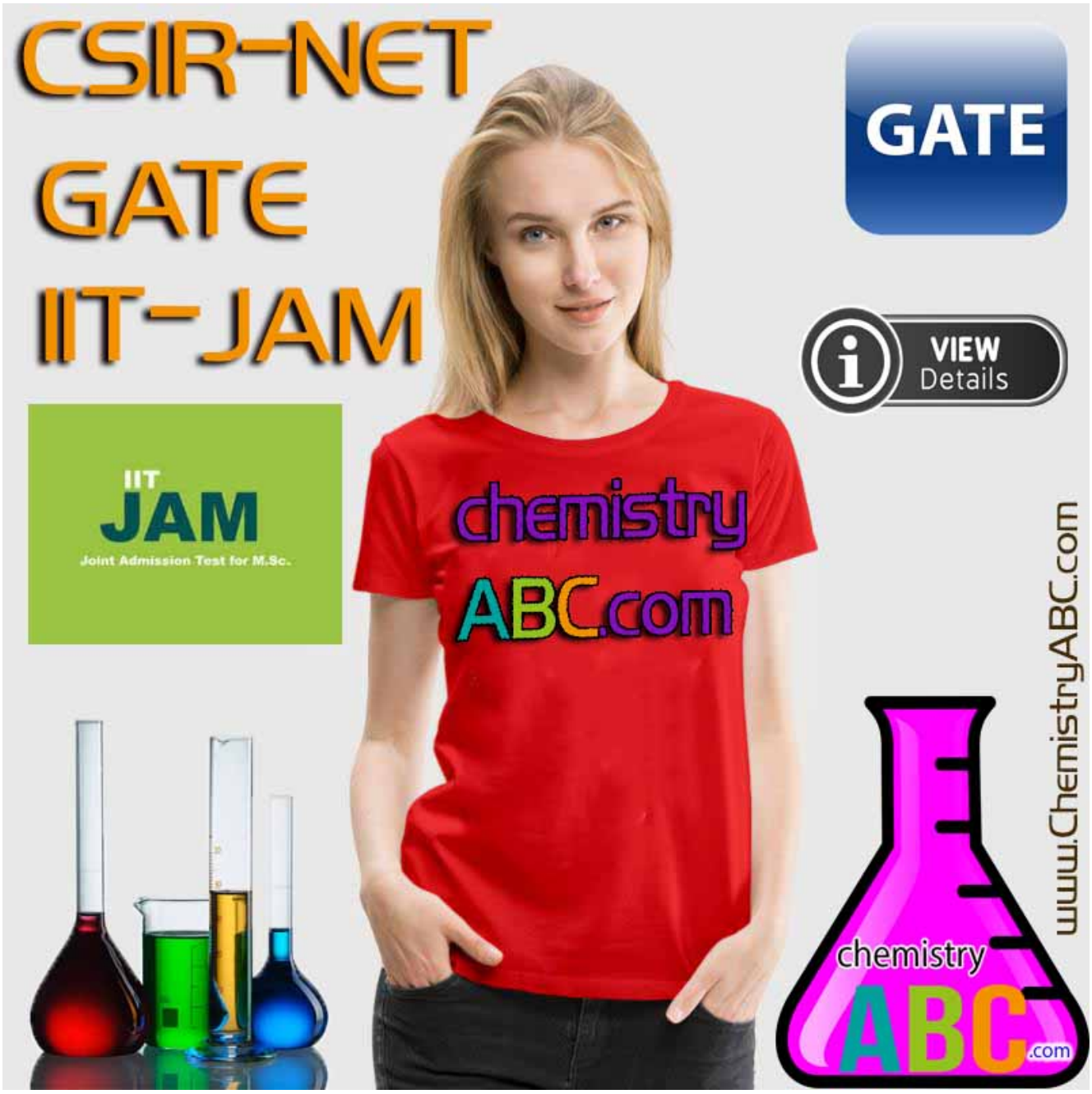
Best G.O.C.
By Nayan



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NARENDRA SINGH "NAYAN" ChemistryABC

BATCH - I

Revise daily otherwise this part will be burden.

Read Ques., think about function of reagent on substrate then solve ques. Never do solve without thinking, it's make wrong Ans.

ChemistryABC

Reactant ⟶ Product

- Substrate: Spp. at which reagent attack
- Reagent (Generally given on arrow): Reagent is an attacking spp.

Organic spp. + Inorganic spp. ⟶ Product

↓ Generally work as Reagent

Org. spp. + Org. spp ⟶ Product

The organic spp. which has max. charge density work as reagent

↳ May be +ve or −ve

Reagent

Electrophile

* e^- deficient spp.
* e^- loving spp.
* attack on e^- rich centre
* Have tendency to accept e^- pair.
* Behave as a lewis Acid.

Nucleophile

* e^- rich spp.
* Nucleus loving spp.
* Aattack at e^- deficient centre
* Have tendency to donate e^- pair.
* Behave as lewis Base.

Note:- spp. given on arrow may be reagent or substrate. don't ~~thick~~ think, It is always reagent.

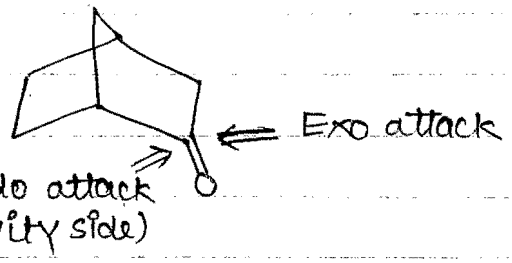
Electrophile

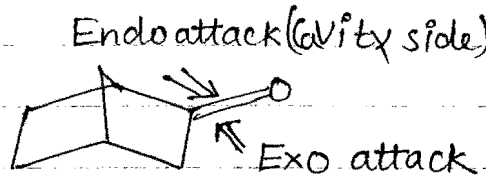
- +ve charged
  - Ex. $H^{\oplus}$, $R^{\oplus}$, $Br^{\oplus}$ etc
- Neutral
  - Ex.
  - ⇒ Incomplete octet
    - $:CH_2$
  - ⇒ Vacant p or d-orb.
    - BF_3, BCl_3, PCl_3
    - ICl, $AlCl_3$, $FeCl_3$
      - ↳ Weidge Reagent (Use in unsaturation Test.
  - ⇒ Comp. having multiple bond. Eg. CO_2
    - Br_2

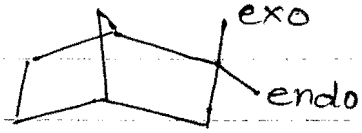
Nucleophile

- Negatively charged.
  - $R^{\ominus}$, $Br^{\ominus}$, $\bar{O}H$, RO^{-}, $\overset{\ominus}{N}H_2$ etc.
- Neutral
  - Having lone pair
    - ROH, RNH_2, etc.
  - Having multiple Bond
    - $CH_2=CH_2$, $CH\equiv CH$
    - Benzene
  - Organometallic comp.
    - $RMgX$, R_2CuLi

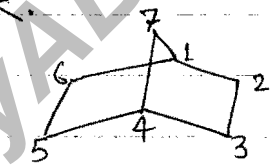
Exo, Endo Attack :-





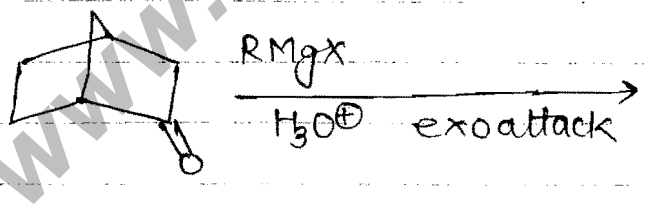


If reagent attack from cavity side then this attack is k/a endo attack, if reagent attack from outer side then that attack is k/a exo attack.

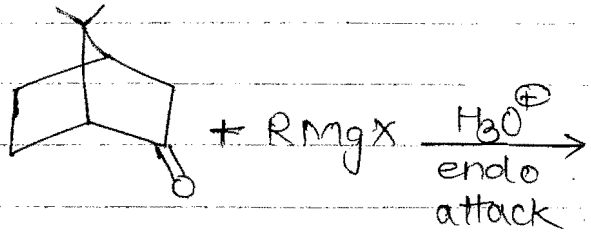


If at 7th position no group or substituent +nt then majorly reagent attack from exo side and if at 7th position substituent +nt then majorly reagent attack from endo side.

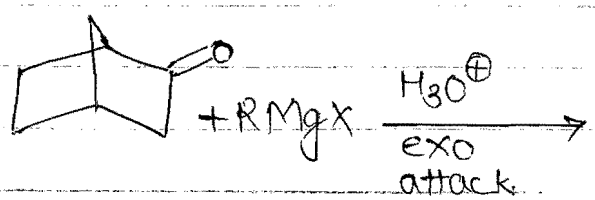
Ex.

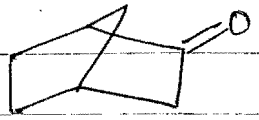


Ex.

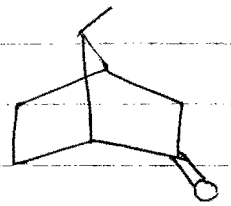


Ex.

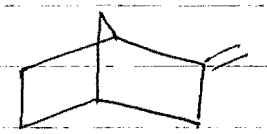




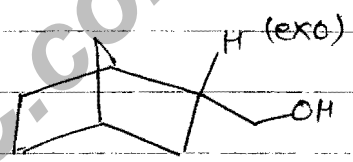
$LiAlH_4$ → exo attack

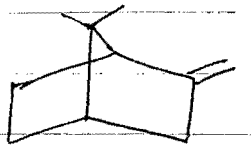


" → endo

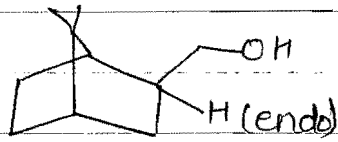


$BH_3 / H_2O_2 / \bar{O}H$ → exo

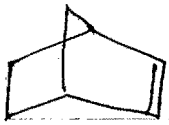




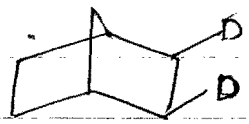
$BF_3 / H_2O_2 / \bar{O}H$ → endo



Antimarkonikoff addⁿ.

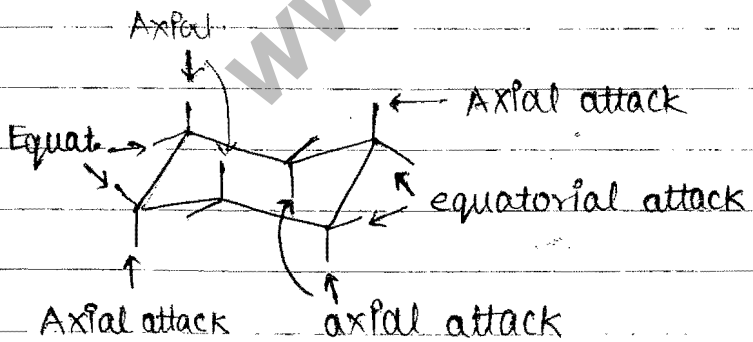


Wilkinson cat. / D_2 →



exo product.

Axial - Equatorial Attack :-



Reagent (Size)

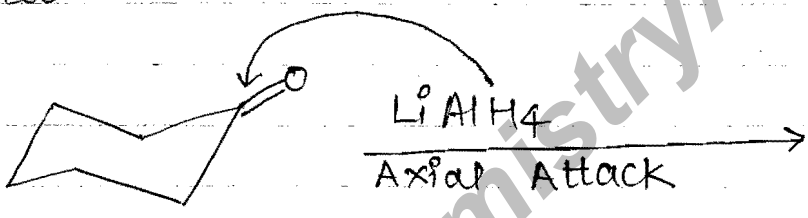
Smaller Reagent

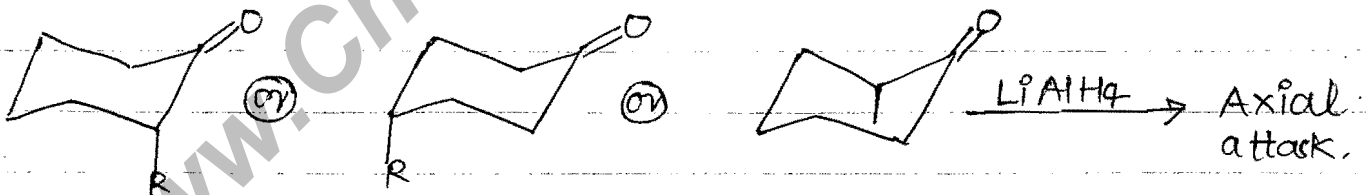
May be attack from axial or equatorial. It depends upon at which position substituent attached. Eg. $LiAlH_4$, $NaBH_4$, BH_3 etc

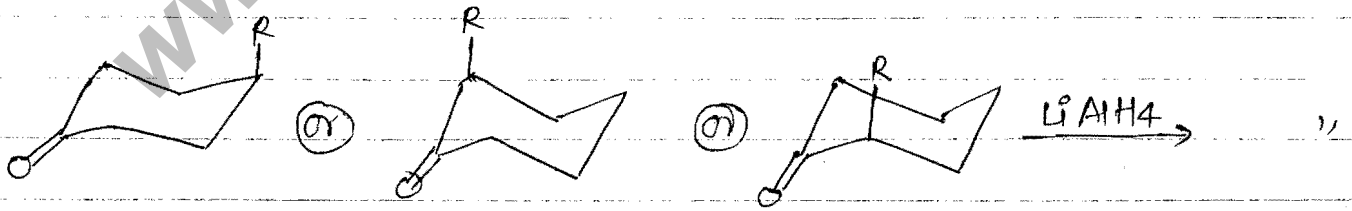
Bulky reagent

Generally ~~Always~~ attacks from equatorial side in all cases. ~~but~~ Eg. R_2CuLi, $RMg{-}X$, DIBAL etc.

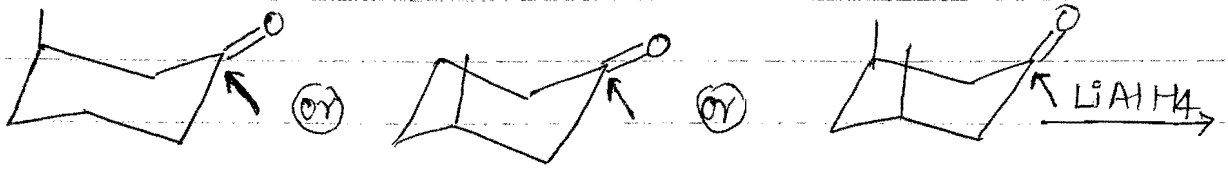
In the following cases smaller reagent attack from axial side.

