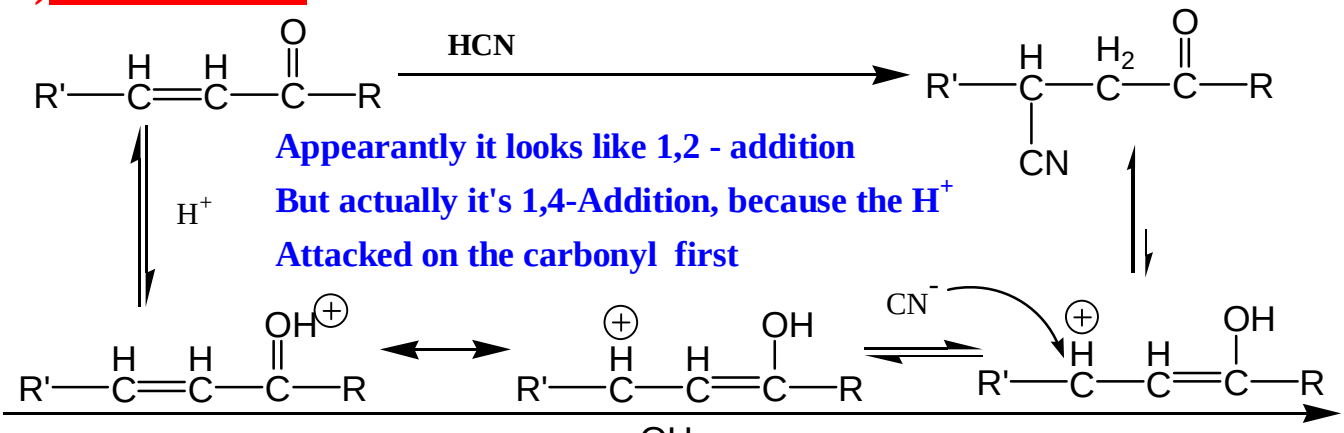
2) 

Reactions with conjugated Carbonyl

1) 1,2-Addition



2) 1,4-Addition

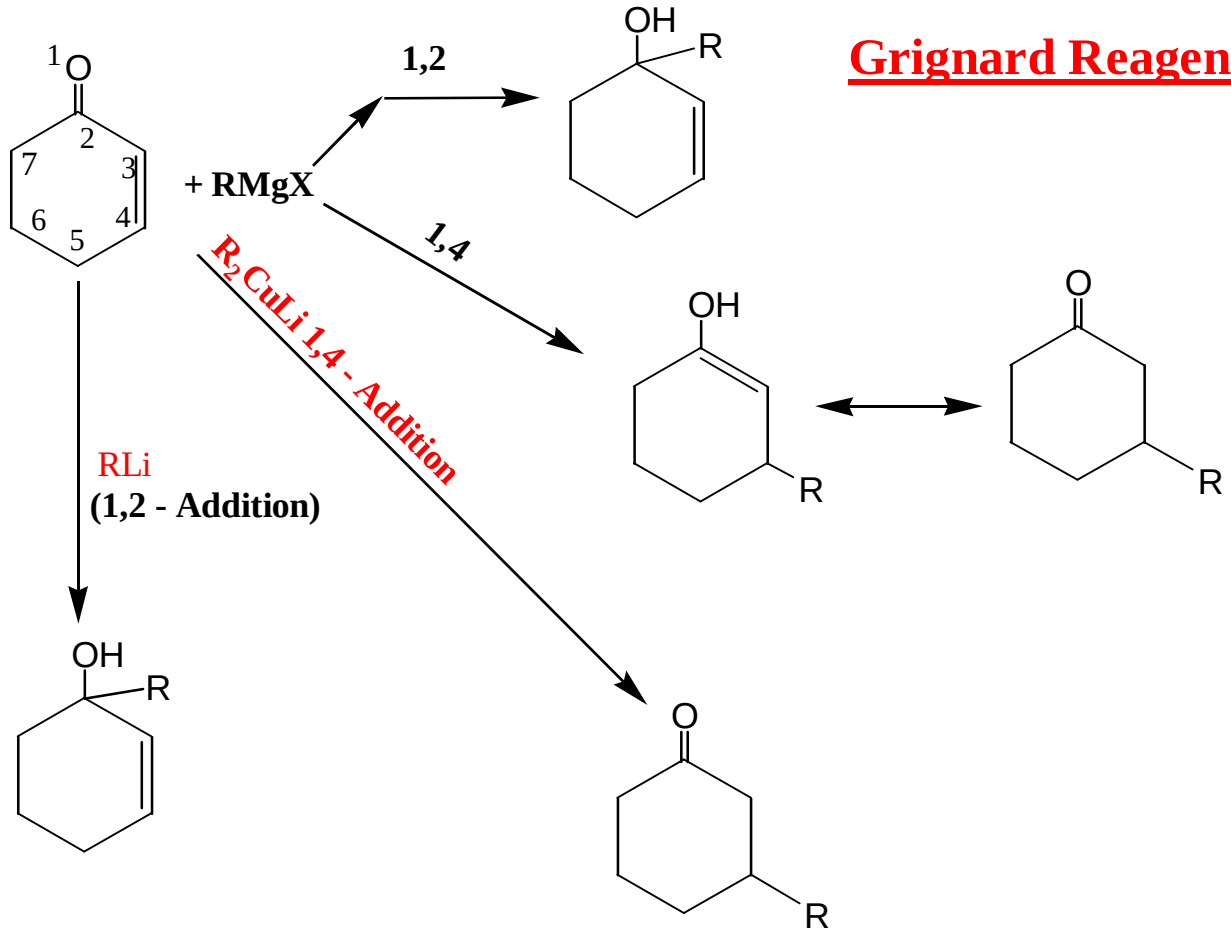


Appearantly it looks like 1,2 - addition

But actually it's 1,4-Addition, because the H^+

Attacked on the carbonyl first

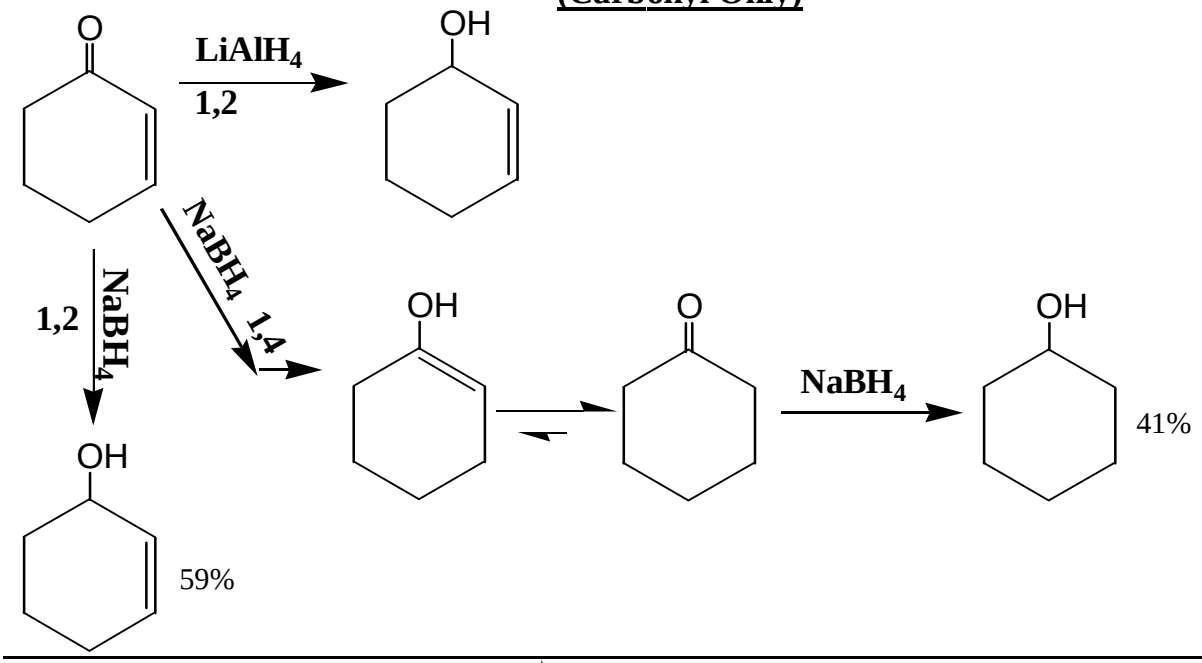
Grignard Reagent



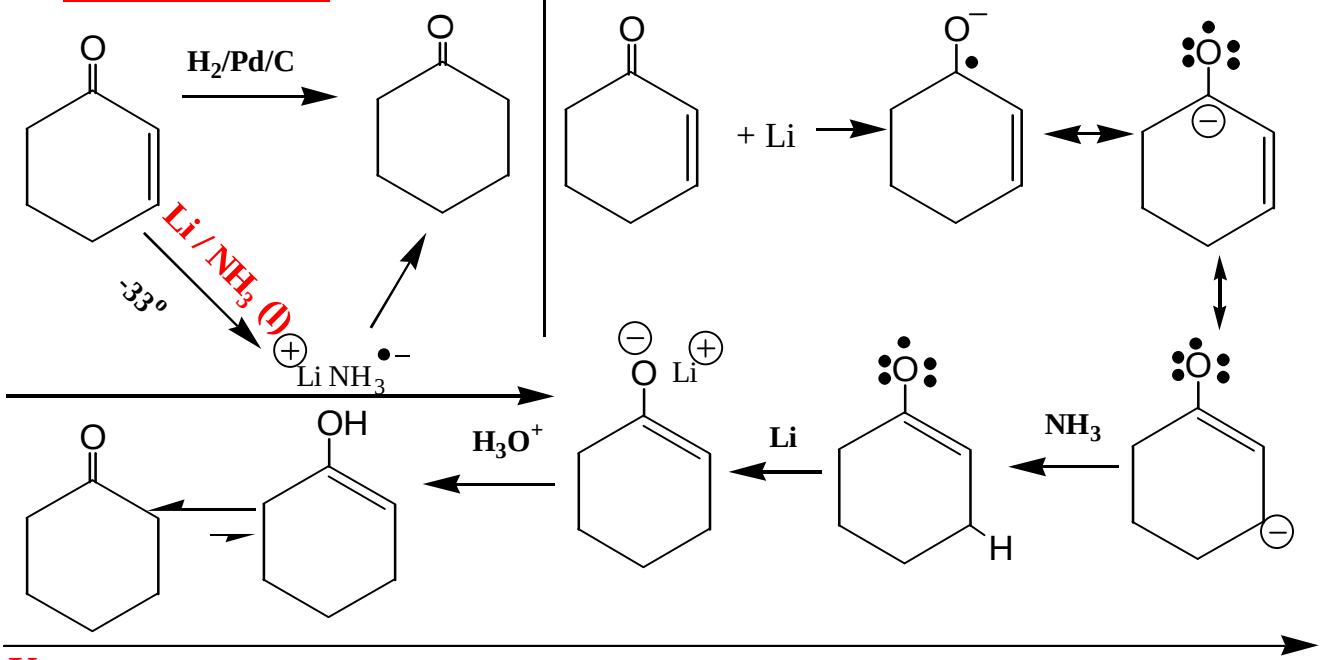
It seems like ordinary 1,2-addition to double bond but it's a delicate reduction reagant for carbonyl conjugated sytems

Reduction ("Hizur")

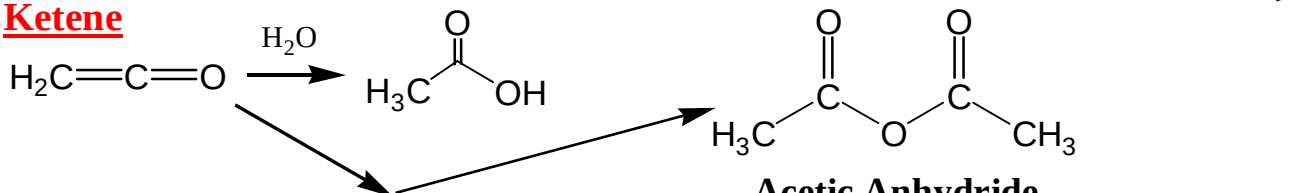
(Carbonyl Only)

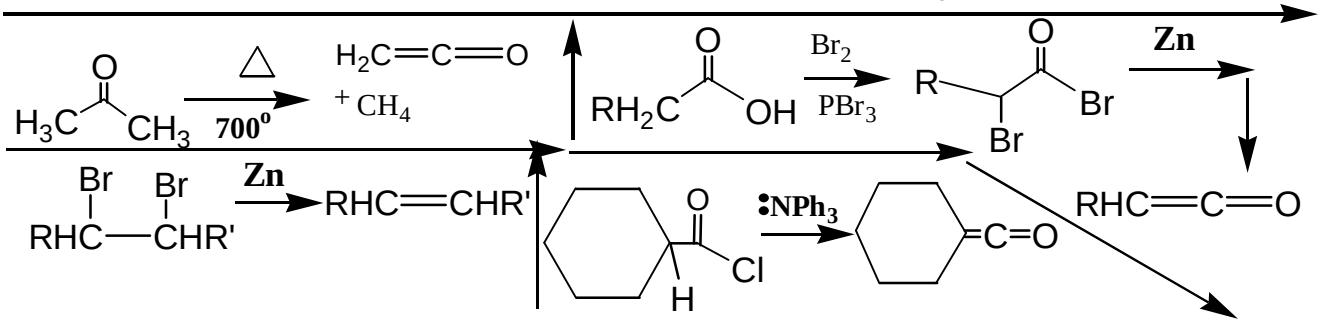


Birch Reduction



Ketene

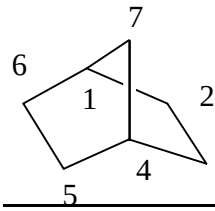




4+2 Cyclo-Addition - Diels Alder

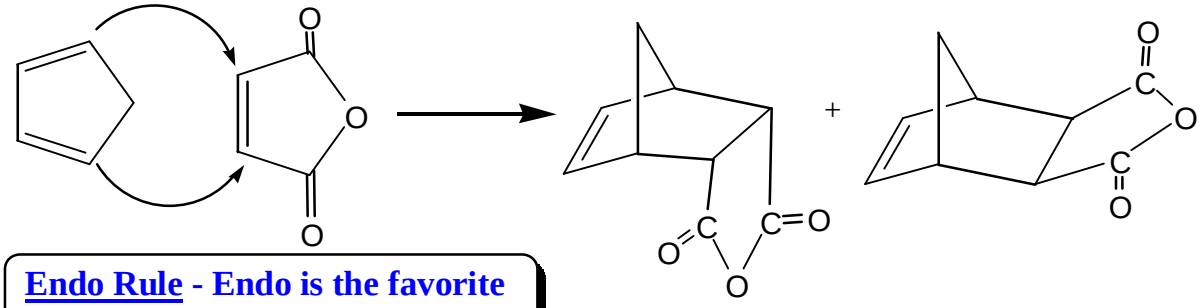
Note: The reactions are at the same time and threfore Streo-specific - Cis And Trans will be preserved - It's named Cis Addition Or Syn Addition

Nomenclature of Bicyclic Molecules



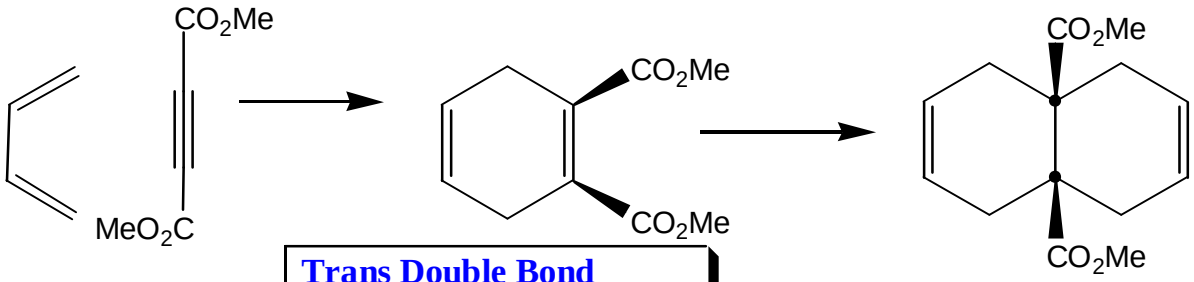
Bicyclo[2.2.1]heptane

Count the number of Carbon atoms to the lefr,right and above the "Bridge" Carbon (No. 1) until the next "Bridge" Carbon (No. 4). e.g. the Number 1 in the name is for the carbon above (No. 7)

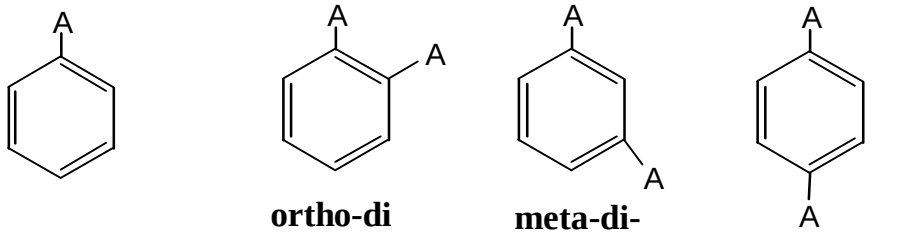


-endo **-exo**

Endo Rule - Endo is the favorite Isomer and in low Temp. we'll get only Endo

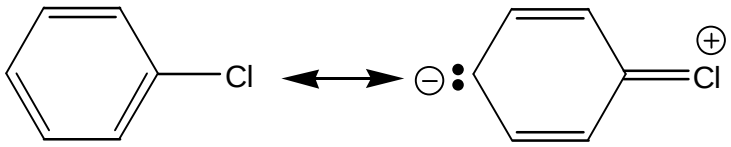


Trans Double Bond in a cyclic molecule causes High cyclic Strain



ortho-di **meta-di-** **Para-di-**

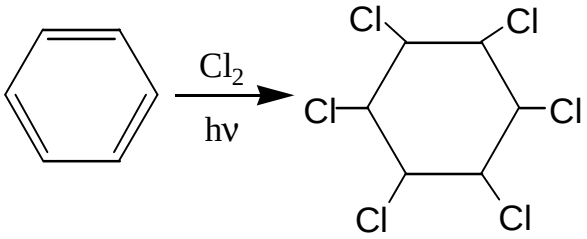
By adding 1 more functional group (to ortho para or meta isomeres) we can identify which isomere we had according to the number of new isomeres: Ortho - 2(A_3) , meta -3(A_3) and para - 1(A_3).

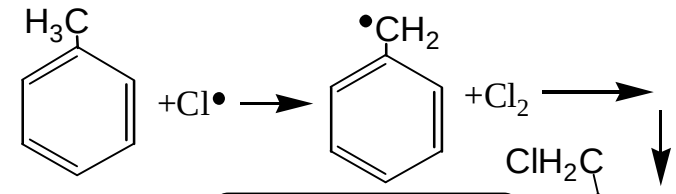


This isomere conributes to the **Moment Dipole** of the molecule

Reactions with Aromatic systems

Radical Reacions



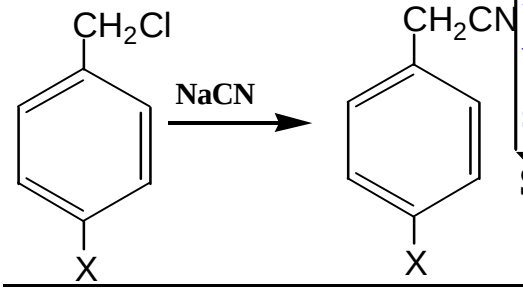


$Cl_2 \overset{h\nu}{\rightleftharpoons} 2Cl^{\bullet}$

attacking the methyl doesn't damage the aromaticity.

There is a resonance of the radical all over the aromatic cycle

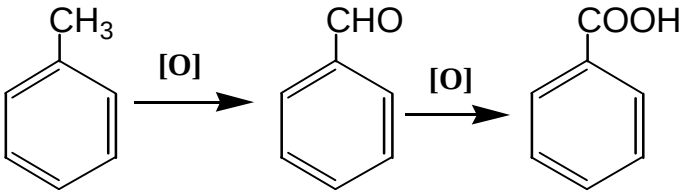
Nucleophilic Substitution



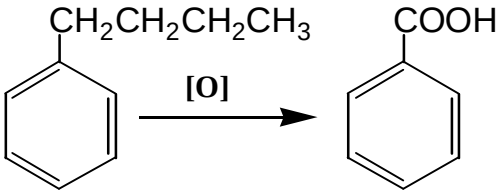
It appears that the reaction is S_N1 and not S_N2. the reason is that **Benzylic Carbocation** is very stable - Even more than 3^o Carbocation.

