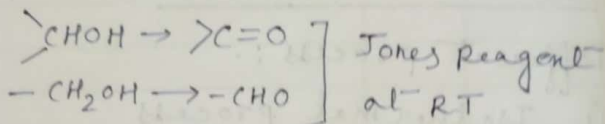


Oxidizing agent:

- (I) Cr(VI)
- (II) Mn(VII)
- (III) Mn(IV)
- (IV) DMSO
- (V) $\text{PB(OAc)}_4, \text{H}_2\text{SO}_4$
- (VI) O_3

Hydroxylate

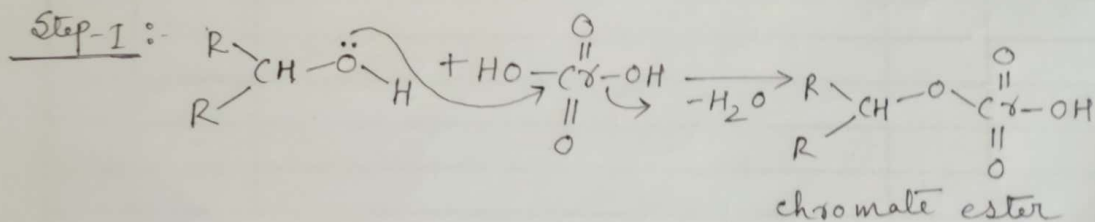
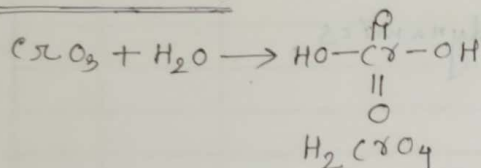
- (I) OsO_4
- (II) KMnO_4
- (III) MCPBA
- Cr(VI) in acidic medium
- CrO_3 in 8N H_2SO_4 in acetone



Role of acetone

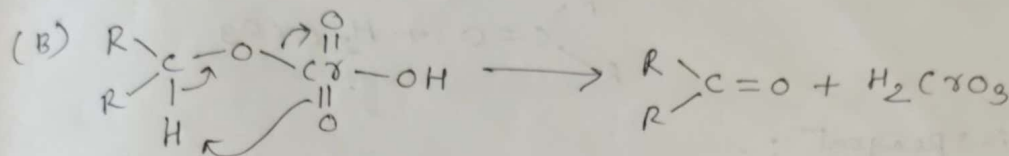
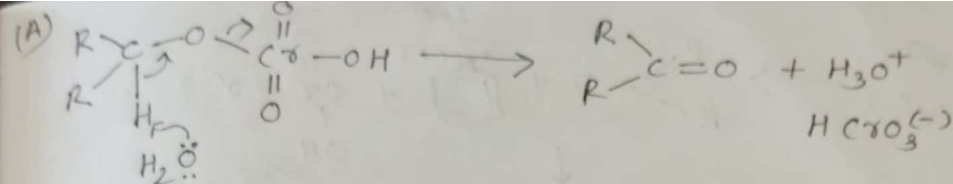
- (I) Excellent solvent for both Cr(VI) and organic substance.
- (II) Prevents further oxidation of aldehyde / ketone

Mechanism:

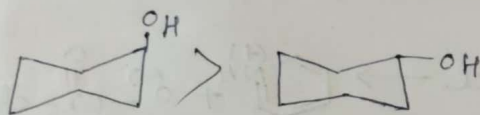
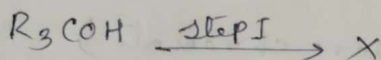
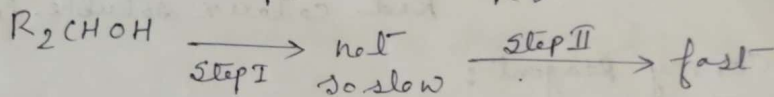
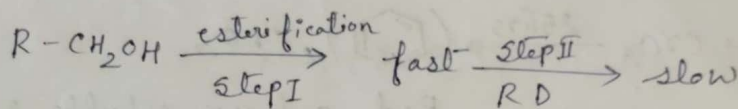


Step II cleavage of ester

- (A) Inter molecular
- (B) Intra molecular



* Difference:-



1, 3 diaxial fast interaction is there

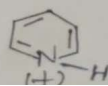
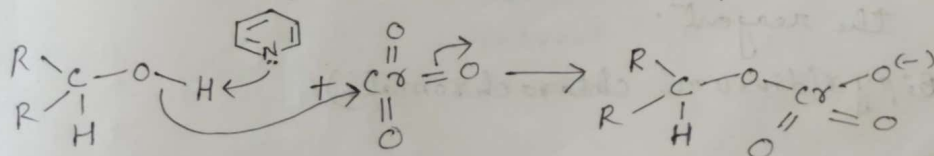
Disadvantage:- (I) strongly acidic for which the migration of $C=C$ takes place.