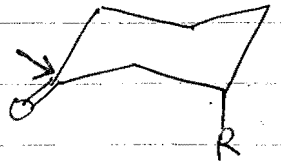




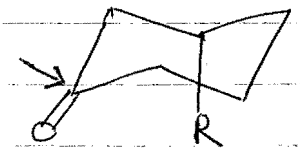


But in the following type cases smaller reagent also can attack from equatorial side.

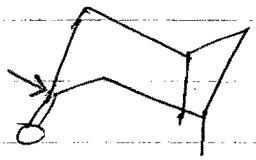




(or)



(or)

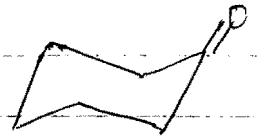


AlH_4Li

Equatorial attack

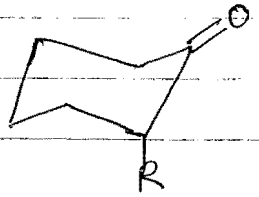
$LiAlH_4$ → Axial attack

" → equatorial

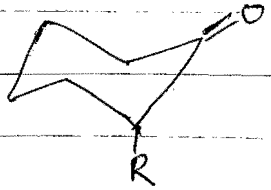


$RMgX$ → equatorial.

" → "

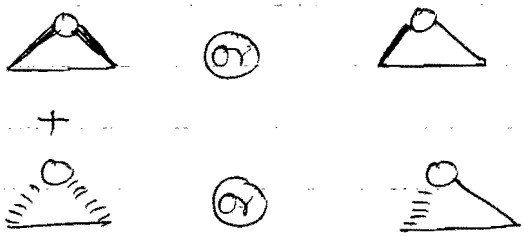


" → "



$LiAlH_4$ → axial attack.

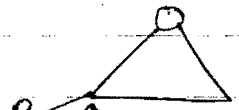
Epoxide ring Opening :-

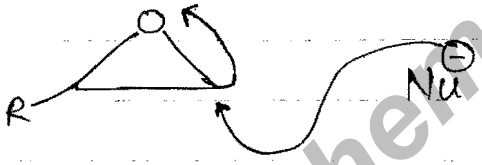
= + m-CPBA ⟶  (or)

+

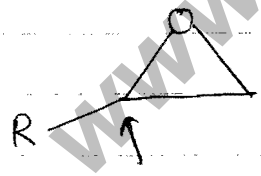
 (or)

Epoxide ring opening in Assymmetric epoxide :-



* 

1, 2 trans prod.

* 

i) $H_2O/H^{\oplus}$ (or)
+ ii) BH_3 (or)
iii) Lewis acid (or)
iv) Mixed Hydride (AlH_3)
$LiAlH_4 + AlCl_3$

⟶ S_N1

In the case of $H_2O/H^{\oplus}$, (or) BH_3 (or) Lewis acid (or) Mixed hydride ⇒ ring opening via S_N1

because these reagents activate to 'O' atom (L.G.)
Attack of $Nu^{\ominus}$ from more hind. side

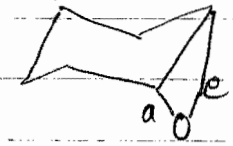
$H_2O/\bar{O}H$ (or)
$LiAlH_4$ (or)
$NaBH_4$ (or)
R_2CuLi etc

S_N2

⟶ 1,2 trans prod.
Stereochemistry of 'OH' & 'Nu' will be trans.

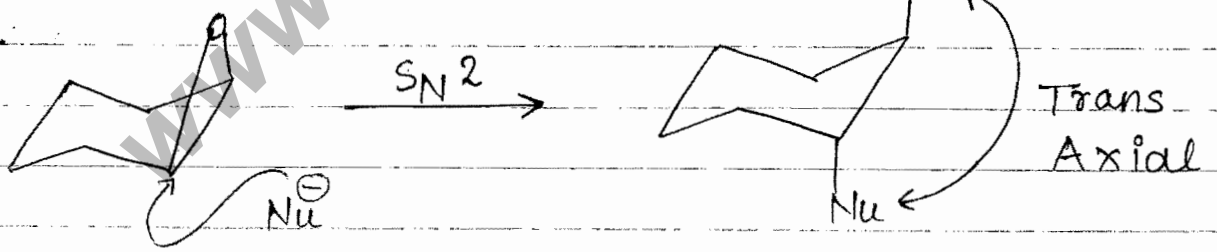
Epoxide Ring Opening in Cyclohexane epoxide:-

1,2 -cis
a,e



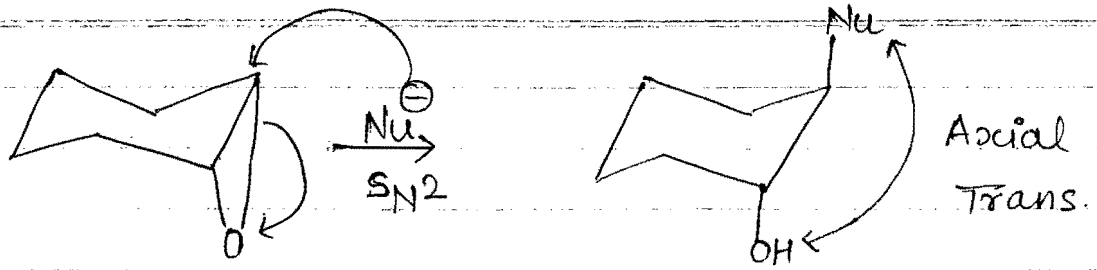
Epoxide ring opening in cyclohexane takes place via Trans Axial.

Ex.



Trans Axial ring opening

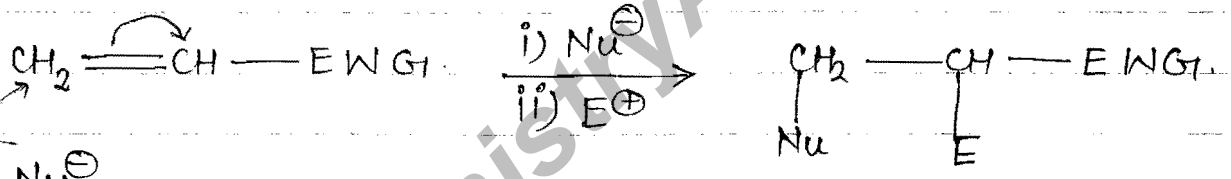
* The above representation (mechanism) is not correct. in actual mechanism so many T.S. take part but finally ring opening takes place via trans opening way.



MICHAEL Add$^{n.}$ V/s Direct Add$^{n.}$

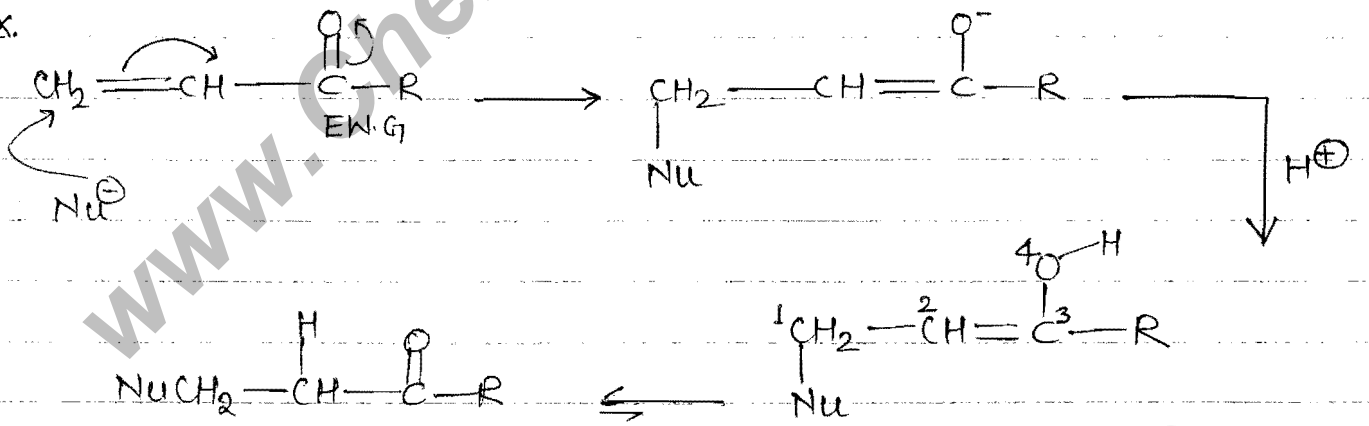
Generally alkene gives electrophilic add$^{n.}$ but activated alkene ($CH_2=CH-EWG$) which have e^- withdrowing group gives nucleophilic Add$^{n.}$ ring & this addition is K/a Micheal Add$^{n.}$

Ex.



Micheal Add$^{n.}$

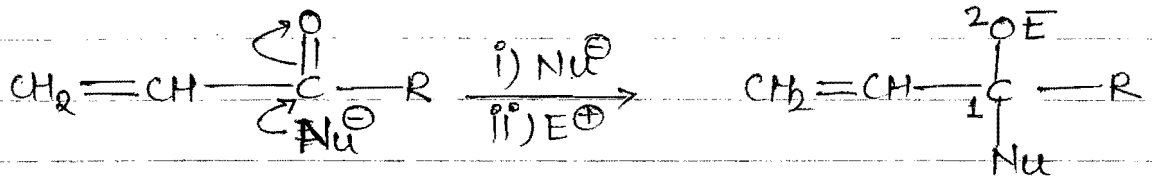
Ex.



1,4 addition.

Micheal addition ⇒ 1,4 Addition
but 1,4 add^{n} is not always Micheal add$^{n.}$

Direct Addⁿ :-

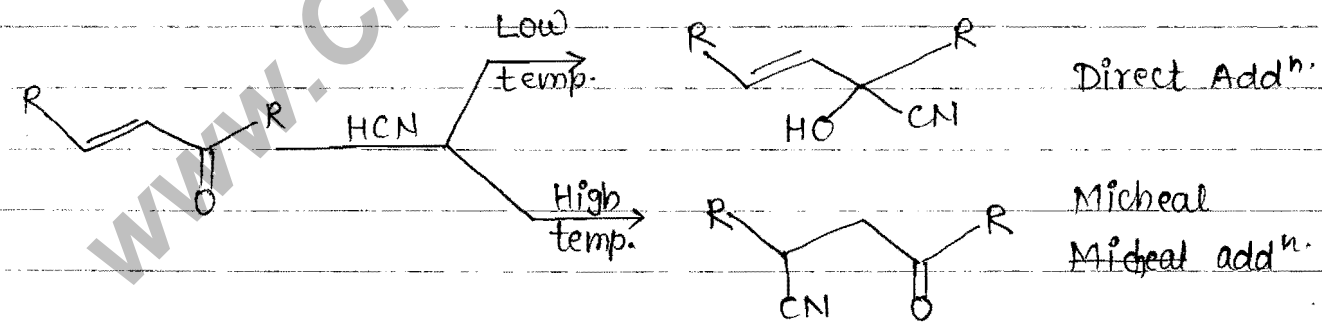


(1,2 - Addⁿ)

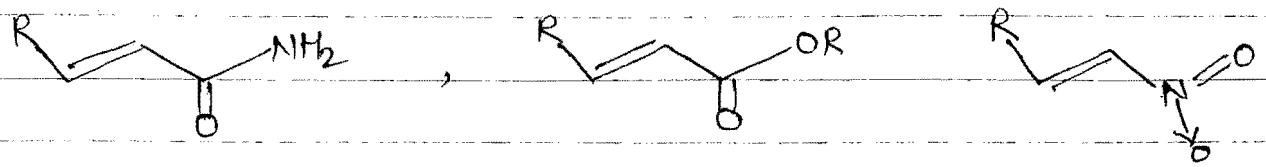
There is competition b/w Direct & Micheal addⁿ and the regioselectivity is controlled by following factors :-

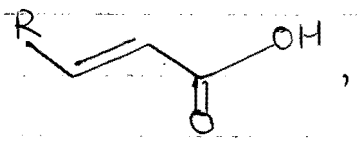
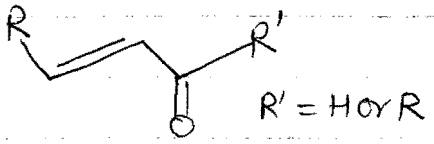
1) Temperature
2) Nature of α,β-unsaturated compound.
3) Nature of reagent.

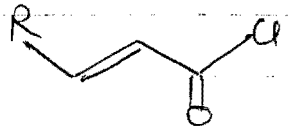
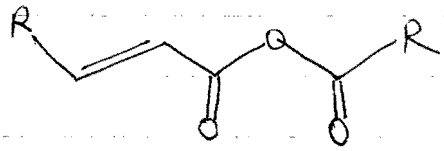
1) Temperature :- At high temp. → micheal addⁿ
At low " → Direct "



2) Nature of α,β-unsaturated Compound :-



In the case of α, β unsaturated amide always Micheal add^{n}. will take place.

In the case of α, β- unsaturated ester, Nitro, acid always Micheal add^{n}. takes place, but $LiAlH_4$ direct add^{n}. will be take place.

In the case of α-β, unsaturated acid halide and α, β- unsaturated anhydride always direct add^{n}. will take place

In the case of α, β- unsaturated carbonyl direct add^{n}. and micheal add^{n}. generally depends upon the temp. & nature of reagent.

Most stable $R-\overset{\overset{O}{\|}}{C}-NH_2$
(Least reactive)

$R-\overset{\overset{O}{\|}}{C}-OR$

$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R$

$R-\overset{\overset{O}{\|}}{C}-X$ Least stable (Most reactive)

Q Write the correct order of Nucleophilic substitution Rxn., reactivity of acid derivatives ?

leaving Group. $NH_2^{\ominus}$ $OR^{\ominus}$ $RCOO^{\ominus}$ $X^{\ominus}$

Conj Acid. $H-NH_2$ $H-OR$ $HO-C(=O)-R$ $H-X$

Acidic order. $HNH_2 < HOR < HO-C(=O)-R < H-X$

Reactivity order towards Nucleophilic Sub^{n} Rxn.