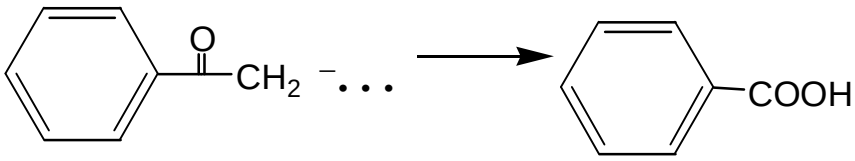
S_N1

Oxydation Reactions

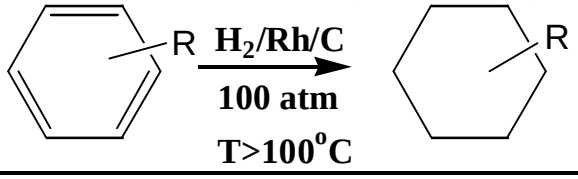


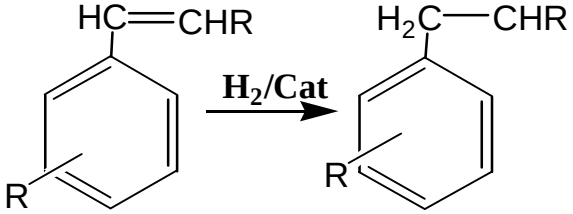
[O] = CrO_3





Reduction Reactions ("Hizur") (Part 1)

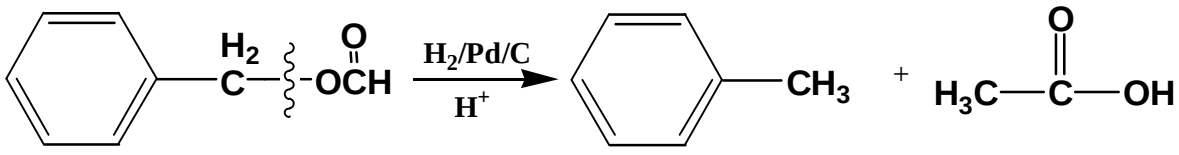




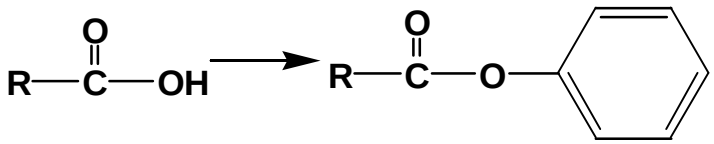
Note: Without the rough conditions of temp. and pressure, the aromatic cycle isn't Reduced as it was in the example above

Reduction Reactions of Aromatic Systems (Part 2)

Hydrogenolysis

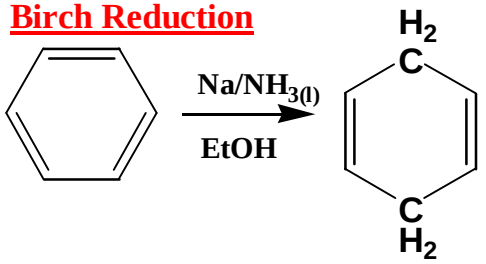


toluene

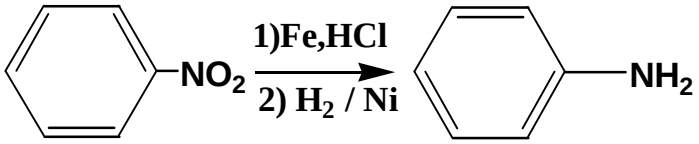


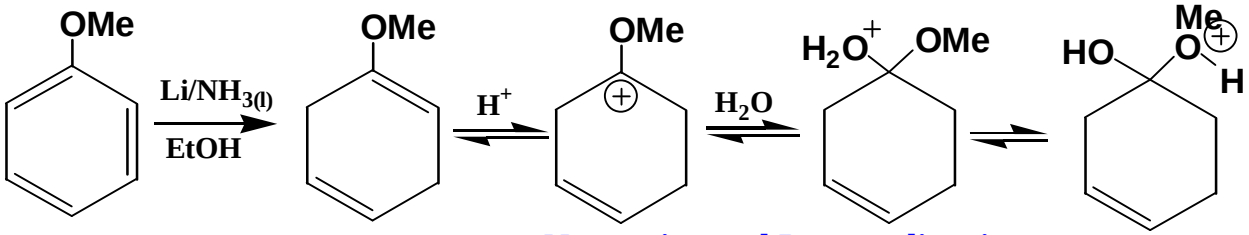
In Order to protect the Carboxyl Group we create a Benzylic Ester that we can Remove by simple hydrogenolysis that doesn't require any tough conditions

Birch Reduction

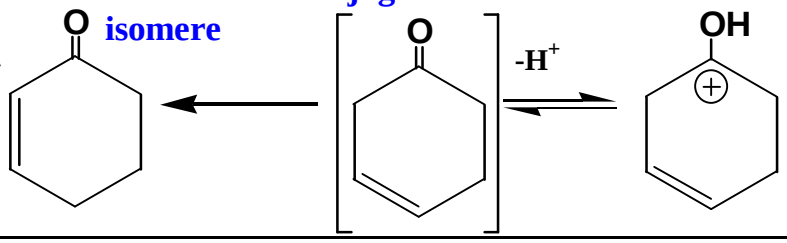


De-Aromatization

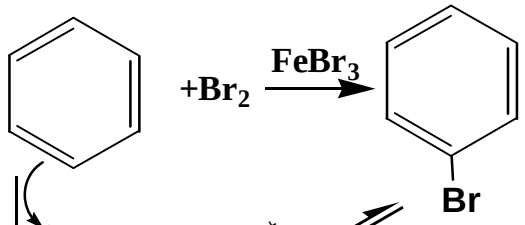


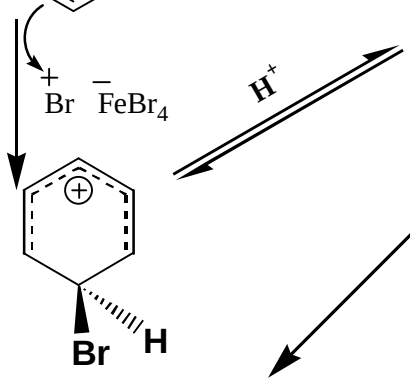


Not conjugated Intermediate is less stable and therefore it's turned intoa conjugated isomere

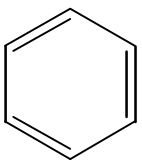


Benzene Reactions Part 1 Halidation

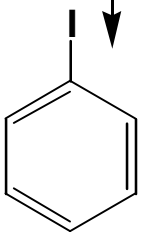




+HBr

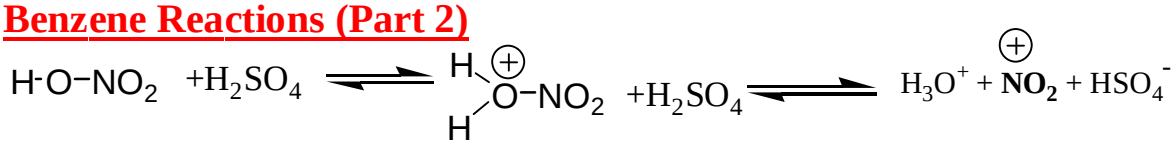


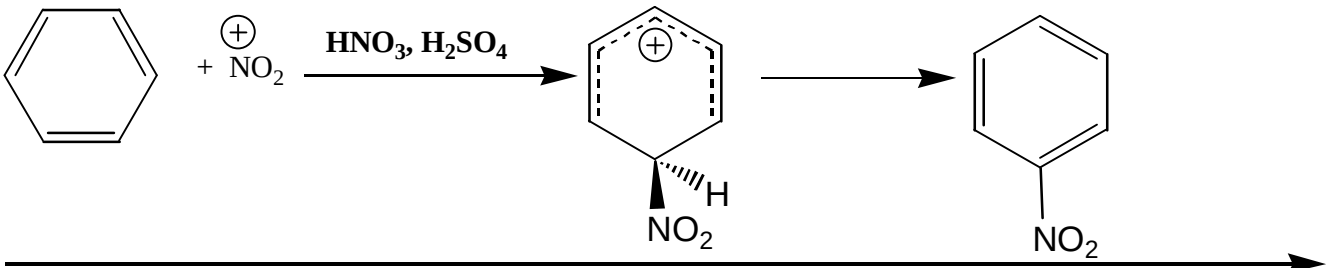
+ I_2 +HNO_3



+NO + NO_2+ HI

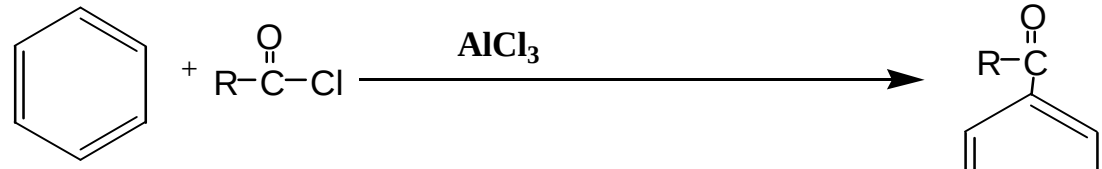
Benzene Reactions (Part 2)

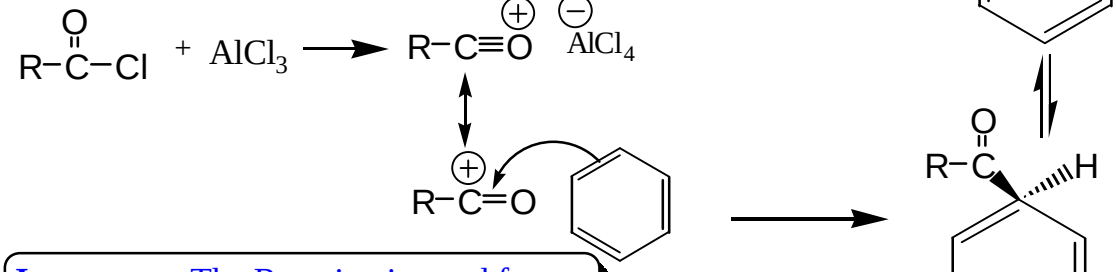




Friedel - Crafts Reactions

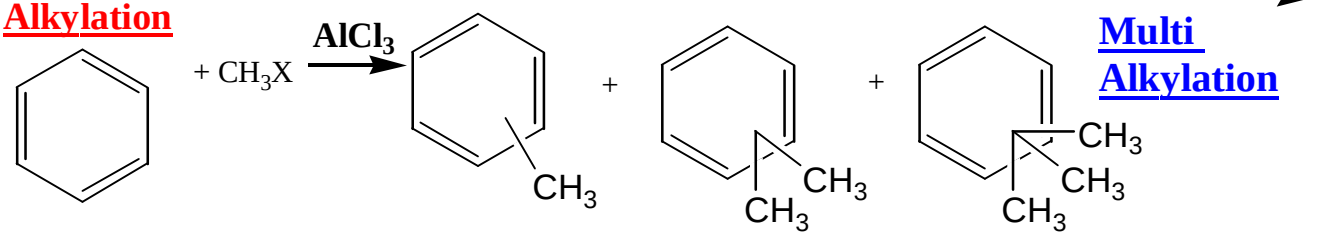
Acylation





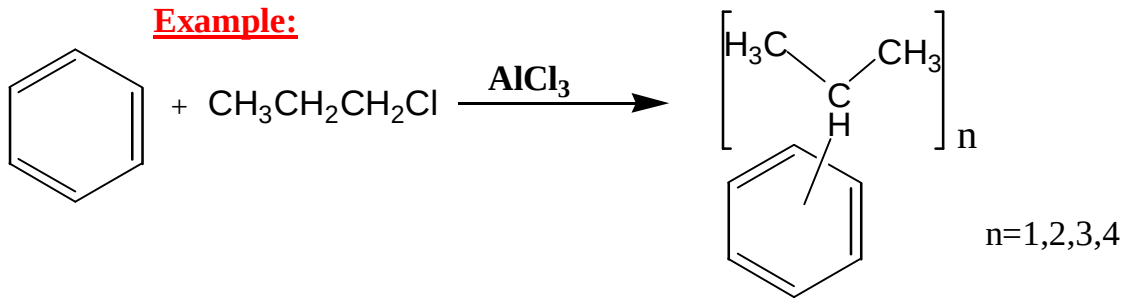
Important: The Reaction is good for Benzene without any Functional groups Or one that don't De-Activate it (See effects of functional groups on Benzene)

Alkylation

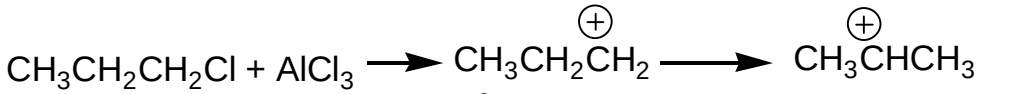


Multi Alkylation

Example:

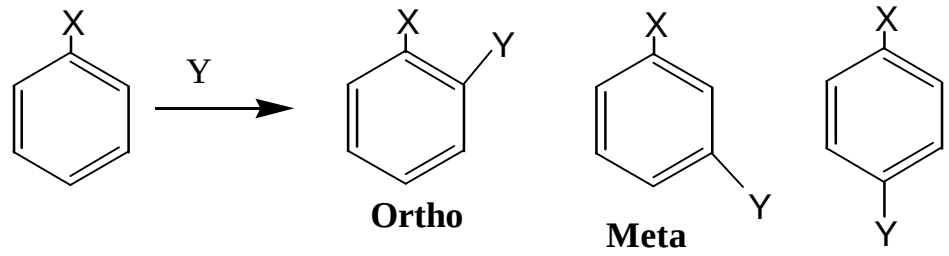


n=1,2,3,4



1° Carbocation **2° Carbocation**

Multiple Electrophilic Aromatic Reactions



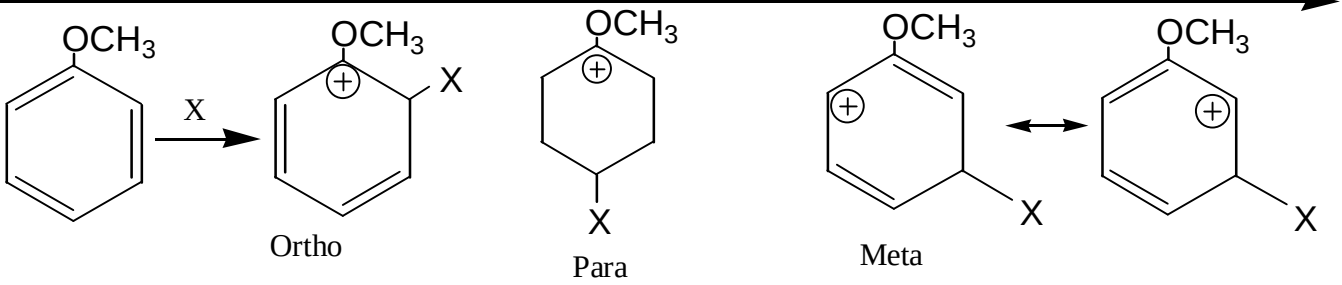
X:

Meta $-NO_2$, $-\overset{O}{\overset{\|}{C}}-R$, $-\overset{O}{\overset{\|}{C}}-OR$, $-\overset{O}{\overset{\|}{C}}-NR$, $-\overset{O}{\overset{\|}{C}}-OH$, CN, CF_3 $\Longrightarrow$ **De-Activation**

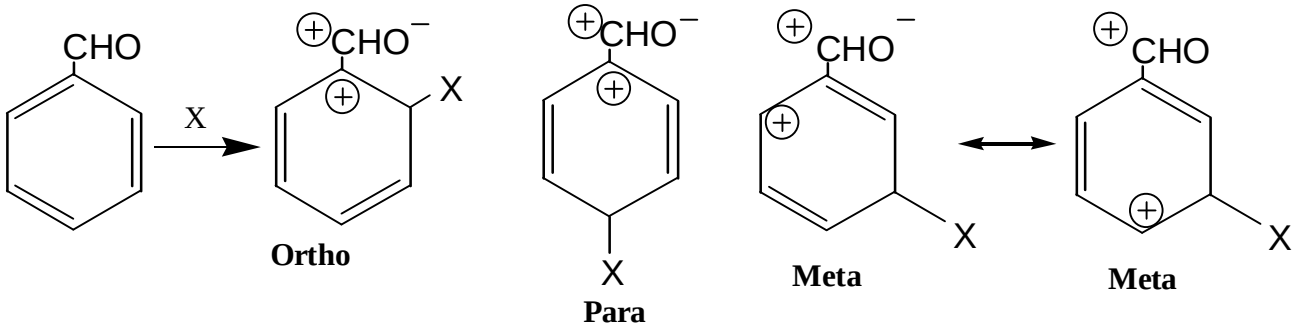
Ortho, Para $R-\overset{O}{\overset{\|}{C}}-O-$, $R-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-$, NH_2, $-OR$, $-R$ $\Longrightarrow$ **Activation**

Hallogenes $\Longrightarrow$ **Activation (Weak)**

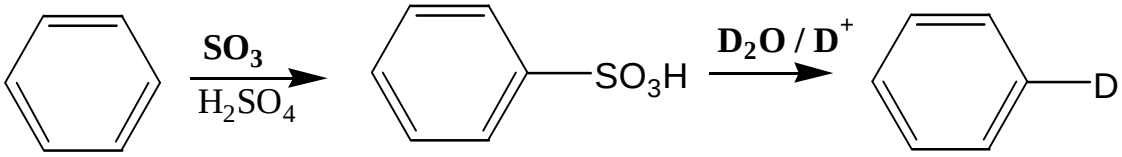
Note: For 3rd Subtitution - If one of the 2 functional groups leads strongly to o,p we'll get o,p ,Otherwise We'll get a mixture of Products

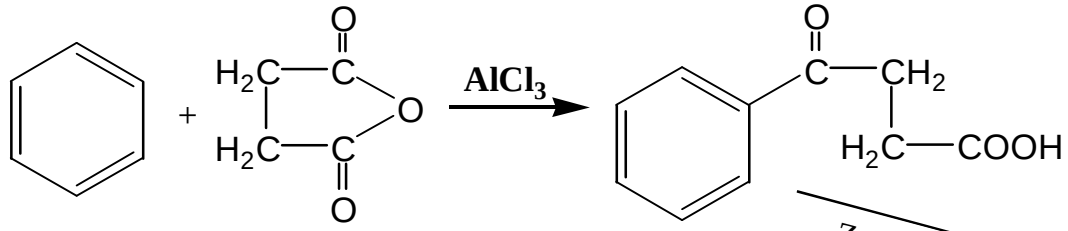


The Resonance of the + charge can give a form with the + on the carbon attached to the Electron Drawing group and stabilizes it. This can't happen on the Meta isomere and therefore Para and Ortho are the favorite isomere.
The **Activation** is resolved by the Electron Donation to the Aromatic system.

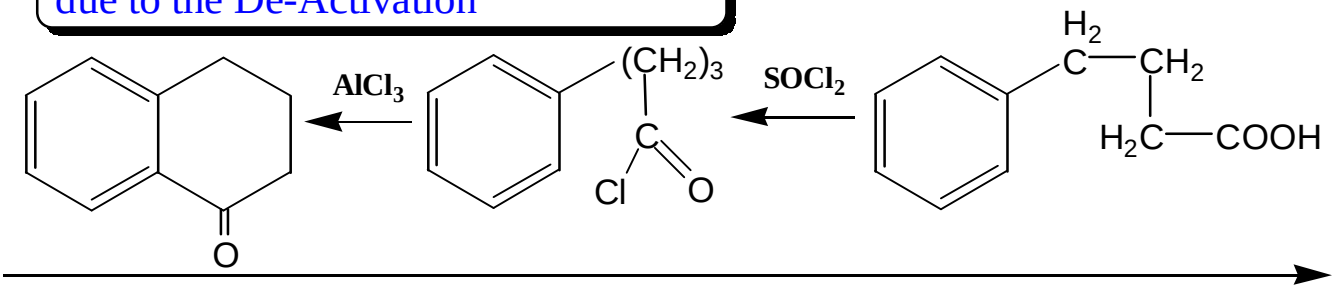


The + charge will never be on the Electron Donating group in Meta Isomere, but on Ortho and Para Isomere it can be. Therefore it De-stabilizes these 2 isomeres and the Meta Isomere is the favorite one.
The **De-Activation** is resolved of the Electron drawing from the Aromatic system.





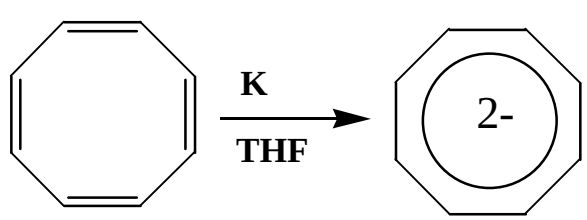
Note: Without the reduction of the Ketone, we wouldn't get thisReaction, due to the De-Activation



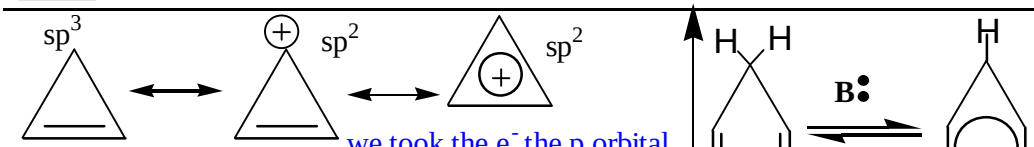
Aromaticity

Huckel Rule: Number of π Electrones: 4n+2 ⟹ **Aromaticity**

4n ⟹ **Anti-Aromatic**



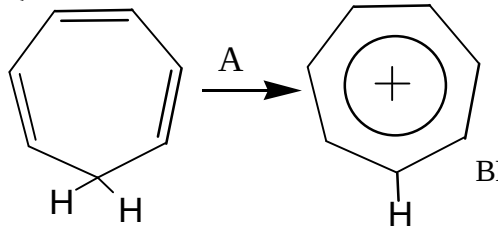
Aromaticity
(4n+2)



Aromaticity

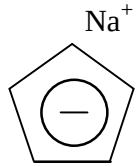
we took the e⁻ the p orbital is now empty for resonance

Aromaticity: $6e^-$
(4n+2)

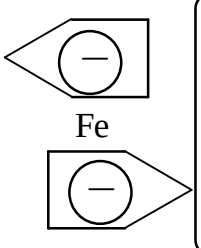


Aromaticity : $6e^-$
(4n+2)

A = HBF_4



$C_{10}H_{10}Fe$:

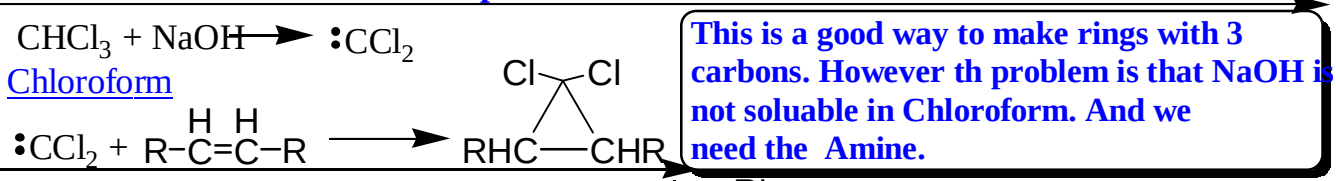


The p Electrones are shared with the Fe atom's empty orbitals (also possible with other Transition Metals such as Ni and Co

Amines

pKa

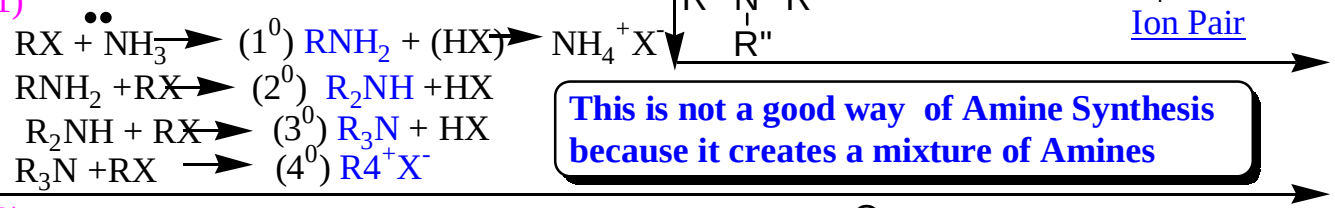
Electron drawing Functional groups such as NO_2,Cl,Br make the Amine to be Less Base and to have a lower pKa



This is a good way to make rings with 3 carbons. However th problem is that NaOH is not soluable in Chloroform. And we need the Amine.

