

Study Material

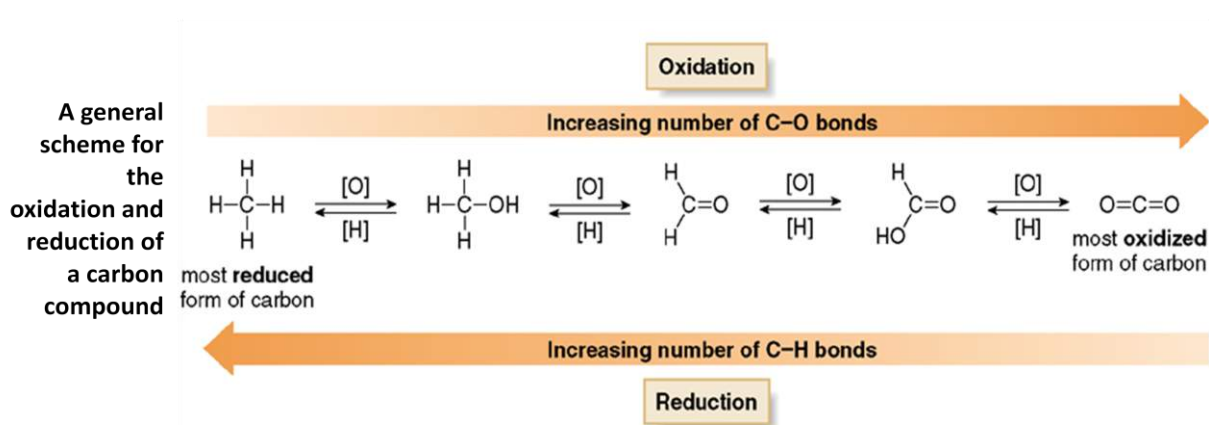
M.Sc. Sem IV

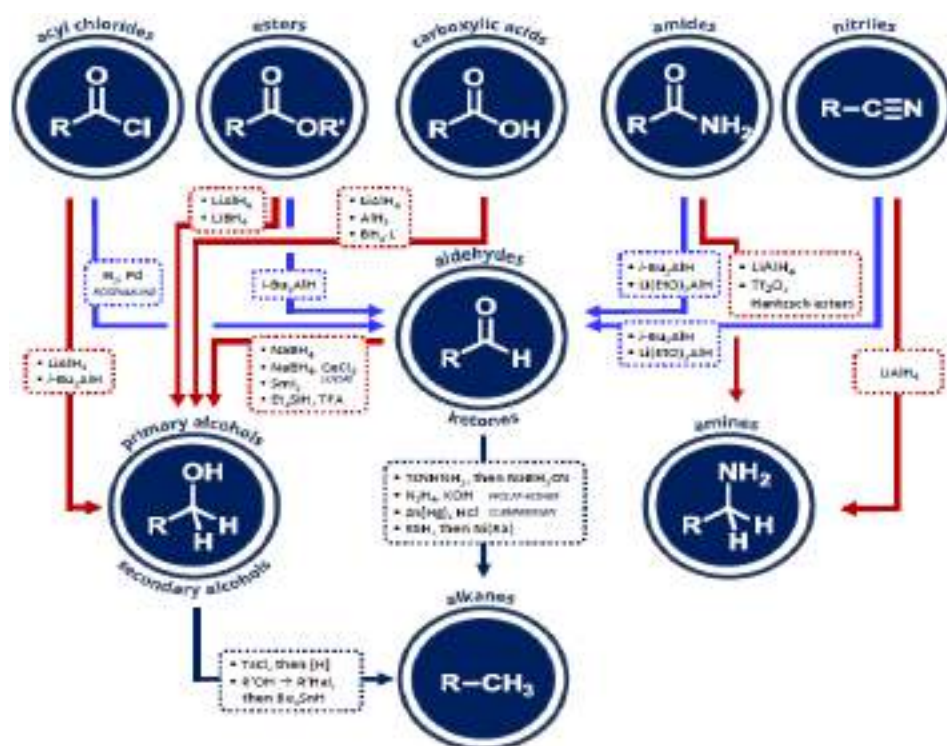
Reduction

Oxidation and Reduction

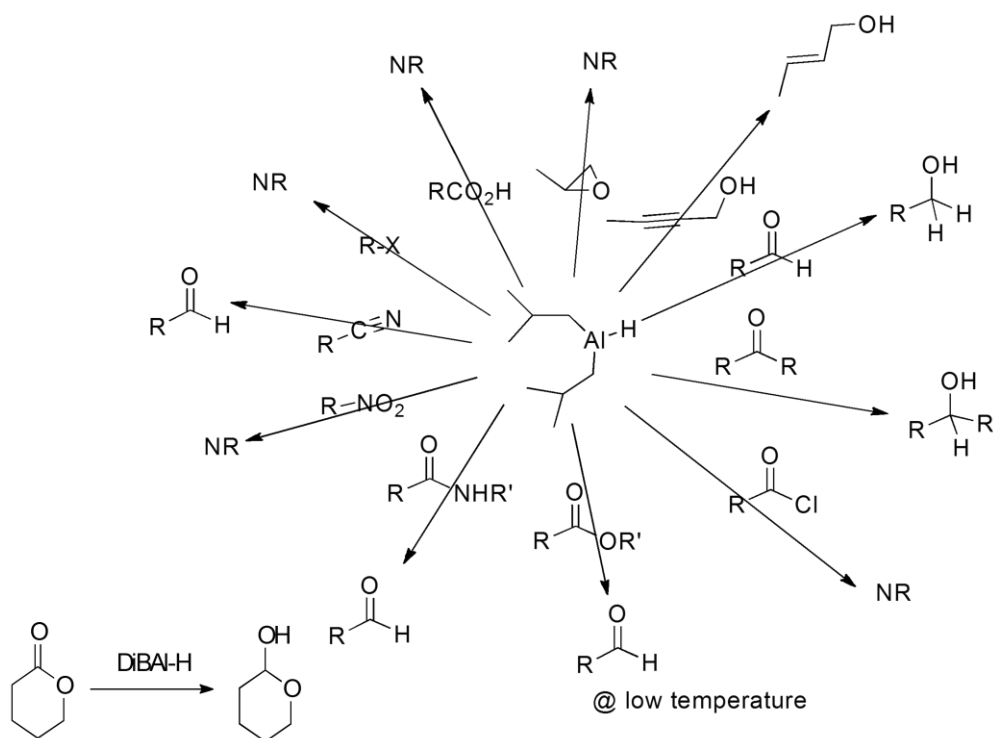
Introduction

- oxidation results in an increase in the number of C—Z bonds (usually C—O bonds) or a decrease in the number of C—H bonds.
- reduction results in a decrease in the number of C—Z bonds (usually C—O bonds) or an increase in the number of C—H bonds.