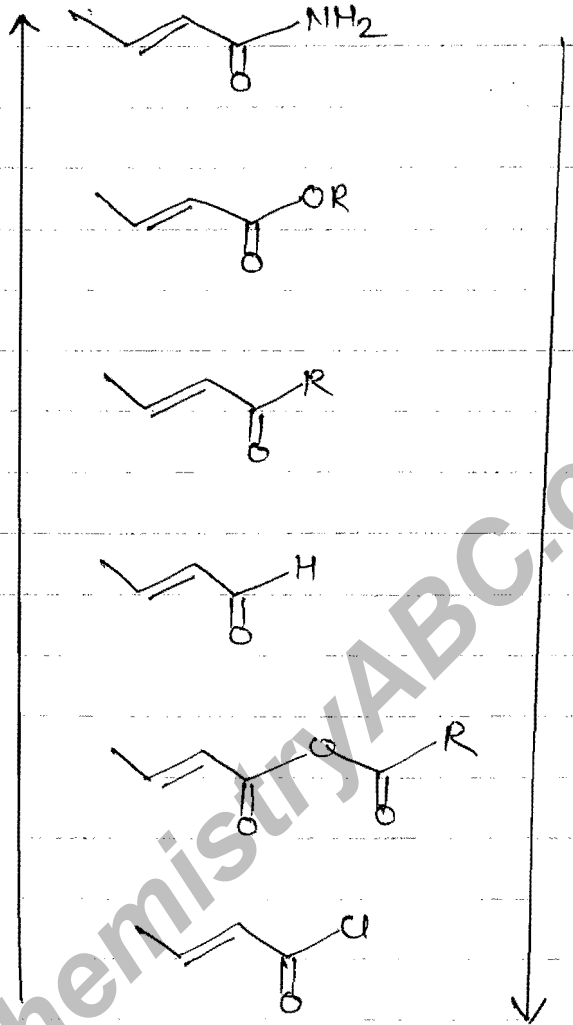
Reactivity order towards Nucleophilic substitution Rxn.

$R-I > R-Br > R-Cl > R-F$

↑ Good leaving Group. ↑ Bad L.G.

$HI > HBr > HCl > HF$

The comp. which whoose conjugate acid is most acidic, conjugate base is good leaving group.



1,4 Addⁿ (or) Micheal Addⁿ ↑

1,2 - addⁿ (or) direct addⁿ ↑

3) Nature of Reagent:- soft reagent micheal addⁿ & hard reagent gives direct addⁿ

Smple.

Reagent

Soft

Micheal Addⁿ

NH_2OH, R_2CuLi, $RMgX/CuI$

$Na/liq.NH_3$, RSH

Hard

Direct addⁿ

$NaBH_4$, $LiAlH_4$, $RMgX$, $\overset{\ominus}{O}H$, $F^{\ominus}$, RLi

Micheal Addition.	Direct Addition
1) Takes place at High temp.	Takes place at low temp.
2) Thermodynamically controlled	Kinetically controlled.
3) Add^{n}. at C=C	Add^{n}. at C=O
4) C=O intact after Rxn.	C=C intact after Rxn.

CRAM's RULE

See in Stereochemistry

Imp.

General order of Rxn.

Acid-Base Rxn. > Add^{n}. Rxn. > Substitution Rxn. > Elimination Rxn.

↑ Very less Ea require

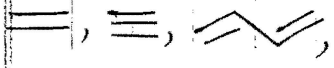
↑ Very much Ea require i.e. why Δ given (Generally)

REACTIONS

Addⁿ. Rxn.

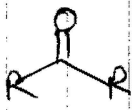
Addⁿ.

Electrophilic Rxn.



R–NC etc.

Nucleophilic Addⁿ. Rxn.



$CH_2=CH-EW.G.$

$CH_2=C=O$, $R-N=C=O$

$R-C\equiv N$

α-haloester ⇒ Always S_N2 gives.

Substitution Rxn.

Aliphatic S. R.

Acid derivatives

Alkyl Halide

S_N1 ←

S_N2 ←

S_Ni ←

Aromatic Substitution Rxn.

→ Ar S_N1

→ Ar S_N2

→ Benzyne

Elimination Rxn. ←

E_1

E_2

Ei

Syn periplanar

Anti periplanar

GILMANN REAGENT (R_2CuLi)

* Gilmann Reagent is an Organo copper reagent.
* It is a source of carbanion ($Nu^{\ominus}$)
* It exist in dimer form in soln.
* It works at low temp. $-78\,^{\circ}C$

Preparation:-

$$2R-Li + CuI \longrightarrow R_2CuLi + LiI$$

Applications:-

R_2CuLi

Nucleophilic Subn. Rxn.

Alkyl Halide Aryl Halide Vinyl Halide Epoxide ring opening

R_2CuLi

S_N Rxn.

- Alkyl Halide → R_2CuLi → S_N2
- Aryl Halide →  → R_2CuLi → Migration of multiple Bond take place.
  - L = OTs, 
- Vinyl Halide → R_2CuLi → Retention.
- Epoxide ring opening
- Allylic Halide @ Propargylic Halide → Migration of double bond or tripple bond will be take place.
- Allylic @ propargylic epoxide → R_2CuLi → Migration of Multiple bond takes place

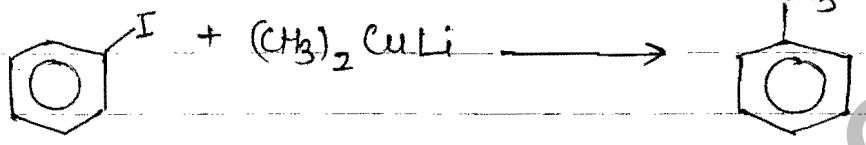
Nucleophilic Addⁿ. Rxn.

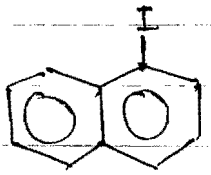
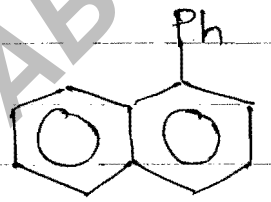
- → Micheal Addⁿ.
- → Addⁿ on Carbonyl. (Cram's Rule)

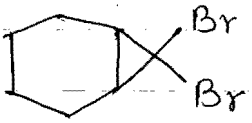
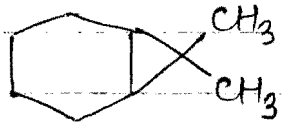
Corey House Synthesis (C-C coupling)

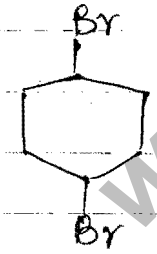
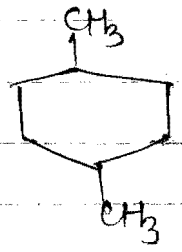
Q $CH_3-(CH_2)_6-CH_2I + (CH_3)_2CuLi \longrightarrow CH_3(CH_2)_6-CH_2-CH_3$

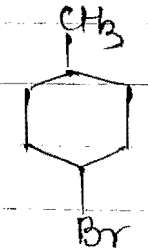
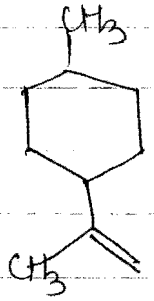
Q $(CH_3-CH_2-\underset{CH_3}{CH})_2CuLi + CH_3(CH_2)_4Br \longrightarrow CH_3-CH_2-\underset{CH_3}{CH}-(CH_2)_4CH_3$