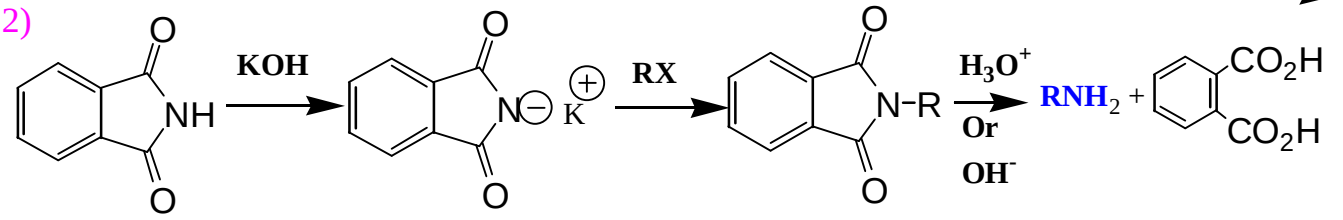
Synthesis Of Amines

1)



This is not a good way of Amine Synthesis because it creates a mixture of Amines

2)

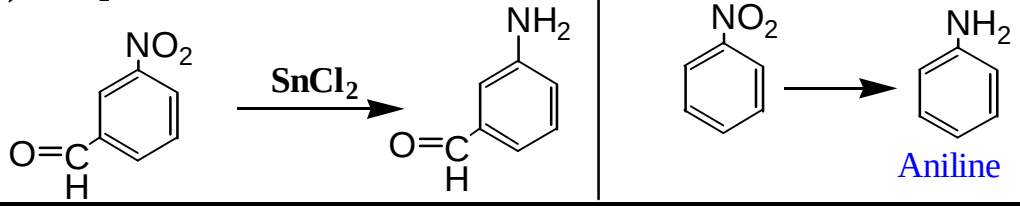


Phtalimide

Reduction

[H] = Fe/HCl , $SnCl_2$, H_2/Pd , H_2/Ni

A) $RNO_2 \xrightarrow{[H]} RNH_2$



B) $RC\equiv N \xrightarrow{[H]} RCH_2NH_2$ [H] = LAH , H_2/Cat

C) $RC(=O)-NH_2 \xrightarrow{[H]} RCH_2NH_2$

D) $RC(=NOH)-R' \xrightarrow{[H]} RC(NH_2)-R'$

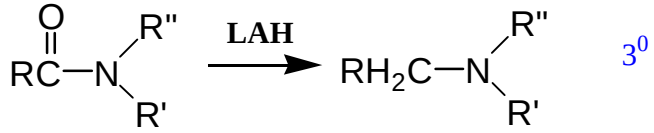
$R-CR'(=O) \xrightarrow{NH_2OH} RC(=NOH)-R'$

E) $R-CR'(=O) \xrightarrow{NH_3} R-CR'(=NH) \xrightarrow{[H]} R-CR'(NH_2)$ 1^0 [H] = H_2/Ni , LAH

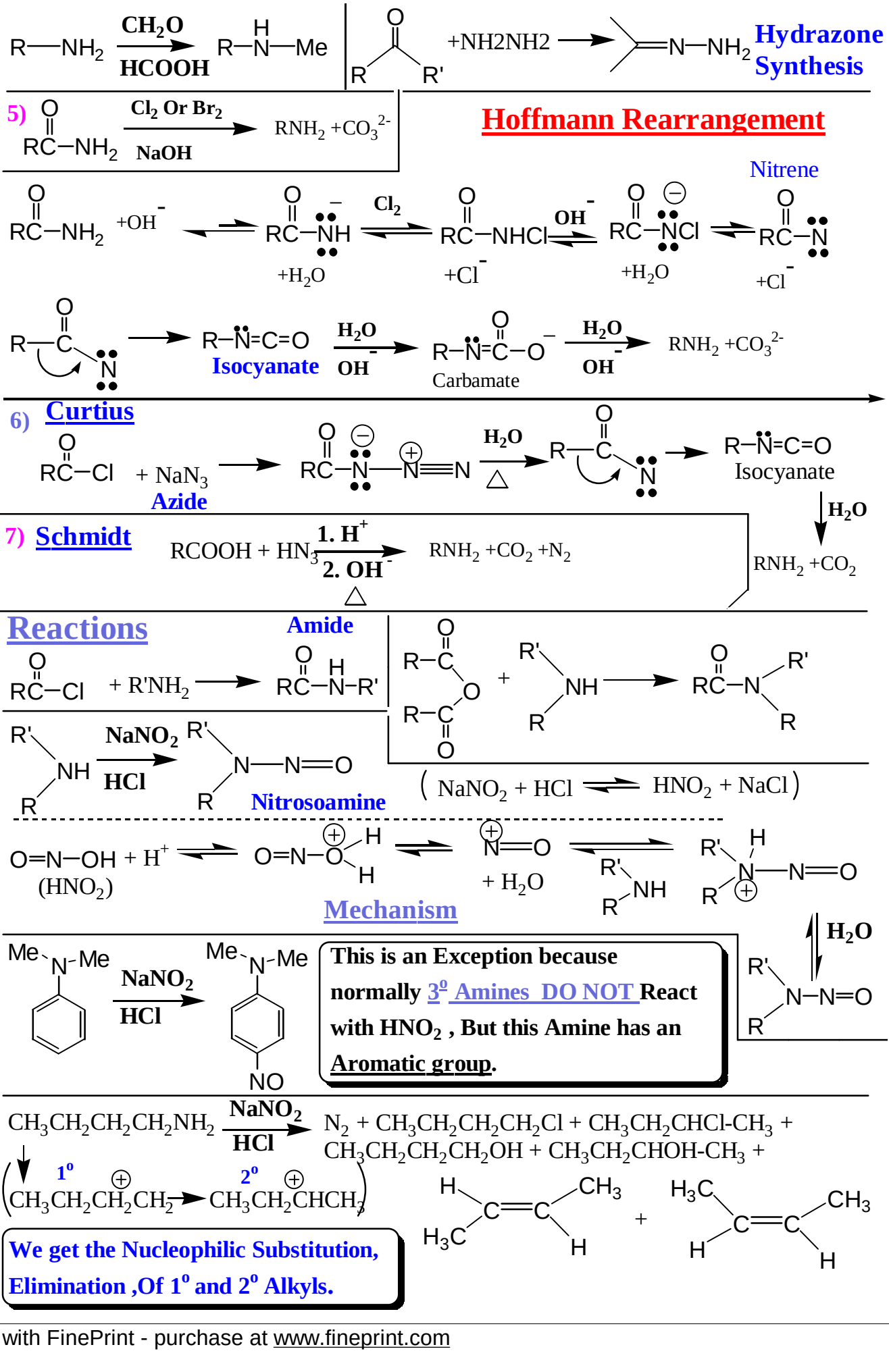
$R-CR'(=O) + R''NH_2 \rightleftharpoons R-CR'(=NR'') \xrightarrow{[H]} R-CR'(NHR'')$ 2^0

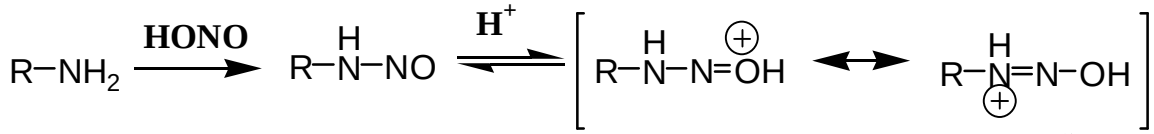
Schiff's Base

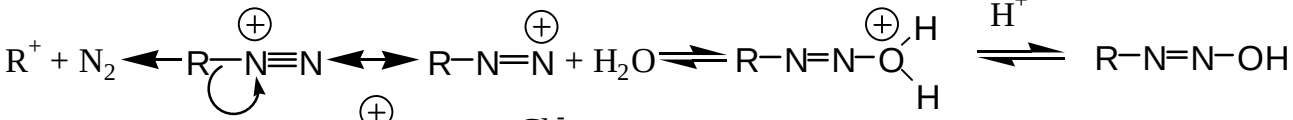
4) $RC(=O)-NHR' \xrightarrow{LAH} RCH_2NHR'$ 2^0

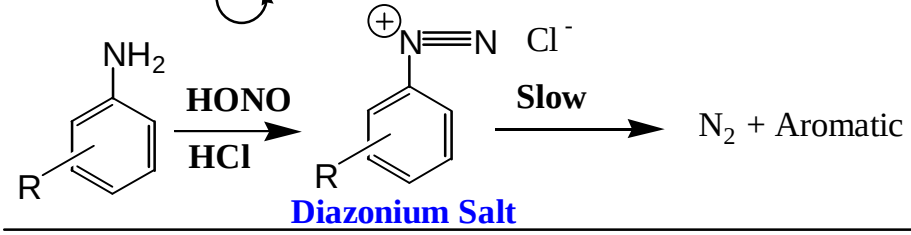


3^0



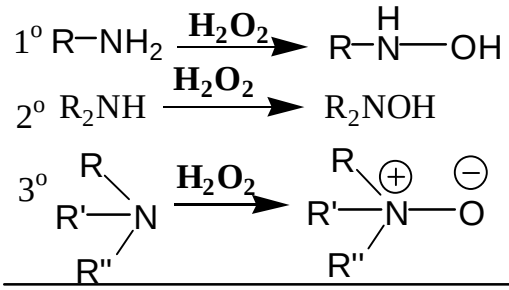


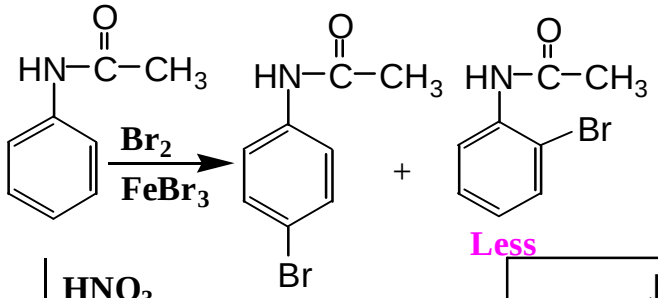


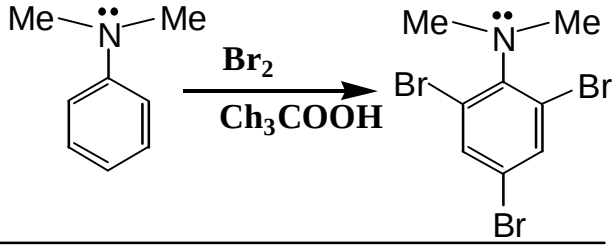


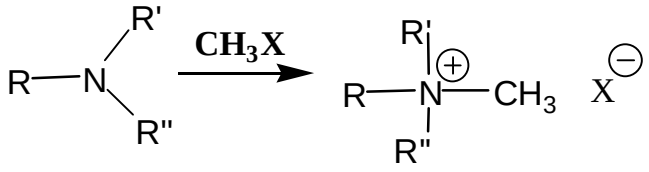
If the R Group of the Amine is Aromatic then the Diazonium Salt is stable

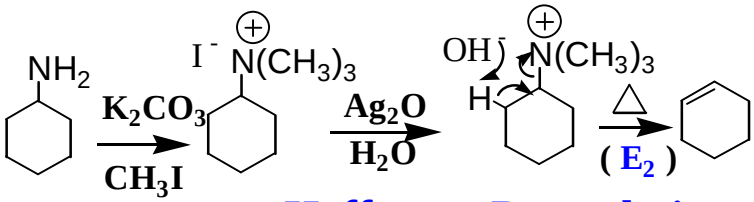
Oxidation Of Amines





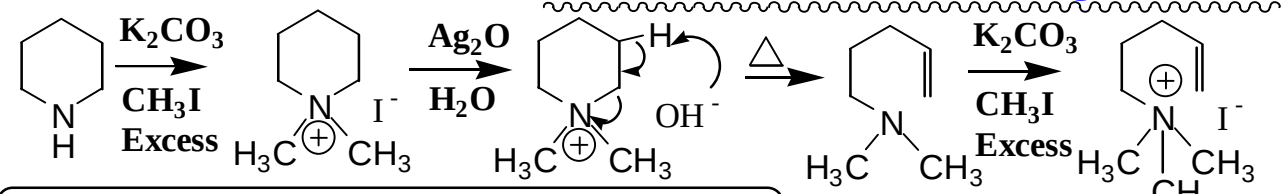




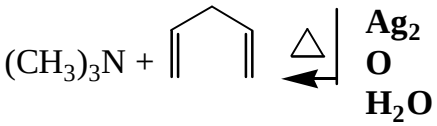


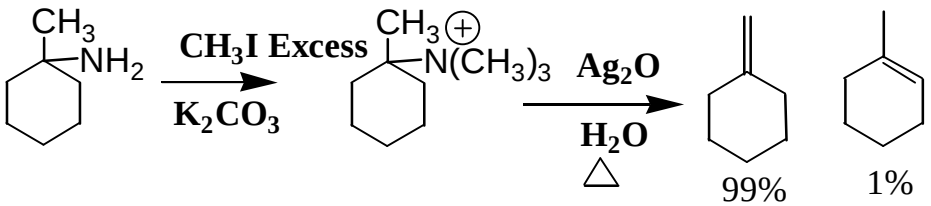
In case we have a Cyclic Amine:

Hoffmann Degradation



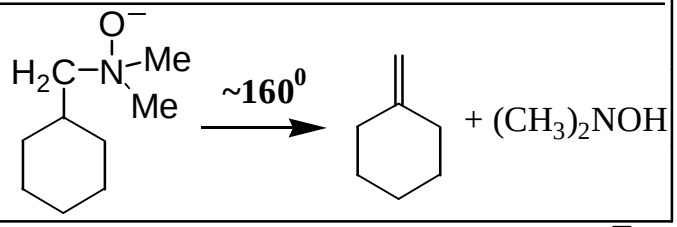
By the number of the double bonds after the degradation we can determine: 1 - Chain Amine, 2 -Cyclic Amine , 3 - Bicyclic Amine

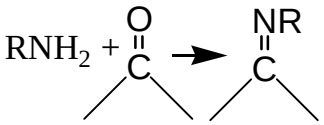




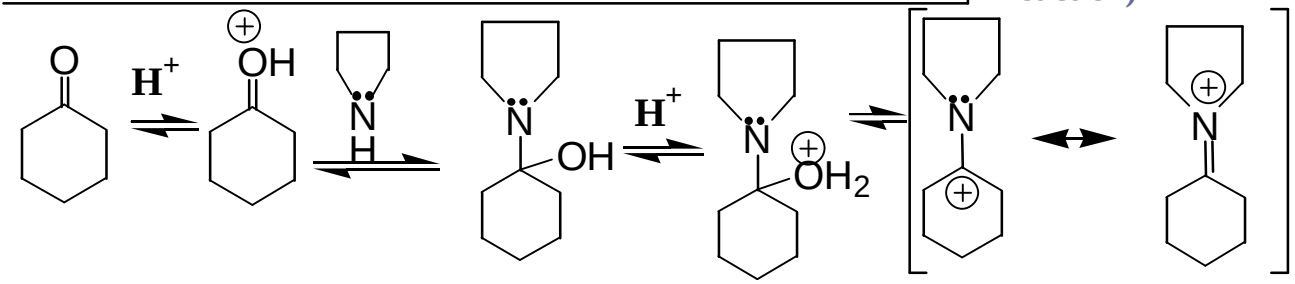
We get the **Anti-Zeizev Product**

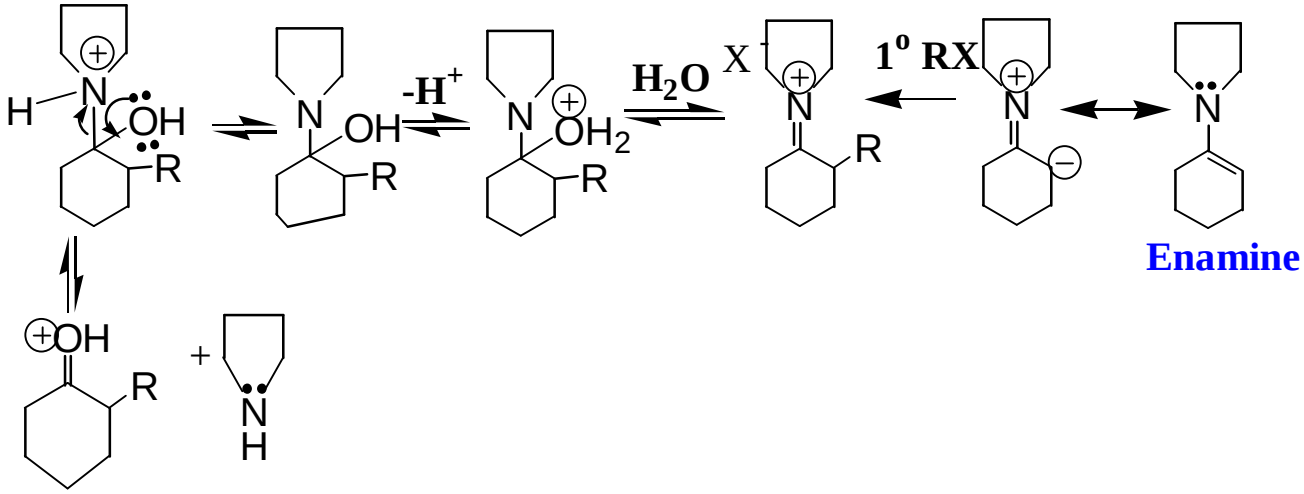
Cope Reaction





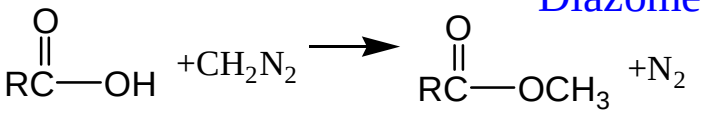
(For the following Reaction)

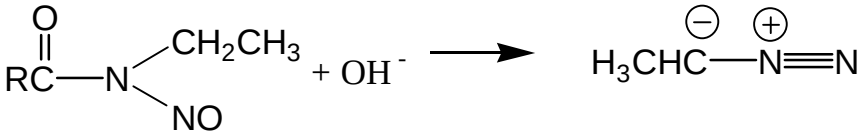


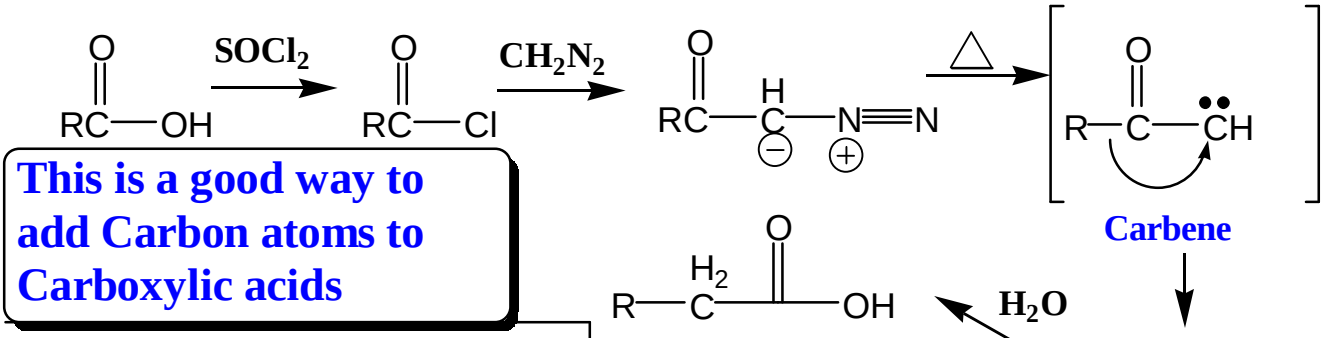


DiazoAlkanes Derivatives

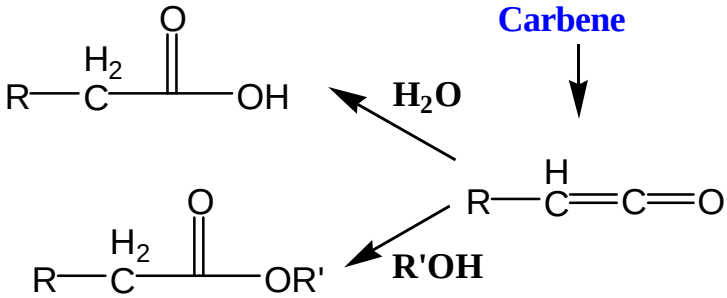
Diazomethane



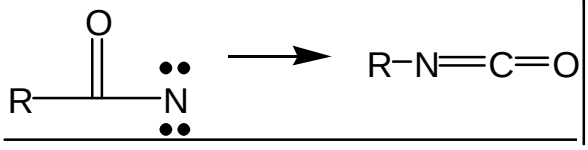


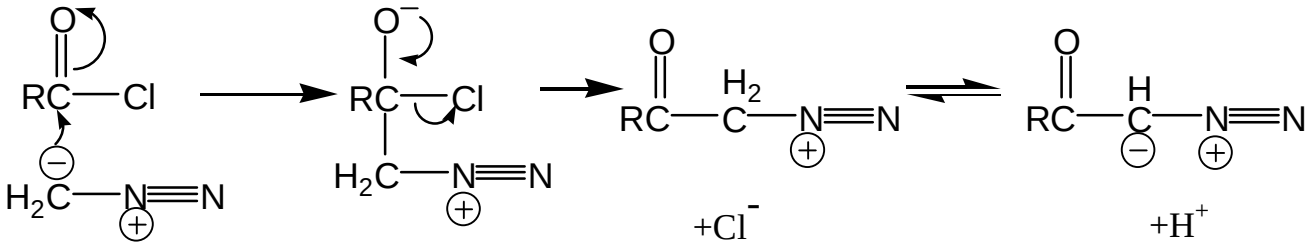


This is a good way to add Carbon atoms to Carboxylic acids

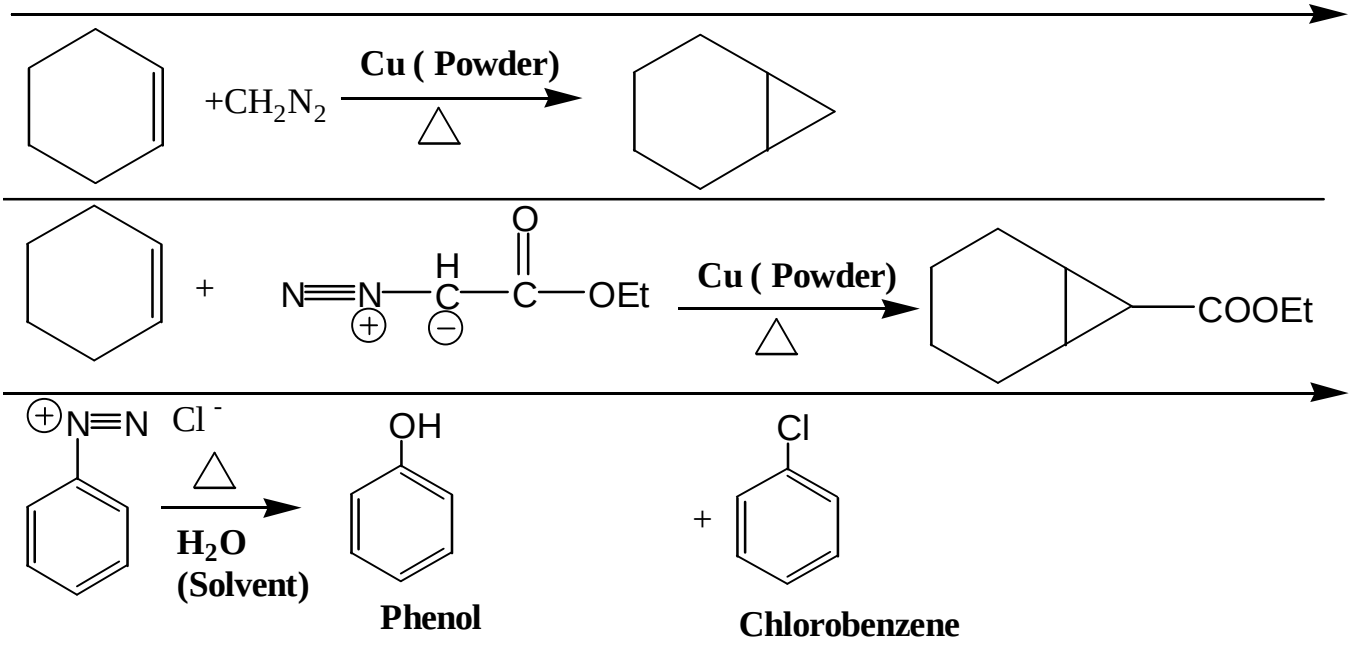


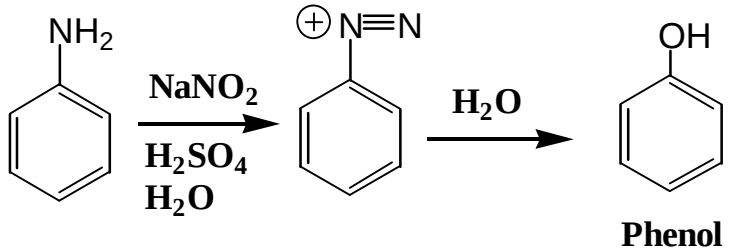
(Works in the same mechanism)