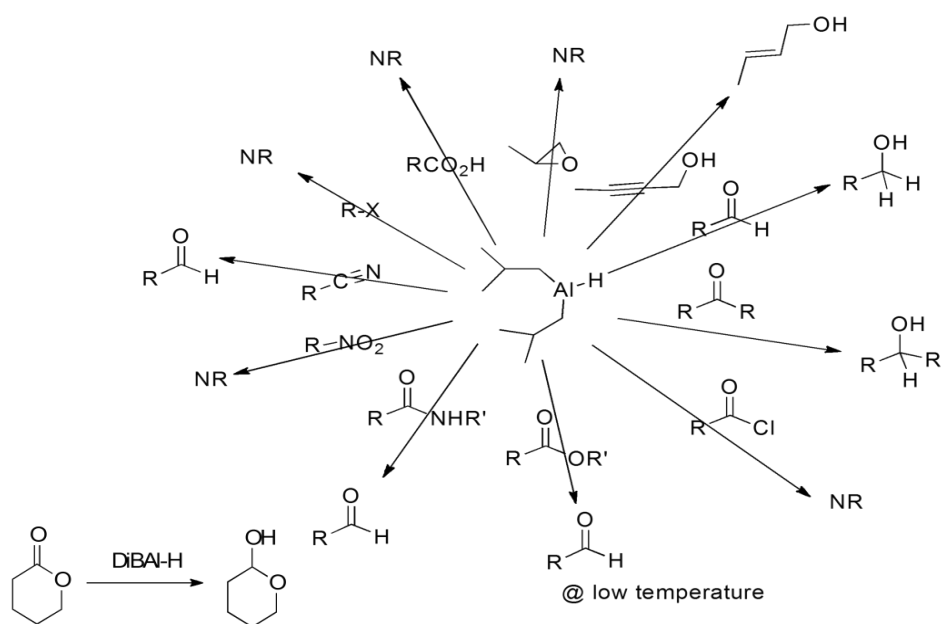




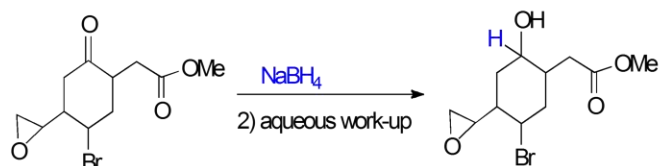
Reductions with DIBAL-H



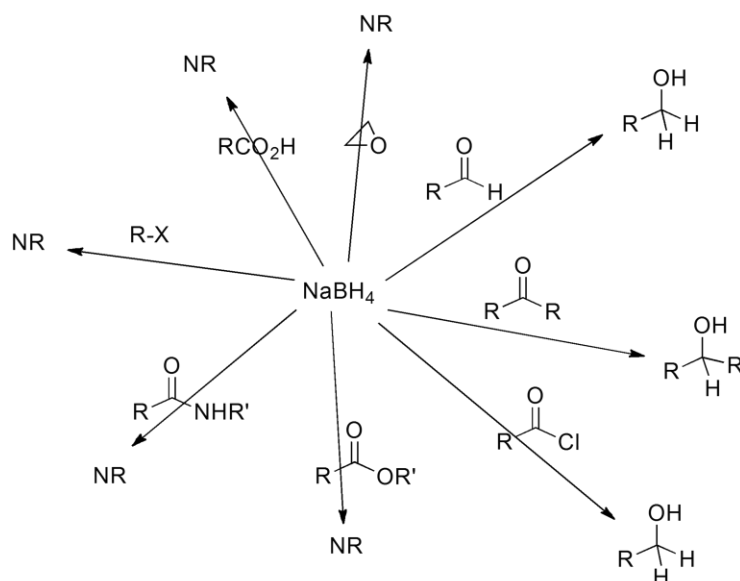
Reductions with DiBAL-H



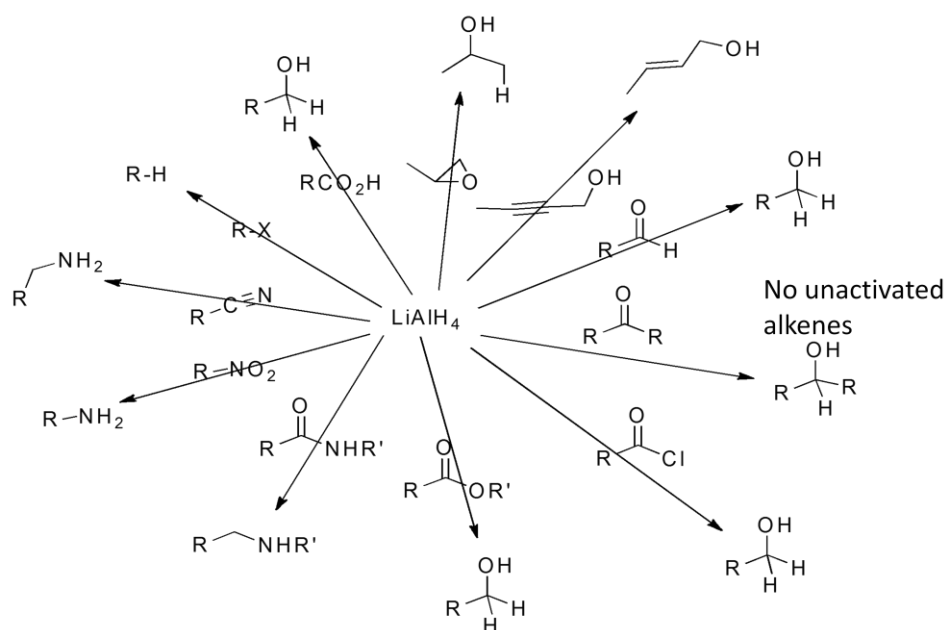
Sodium Borohydride Reductions in Synthesis



Less reactive;
More selective
Than LiAlH_4



Lithium Aluminum Hydride

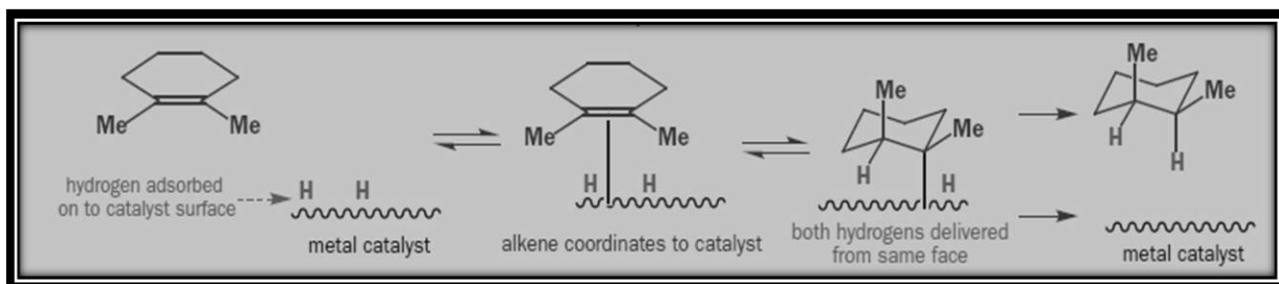
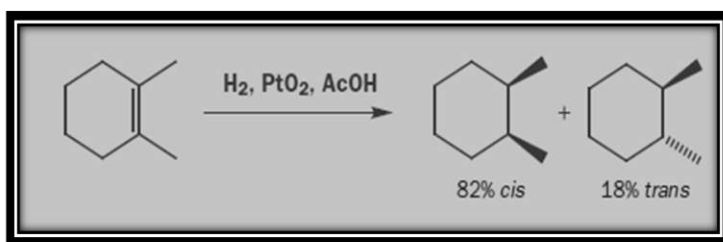


Strong reducing agent. Not very selective

Reduction of hydrocarbon(reduction of alkenes)