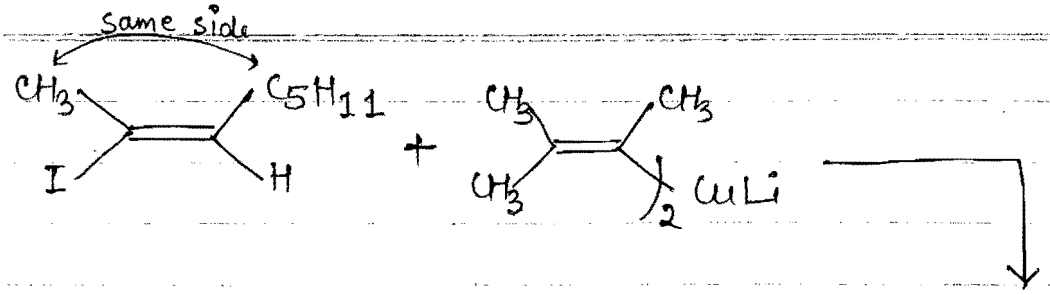
Q  + $(CH_3)_2CuLi$ ⟶

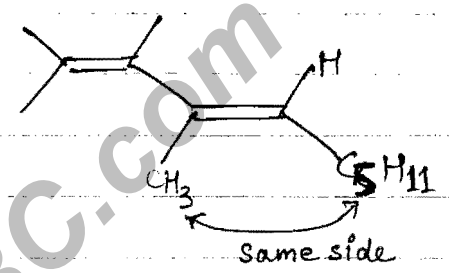
Q  + Ph_2CuLi ⟶ 

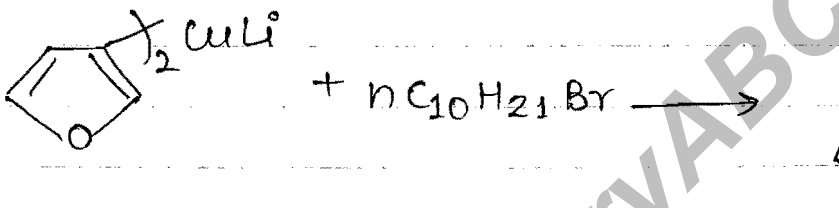
Q  + $CH_3(CH_3)CuLi$ ⟶ 

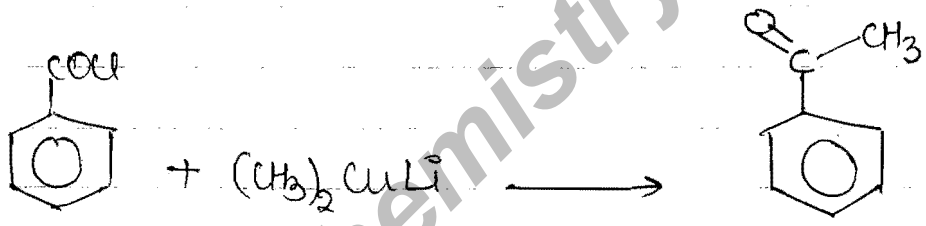
*  $(CH_3)_2CuLi$ ⟶ 

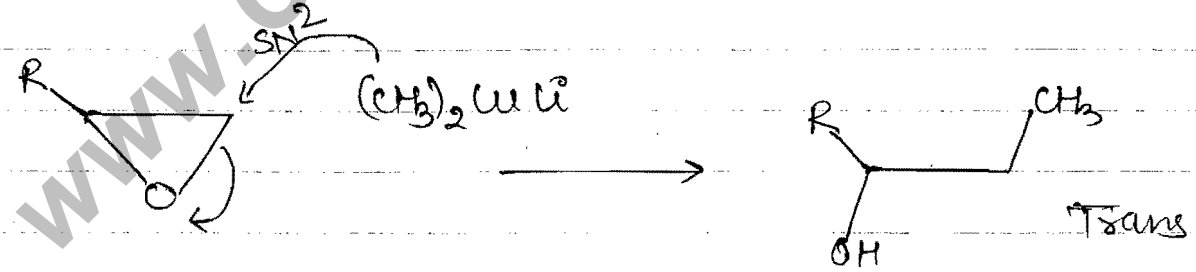
Q  $\left(CH_2=C(CH_3)-\right)_2CuLi$ ⟶ 

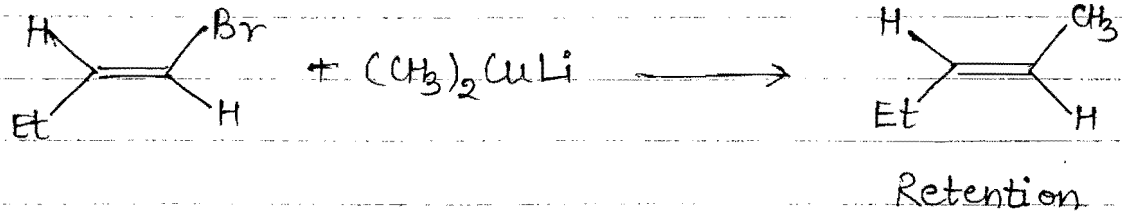
Q 



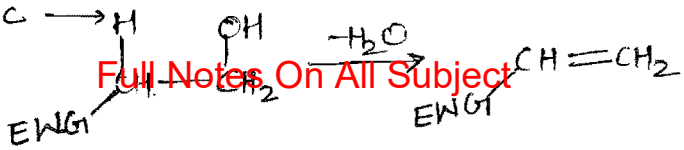
Q 

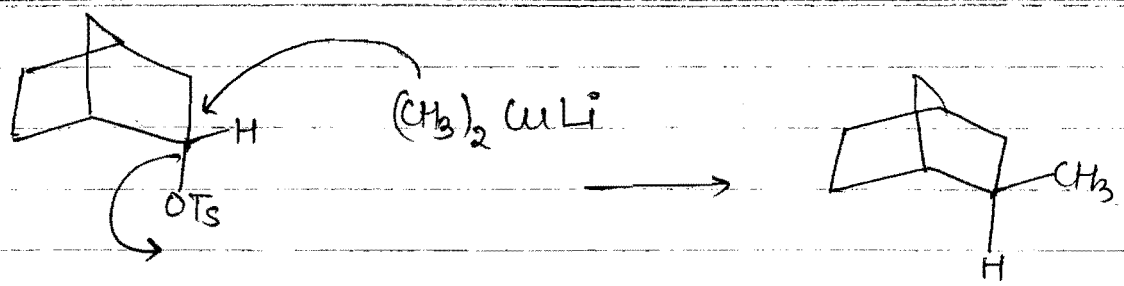
Q 

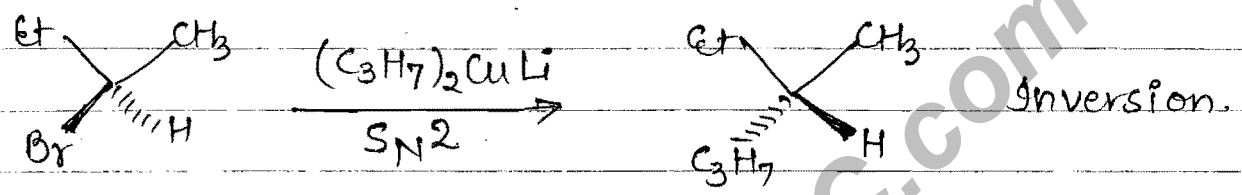
Q 

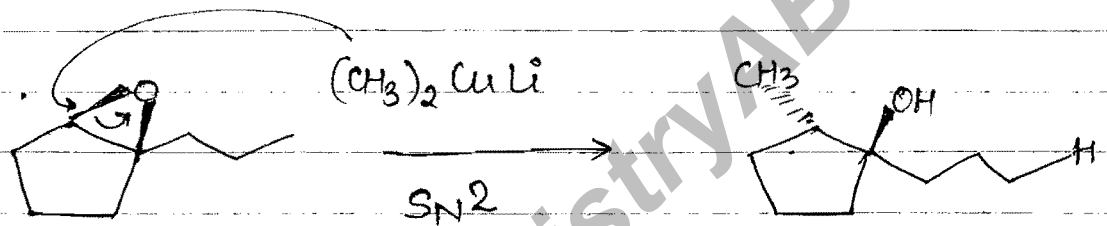
Q 

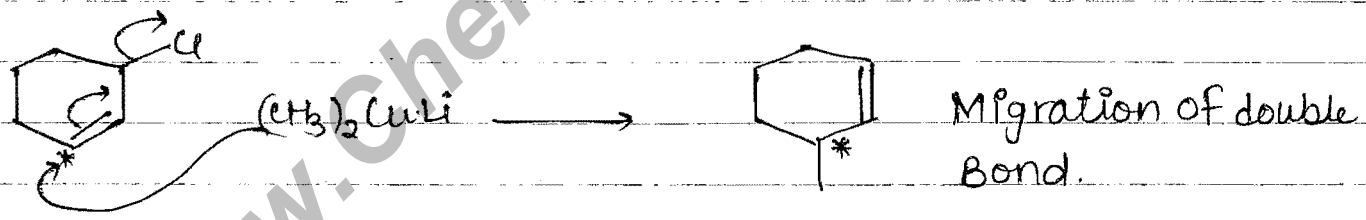
Retention

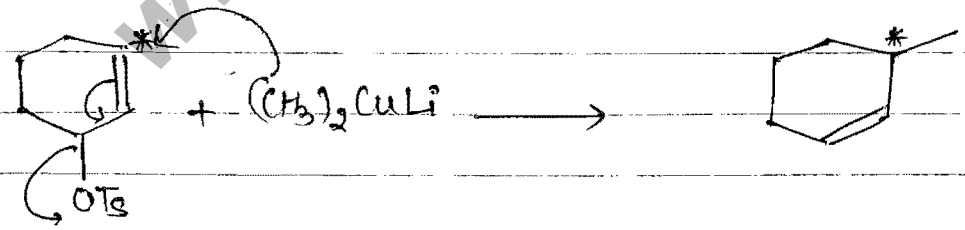
Acidic → 

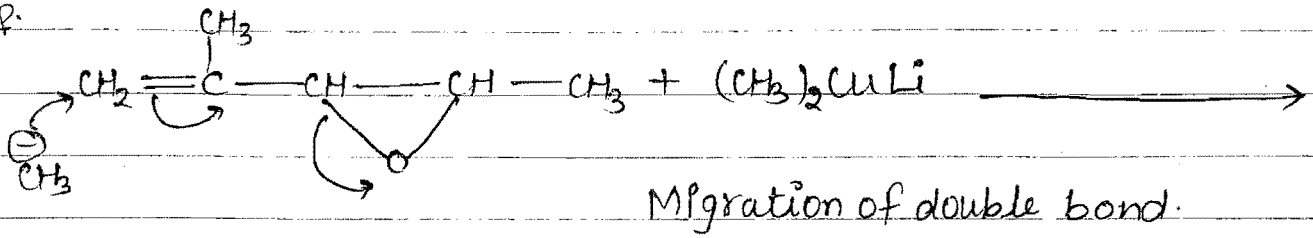
Q 

Q 

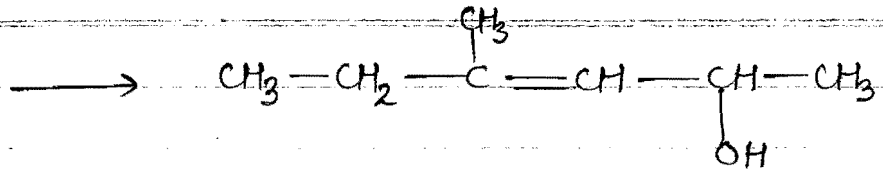
Q 

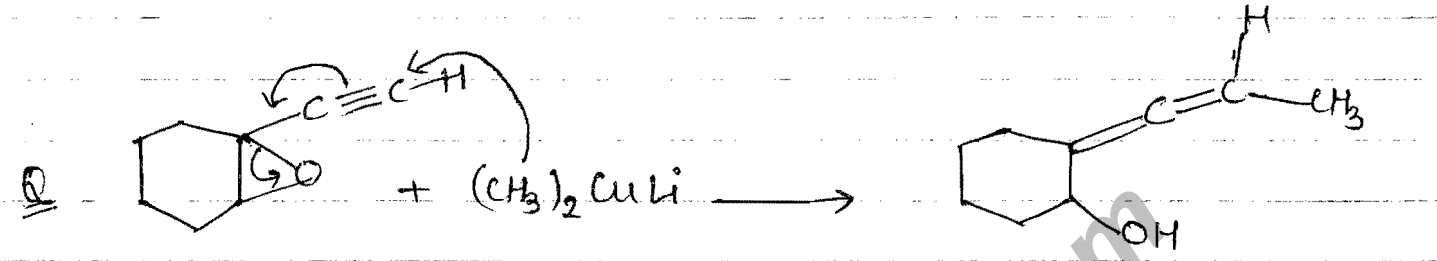
Imp. Q 

Q 

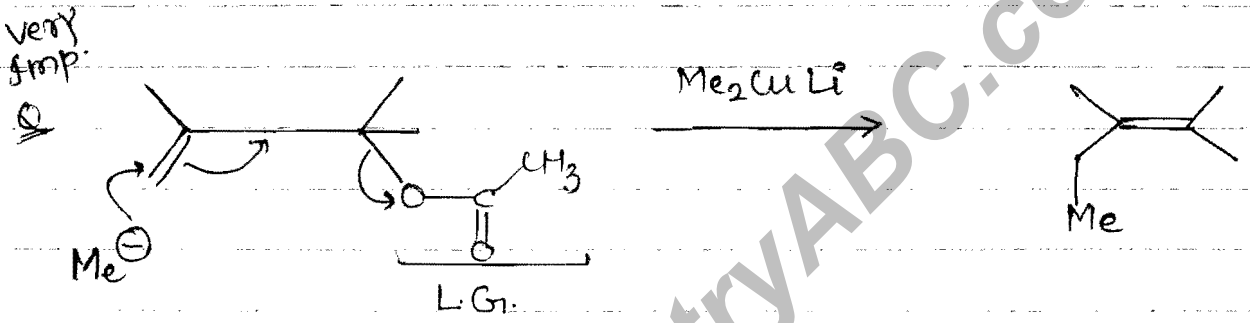
Imp. Q 

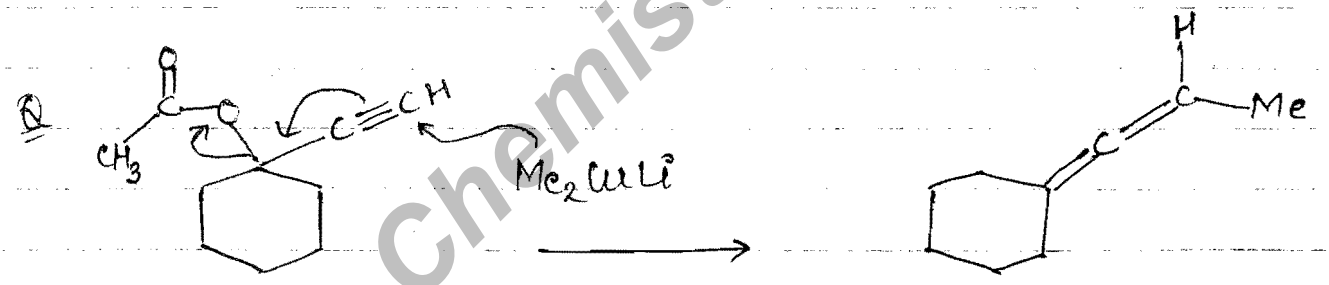
Migration of double bond.

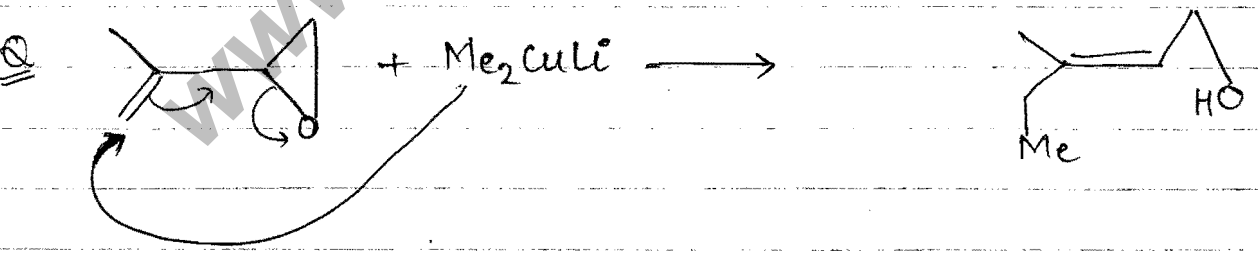


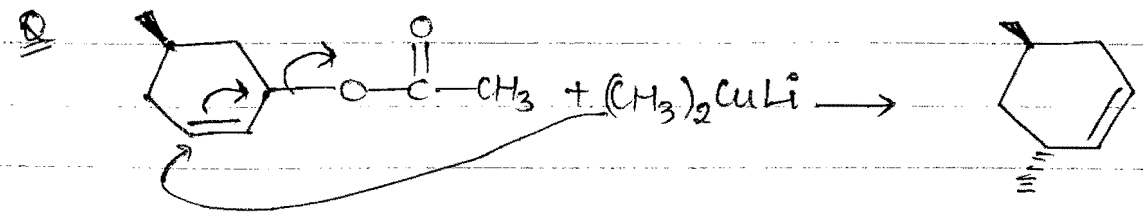


very imp.



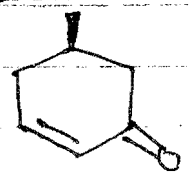




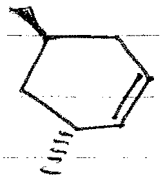


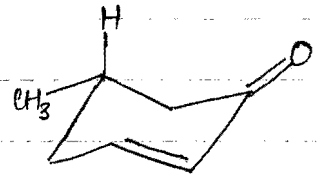
GATE

Q



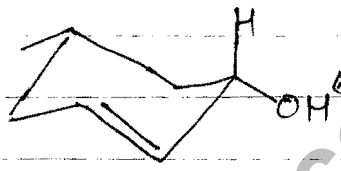
i) $LiAlH_4$
ii) Py , Ac_2O
iii) $(CH_3)_2CuLi$