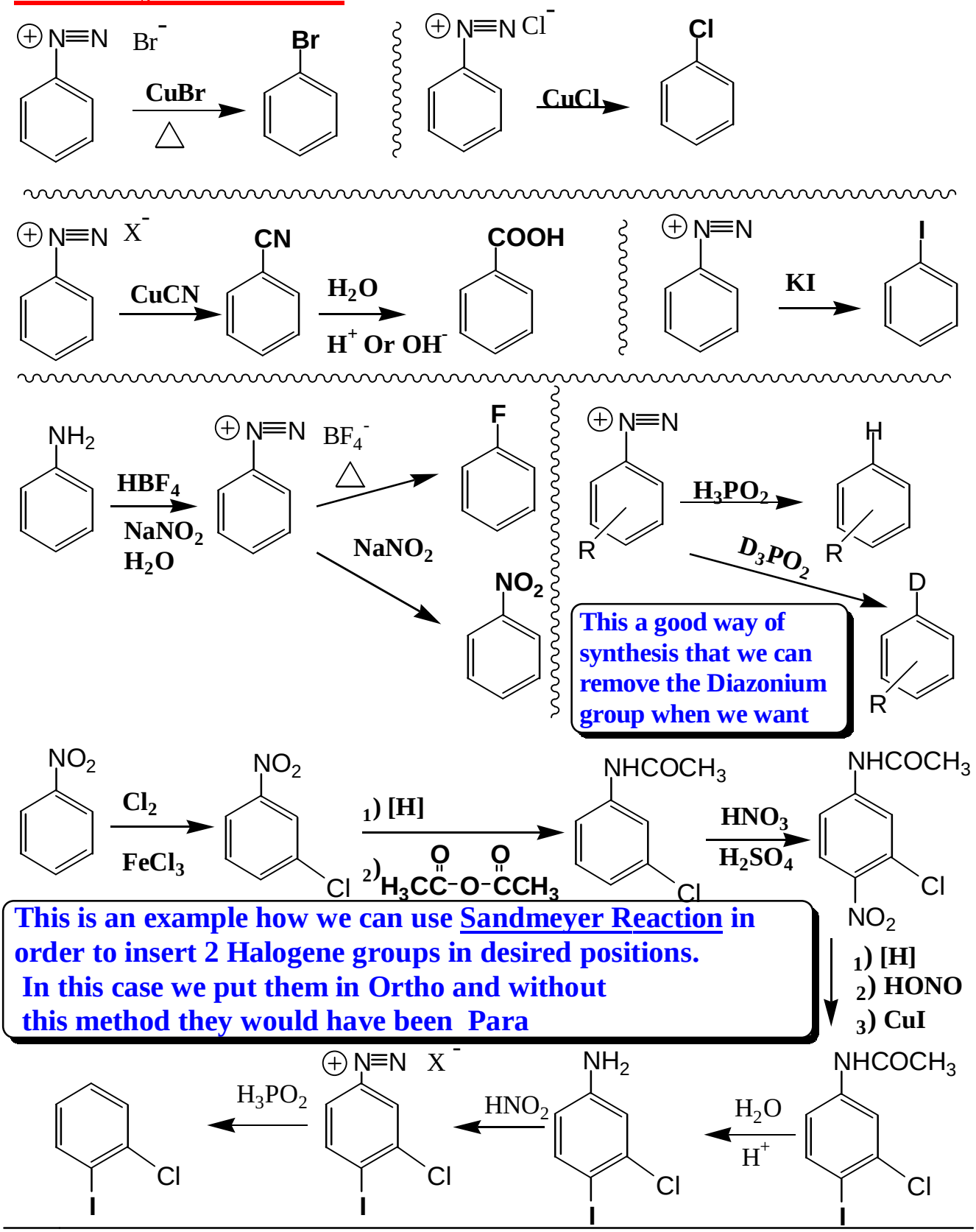
This is the mechanism of the Reaction above



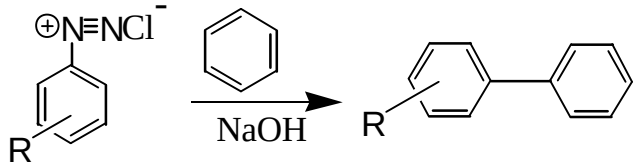


Synthesis of only the Phenol

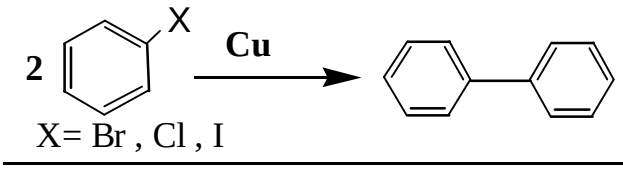
Sandmeyer Reaction



Biaryls - Synthesis

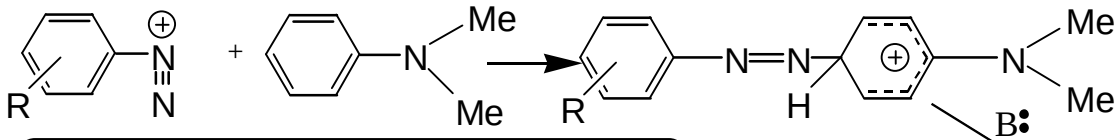


1) Gomberg - Bachman

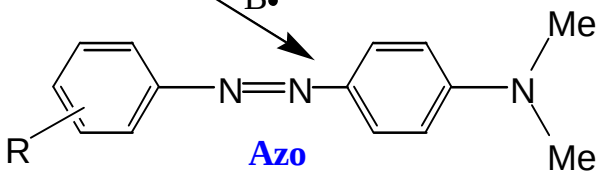


2) Ulmann

Electrone Drawing groups (like NO_2) or Simetric materials help this Reaction

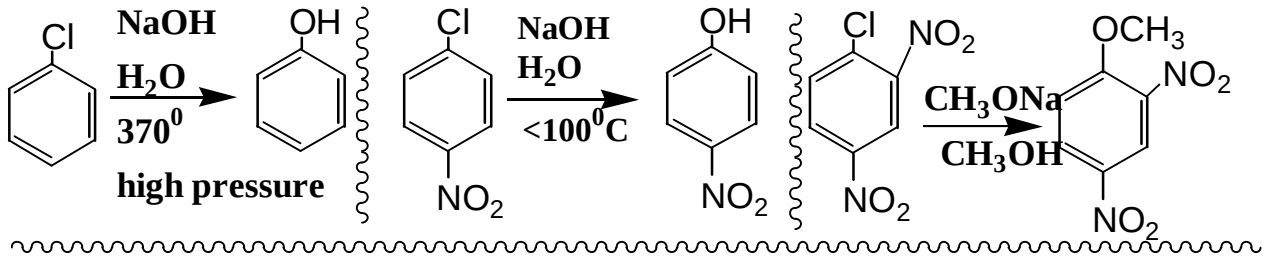


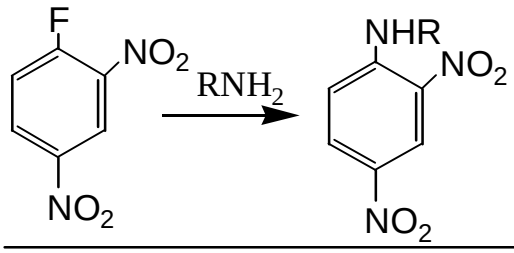
The Azo compounds are colorful and absorb UV light in wavelengths close to the Seen Light



Coupling Reactions

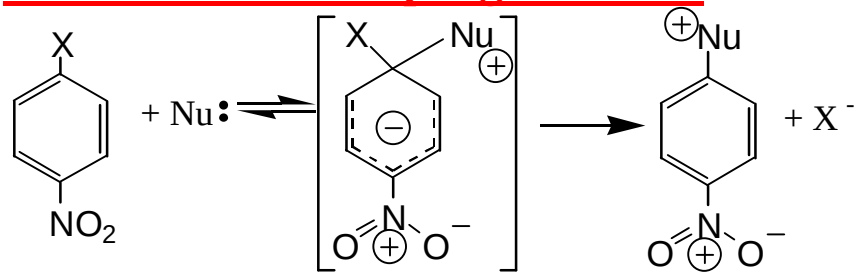
Haloaromatic Compounds

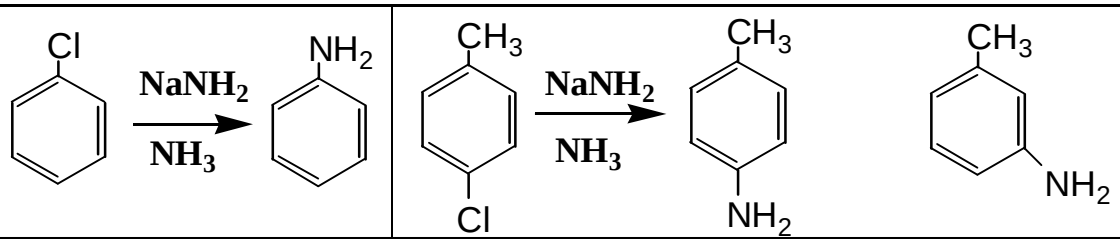


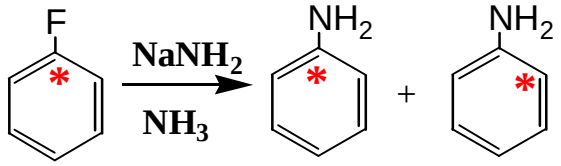


NO_2 and CN are Electrone Withdrawing groups that can help the reaction go.

Mechanism For Coupling Reactions



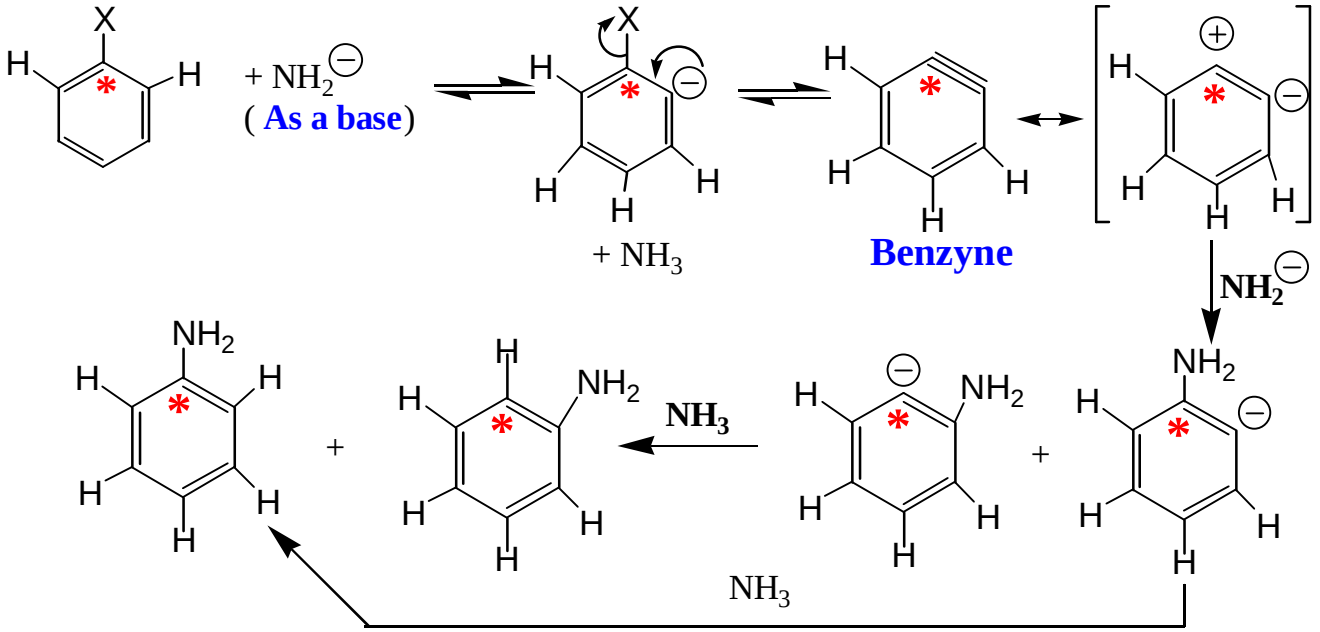


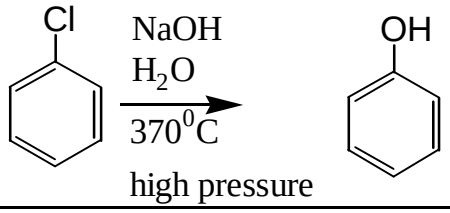


* - ^{14}C

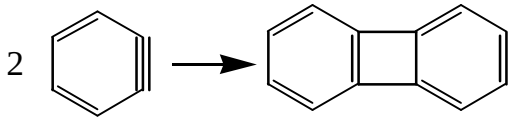
The mechanism is shown in the next page

Mechanism for the coupling reaction from the previous page

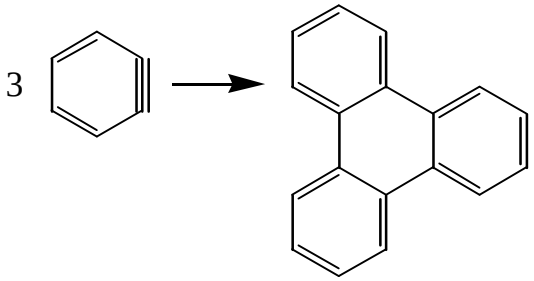




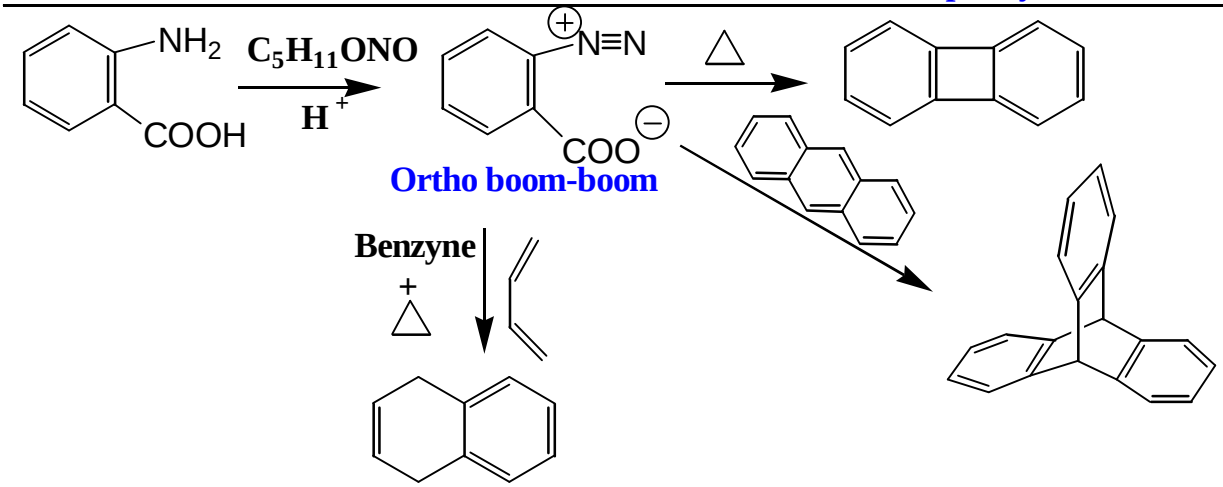
This reaction (was shown on the previous page) also goes through the benzyne intermediate



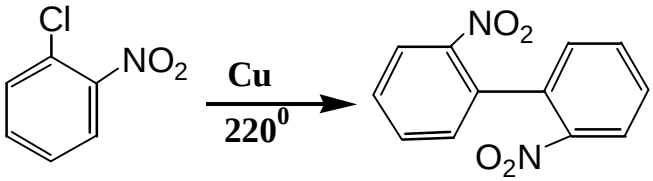
Biphenylene



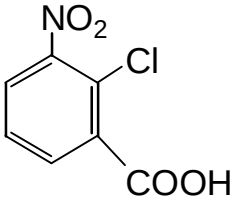
triphenylene

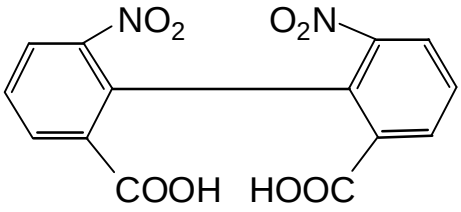


Ortho boom-boom

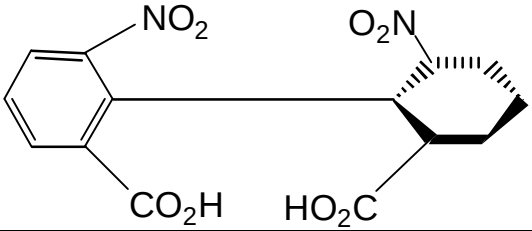


Ullmann

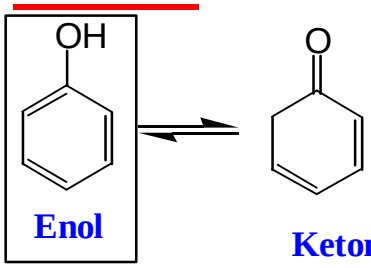




We get this product inspite of the steric effect. The rings are, in avarage at 90^0 One to the other



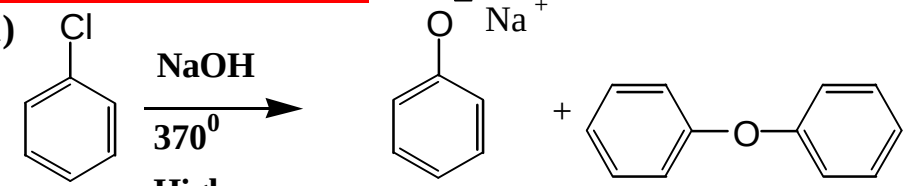
Phenols



In opposite to the regular Keto-Enol Tautomerization, This Enol is the more stable form due to the aromatic stabilization

Phenols Synthesis

1)



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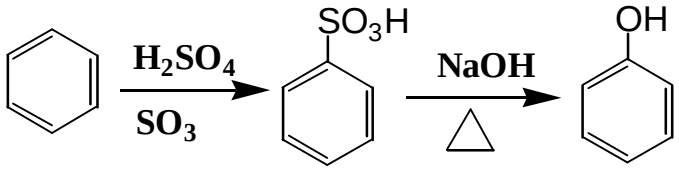
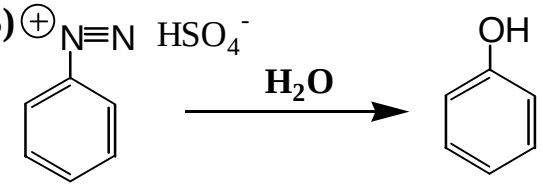


3)



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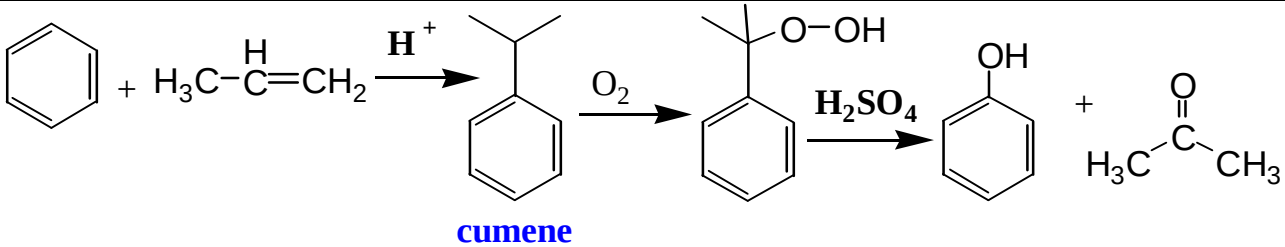
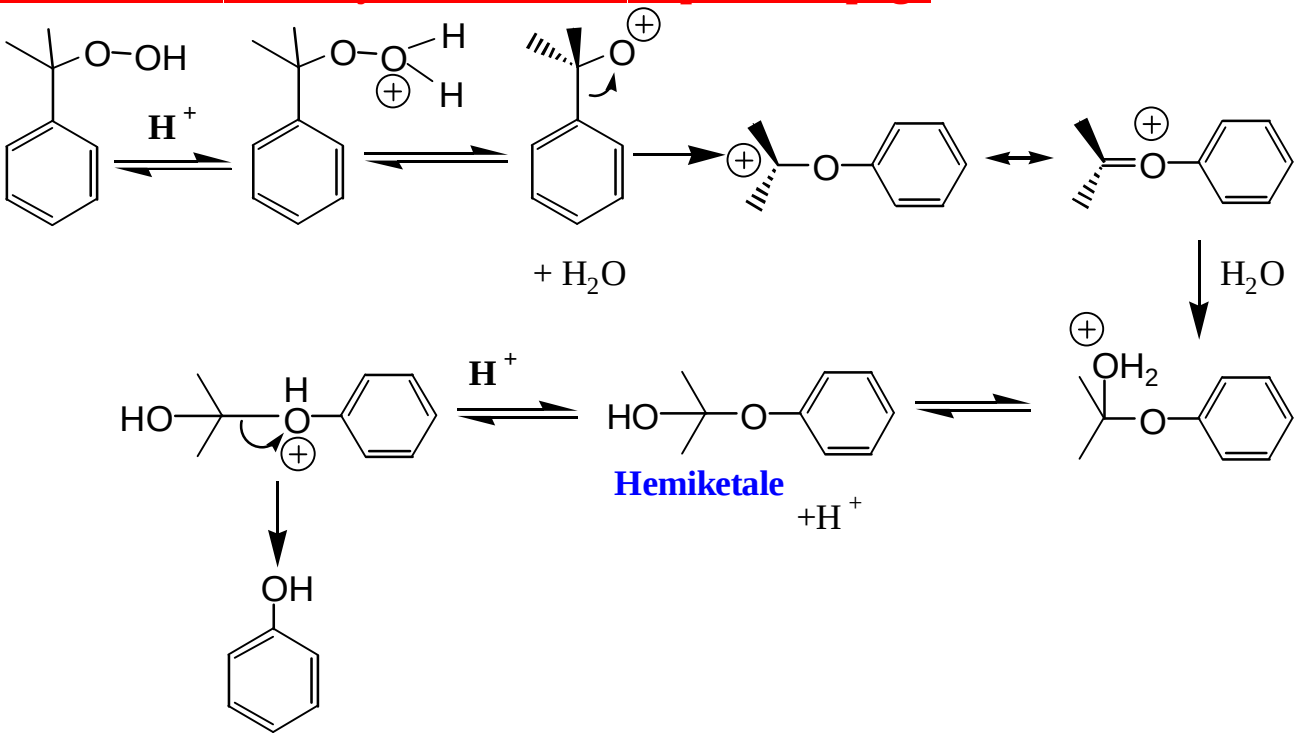


cumene

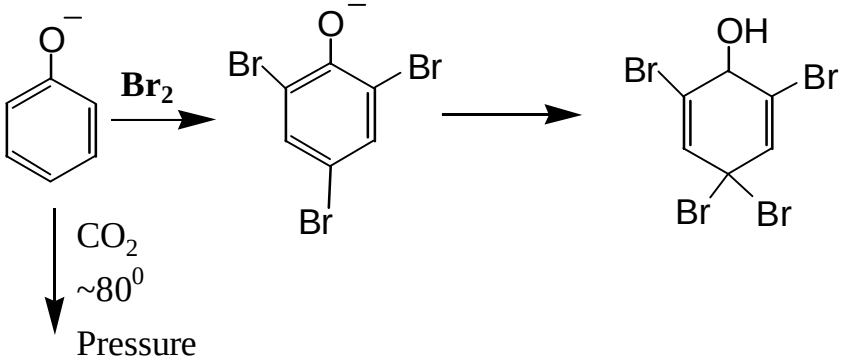
The Mechanism will be shown in the next page