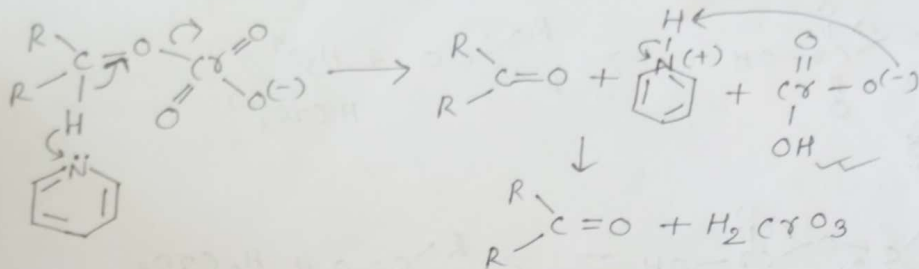
(II) Allylic and benzylic position may be affected

(III) Group such as ester, ketones, amines also affected.

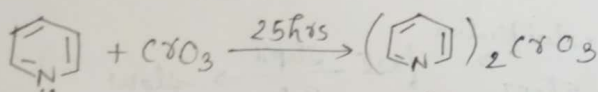
Secret Reagent:-

CrO_3 is added to pyridine Sparingly solution is (not in reverse order) chloroform is solvent.





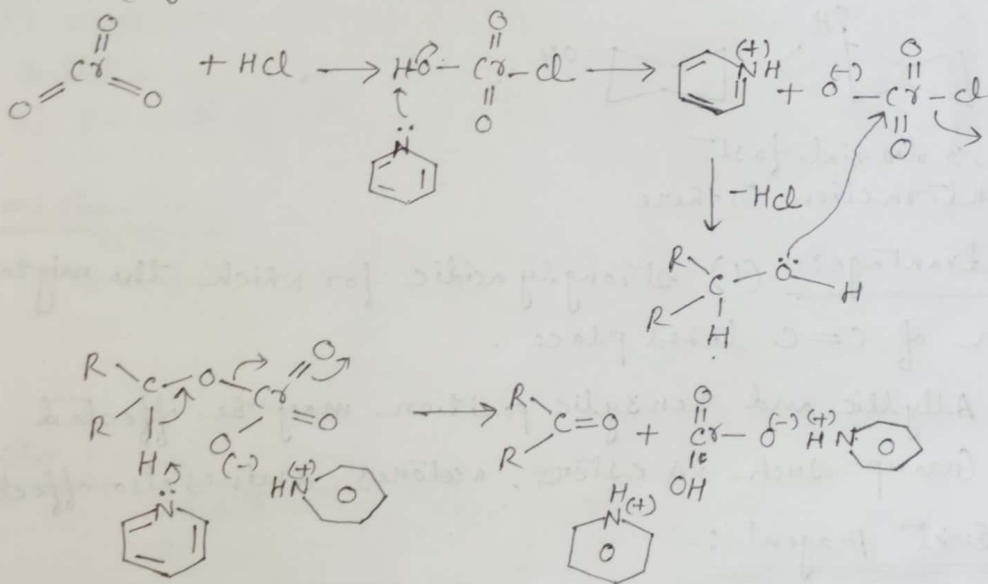
Collins reagent : -



Red colour soluble in DCM, $CHCl_3$

Correy reagent :

PCC (pyridinium chlorochromate)



→ Strongly acidic buffered with NaOH to control the acidity of the reagent.

BPC (Bipyridinium chlorochromate).

* $Mn(VII)$ oxidation of alcohol

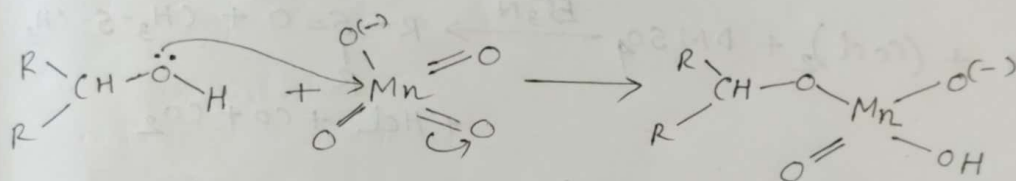
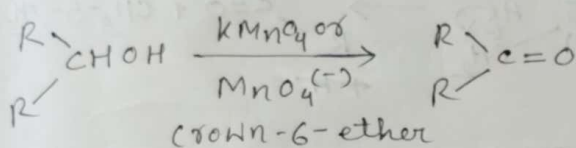
KMnO_4 (acidic, basic, neutral)