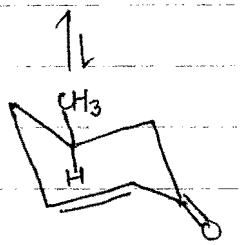


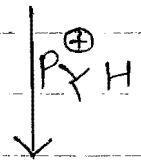


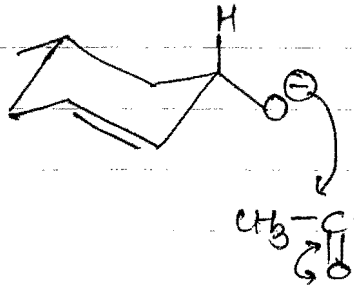
$LiAlH_4$

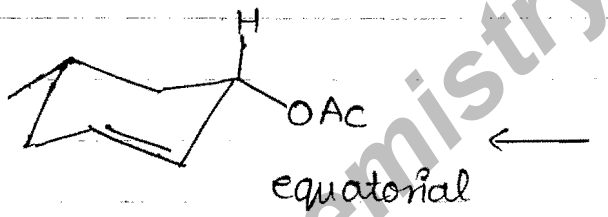
axial attack





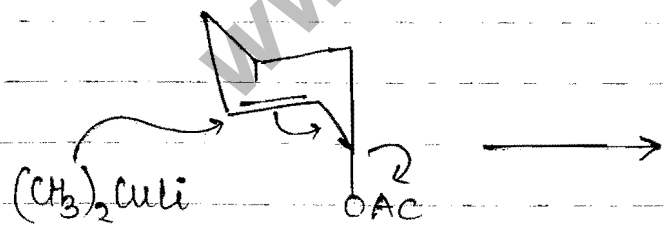




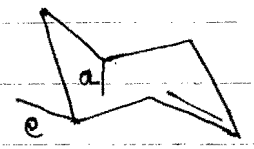


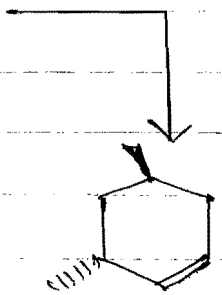
equatorial

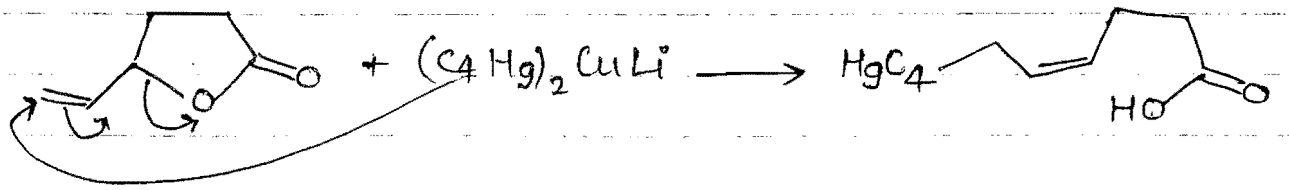
Flipping

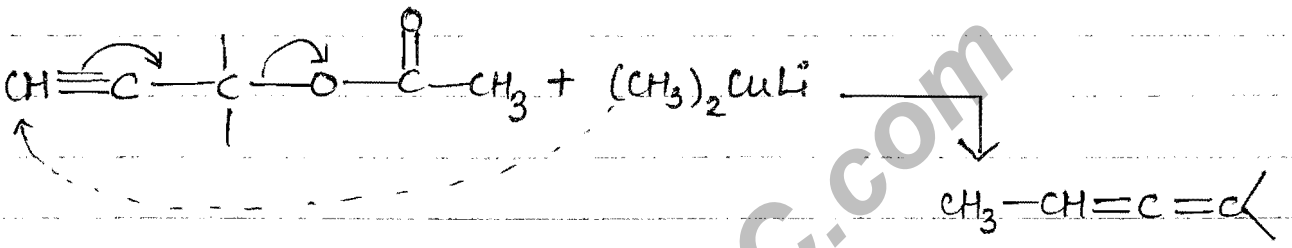


equatorial attack





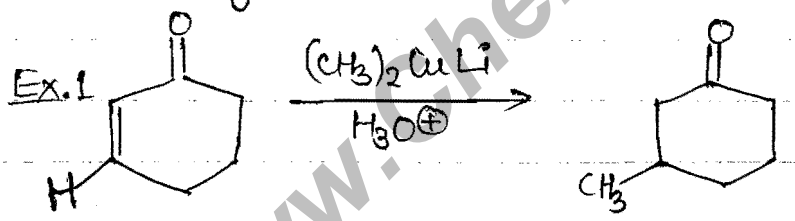
Q 

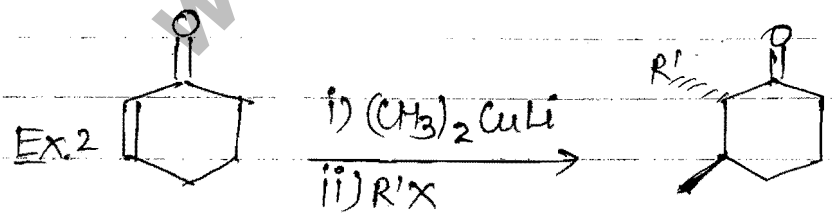
Q 

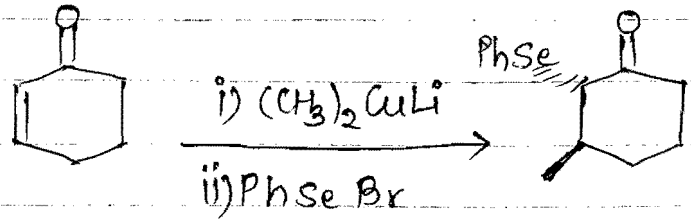
Nucleophilic addition Rxn.

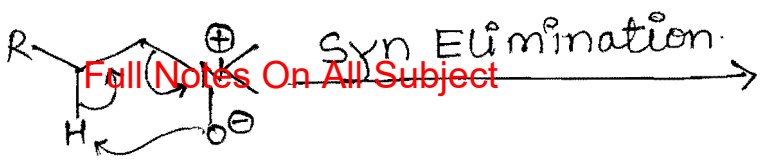
Imp. MICHAEL Addⁿ.

Gilmann reagent is soft reagent so it gives 1,4 addition at α,β- unsaturated carbonyl compound.

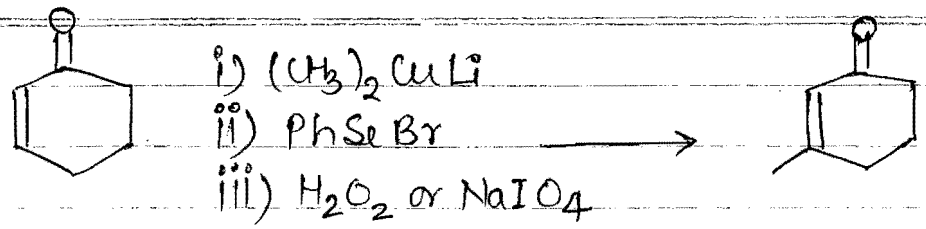
Ex.1 

Ex.2 

Ex.3 

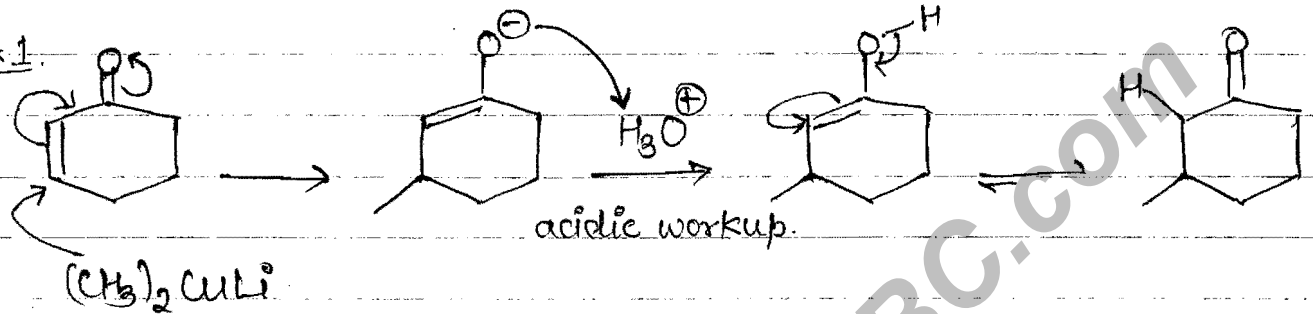


Ex.4

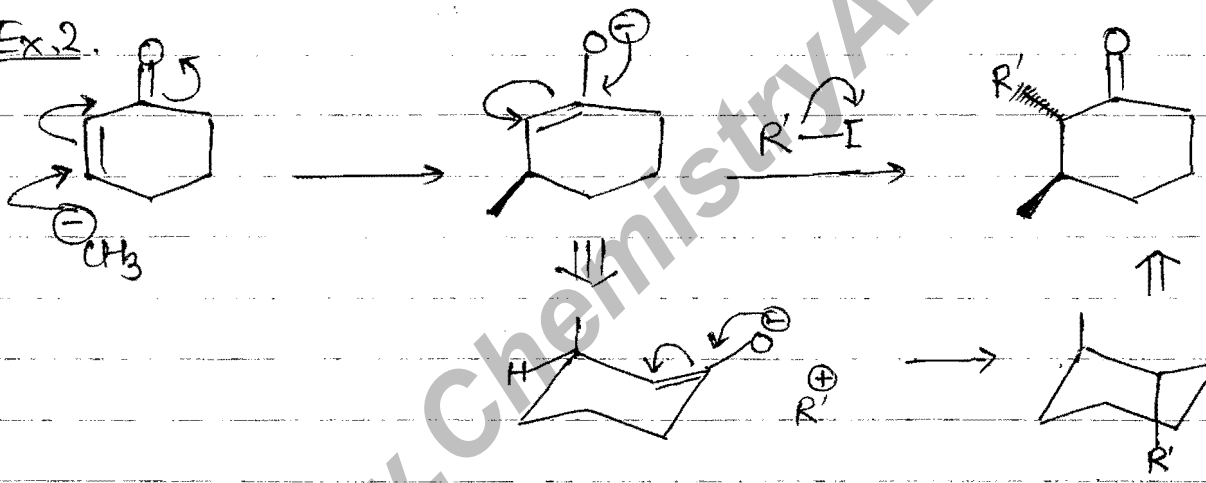


Mechanism

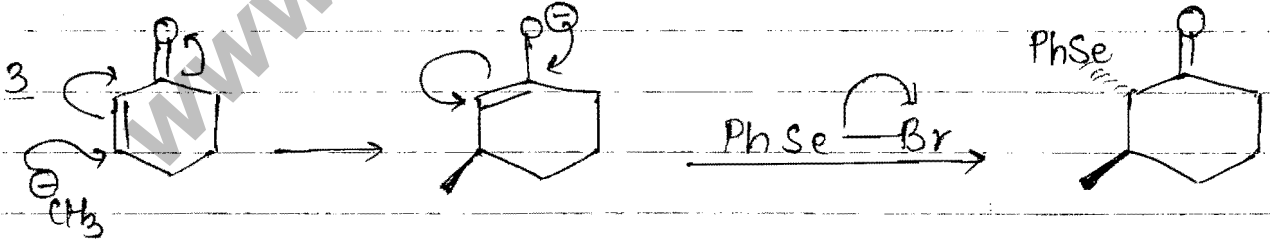
Ex.1



Ex.2

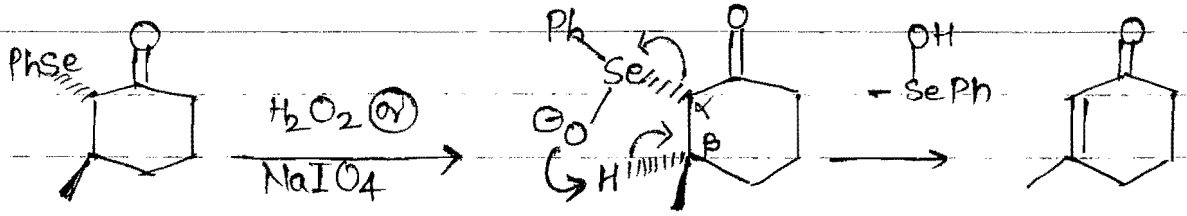


Ex.3



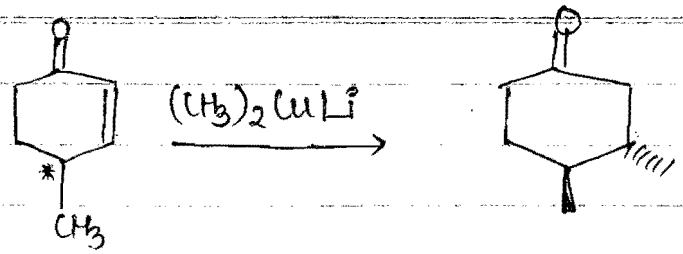
Most imp.

Ex.4

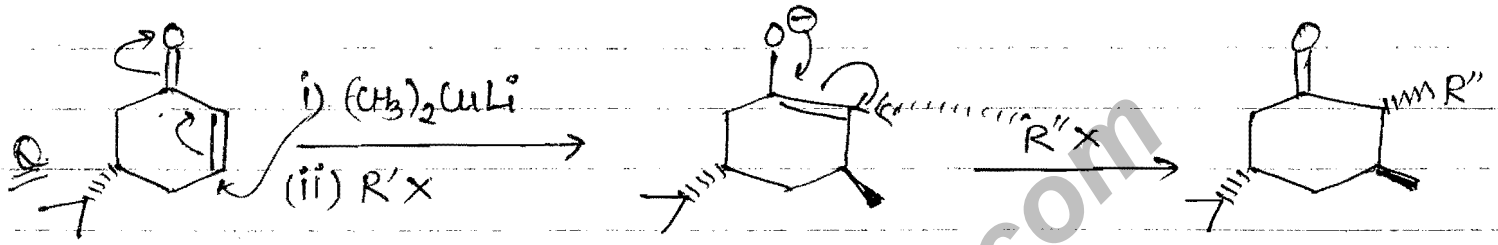


Syn Elimination of β-H

Q



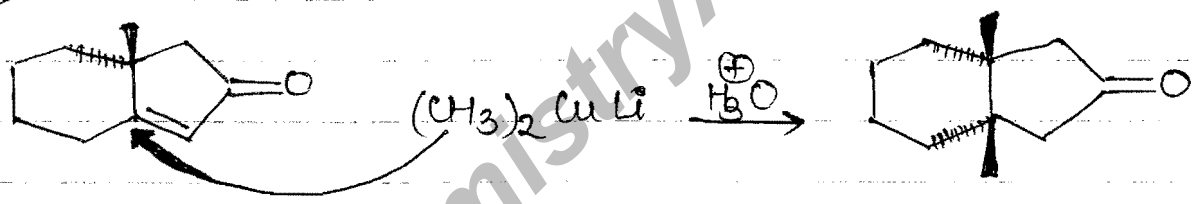
Q



At ring junction cis stereochemistry will be occur.

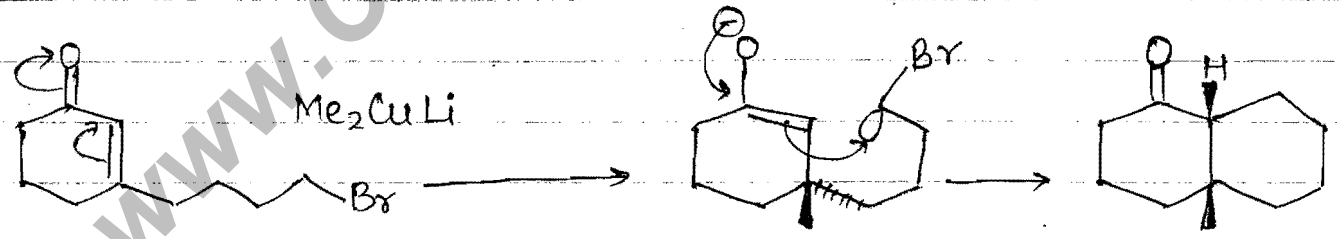
M. Imp

Q

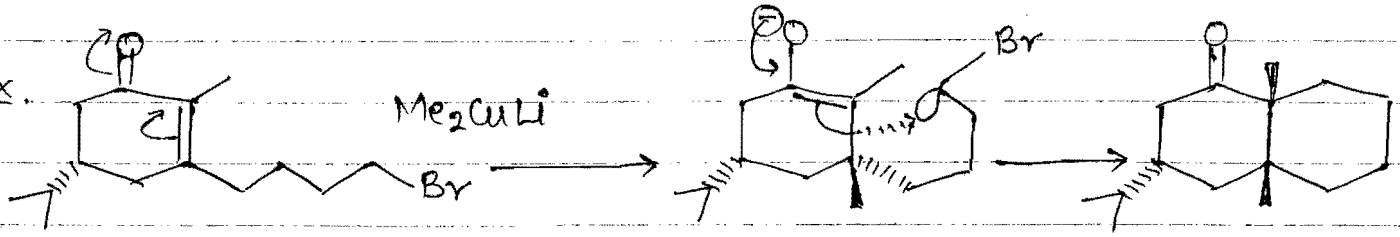


V.V.Imp: Gilmann reagent also used in cyclisation Rxn.