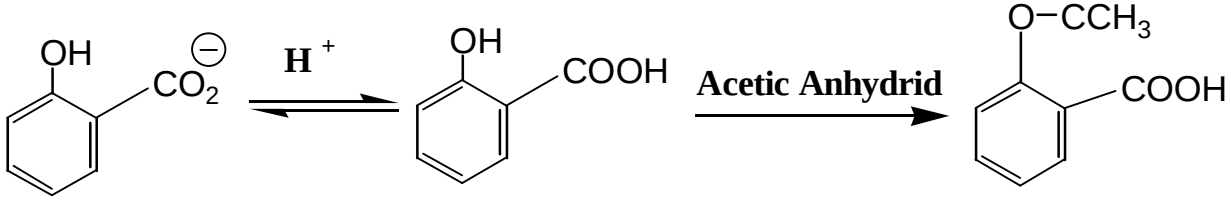
Mechanism for the synthesis from the previous page



Reactions

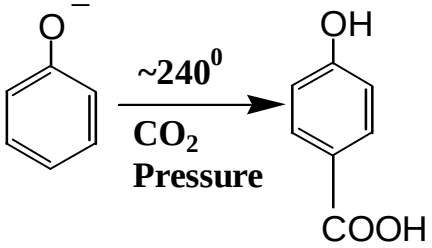
Kolbe Reaction





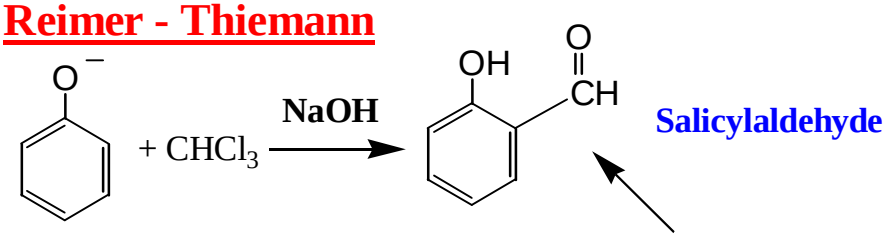
Salicylic Acid

Acetylsalicylic acid (Aspirin)



Kineticly we get the Ortho product (shown above) but Themodynamicly we get the Para product and if we heat the reaction to 240^0, we'll get the Para Product

Reimer - Thiemann



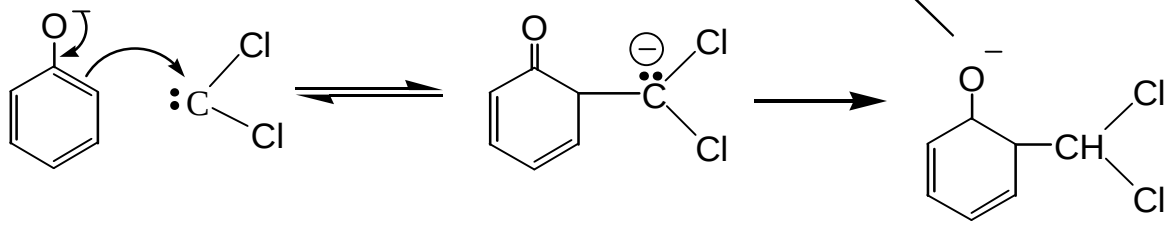
Salicylaldehyde

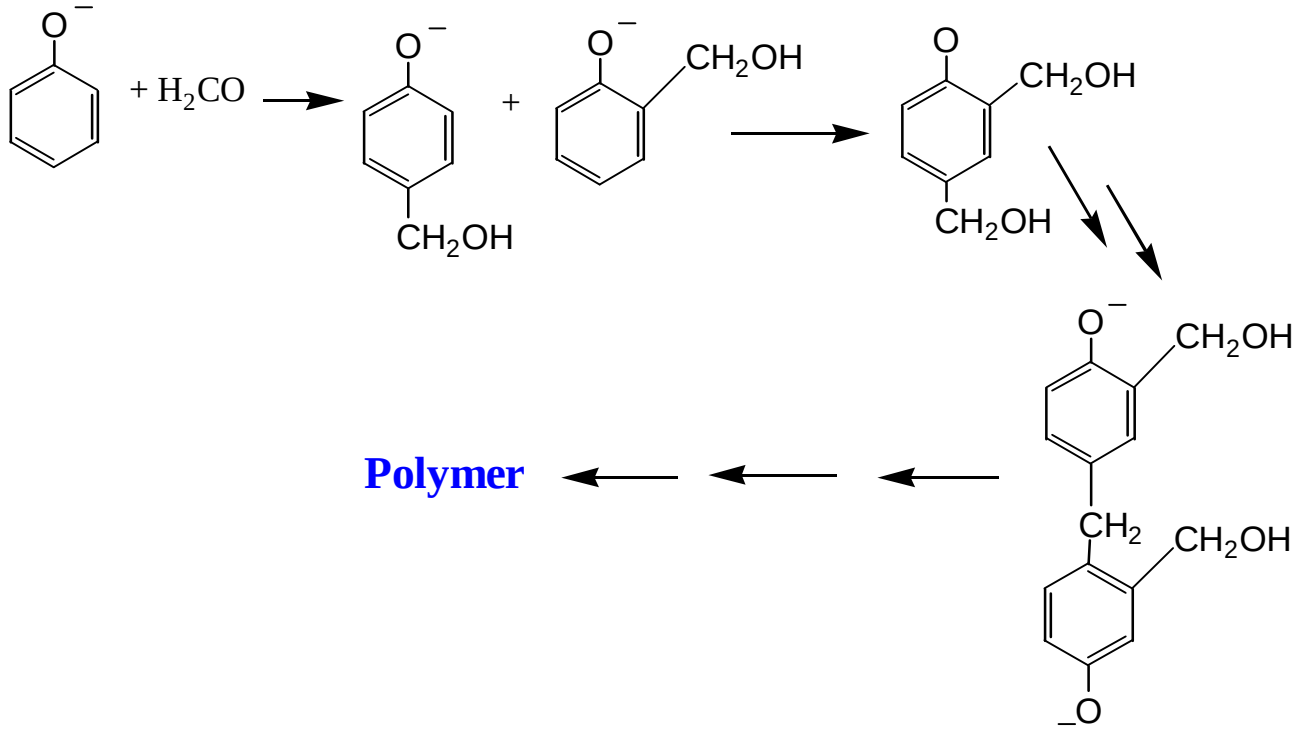
Mechanism

$CHCl_3 + OH^- \rightleftharpoons CCl_3^- + H_2O$

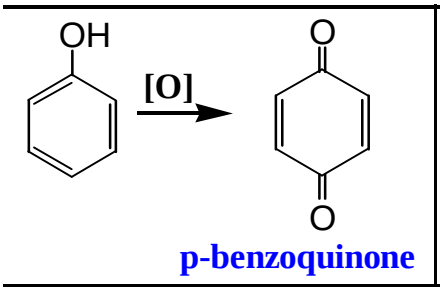
$CCl_3^- \rightleftharpoons Cl^- + :CCl_2$

Carbene

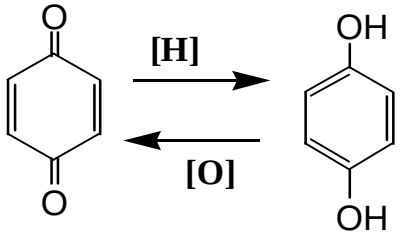


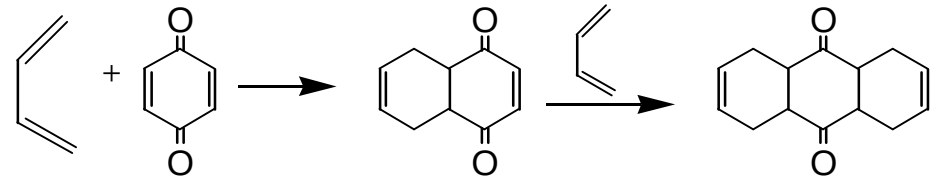


Polymer



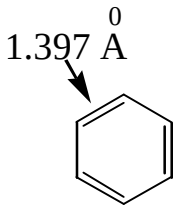
p-benzoquinone

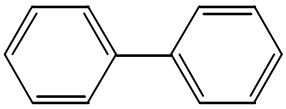




Diels-Alder

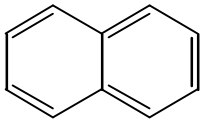
Polycyclic Aromatic Hydrocarbons



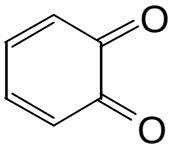


Biphenyl

p-Terphenyl



Naphthalene



o-quinone

The Naphtalene has a similar structure as the o-quinone 's structure

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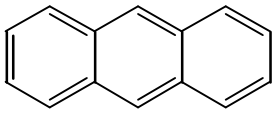
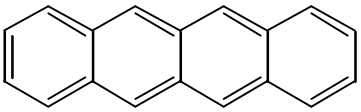
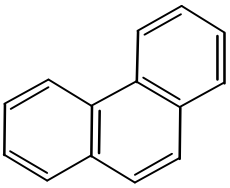


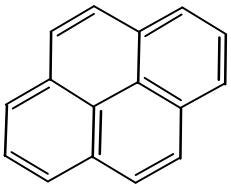
Anthracene



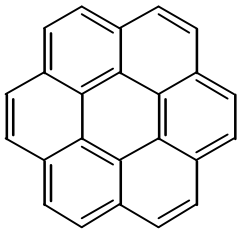
Naphthacene



Phenanthrene



Pyrene



Coronene

As we enlarge the system, the number of the Hydrogen atoms is getting smaller, compared to the number of the carbon atoms

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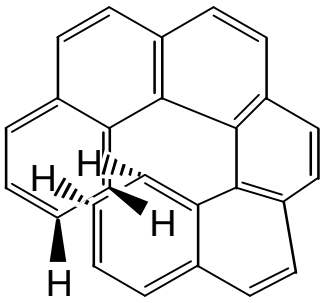

The more we add rings, we'll get a spiral structure and the molecule will be Chiral. This systems are called Helicenes. Their optical activity is different than the usual

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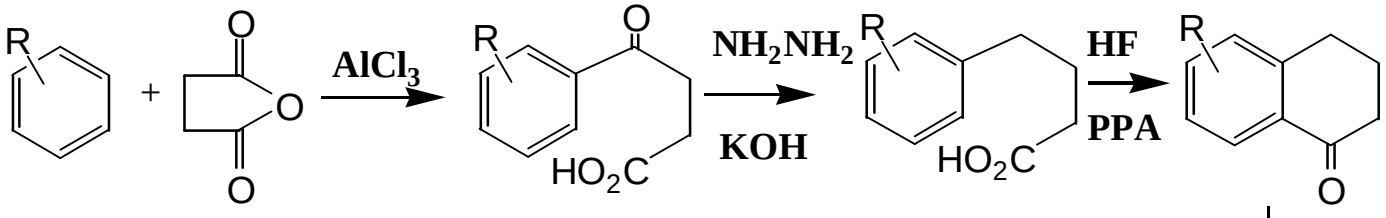
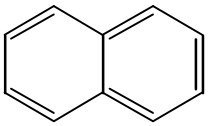
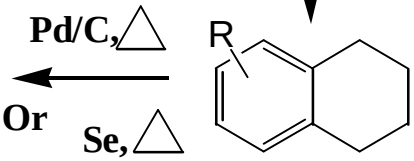
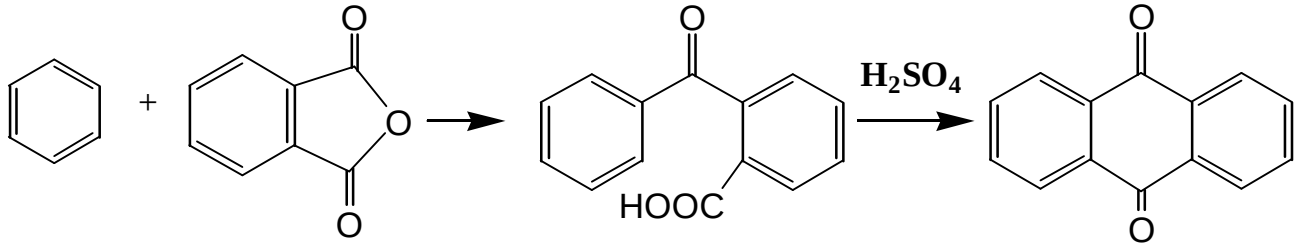
Synthesis of Polycyclic Aromatic Hydrocarbons



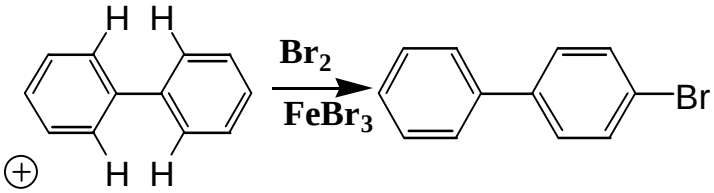




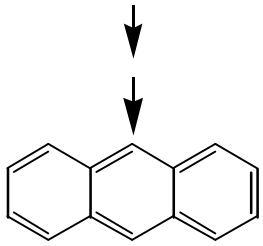
PPA = Polyphosphoric acid
$H_3PO_4 + P_2O_5$



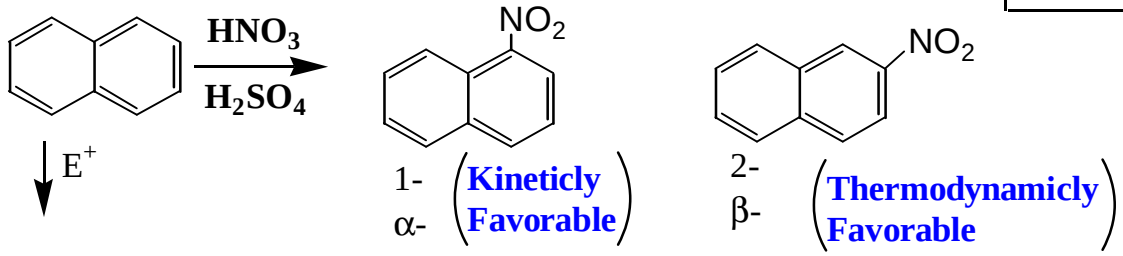
Electropilic Substitution



In the Ortho position there is a steric effect because of the hydrogenes

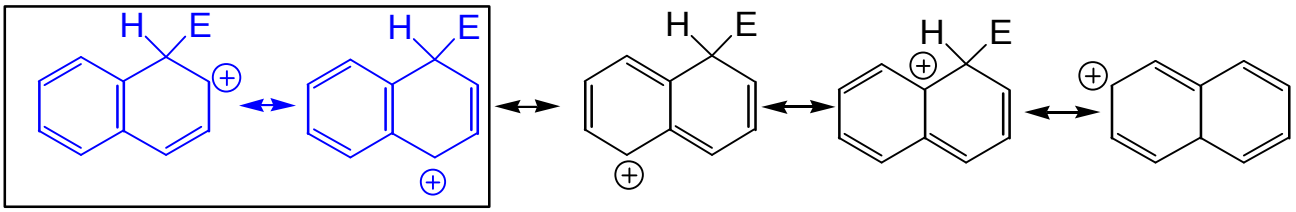


anthracene

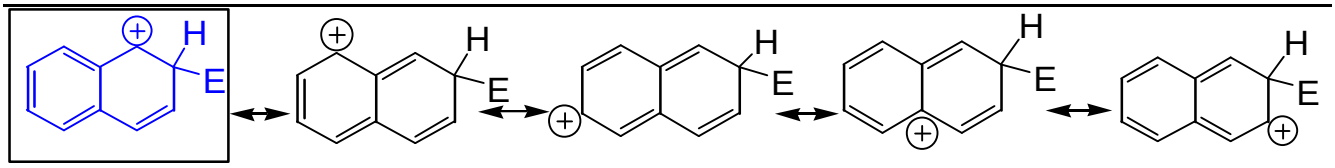


1- α- **(Kineticly Favorable)**

2- β- **(Thermodynamicly Favorable)**



There are 2 Resonance forms that have one benzene ring

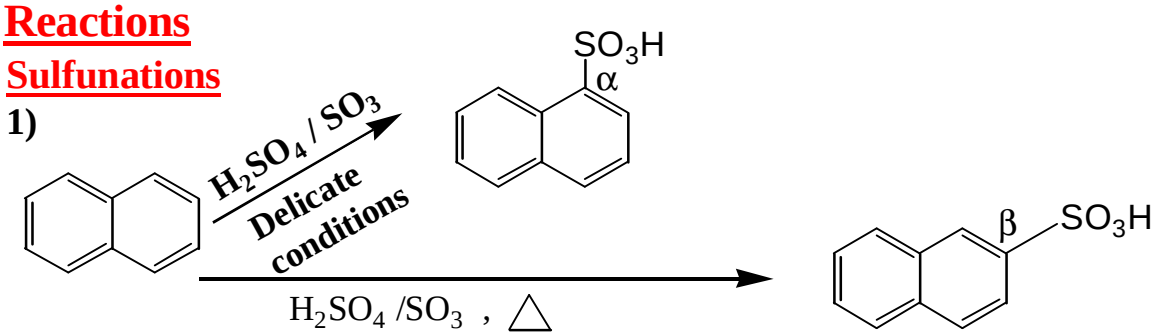


There is only 1 resonanace form with one benzene ring

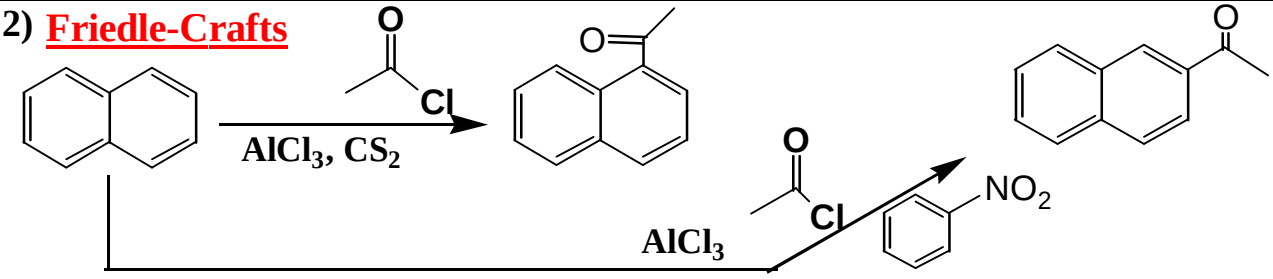
Reactions

Sulfunations

1)

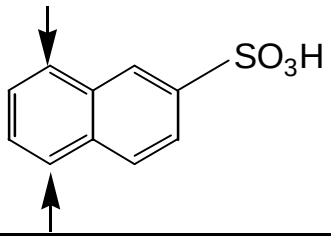


2) Friedle-Crafts

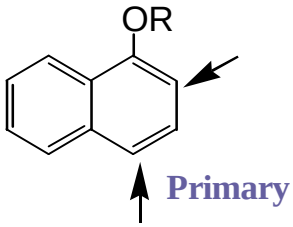


Guidance in Naphtalene

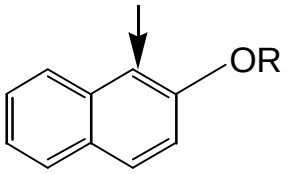
1) **Meta guiding group :**
   a **position on the other ring**



2) **Ortho,Para guiding group in No.1 Position:**
   Para is favorable because it's a



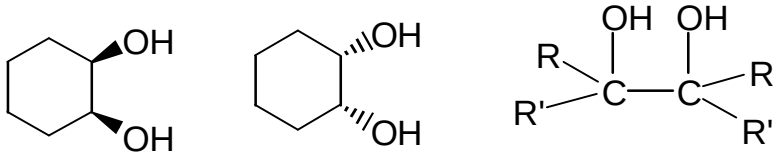
3) **Ortho,Para guiding group in No.2 Position:**



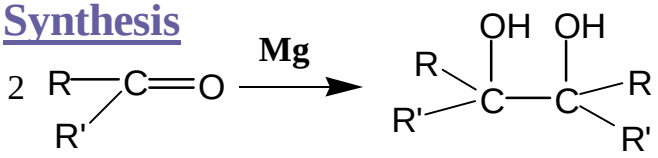
Difunctional Compounds

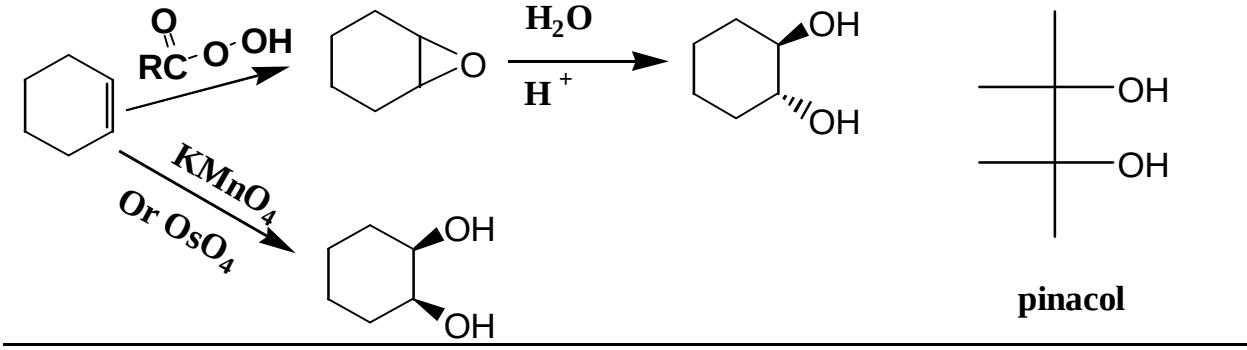
1,2 - Diols

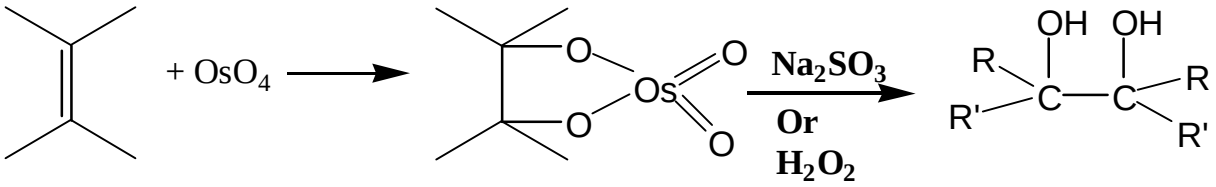
Examples



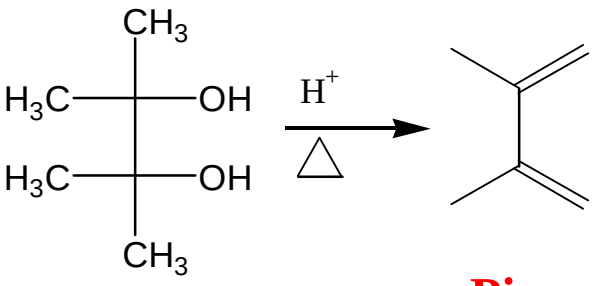
Synthesis





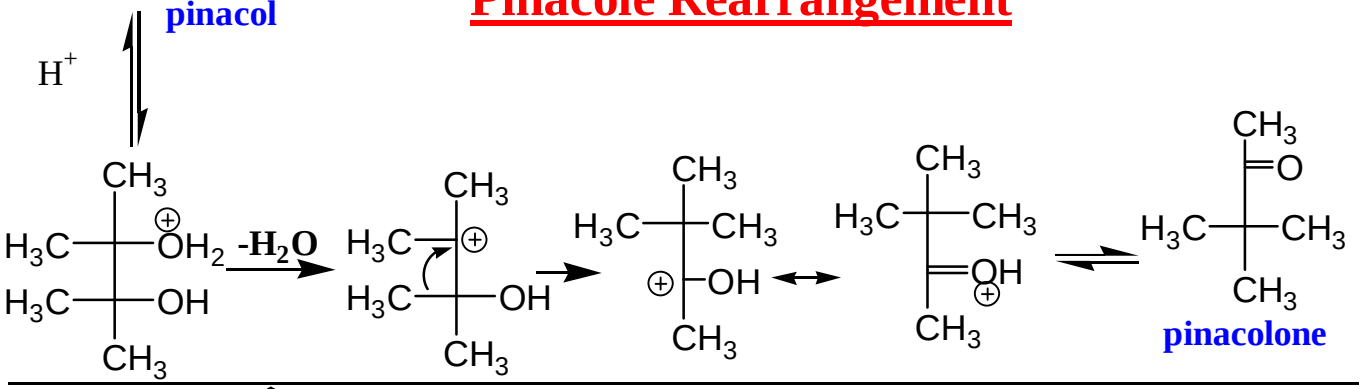


We can see that with OsO_4 and $KMnO_4$ we get the Cis Product. This happens due the formation of the ring.