KMnO_4 is insoluble in non-hydroxylic solvent,

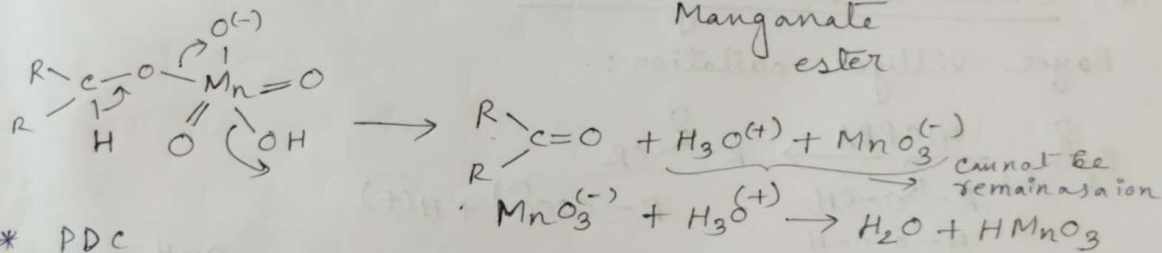
Common hydroxylic solvent like alcohol undergo oxidation.

* PTC eg: $[(R_4N)^+ Bx^-]$ or $[(R_4P)^+ Bx^{(-)}]$ or crown-8-ether

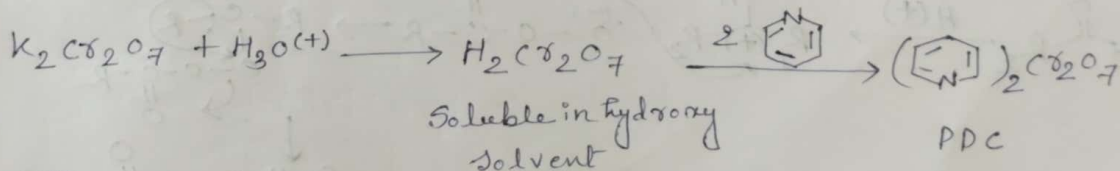
with KMnO_4 to make it soluble in Hydroxylic solvent



Manganate ester



* PDC

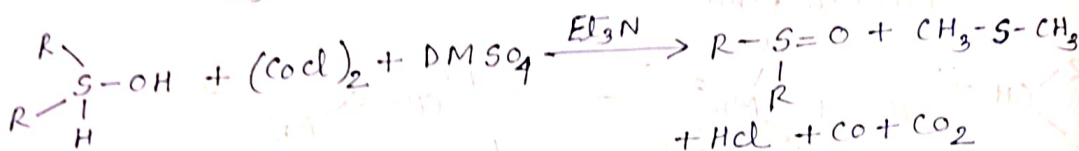
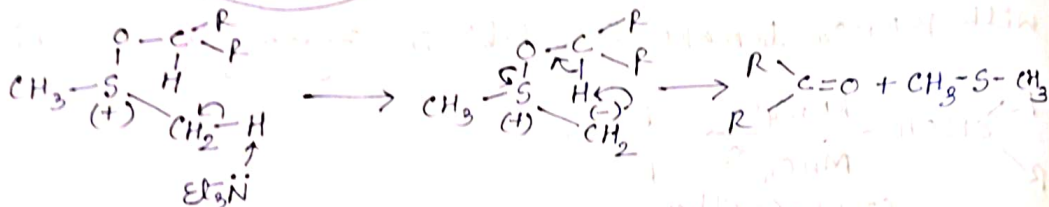
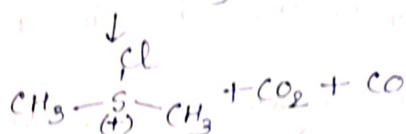


The reactivity is enhanced by adding 3AMS ^{solvent}

PDC / PCC

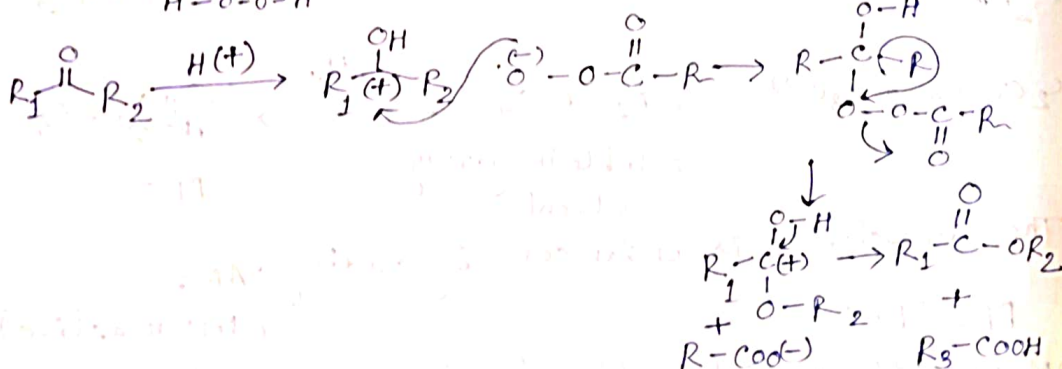
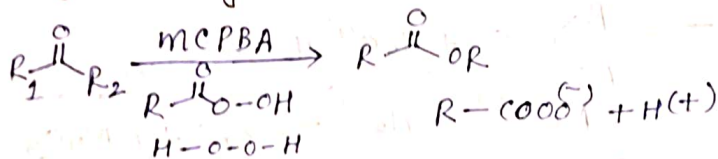
(less reactive)