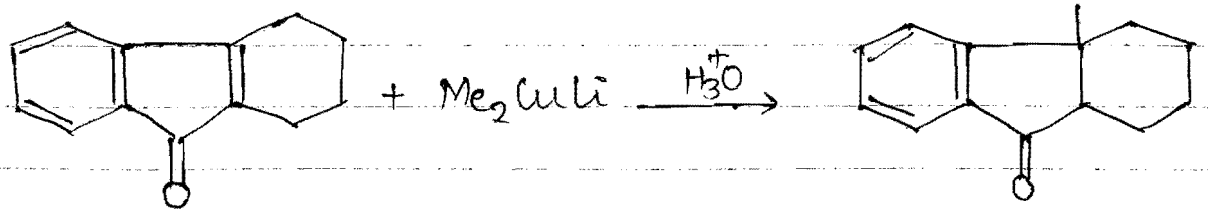
Ex.

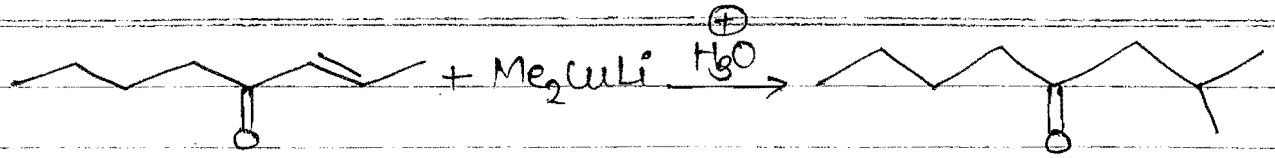


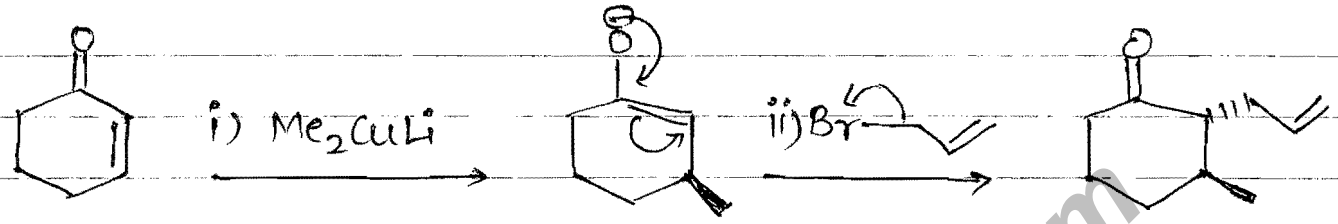
Ex.

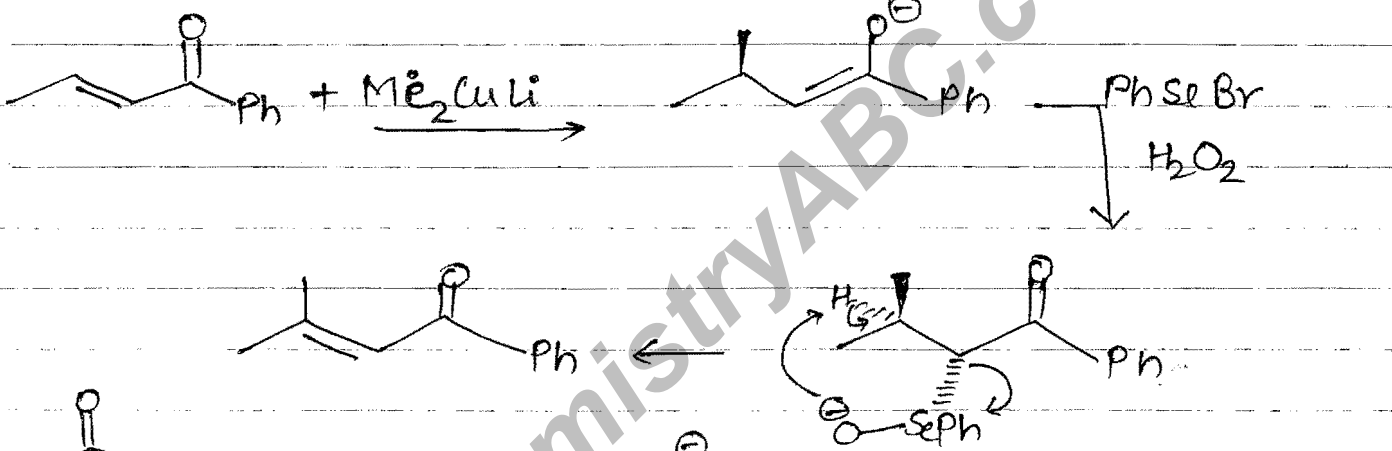


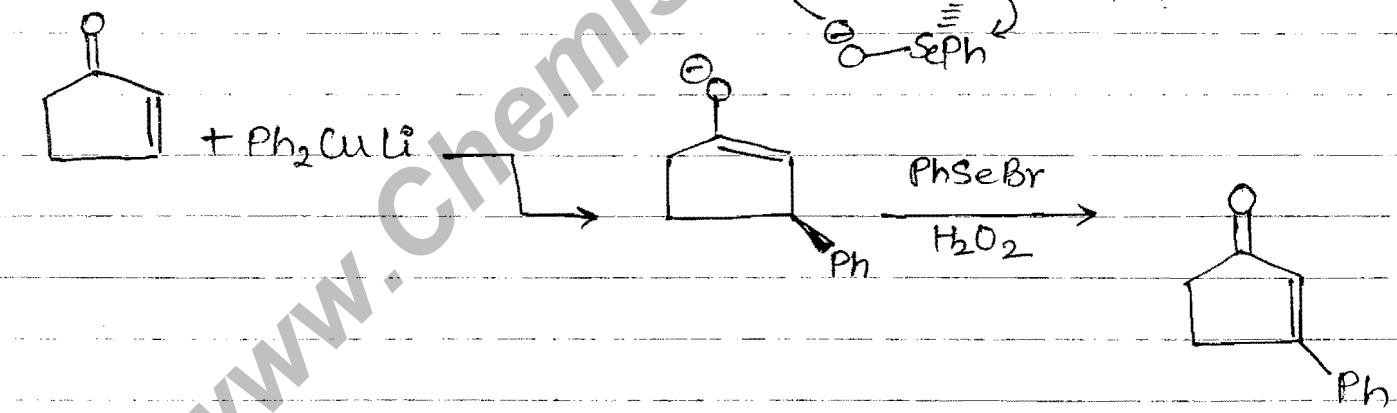
Q



Q 

Q 

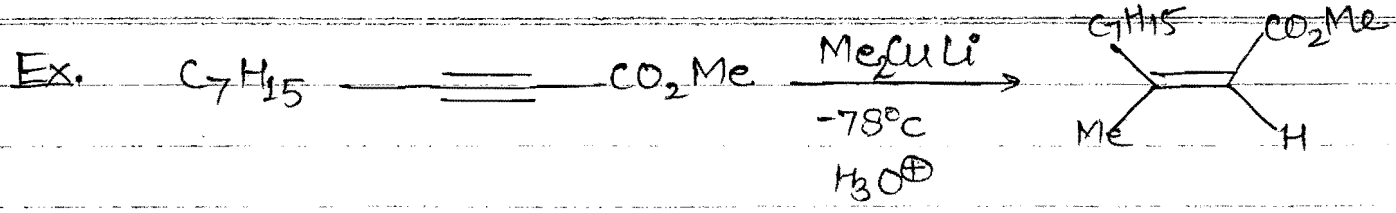
Q 

Q 

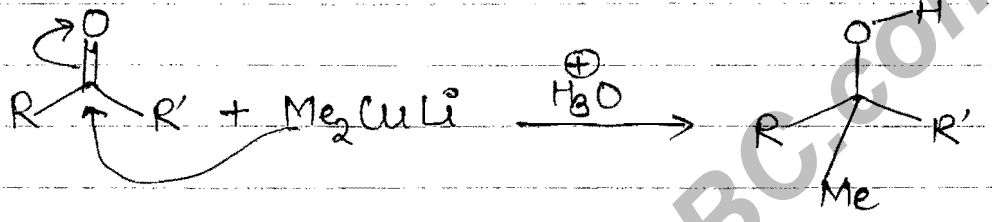
In 1,4 addition gilmann form a complex with α-β- unsaturated compound and copper is in +3 oxidation state. Gilmann also gives 1,4 addⁿ with acetylenic carbonyl comp. & cis addⁿ will be take place.

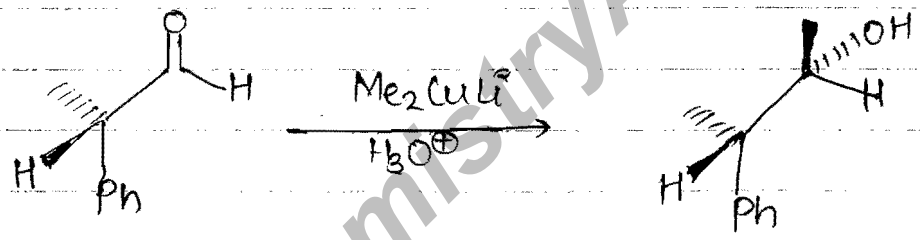
Gilmann ⇒ Cu(III)

Click Rxn ⇒ Cu(I)

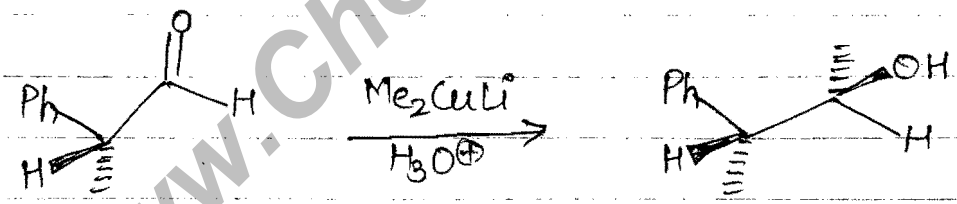
Ex. 

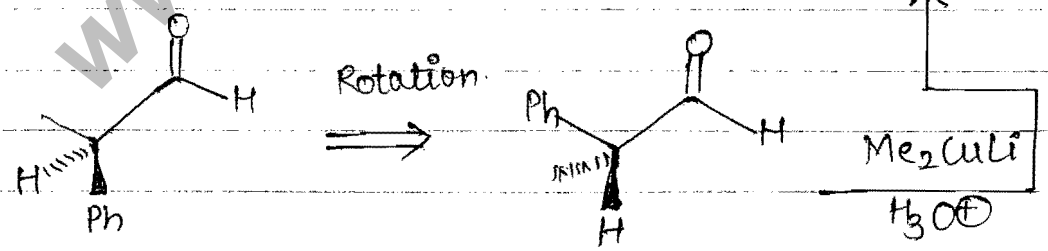
Gilmann Reagent gives addition reaction on carbonyl.

Ex. 

Ex. 

Apply Cram's Rule.

Ex. 

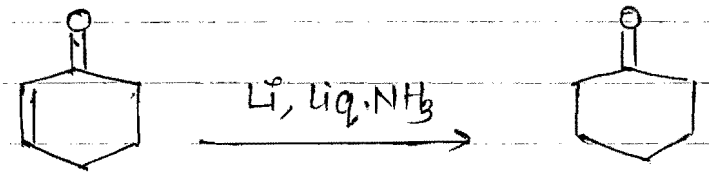
Ex. 

Q 49

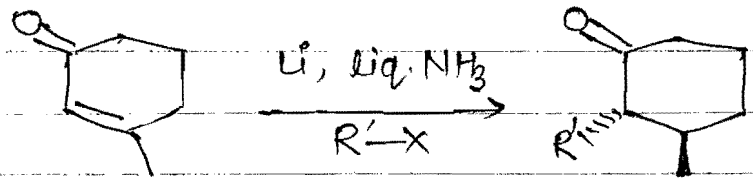
V. imp.

Rxn. of α,β-unsaturated carbonyl comp. with Metal in liq. Ammonia.

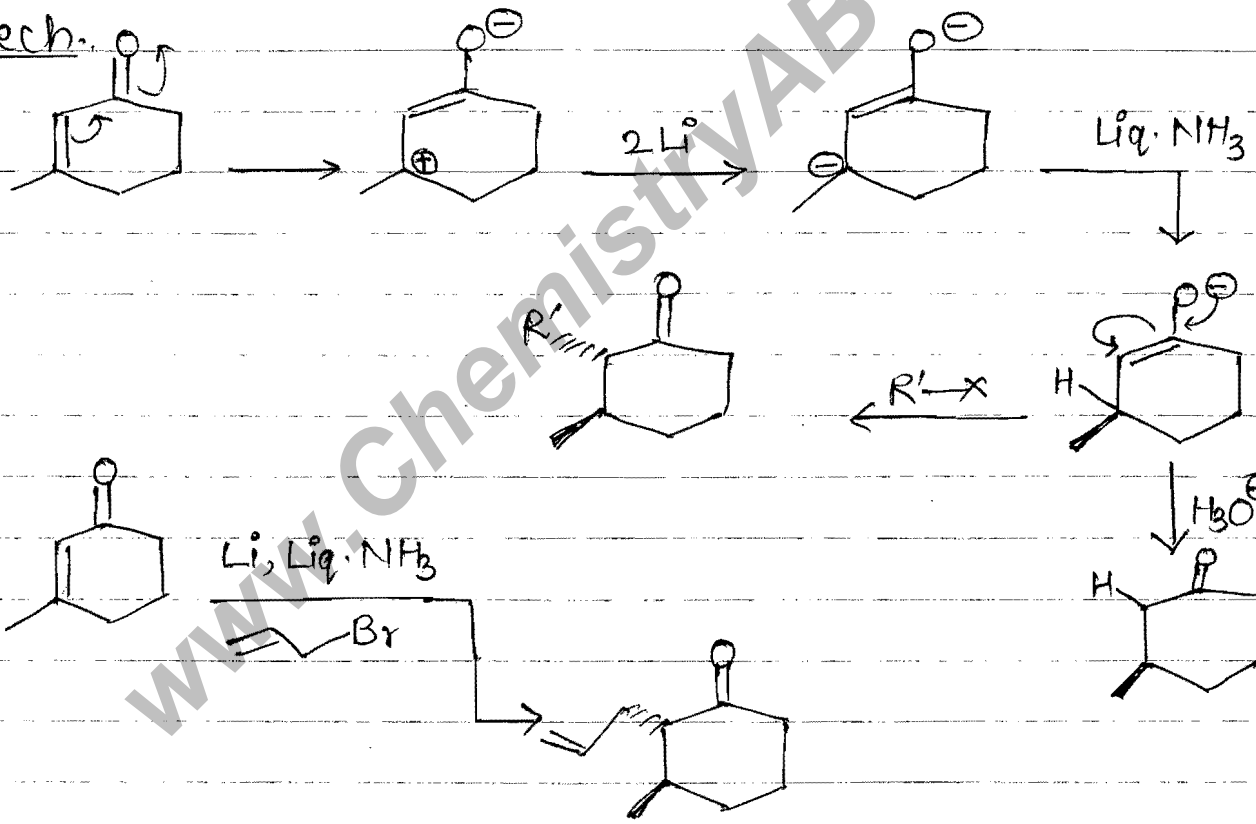
Ex.