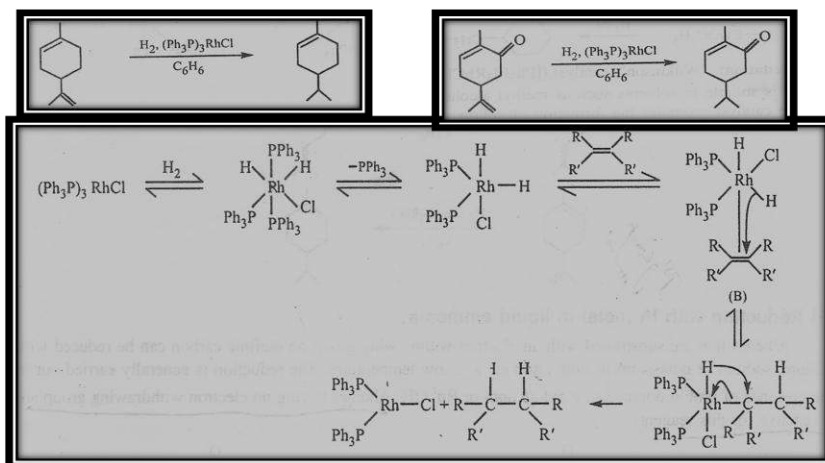
(1)Catalytic Hydrogenation

(a) Heterogeneous hydrogenation

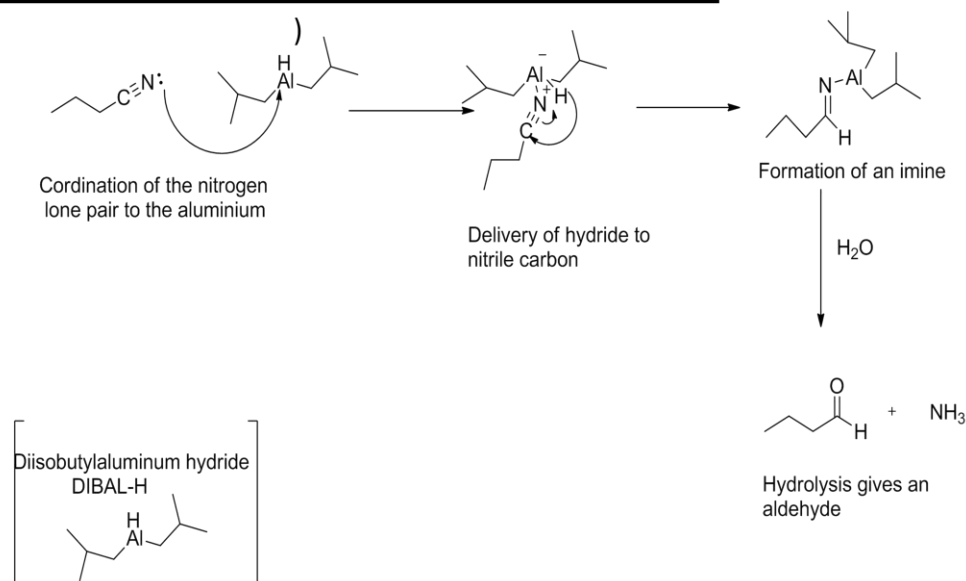
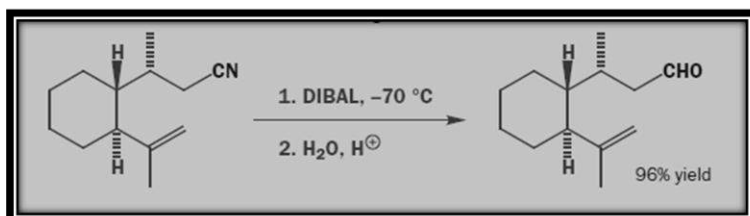


Homogeneous hydrogenation

- Wilkinson's catalyst is useful homogeneous catalyst of alkene.
- Mono- and disubstituted double bonds are reduced much more rapidly than tri- and tetrasubstituted one, permitting the partial hydrogenation of compounds.

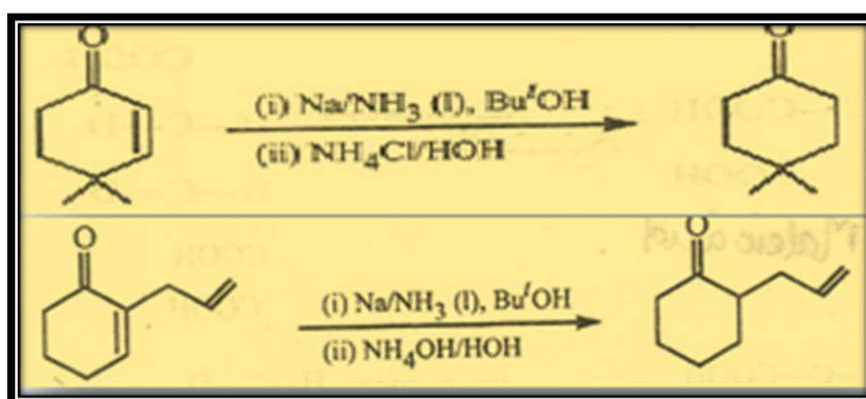


Reduction of nitriles to aldehyde

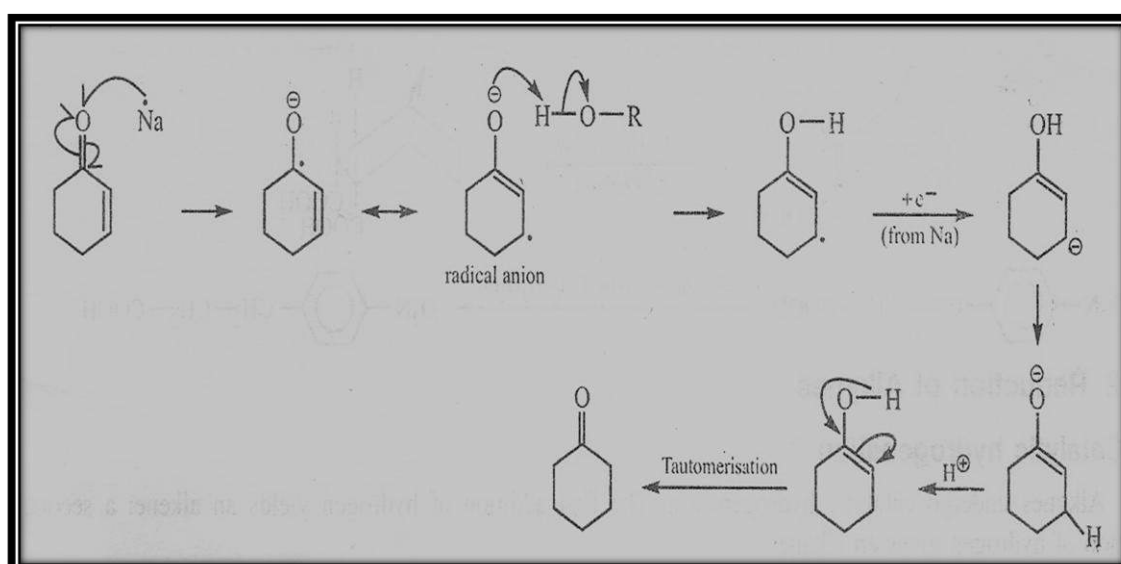


Reduction with IA metal in liquid ammonia

- Alkenes substituted with electron withdrawing group on olefinic carbon reduced with sodium in liquid ammonia.

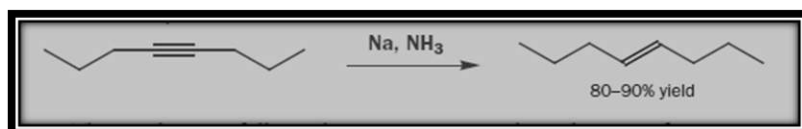
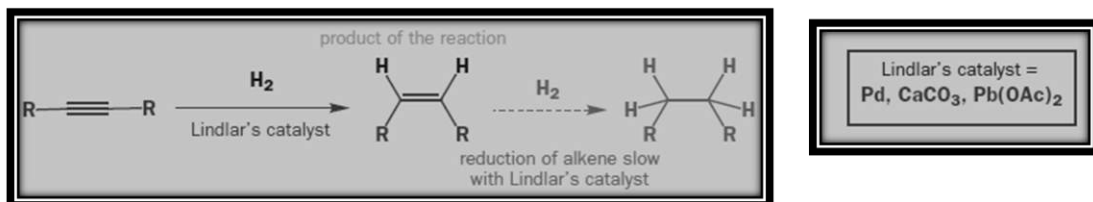