* DM SO with oxalyl chloride (Swern's oxidation)

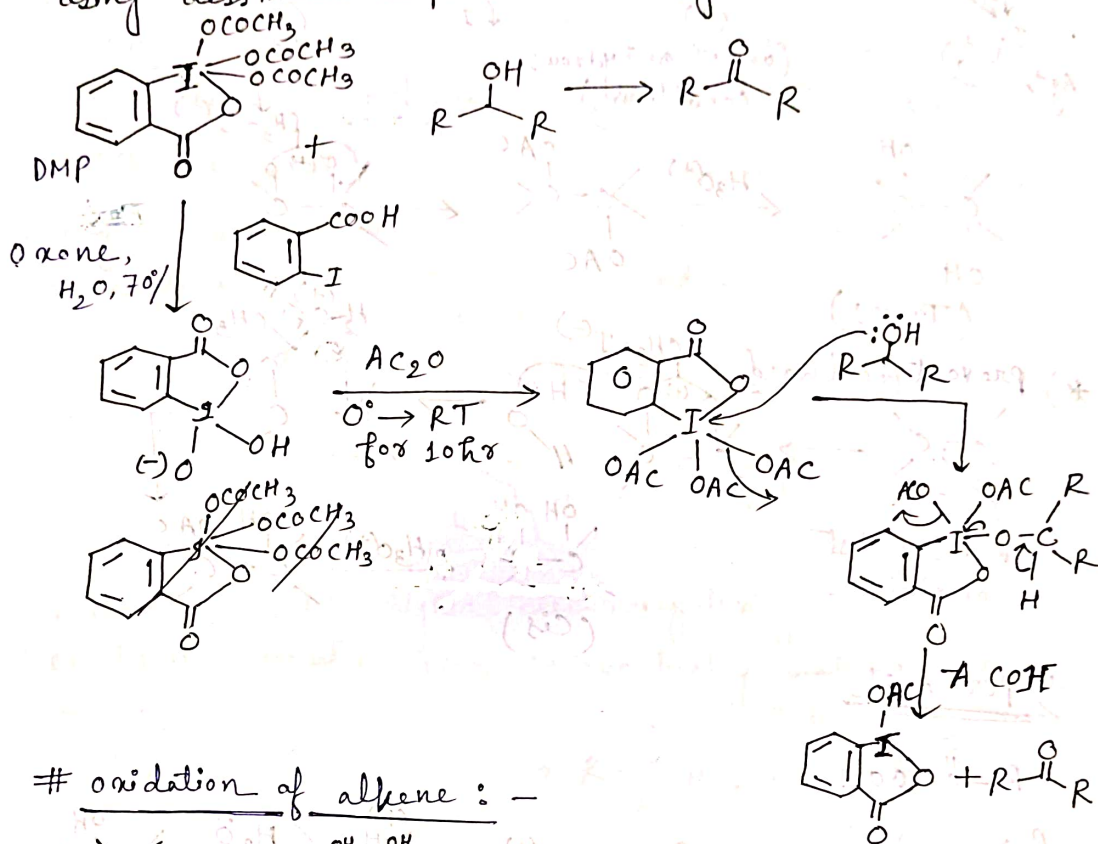


(*) Oxidative Rearrangement

Bayer-villiger oxidation:-



Dess martin periodinane oxidation :- involves the primary alcohol to aldehyde and 2° alcohol to ketone using dess martin periodine reagent.