Ex.



Mech.



Ex.

Red^{n} of C=C of α,β-unsaturated carbonyl comp. Li or Na and liq. NH_3 is the best reagent.

GRIGNARD REAGENT "RMgX"

Grignard reagent is an organometallic comp., Metal directly connected to carbon. It is an example of umpolung reagent. (Reversible in polarity)

Preparations of Grignard Reagent:-

$$R-X \xrightarrow[\text{Dry ether}]{Mg} R-Mg-X$$

Mechanism:-

$$\overset{\delta+}{R}-X^{\delta-} \longrightarrow R^{\oplus} + X^{\ominus}$$

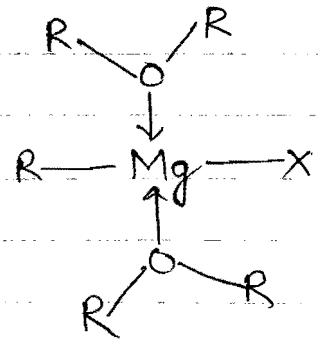
$$Mg \xrightarrow{-2e^-} Mg^{2+}$$

$$R^{\oplus} + 2e^- \longrightarrow R^{\ominus}$$

$$R^{\ominus} + Mg^{2+} \xrightarrow{X^-} \overset{\delta-}{R}-\overset{\delta+}{Mg}-X$$

↑ charge reversed.

In grignard Rxn. dry ether used as a solvent. In etheral soln Grignard reagent exist in the following type structure.



In etheral soln. Grig. reagent exist in following eqm.

V. Imp.

$$2\,RMgX \rightleftharpoons R_2Mg + MgX_2 \text{ (Lewis Acid)}$$

Schlenk Equilibria.

The formation of Grig. reagent is the redox rxn. In Grig. reagent there is a polar covalent bond in b/w carbon atom and Mg.

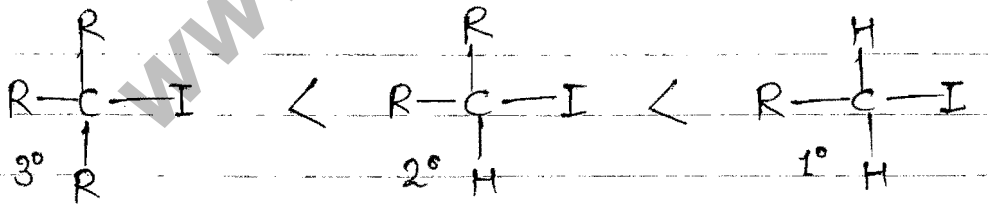
Reactivity of Alkyl Halide for formation of Grignard Reagent

$$R-X \Rightarrow R-I > R-Br > R-Cl > R-F$$

R–I: Weak bond easily break to form Grig. Reagent.

R–F: strong bond.

Q Write the correct order for formation of Grig. reagent of following Alkyl halide. R_3CI, R_2CHI, RCH_2I

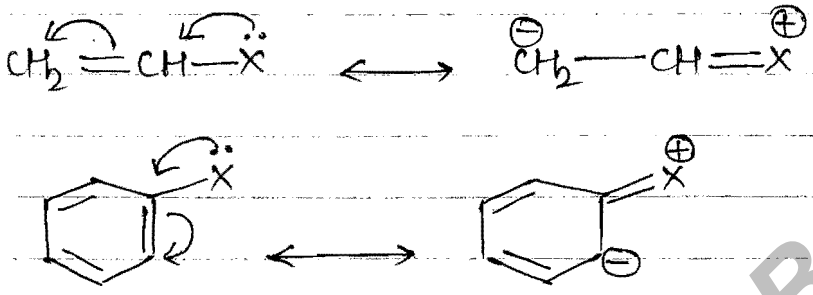


1° is more suitable because after formation of Grignard reagent 1° $R^{\ominus}$ is more stable than 3° $R^{\ominus}$

$$R-CH_2-MgX \longrightarrow R-\overset{\ominus}{C}H_2 \quad \text{More stable}$$

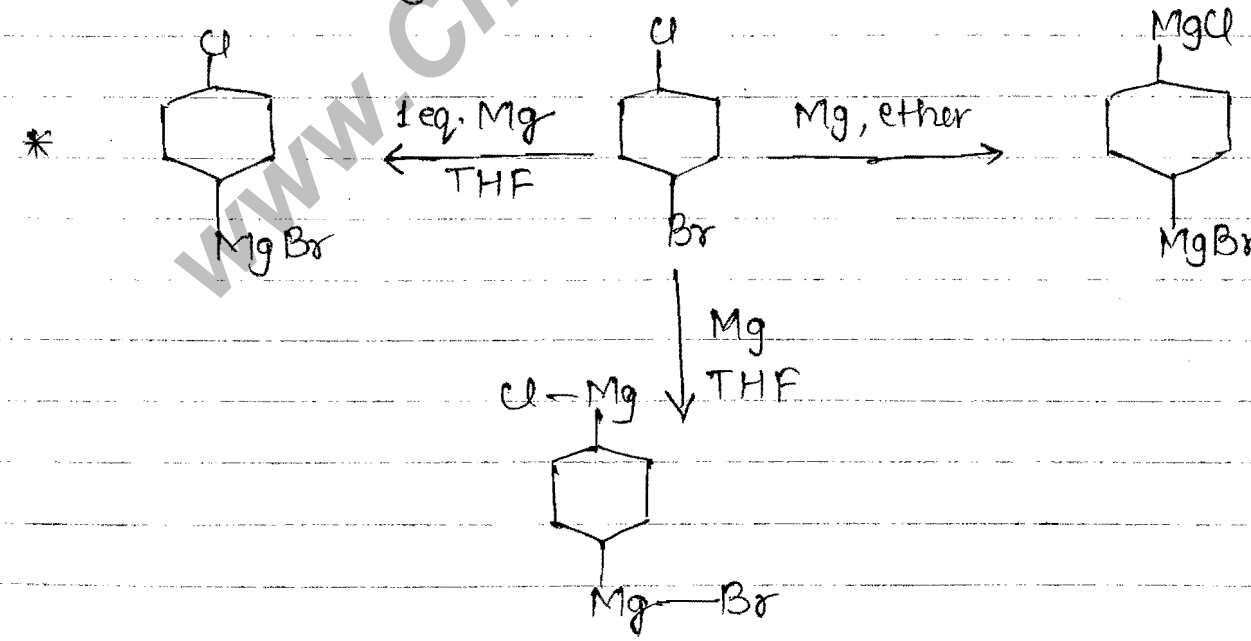
$$R_3C-MgX \longrightarrow R_3\overset{\ominus}{C} \quad \text{Unstable.}$$

In the case of vinyl halide or aryl halide there is a double bond character in b/w 'C' & 'X' so more amount of 'E' require to break C---X bond, so high temp. is required. In these cases ether can't be heated so tetrahydrofurane (THF) used as a solvent.

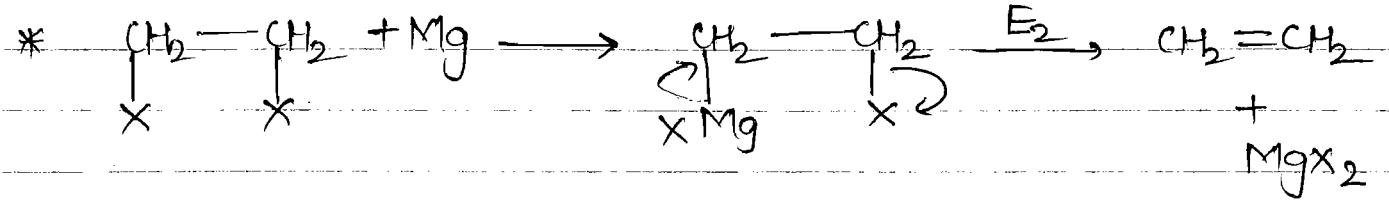


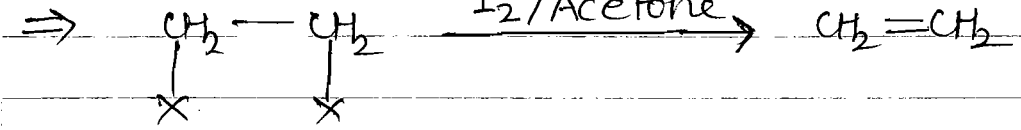
* $CH_2=CH-X \xrightarrow[\text{Dry ether}]{Mg}$ No rxn. or very low yield.

$CH_2=CH-X \xrightarrow[THF]{Mg} CH_2=CH-MgX$

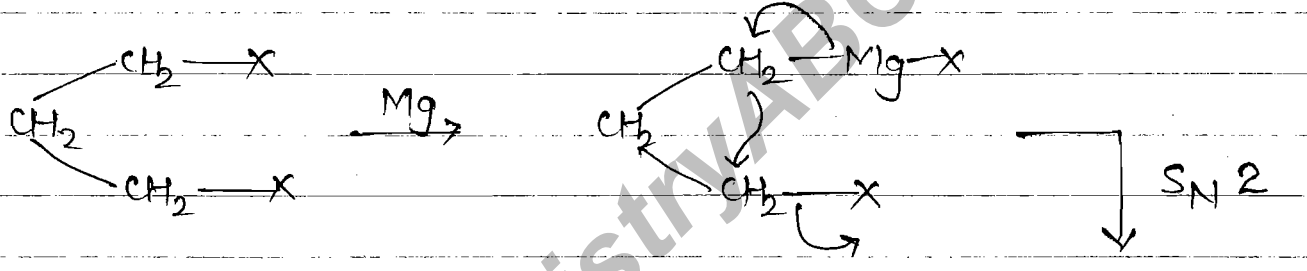


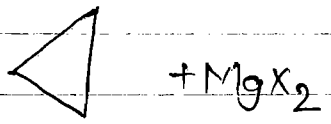
1,2-dihalide (Vicinal) are not used to form Grignard reagent, because they gives elimination Rxn.



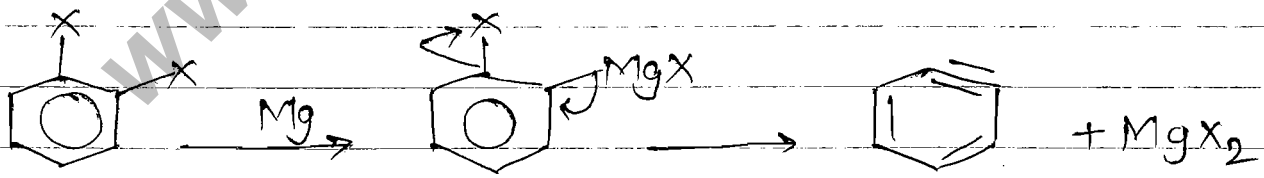


1,3 dihalide are also not used to form Grig. Reagent because they gives substitution Rxn.

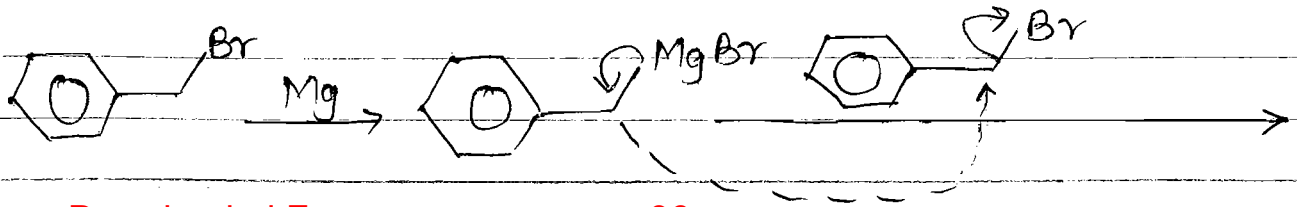


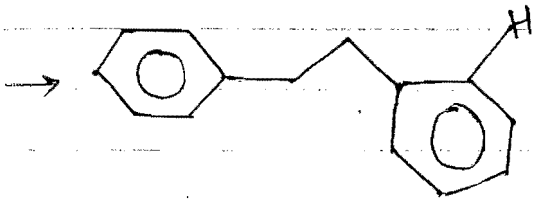


* 1,4-dihalide can form Grignard Reagent.
* Ortho dihalobenzene doesn't form Grignard Reagent.



* Meta and para dihalobenzene can form Grig. Reagent.
* Allylic and benzylic halides also not form G.R. because of high reactivity of these compounds.



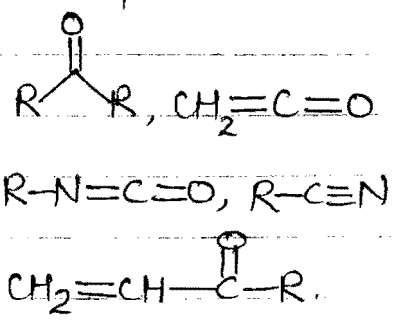


REACTIONS OF GRIGNARD REAGENT :-

Acid Base Rxn. (Zeriwitanoff Rxn)

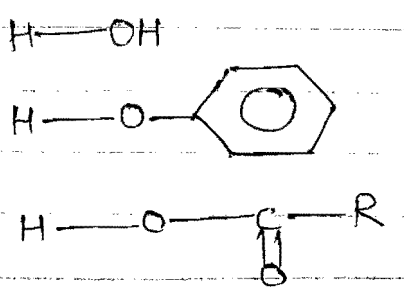
Nucleophilic Substitution
- Allyl halide
- Acid derivatives

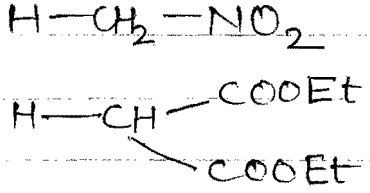
Nucleophilic Addⁿ.



Zeriwitanoff Rxn:- G.R. alkyl group basic in nature. When the G.R. react with the comp. having active hydrogen atom, first of all Acid-base rexⁿ. take place and Alkane is foom. this method is kya Zeriwitanoff Rxn.