Mechanism for reduction with IA metal in liquid ammonia



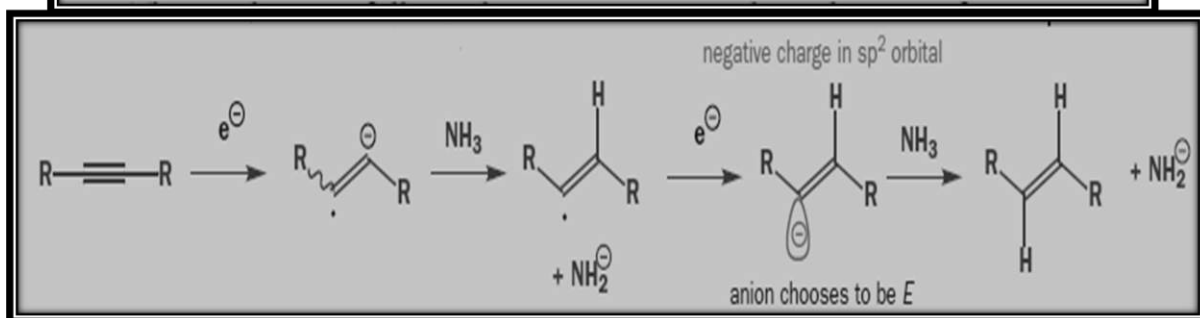
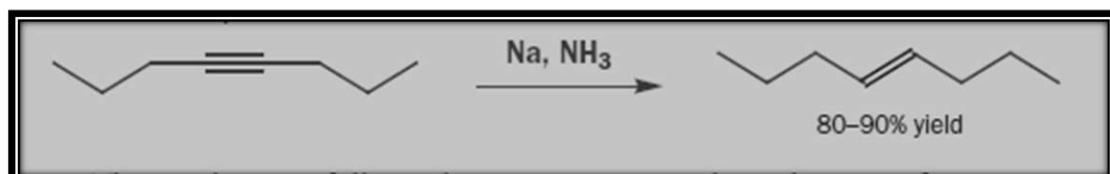
Reduction of alkyne

- Alkyne undergo catalytic hydrogenation to give alkane.
- Non terminal alkyne in the presence of Lindlar's catalyst is converted into cis alkene



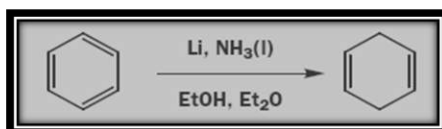
Reduction of alkyne with IA metal in liquid ammonia

- Nonterminal alkyne is converted into trans alkene with a solution of an alkali metal in liquid ammonia.

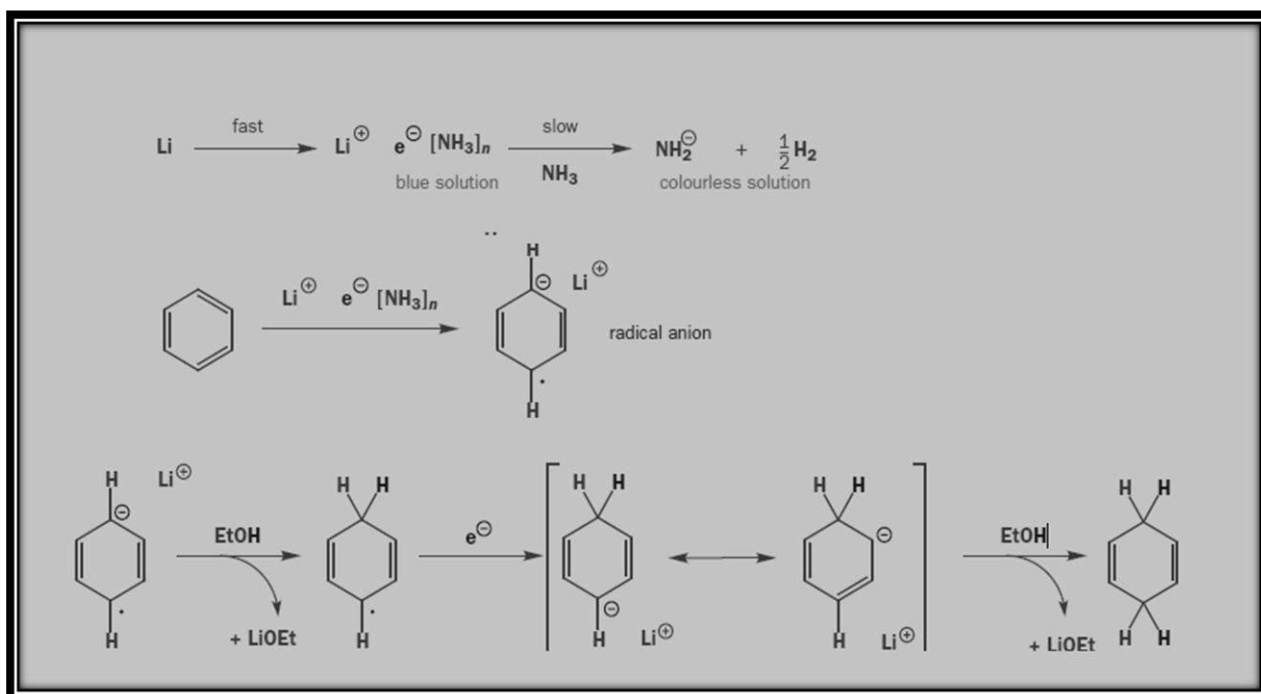


Reduction of aromatic ring “Birch reduction”

- Birch reduction is partial reduction of aromatic ring.
- Aromatic rings are reduced by Li in liq ammonia in alcohol.
- 1,4- addition of hydrogen takes place.
- Product is non-conjugated cyclohexadienes.



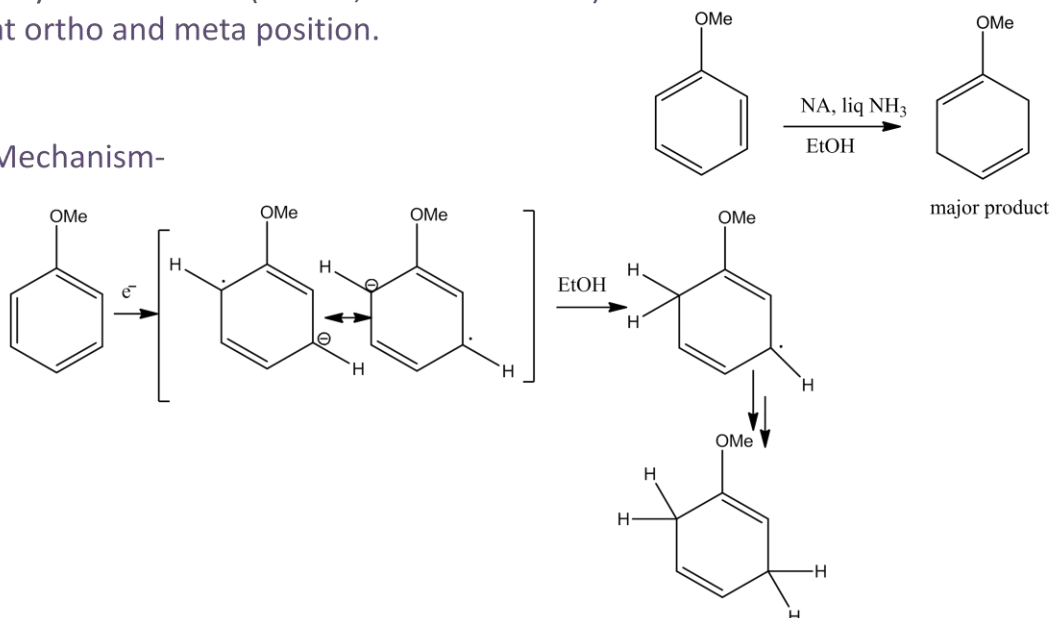
Mechanism



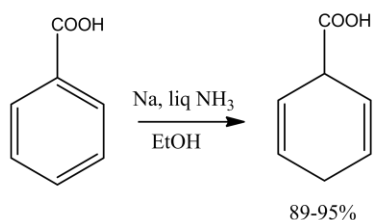
Reduction of substituted aromatic compounds with IA metal in liquid ammonia

- The birch reduction of a benzenoid comp. having an electron donating group (eg-methoxy), should lead, as it indeed does, to the 1-substituted 2, 5-dihydrobenzenes. (ortho, meta reduction) because it stabilise electron density at ortho and meta position.