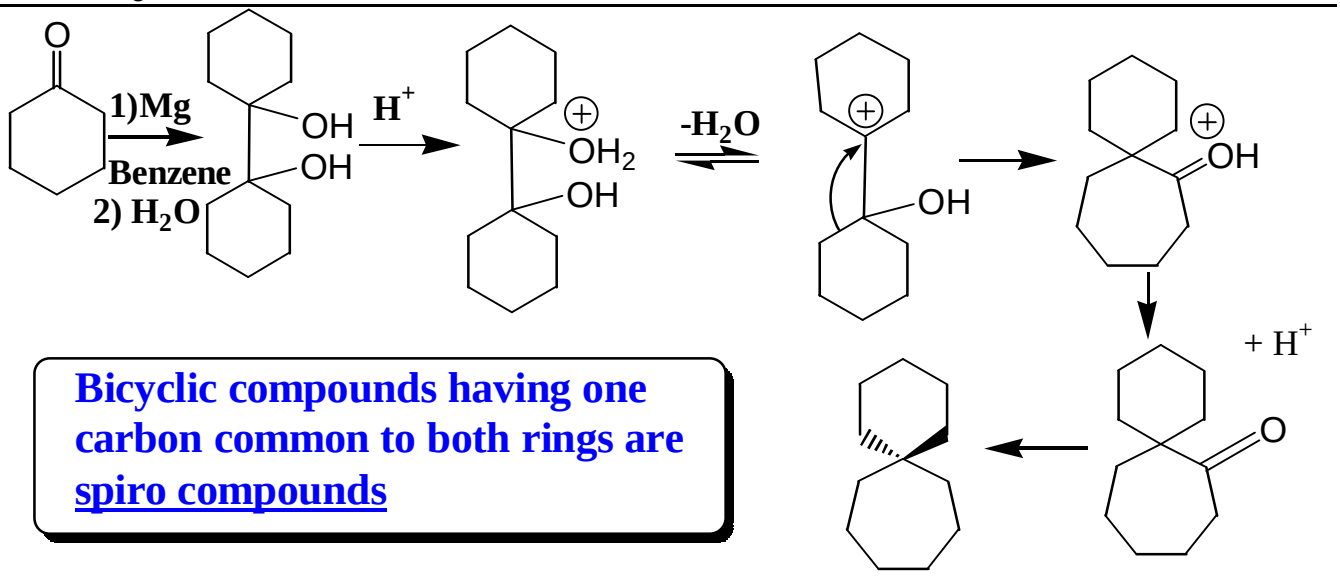


pinacol

Pinacole Rearrangement



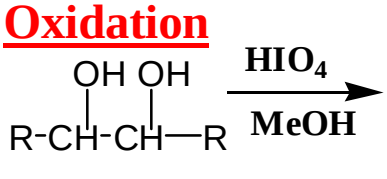
pinacolone



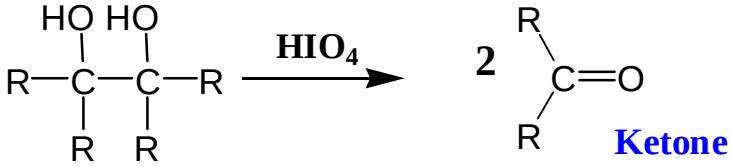
Bicyclic compounds having one carbon common to both rings are spiro compounds

Spiro[5.6]dodecane

Oxidation



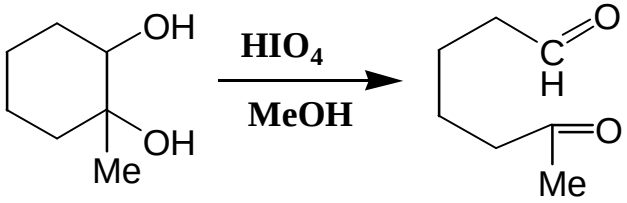
Aldehyde



Ketone

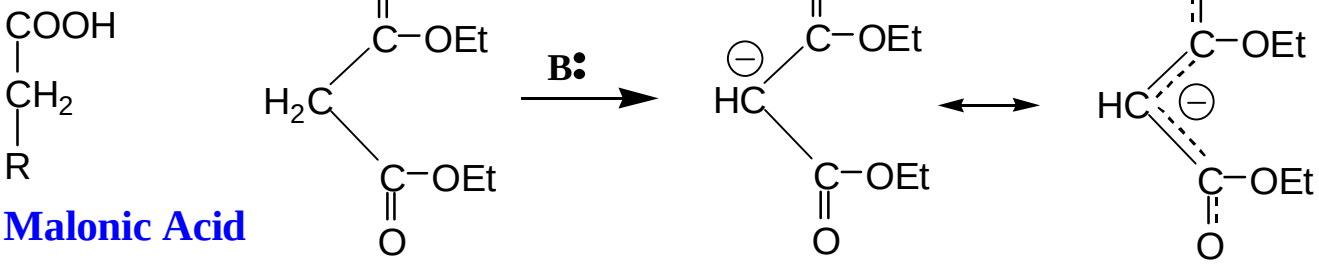
Another Reagent is Lead tetracetate

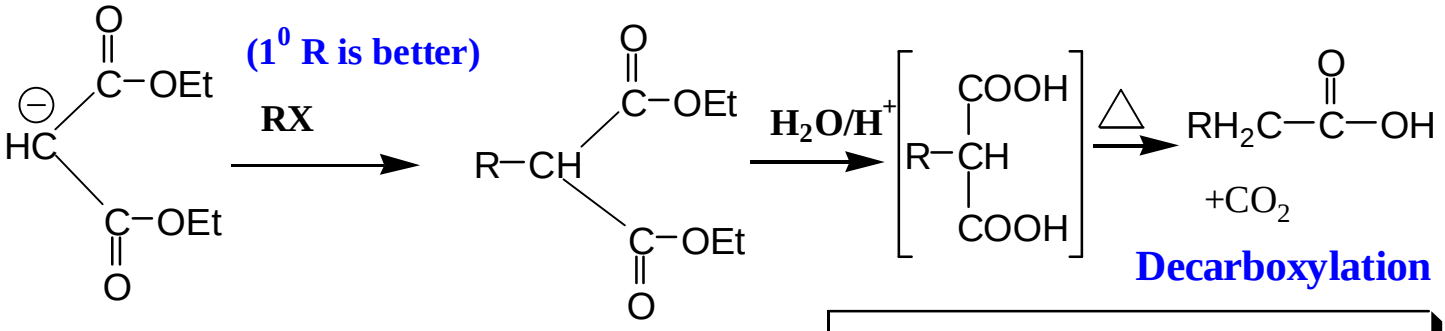
$Pb(CH_3COO)_4$



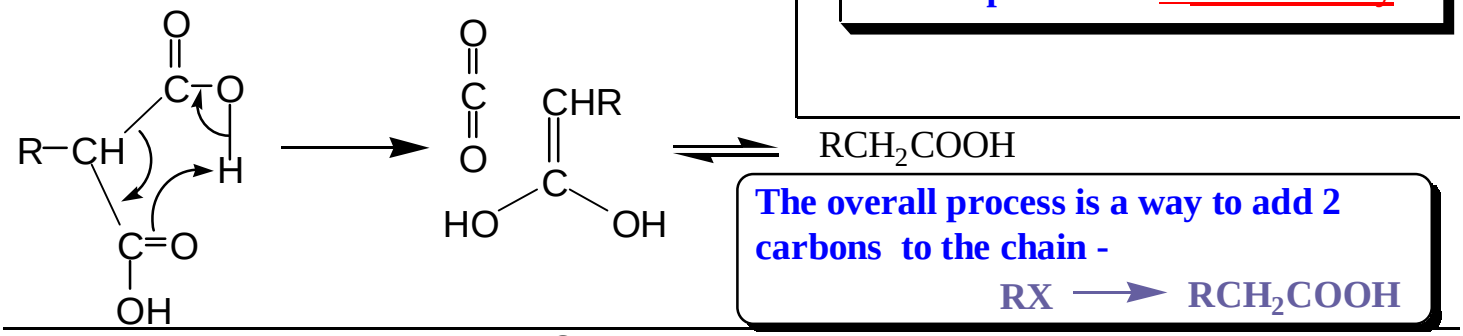
HIO_4 is specific to 1,2 Diols and doesn't oxidate other groups

Diacids



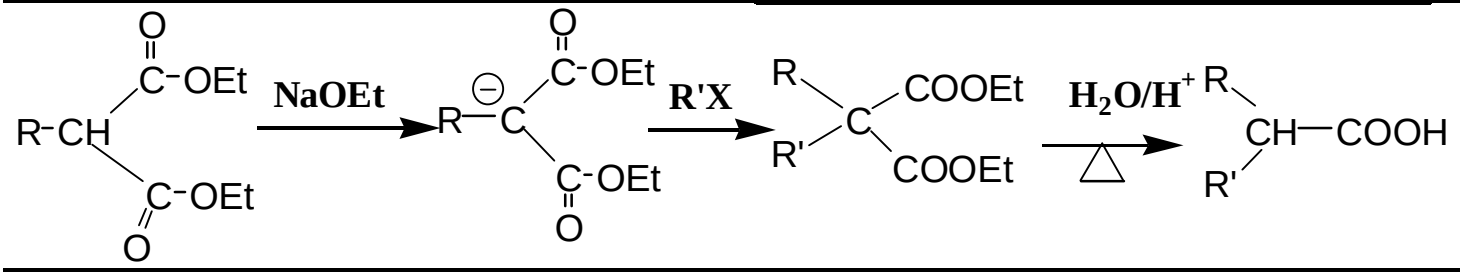


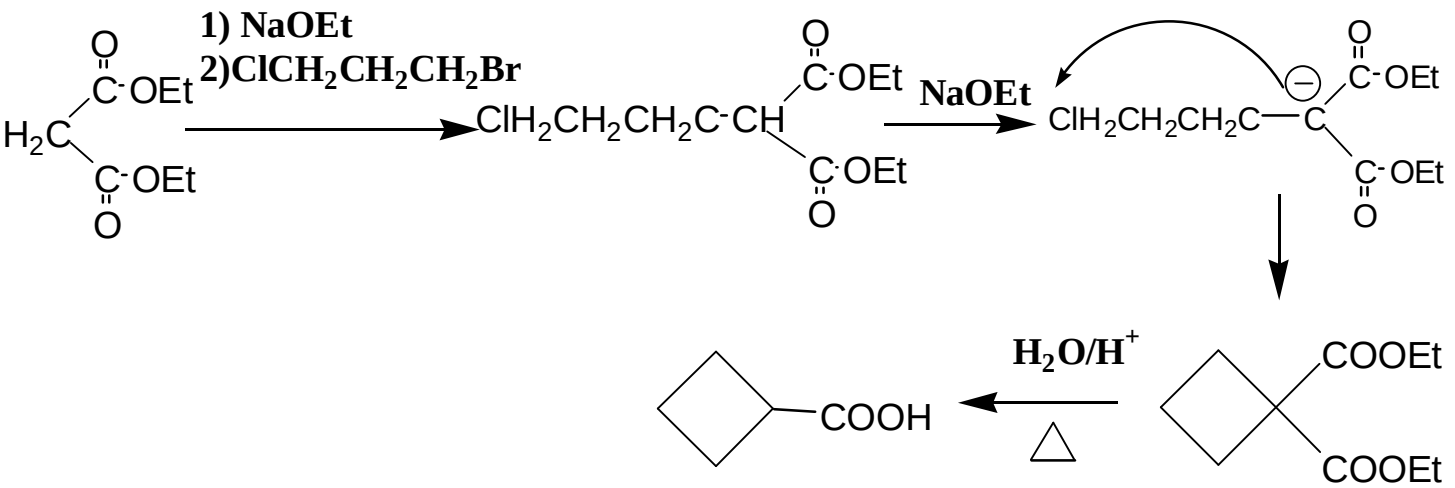
This is Specific for b Diacids Only



The overall process is a way to add 2 carbons to the chain -

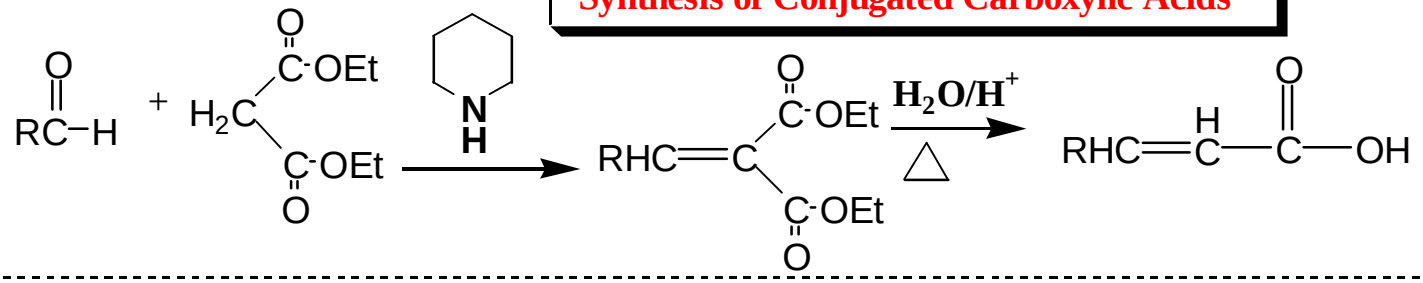
RX → RCH_2COOH

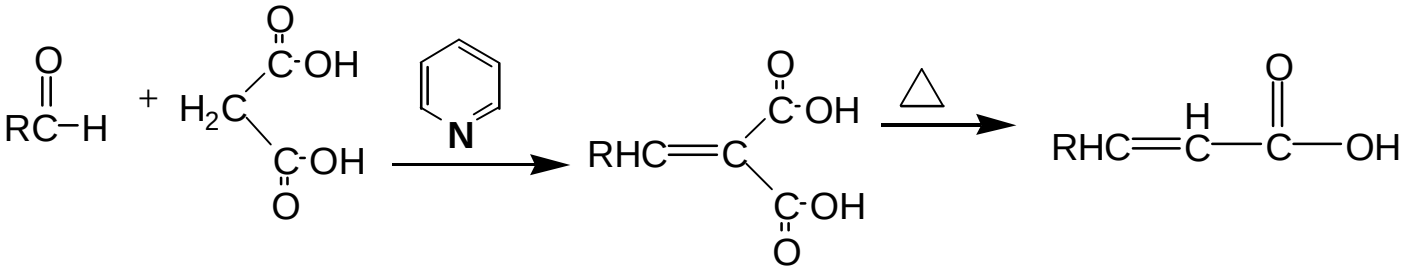


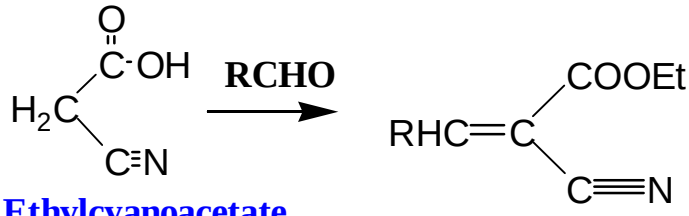


Knnovenagel Reaction

Synthesis of Conjugated Carboxylic Acids

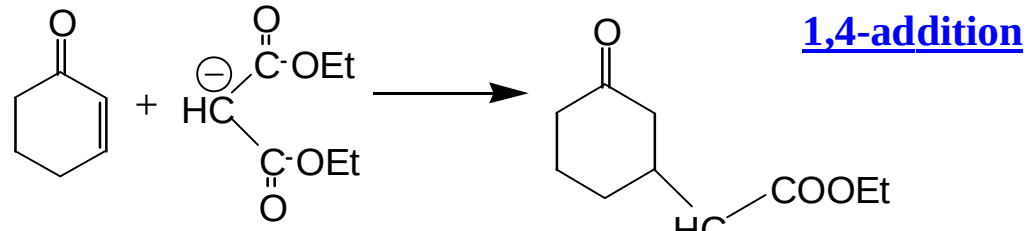




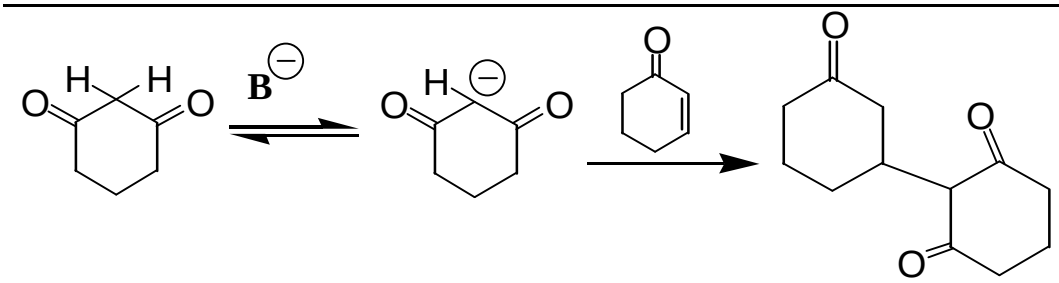


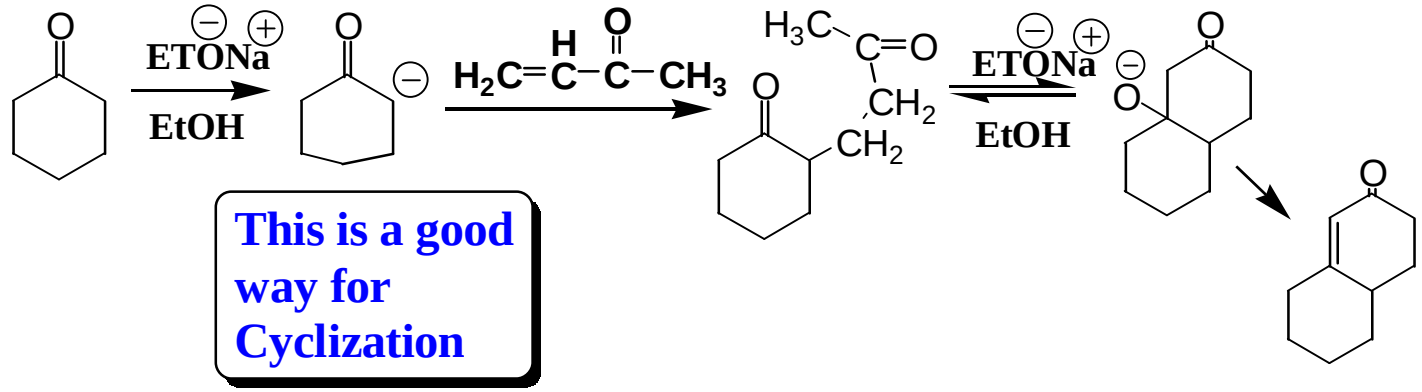
Ethylcyanoacetate

Michael Addition



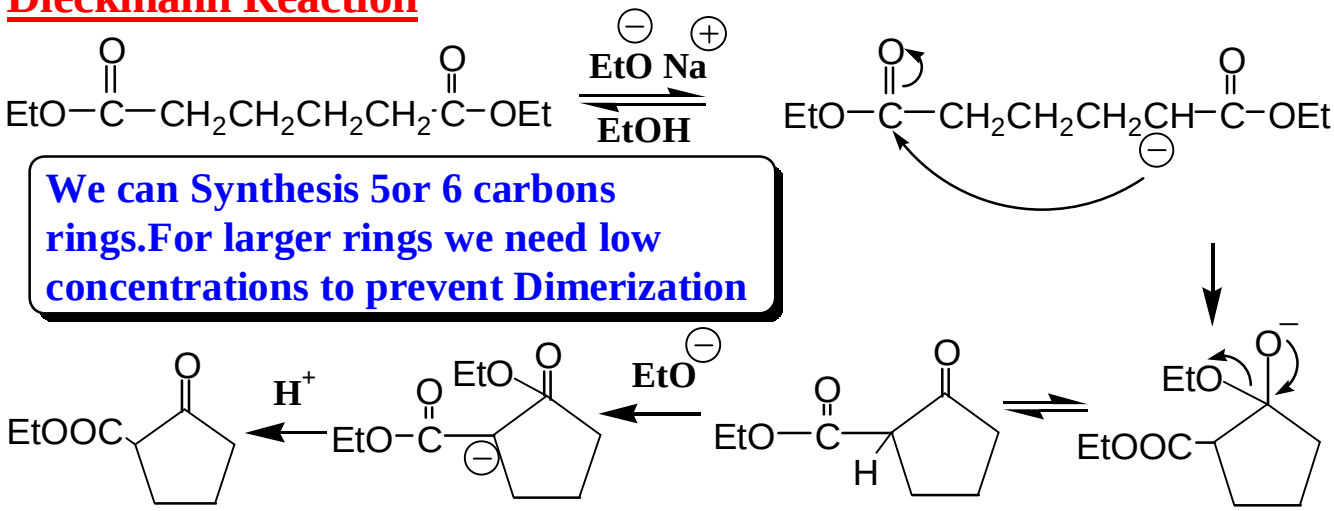
a,b-**unsaturated**
Ketone





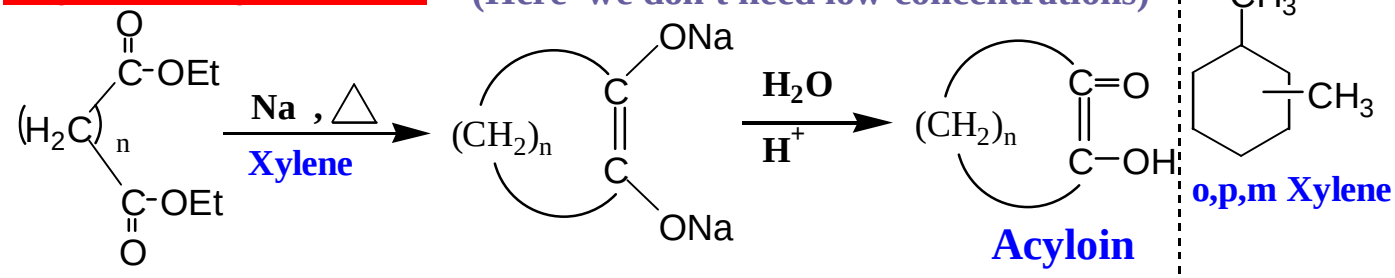
This is a good way for Cyclization

Dieckmann Reaction

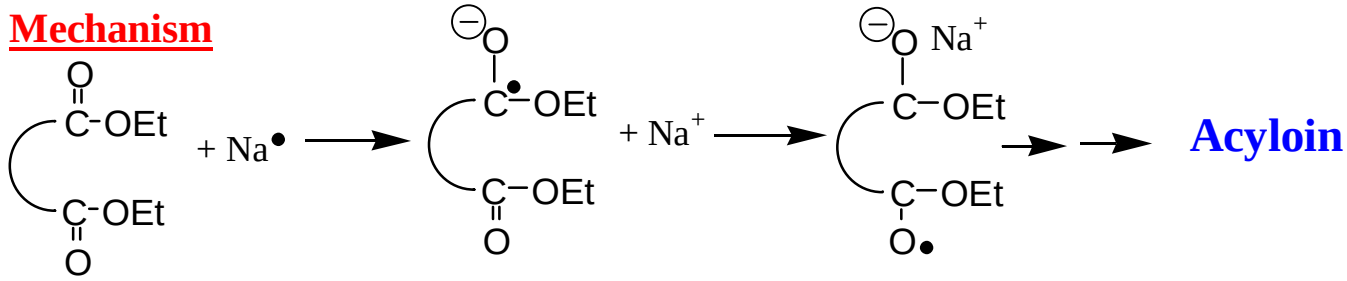


Acyloinic Cyclization

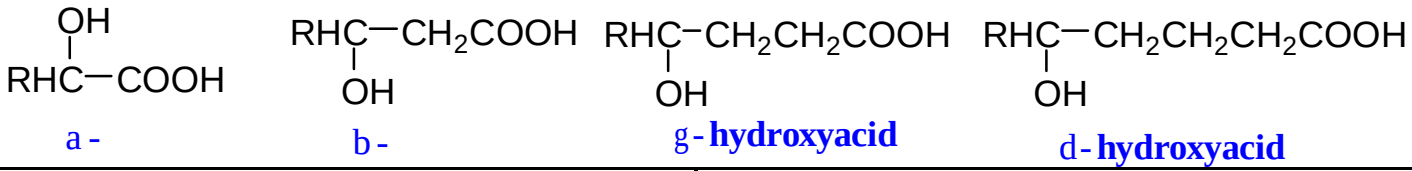
(Here we don't need low concentrations)