oxidation of alkene :-



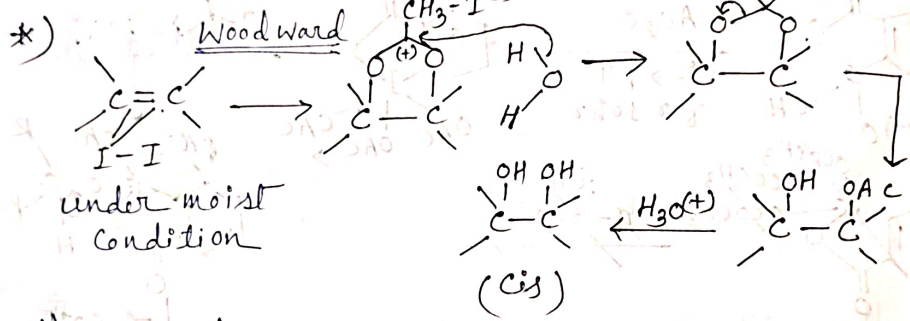
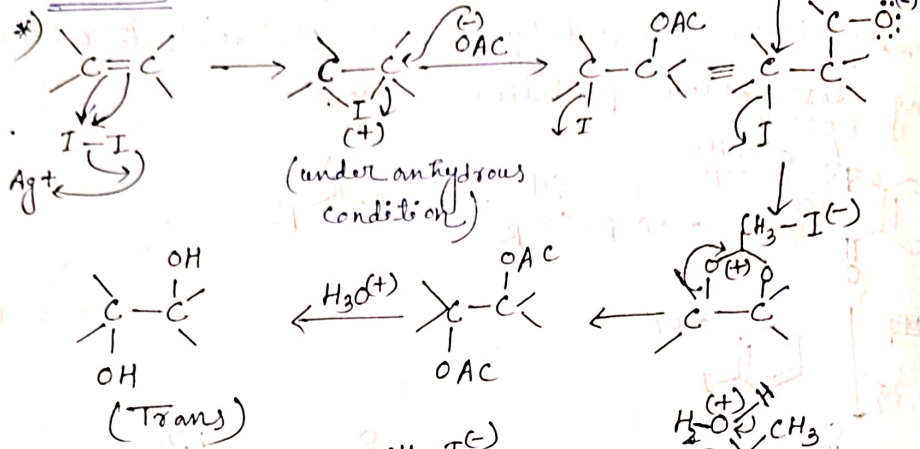
(a) per acid followed by H_3O^+

(b) $I_2 / AgOAc$ in anhydrous condition (prevost)