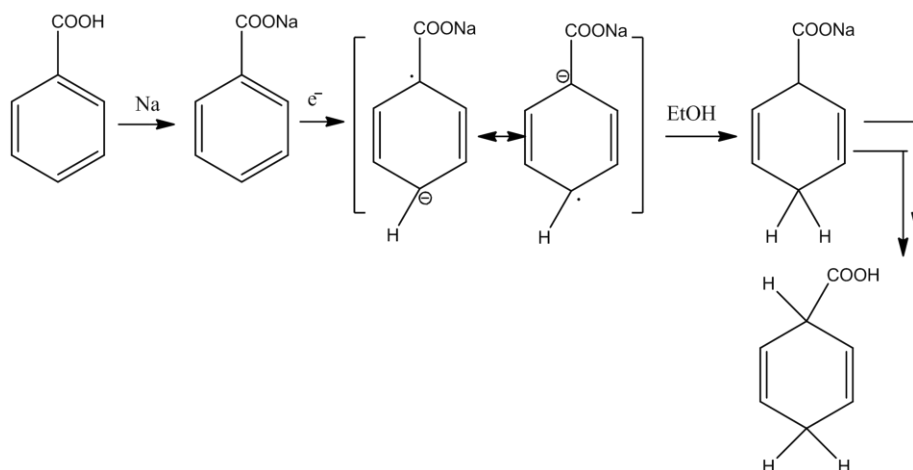
Mechanism-



- Electron withdrawing group(eg- carboxylic acid) gives 1-substituted 1, 4-dihydro benzenes (ipso, para reduction) because it stabilise electron density at ipso position.

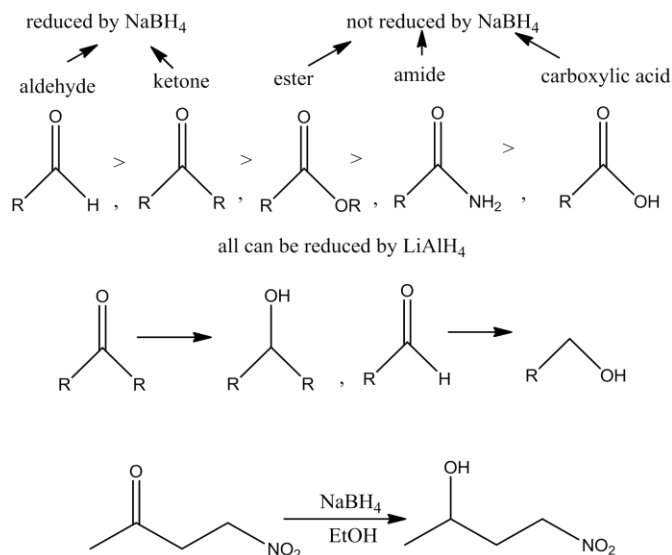


Mechanism -



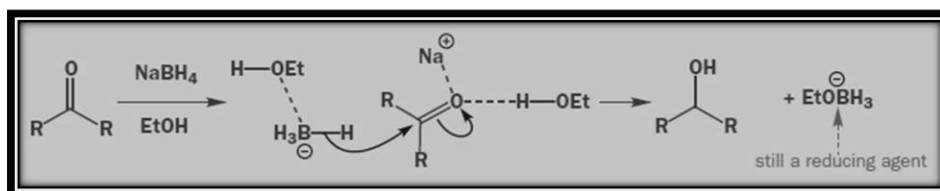
Reduction of aldehydes and ketones

- Sodium borohydride reduces aldehydes and ketones to alcohols.
- It reduces the compounds only in protic solvents.
- It is a more selective reducing agent as it reduces the nitroketones to nitroalcohols whereas LiAlH_4 reduces the nitro group as well.



Mechanism

- Importance of the reaction is transfer of hydrogen atom with two electrons (hydride transfer without involving hydride ion).



Reduction of α,β -unsaturated carbonyl compound

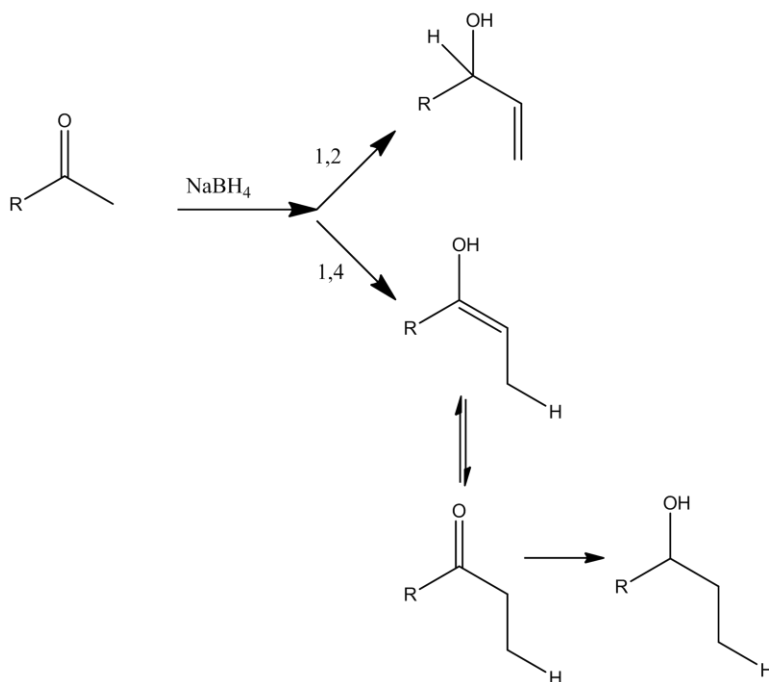
Red of cyclopentanone by NaBH_4 can lead to two products A and B. The allylic alcohol A derives from 1,2-attack of hydride onto ketone. While fully reduced comp originates from 1,4-attack tautomerism of the enol and further red of the ketone product.

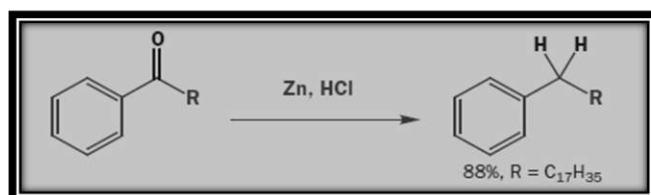
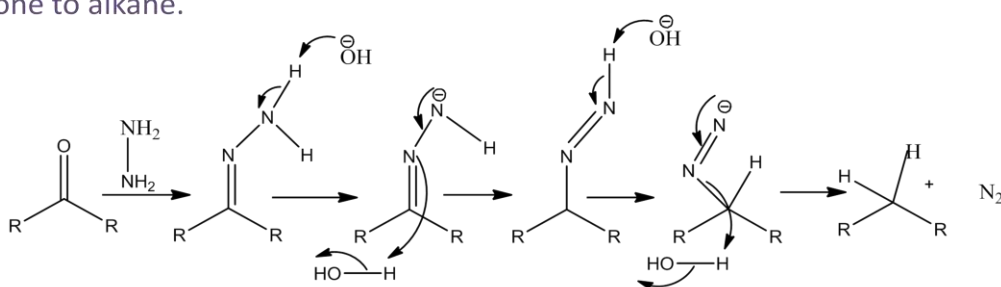
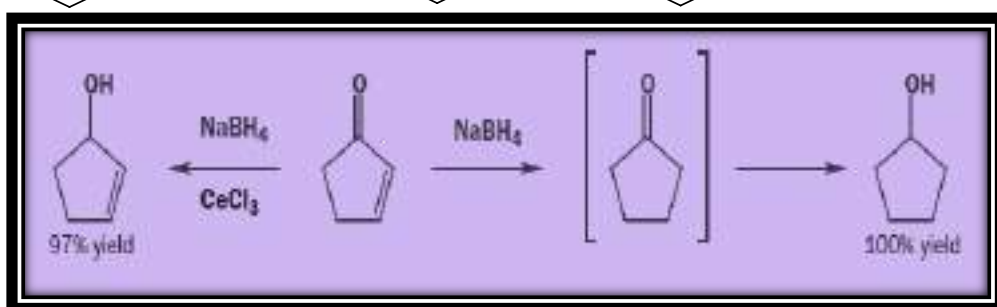
Reduction of cyclopenten-3-one with sodium borohydride in alcohol produces cyclopentanol.