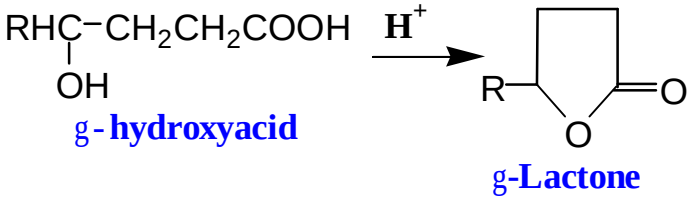


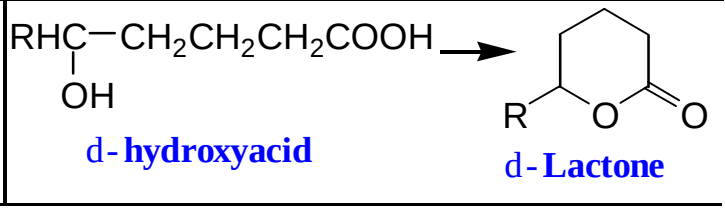
Mechanism

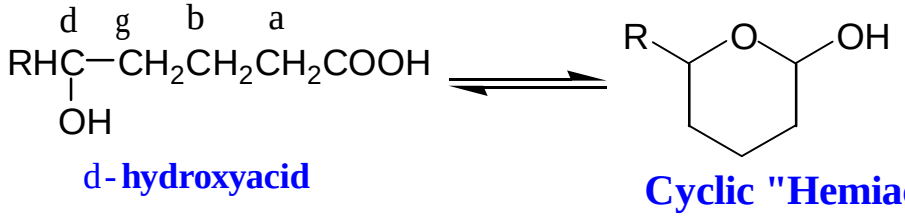


Hydroxyacids

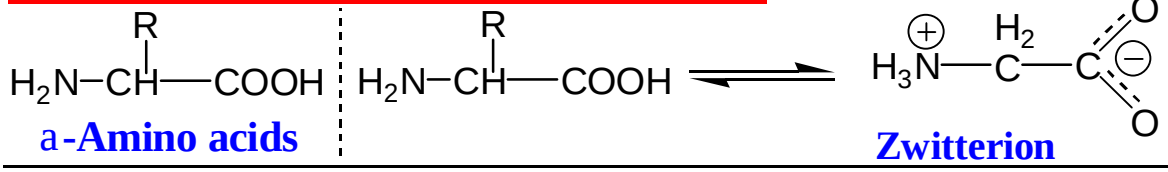


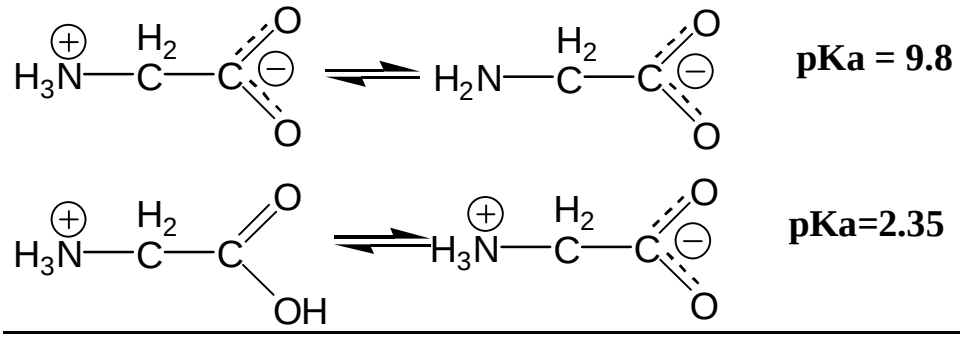


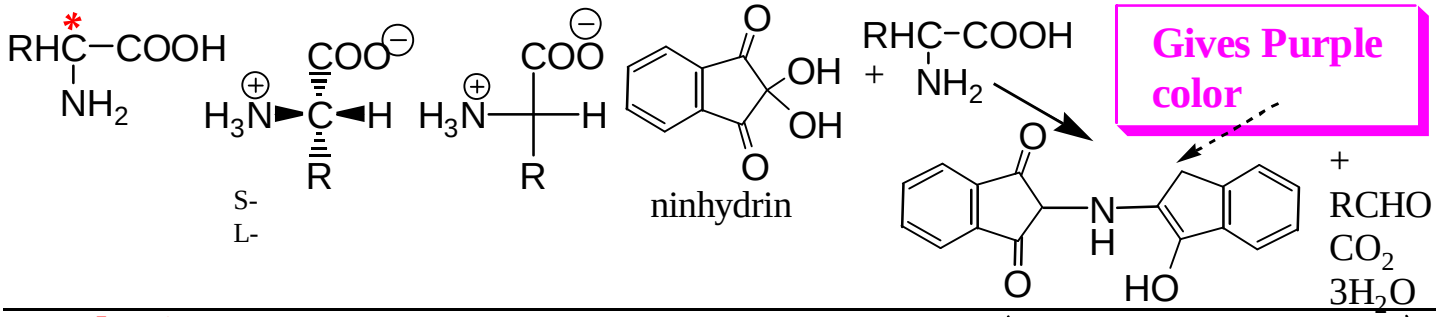




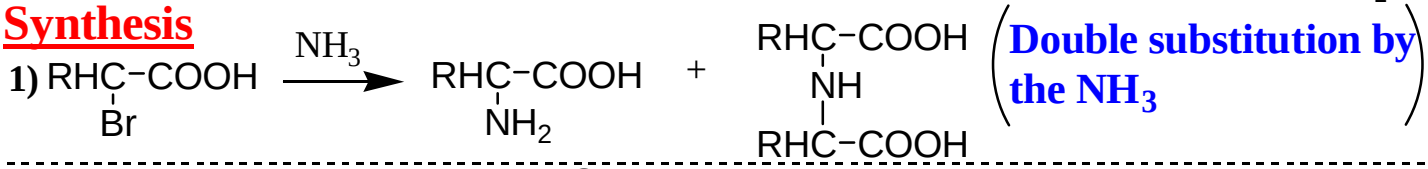
Amino-Acids , Peptides , Proteins

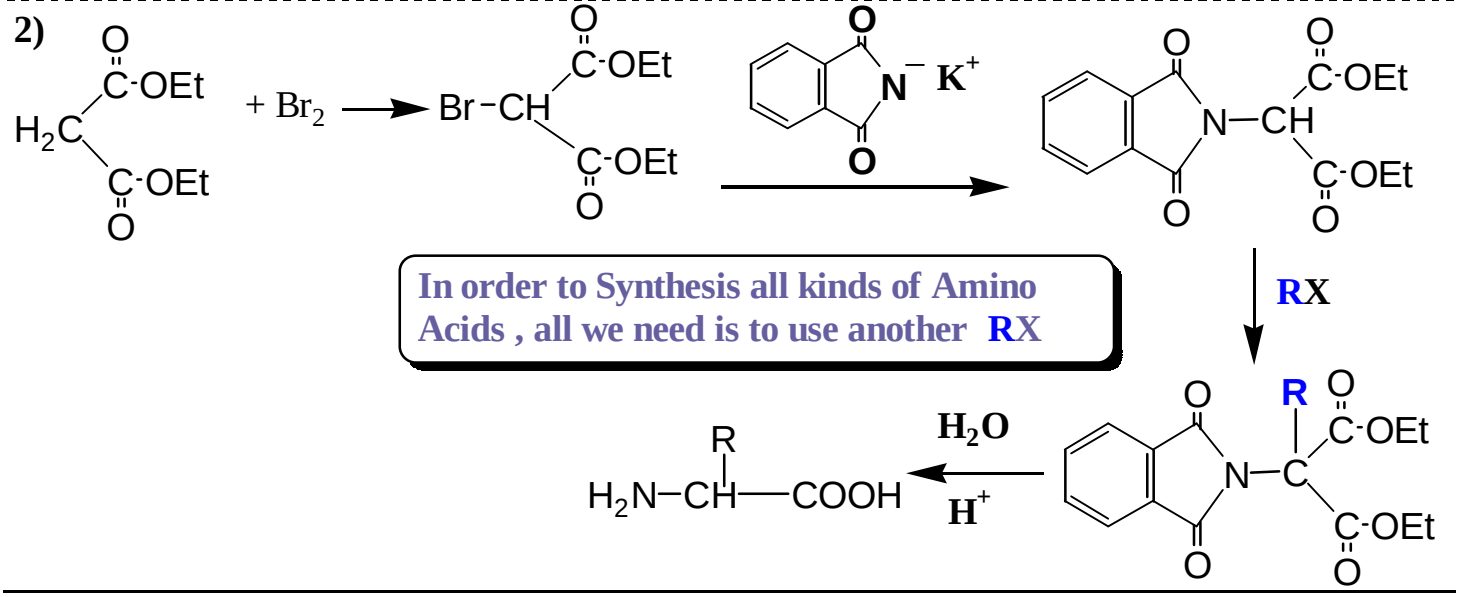


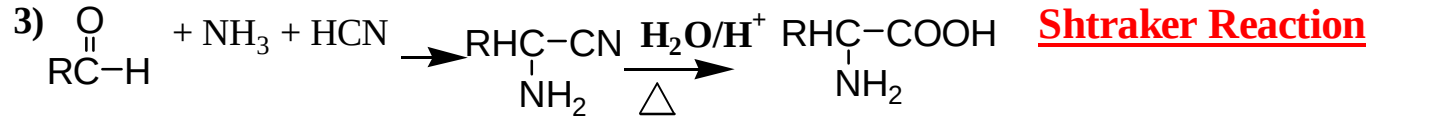


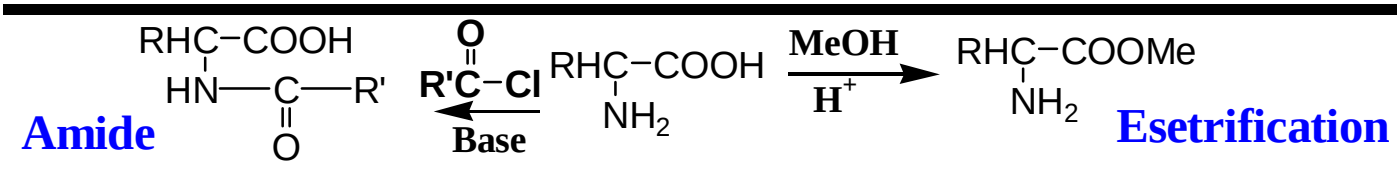


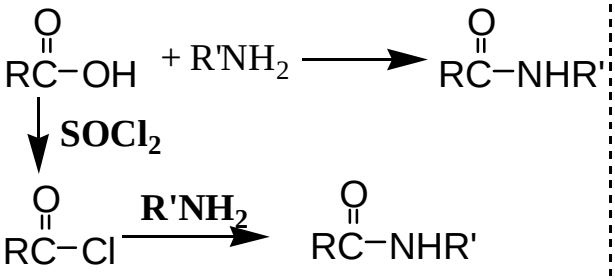
Synthesis

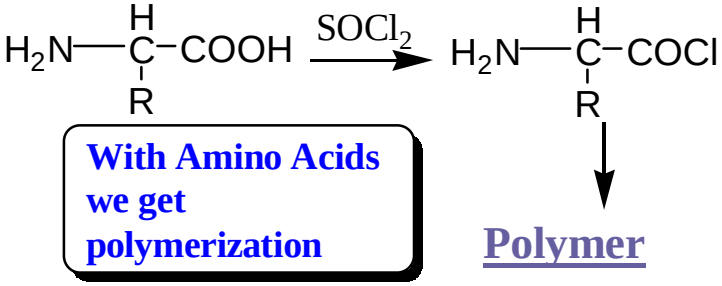












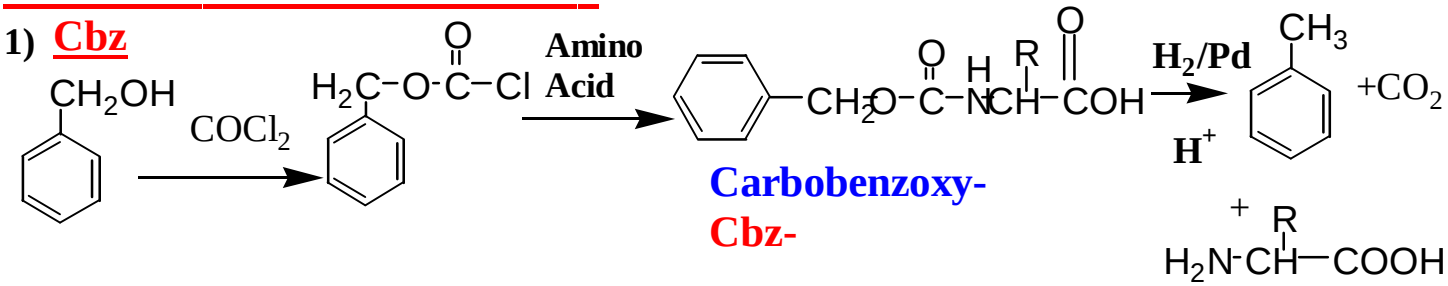
With Amino Acids we get polymerization

Polymer

Protection for Amino Acids

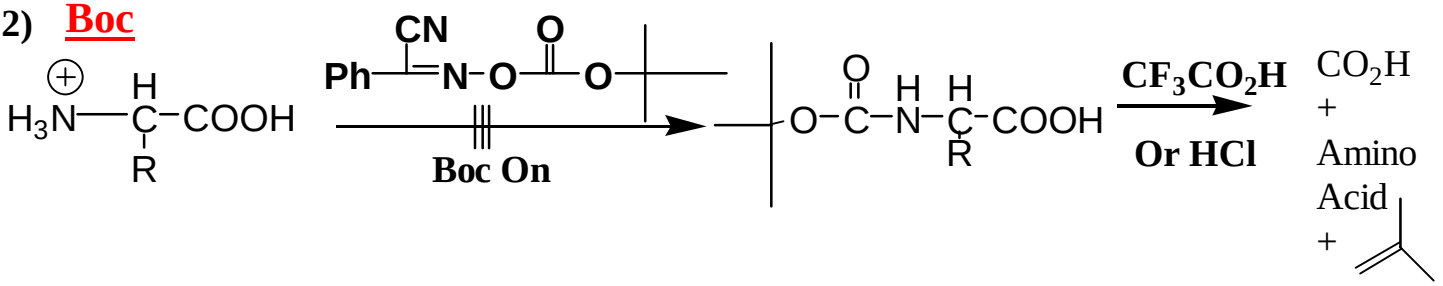
Protection For The Amino side

1) Cbz



Carbobenzoxy-
Cbz-

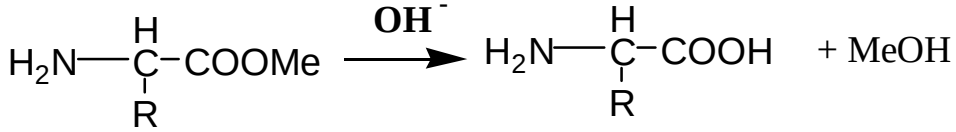
2) Boc



Protection For The Carboxylic side

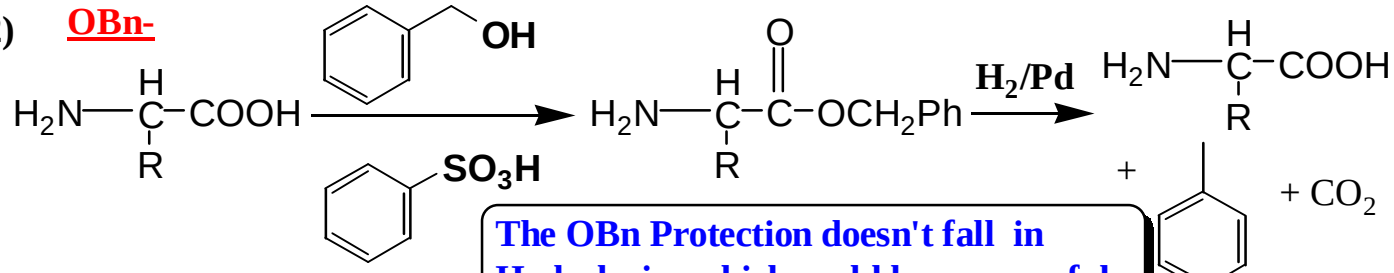
For the protection we create the Ester (Me,Et or Ph) with the Carboxylic Acid and when we want to remove it there are 2 options:

1)