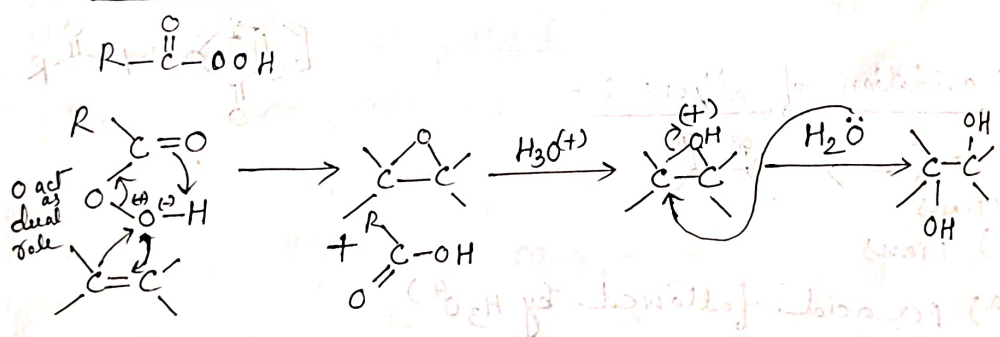
(1) cis-hydroxylation :- Woodward

$KMnO_4, OsO_4, I_2 / AgOAc / moist$

Prevost



per acid



Reduction:-

$\text{LiAlH}_4, \text{NaBH}_4, \text{H}_2/\text{Pd}, \text{Zn}/\text{Hg HCl}$

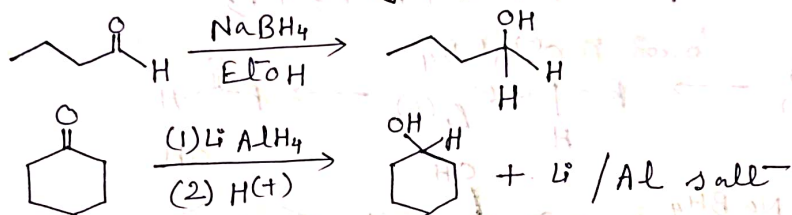
DIBAL-H

$\text{NH}_2\text{NH}_2/\text{KOH}$

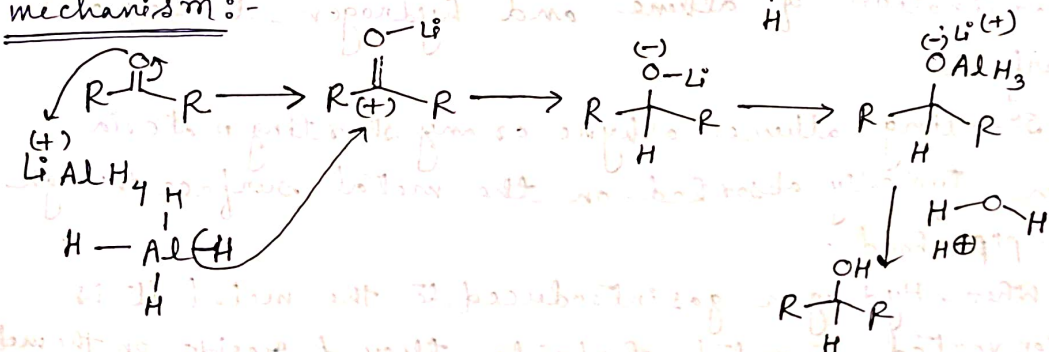
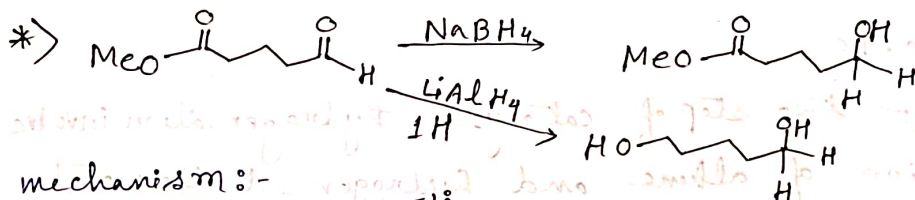
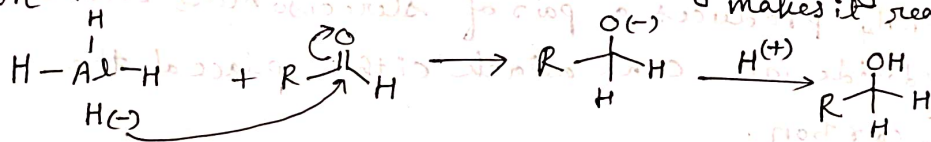
↓
mildest reagent

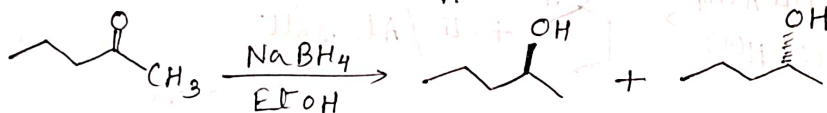
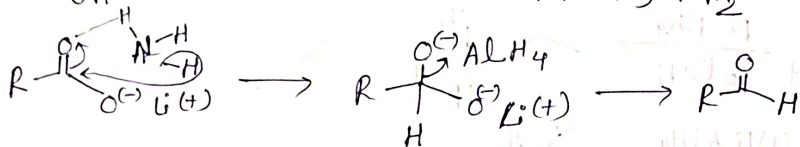
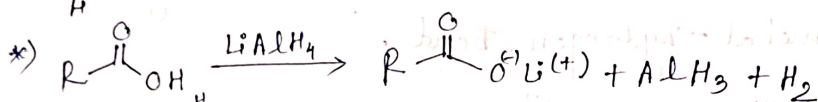
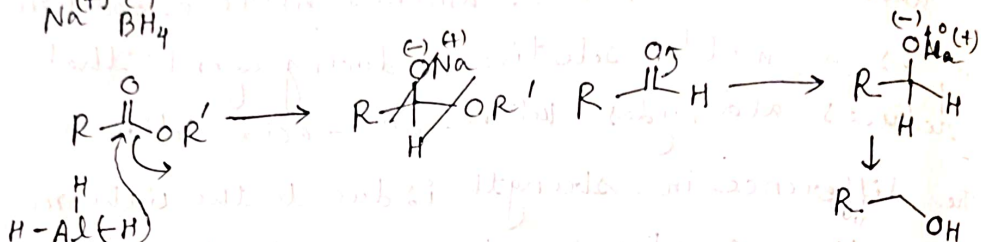
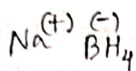
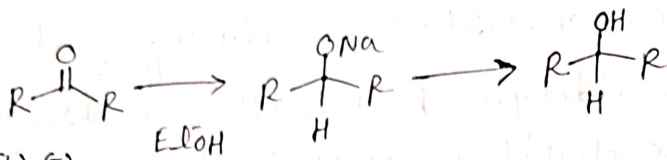
$\text{LiAlH}_4 \rightarrow$ Strong non-selective reducing agent that reduces aldehydes, ketones, esters, acids, amides, acid halide to alcohol or amines where as sodium NaBH_4 is a mild selective reducing agent that only reduces aldehydes, ketones and acid halide.