Product is formed by the initial conjugate addition of hydride to the β –carbon atom, followed by ketonization of the enol product and reduction of the resulting saturated ketone.

Luche reduction- Reduction of cyclopenten-3-one in the presence of ceric chloride yields the unsaturated alcohol.

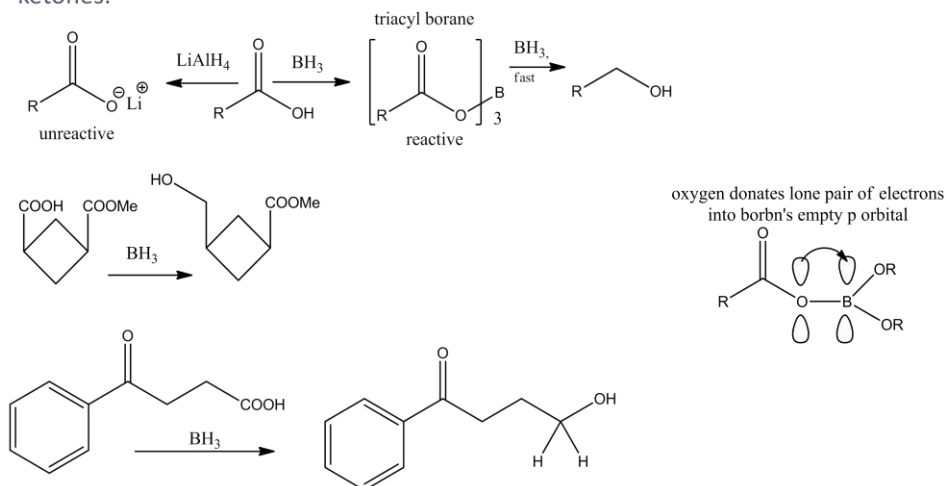
Mechanism





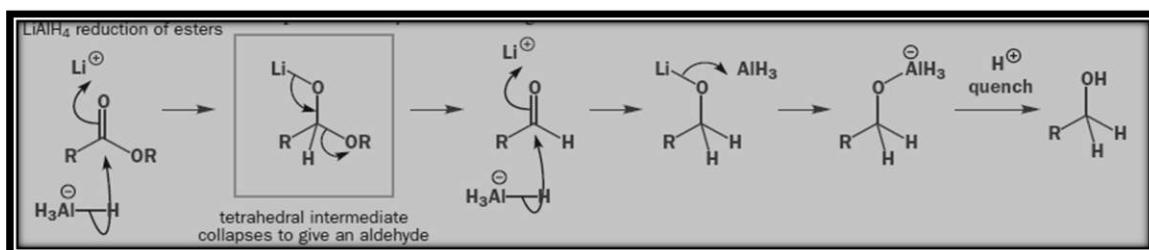
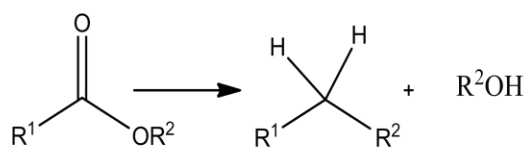
Reduction of carboxylic acid

• Borane is a chemoselective reagent for the reduction of carboxylic acid in the presence of other reducible functional groups such as esters and even ketones.



Reduction of esters to alcohol

Esters reduces to alcohol by LiAlH_4



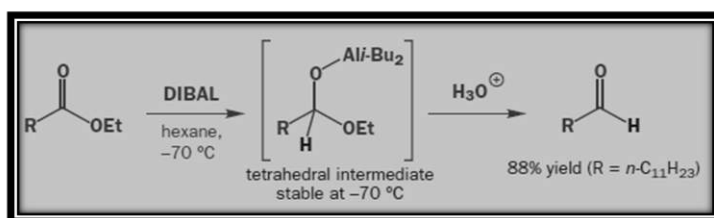
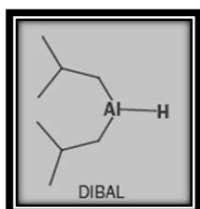
Selective reduction of esters to alcohol

Lithium borohydride in alcoholic solution reduces esters. It has selectivity for esters over acids or amides that LiAlH_4 does not have.

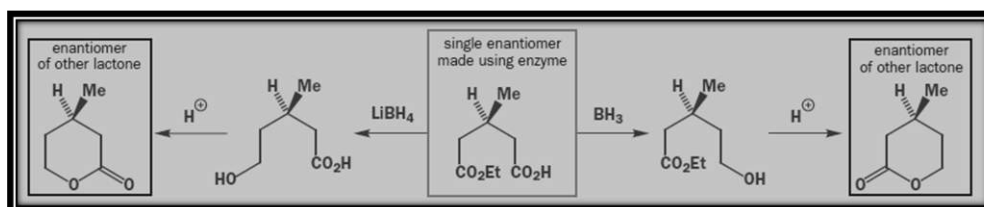


Reduction of esters to aldehyde

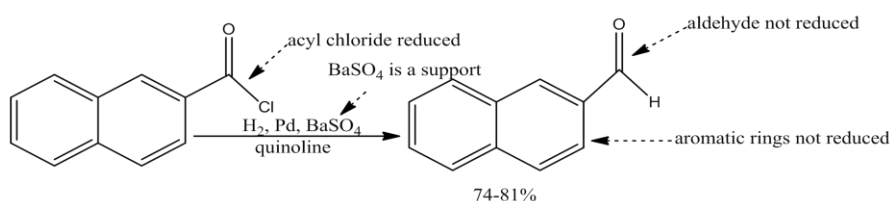
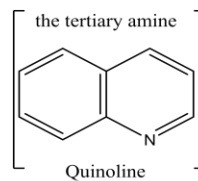
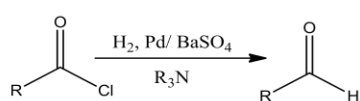
•DIBAL reduces esters to aldehyde at -70°C . At this temperature tetrahedral intermediate is stable.