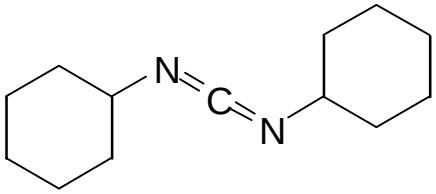


We can use this method to remove Et Ester and we'll get EtOH

2) OBn-

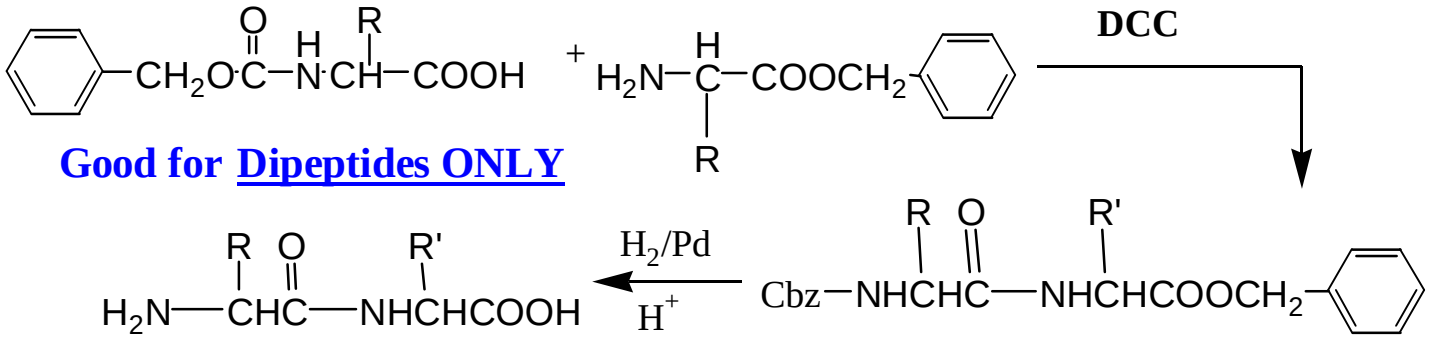


The OBn Protection doesn't fall in Hydrolysis , which could be very useful

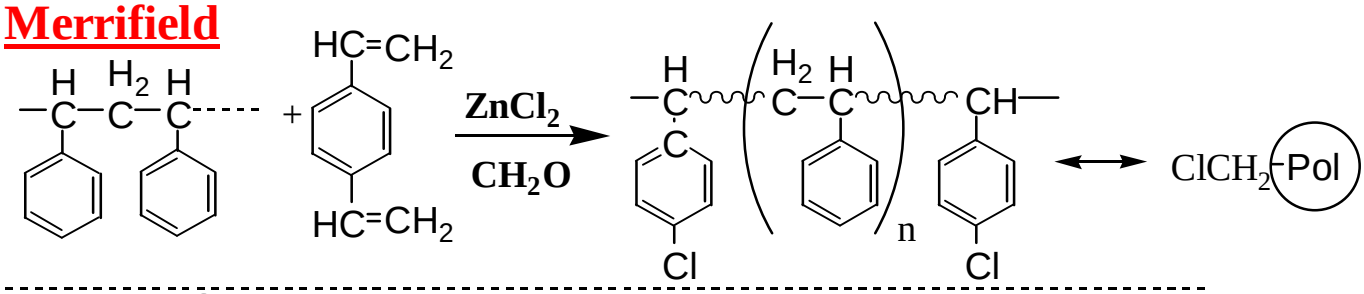


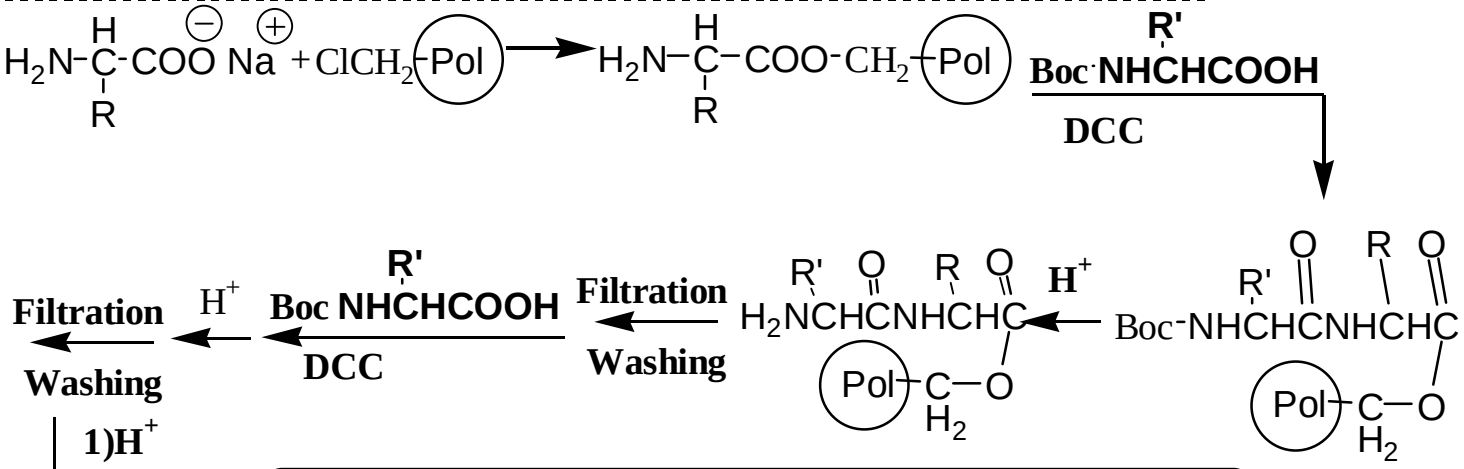
dicyclohexylcarbodiimide

DCC- A catlyst for the condensation of 2 Amino Acids into a Peptide



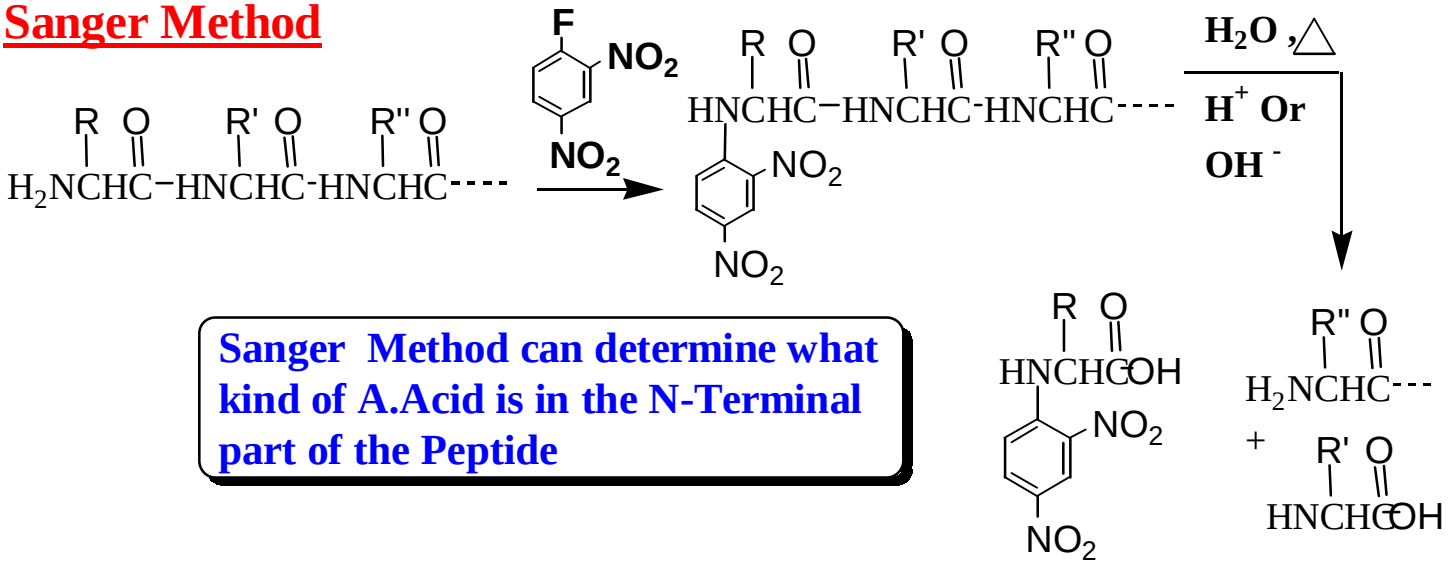
Merrifield





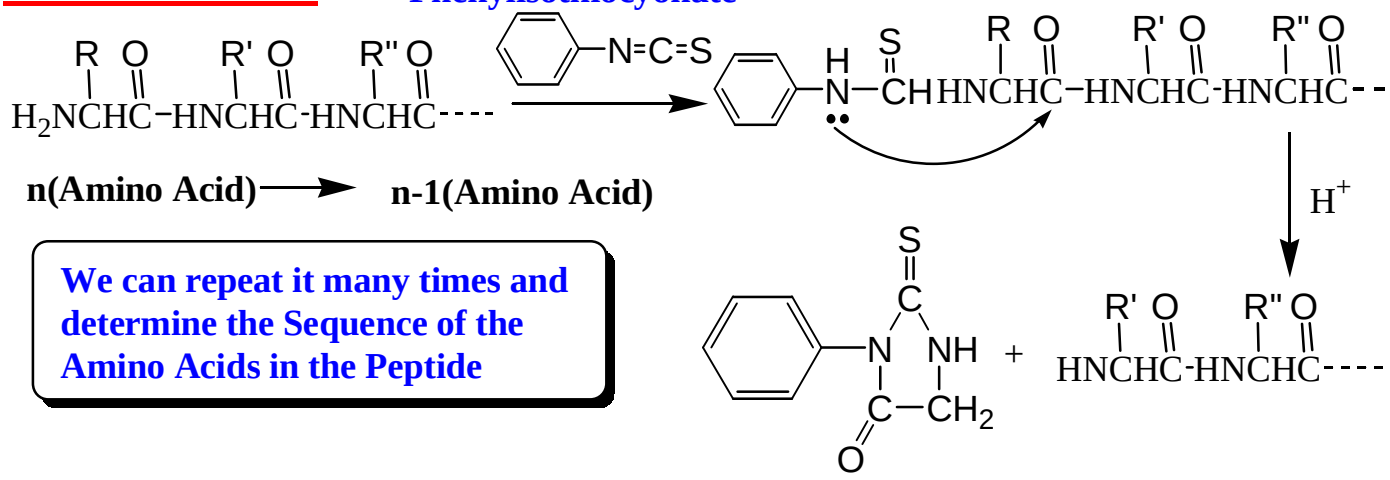
In order to add more A.Acids we need to add another A. Acid with Boc.It's Important to wash and Filter after every time.

Sanger Method



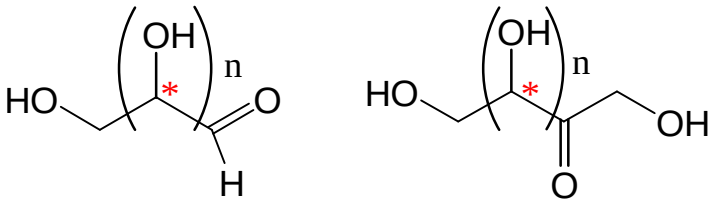
Sanger Method can determine what kind of A.Acid is in the N-Terminal part of the Peptide

Edman Method

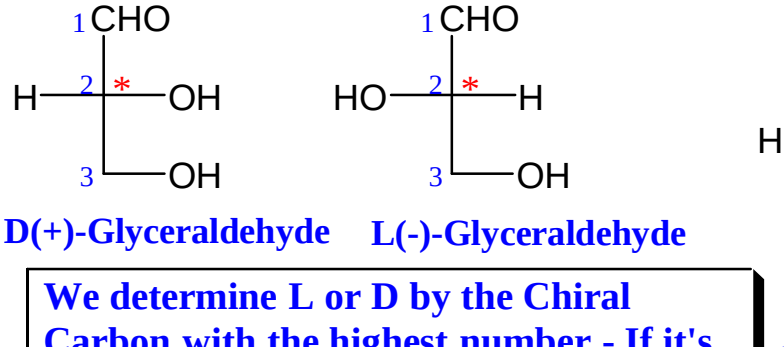


Carbohydrates - $Cn(H_2O)n$

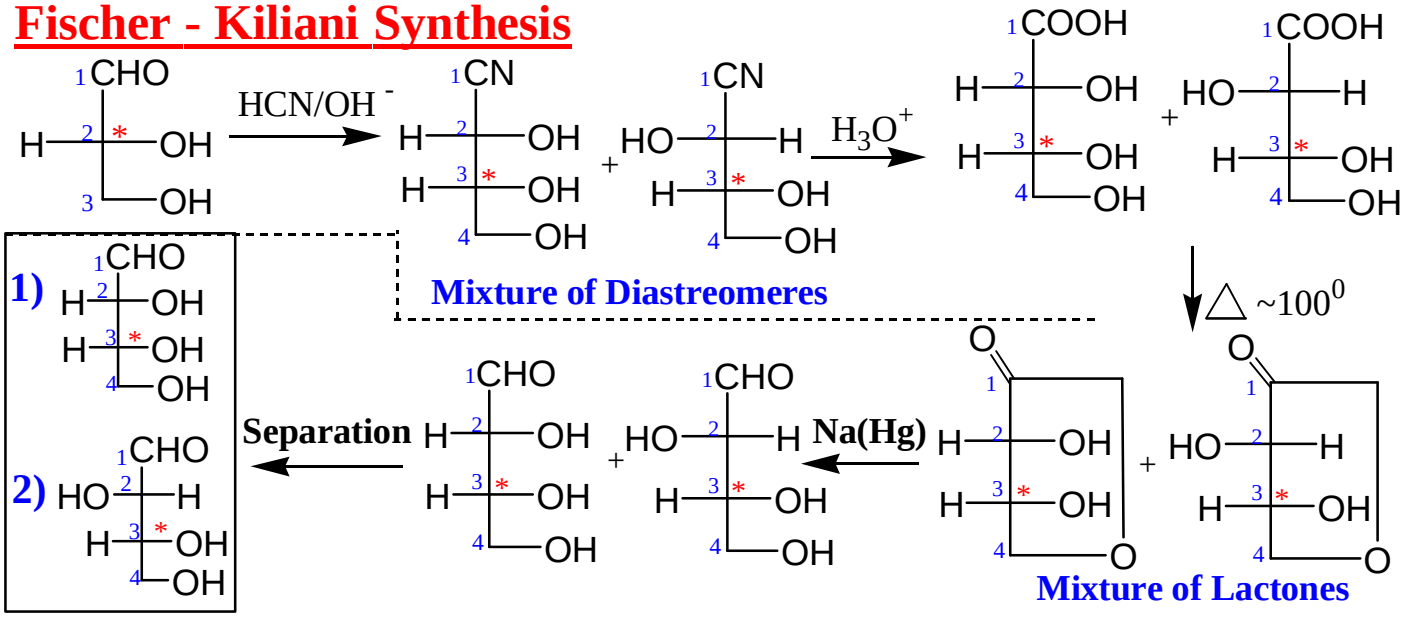
1) Monosacharides
2)Oligosacharides - 2-7 monomers
3)Polysacharides -7+ monomers



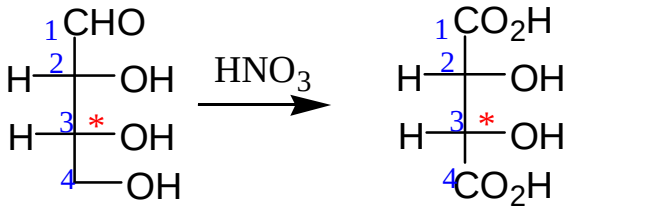
Aldose Ketose



Fischer - Kiliani Synthesis



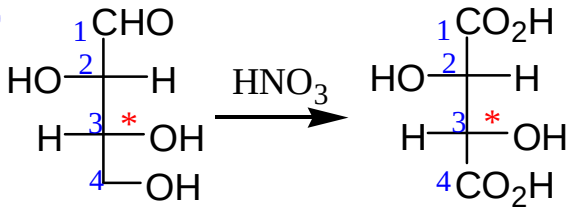
1)



Erythrose — **Meso-tartaric Acid**

$[a]_D = 0$

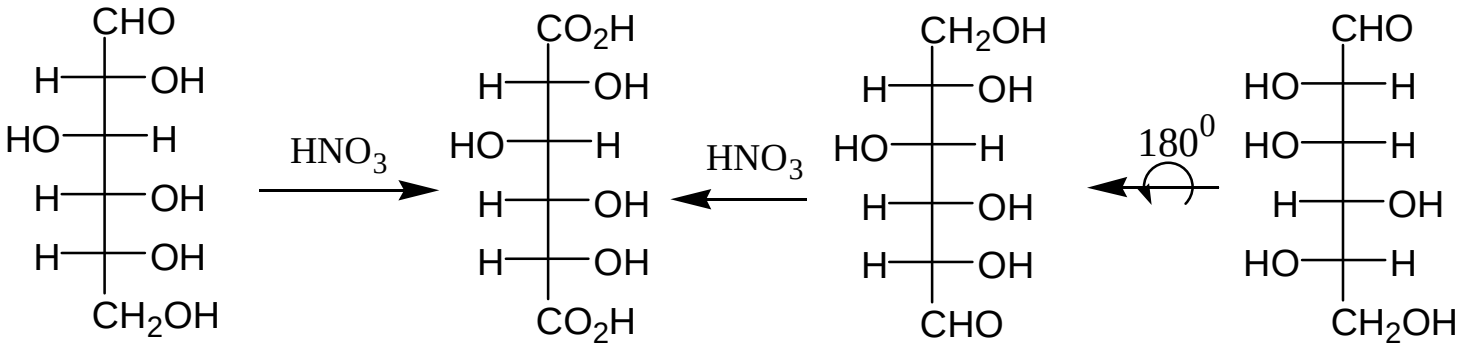
2)



Threose — **$[a]_D \neq 0$**

HNO_3 oxidates only 1^0-Alcohols and Aldehydes to Carboxylic Acids. This helps the separation process, because here we get a Chiral product and an a-Chiral product.

Identifying Glucose and Manose



D-Glucose — **L-Gulose**

If we have L-Gulose we can oxidate it and then if we oxidate Glucose and Mannose -Only Glucose will give the same product as the L-Gulose

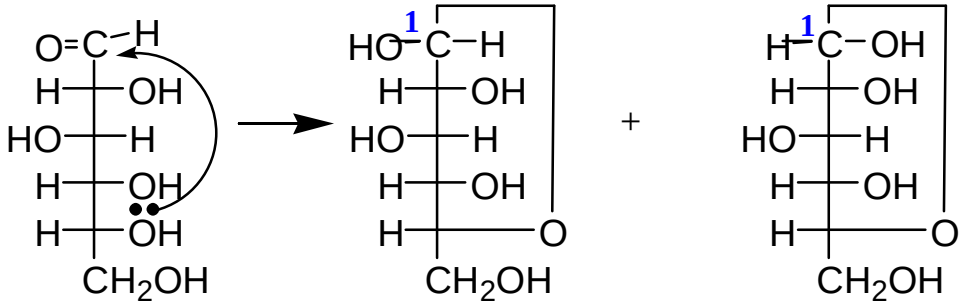
---

If we Crystalize Glucose from an H_2O solution we'll get 2 Different materials:

1) $[a]D = 112^0$ —Equlibration Time→ **$[a]D = 52^0$**

2) $[a]D = 19^0$ —Equlibration Time→ **$[a]D = 52^0$**

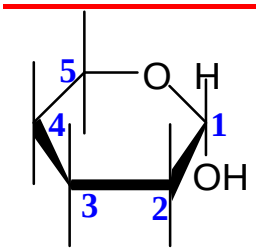
Appearantly these 2 materials are shifting from one form to the other until they reach Equlibrium and we get the 52^0. This lead to the conclusion that glucose is mostly in a Cyclic Form:

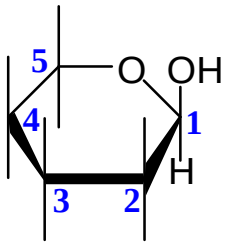


We get a mixture of these 2 Diastreomeres

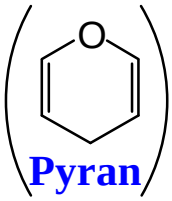
Haworth Projections

Carbon No. 1 is Named The Anomeric Carbon

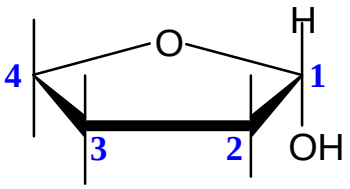


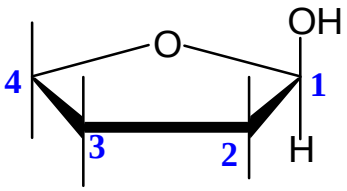


a- Pyranose



b- Pyranose

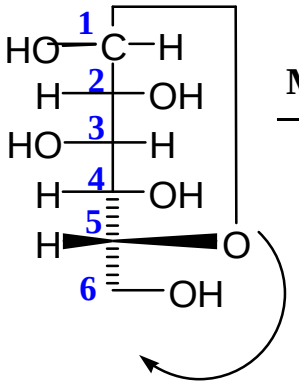




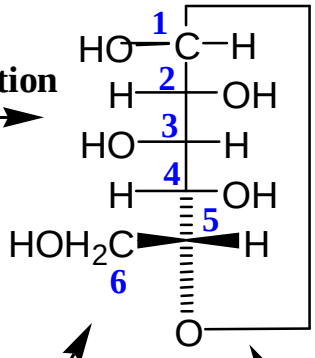
a- Furanose

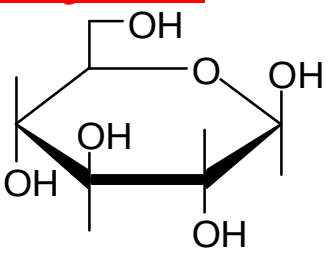
b- Furanose

Transformation from Fischer ro Haworth Projection



Modification





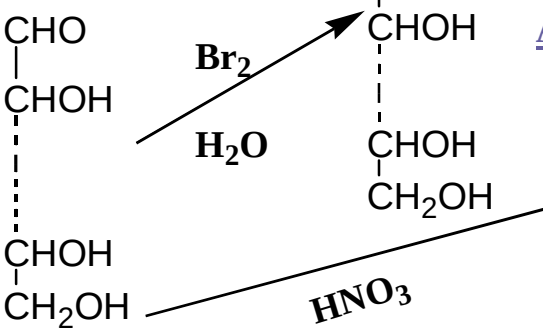
All the groups Right of the middle are Below the ring and the Left ones are above the ring

Above the ring

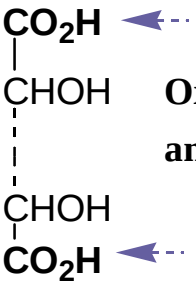
Below the Ring

Reactions

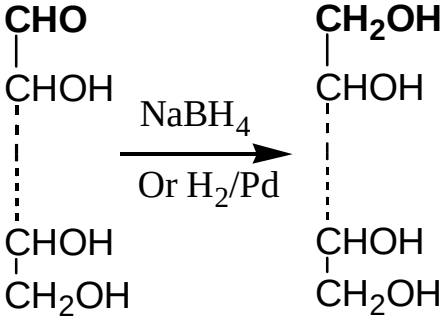
Oxidation



Oxidates the Aldehyde Only



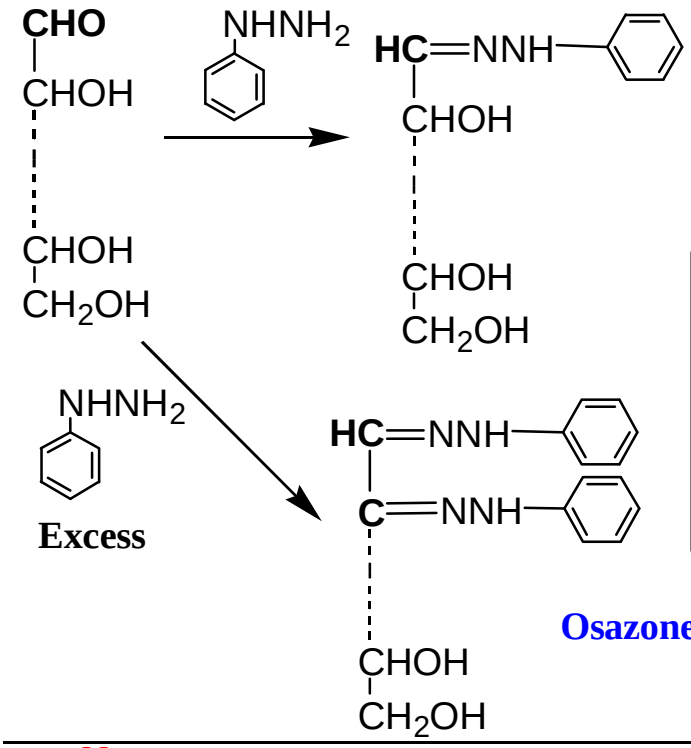
Oxidates Both Aldehyde and 1^0 Alcohol



Reduction

These Reagants reduce the Aldehyde to Alcohol.

If we use HNO_3 or H_2/Pd or $NaBH_4$ on Allose or Galactose we would get Meso form and lose Chirality

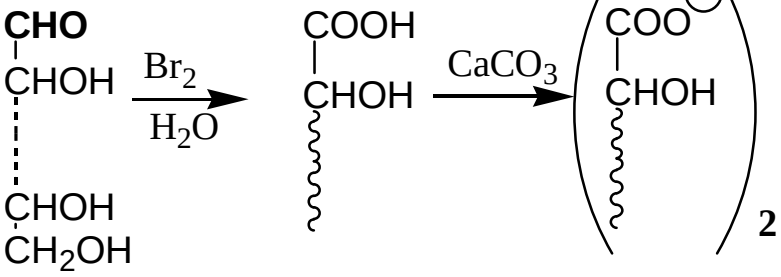


Phenylhydrazone

This reaction occurs only on carbons 1 & 2.It helps us to identify the Carbohydrates that have a difference only in carbon No. 2, because they'll give the same Osazone

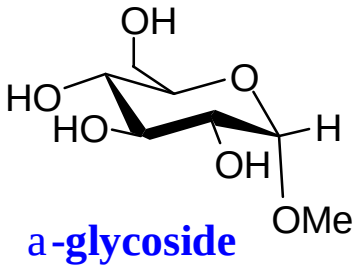
Osazone

Ruff Reaction

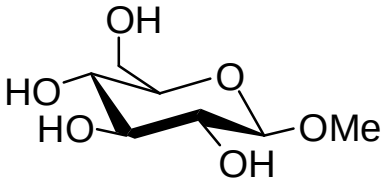


This reaction removes one carbon from the aldehyde end

Glucose $\xrightarrow[H^+]{MeOH}$

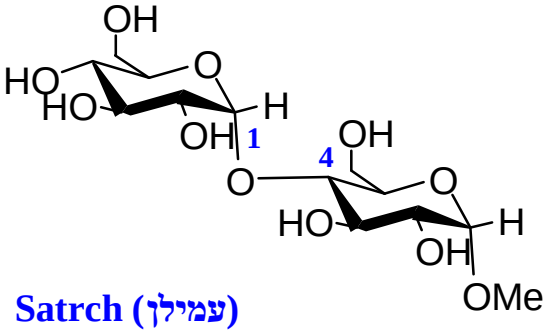


a-glycoside

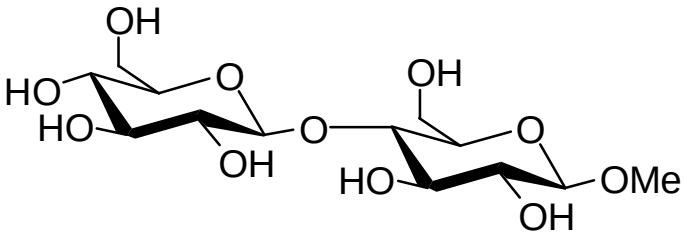


b-glycoside

These Ketals don't change between the a, b **Mutarotations and therefore we can seperate them**



Satrch (עמילן)
Polymer of b**(1-4) Glucose**



Cellulose (תאית)
Polymer of a(1-4) Glucose