The difference in strength is due to the lithium being a better counterion than Na leading to a more polar metal-hydrogen bond.



Because of the higher electronegativity H_A bears highest electron density which is eventually making an H^- hydride ion. H_B bears lowest electron density which makes it react as an atom.





The reduction of unsymmetrical ketones with LiH or $NaBH_4$ produces a pair of stereoisomers because the hydride ion can attack either place of the planar carbon.

* H_2 / Zn or Fe

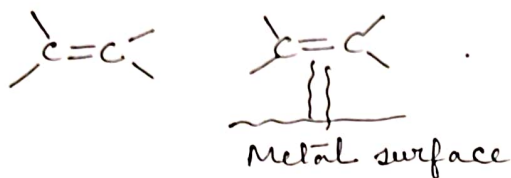
→ The first two steps of catalytic hydrogenation involve coordination of alkene and hydrogen to the metal surface.

→ Starting alkene, alkyne or any starting material can typically be absorbed on the metal surface through the pi bond.

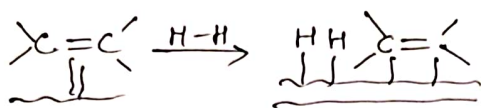
→ When hydrogen gas is introduced to the metal it is converted to metal hydride and resides on the metal surface.

Mechanism for catalytic hydrogenation (H_2/Pd): -

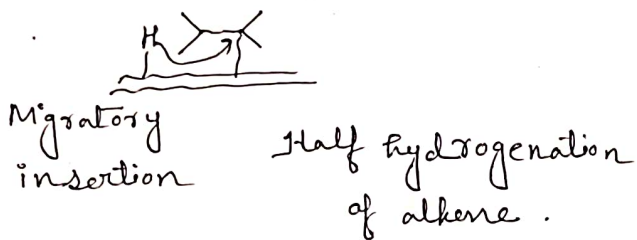
Step I: - Adsorption of alkene on Metal surface



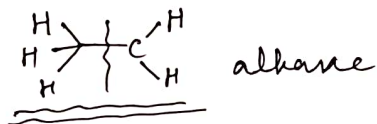
Step II



Step III Formation of First C-H Bond.

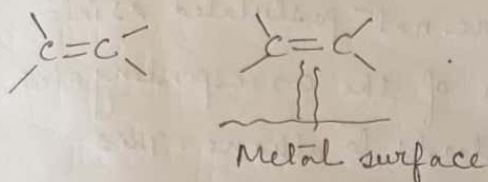


Step IV

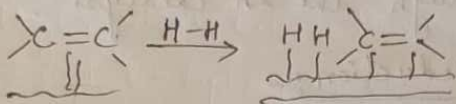


mechanism for catalytic hydrogenation (H_2/Pd): -

Step I: - Adsorption of alkene on Metal surface



Step II



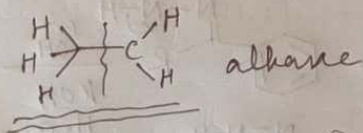
Step III Formation of first C-H bond.



Migratory
insertion

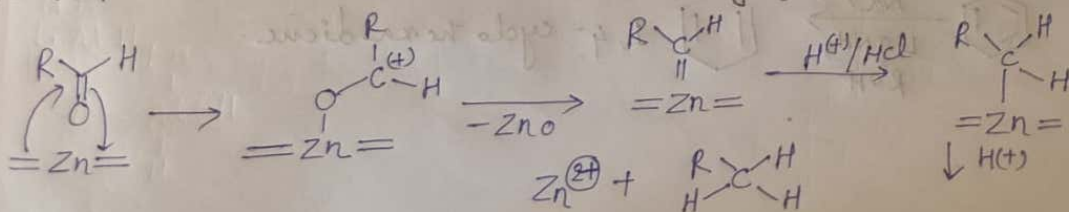
Half hydrogenation
of alkene.

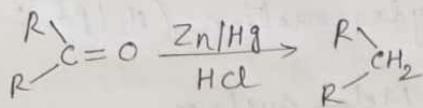
Step IV



* Clemenson Reduction: -

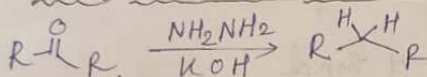
The clemenson reduction allows the deoxidation of aldehyde, ketone to form the corresponding hydrocarbon. The substrate must be stable to the strong acid. The clemenson reduction is complementary to the Wolf-Kishner reduction which is done in strongly basic condition.