Chemoselective reduction

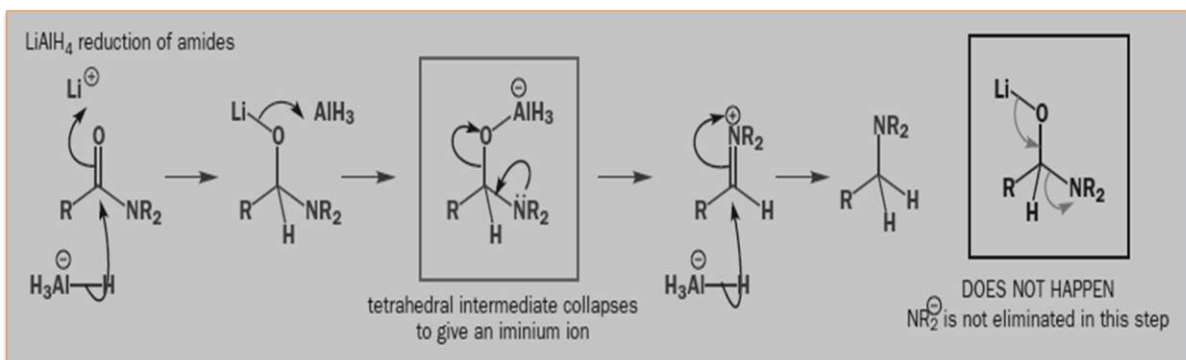
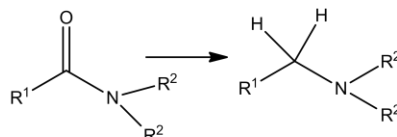


Reduction of acid chloride to aldehyde

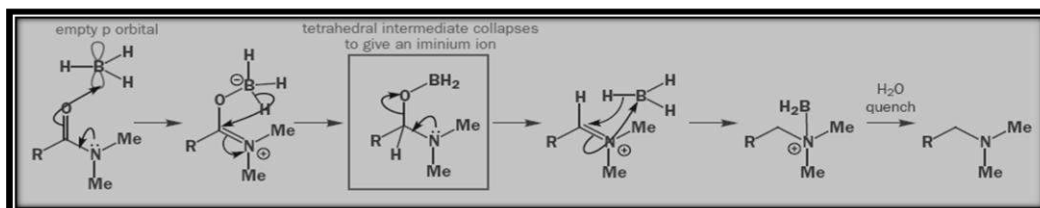
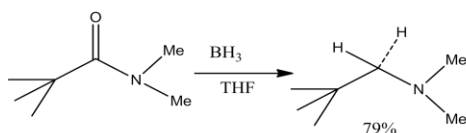


Reduction of amide to amines

•LiAlH₄ reduces amide to amine.



Reduction of amide to amine with borane



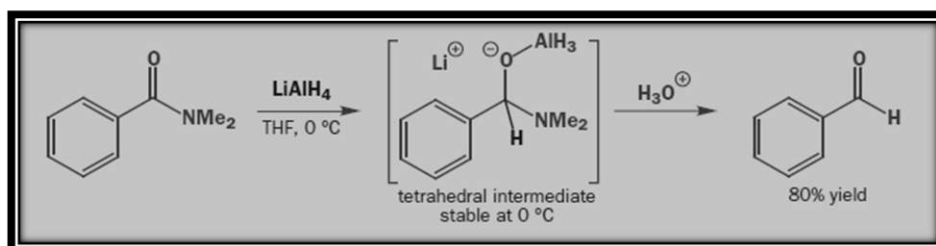
Chemoselective Reduction

- Borane reduces amide to amine in the presence of an ester

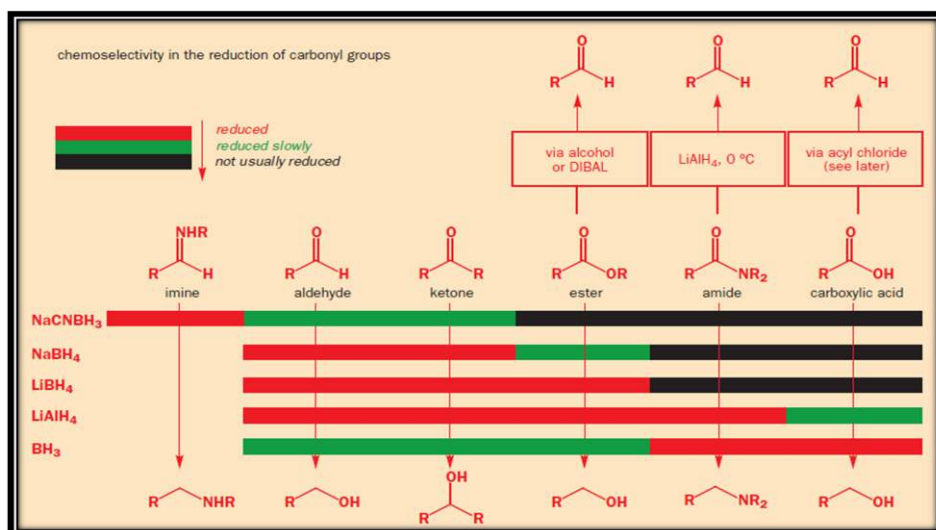


Reduction of amide to aldehyde

- Lithium aluminium hydride at 0°C reduces amide to aldehyde.

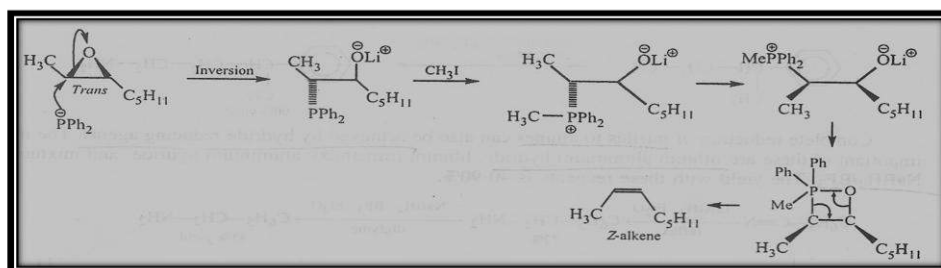


Carbonyl reduction using hydride reducing agent

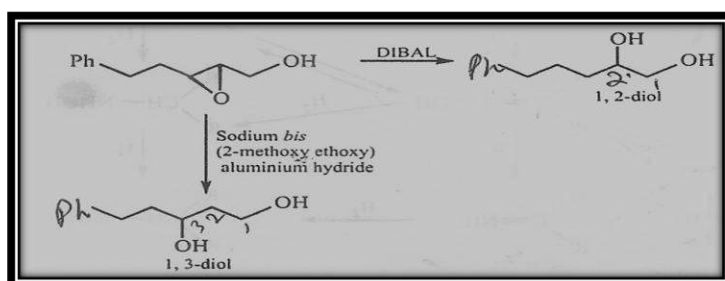
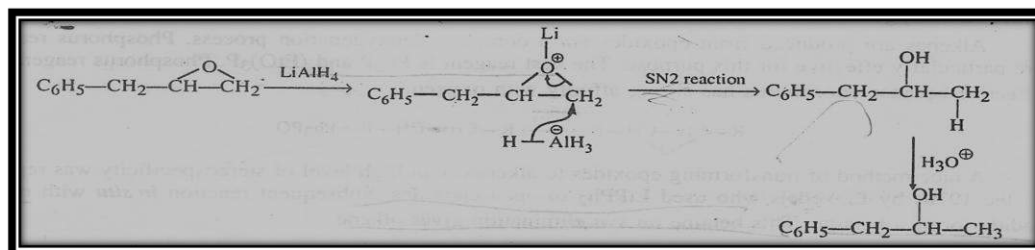


Reduction of epoxide to alkene

- First step is the reaction of epoxide with LiPPh₂ which opens the epoxide ring.
- Second step is the subsequent reaction *in situ* with methyl iodide which gives betaine.
- Betaine on *syn* elimination gives alkene.