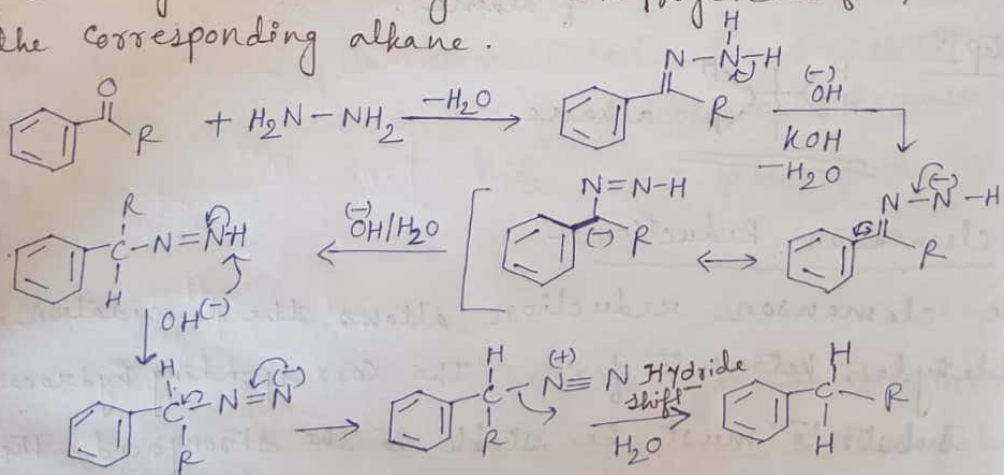


In this reaction, alcohols are not postulated as intermediates because subjecting the corresponding alcohol to this reaction conditions leads to alkane. This can be composed through the Zn catalyst.

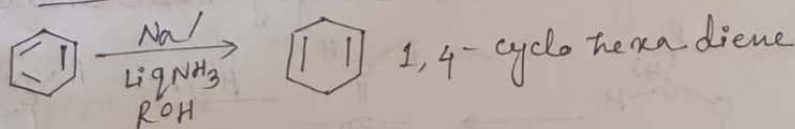
Wolf Kishner Reduction:-

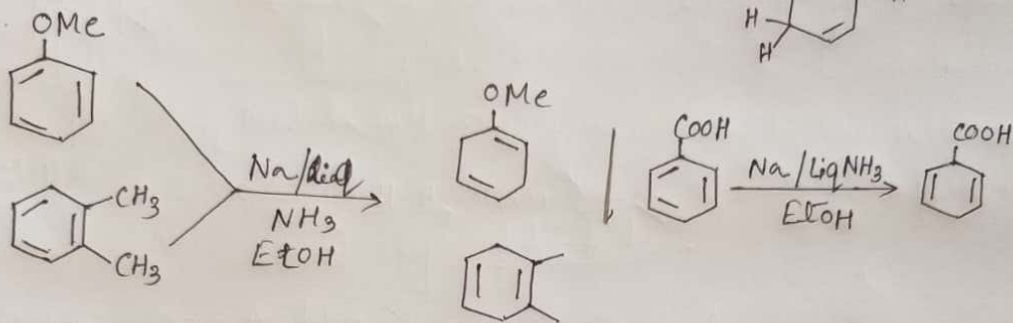
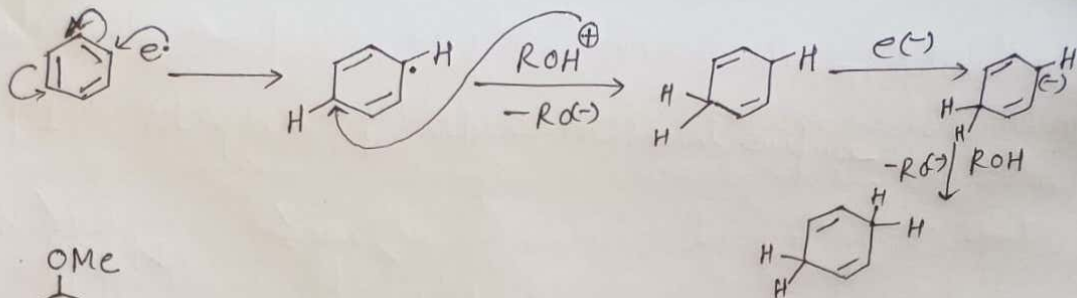


Condensation of the carbonyl compound with hydrazine forms hydrazone and treatment with base induces the reduction of the carbon coupled with oxidation of the hydrazine to gaseous nitrogen to form the corresponding alkane.

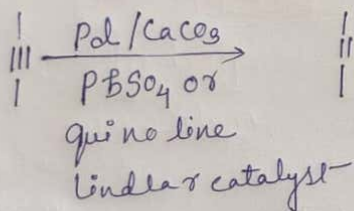


Birch Reduction:-





Carboxylic acid stabilise the adjacent anion.



* > **DI BAL** \rightarrow Diisobutyl Aluminium Hydride.