Reduction of epoxide to alcohol

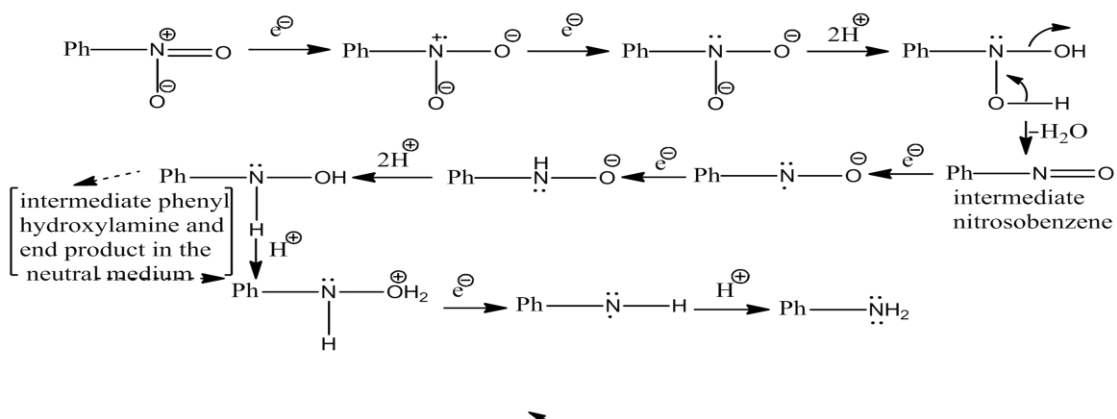


Reduction of nitro group

- Amino gp. can not be introduced into benzene ring directly, nitro gp. Is initially introduced and then it is reduced to get aromatic amine.
- Different types of reduced products are obtained under different conditions and under different pH.
- Exact order of addition of electrons and protons depends on source of electrons and pH of the medium.

Mechanism-

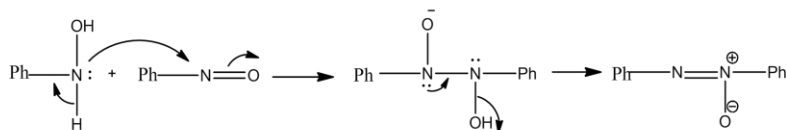
In the acid and neutral medium-



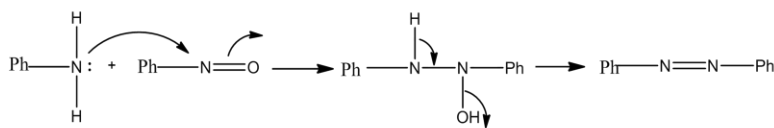
Mechanism-

In the alkaline medium-

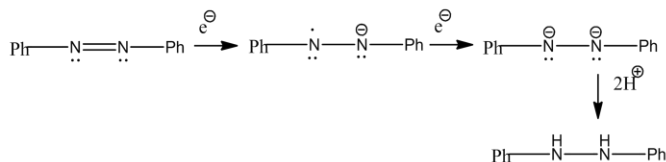
-in the alkaline medium and in presence of sodium arsenite (which is an electron source: $\text{AsO}_3^{3-} \rightarrow \text{AsO}_3^{4-} + 2e^-$), the final product azoxybenzenen is formed by condensation of intermediates phenyl hydroxylamine with nitrosobenzene.



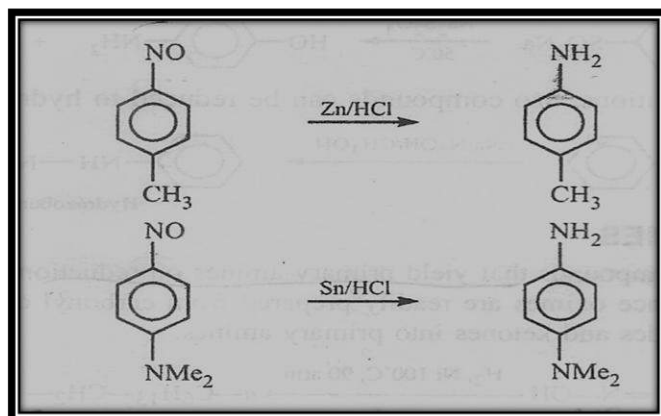
in the alkaline medium and in presence of iron, azobenzene is obtained probably by the condensation of aniline with intermediate nitrosobenzene .



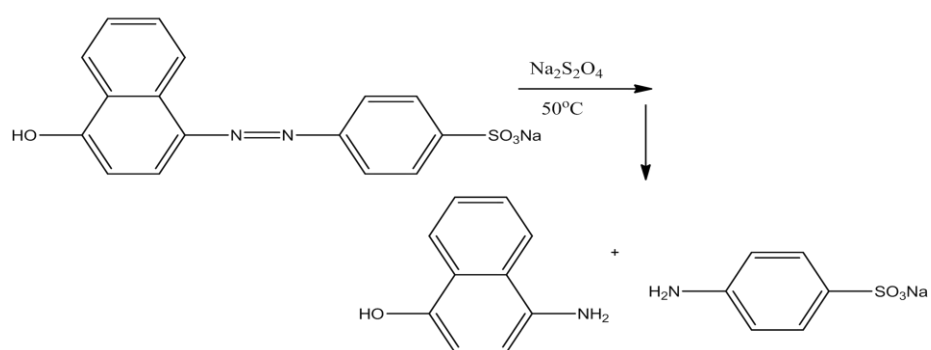
in the alkaline medium and in presence of zinc, hydrazobenzene is obtained by the reduction of azobenzene.



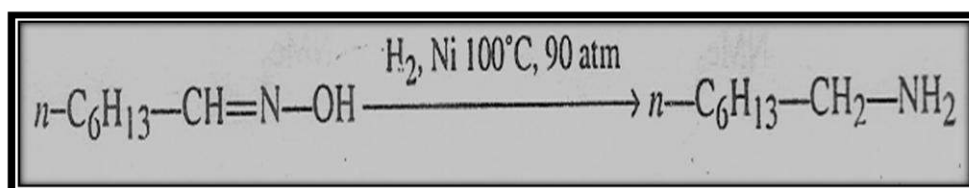
Reduction of nitroso compound with metal and acid



Reduction of azo compounds

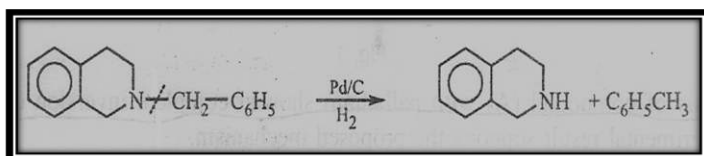


Reduction of oximes

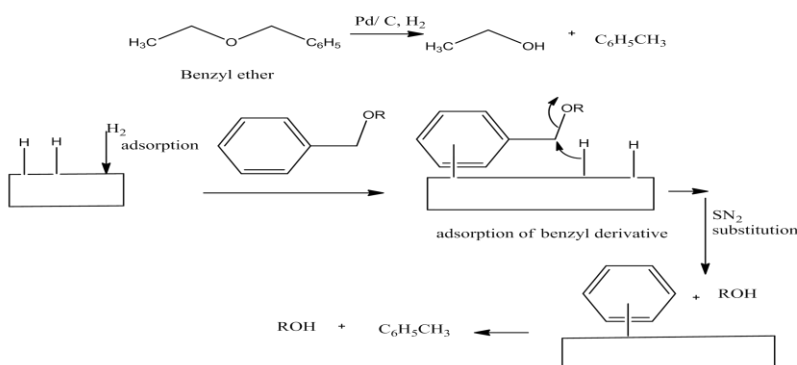


Hydrogenolysis of amines

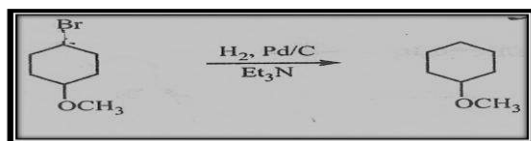
- Reductive cleavage reaction:
- Reaction which completely cleaves the bonds between carbon and electronegative elements, replacing them with bonds to hydrogen are known as reductive cleavage.
- Reductive cleavage when carried out with hydrogen and catalyst is known as hydrogenolysis.



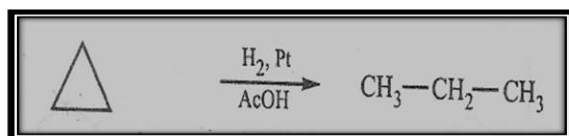
Hydrogenolysis of benzyl ethers



Hydrogenolysis of C-X bonds



Hydrogenolysis of cyclopropane ring



**Material has been taken from various sources for the purpose of class room teaching.*