H—Z are given below



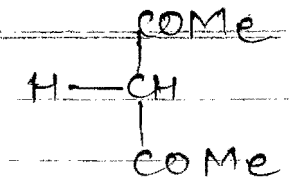


HSR

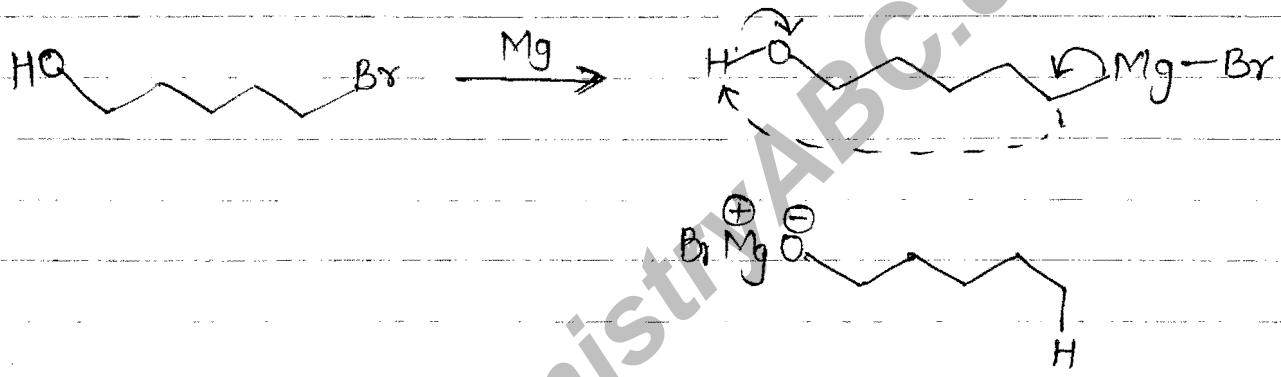
H—OR

H—C≡CH

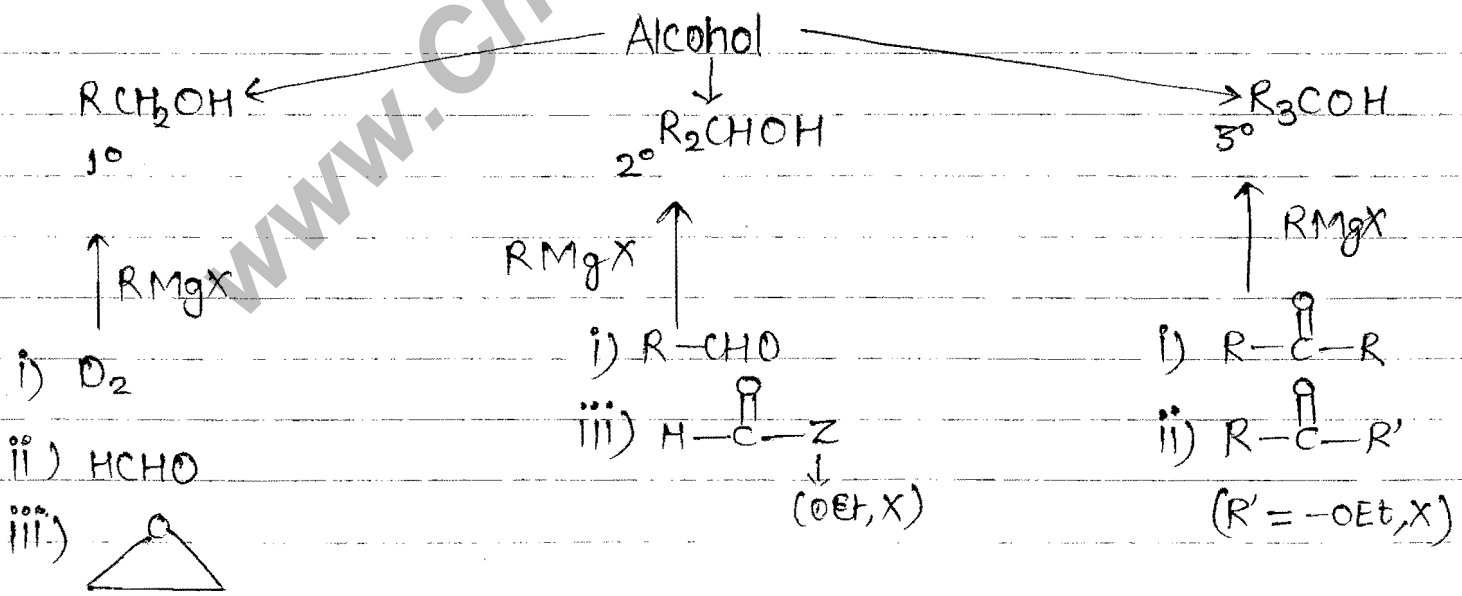
H—NHR



The ~~comp~~ ~~wh~~ alkyl halide comp. which has acidic proton are not used to form grignard reagent becoz. acid-base rxn will take place.



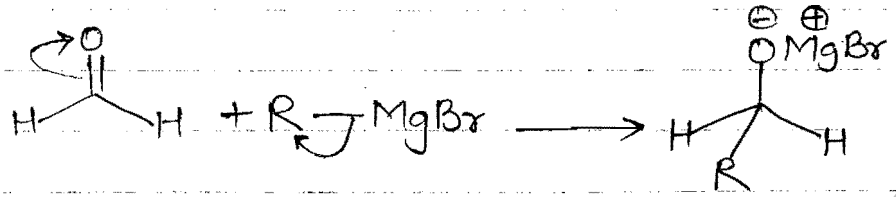
Formation of Alcohol by Grignard Reagent :-



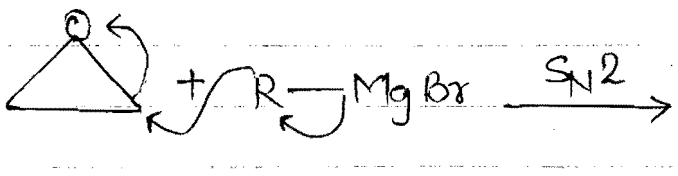
Formation of 1° Alcohol:-

* $R-MgX + \frac{1}{2}O_2 \longrightarrow R-O-MgX \xrightarrow{H_3O^{\oplus}} R-OH + HOMgX$

($R-MgX$: 1°)

* 

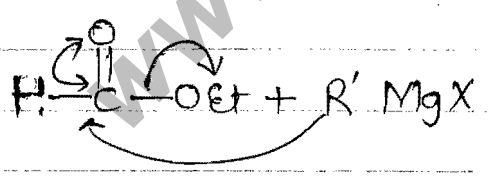
$\xrightarrow{H_3O^{\oplus}}$ RCH_2-OH + $HO-Mg-Br$

* 

$\xrightarrow{H_3O^{\oplus}}$ $R-CH_2-CH_2-OH$

Formation of 2° Alcohol.

* $R-\underset{\underset{O}{\|}}{C}-H + R'MgX \xrightarrow{H_3O^{\oplus}} R-\underset{R'}{\overset{OH}{C}}-H + HOMgX$

* 

$\xrightarrow{H_3O^{\oplus}}$ $R'MgBr$

$H-\underset{R'}{\overset{OH}{C}}-R' + HOMgBr$

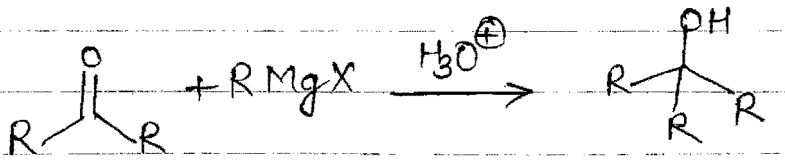
* $H-\underset{\underset{O}{\|}}{C}-Cl + 2R'MgX \xrightarrow{H_3O^{\oplus}} H-\overset{OH}{C}R'_2$

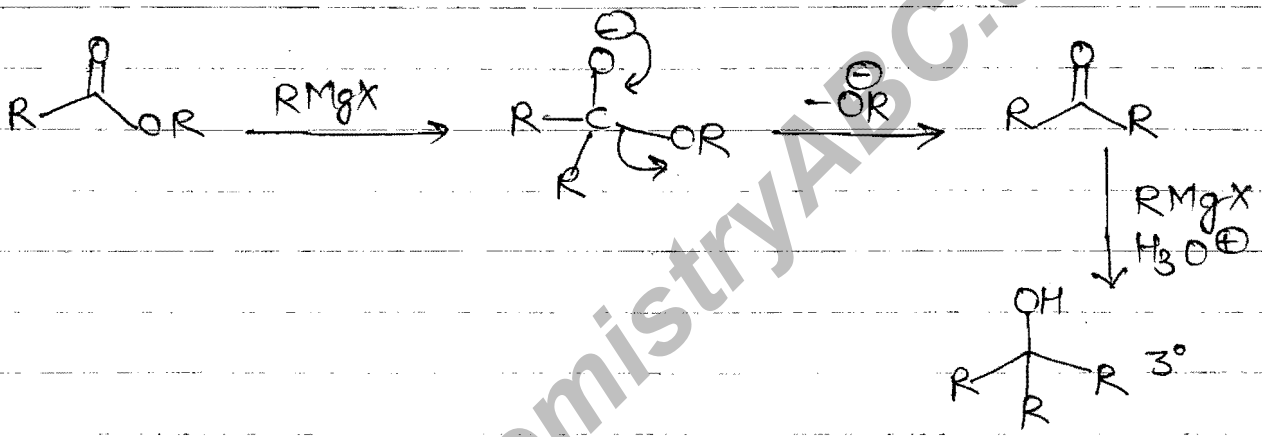
Acid derivative : Grignard Reagent

1 : 1 ⇒ Formation of Carbonyl comp.

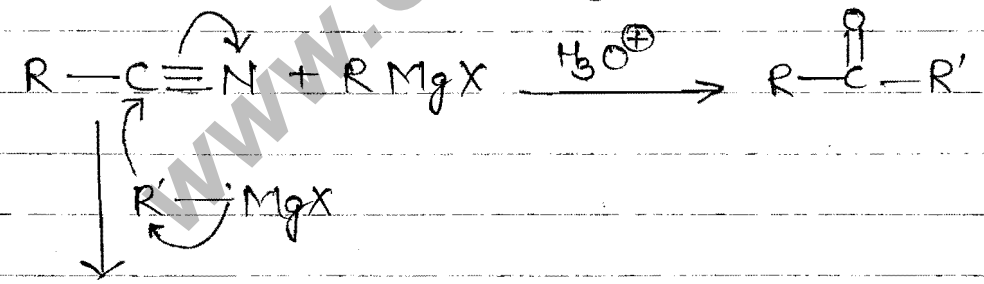
1 : 2 ⇒ Alcohol.

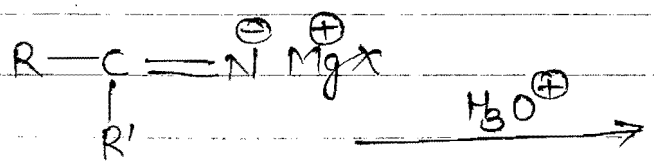
Formation of 3° Alcohol :-



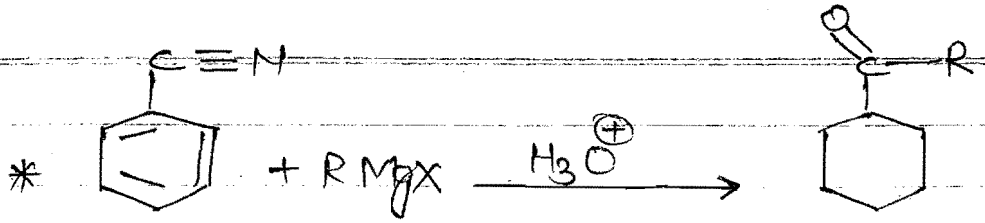


Rxn with Alkyl Cyanide :-

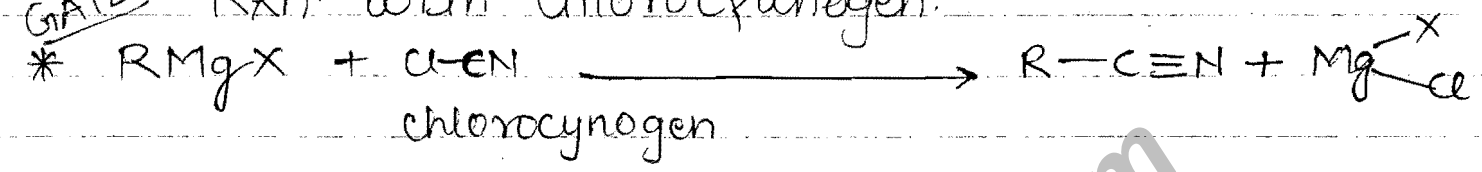




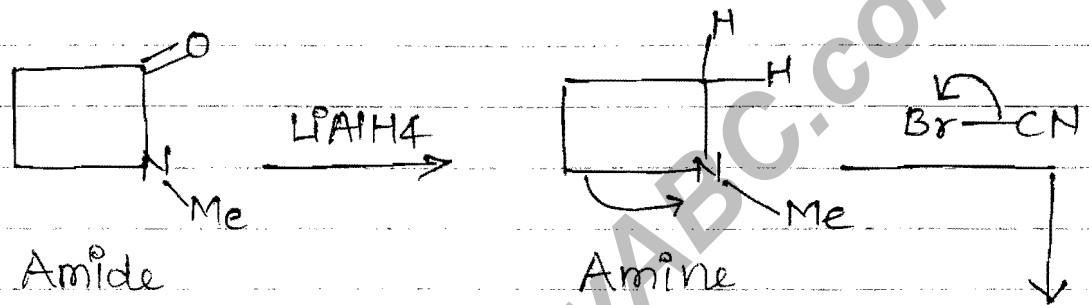
Further no Rxn with RMgX becoz it is inactive in +nce of H_2O.

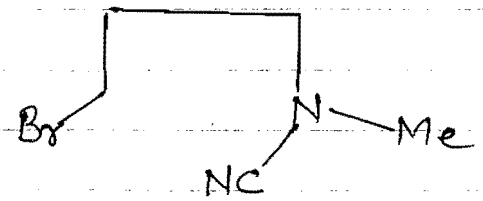


GATE Rxn. with Chlorocyanogen.

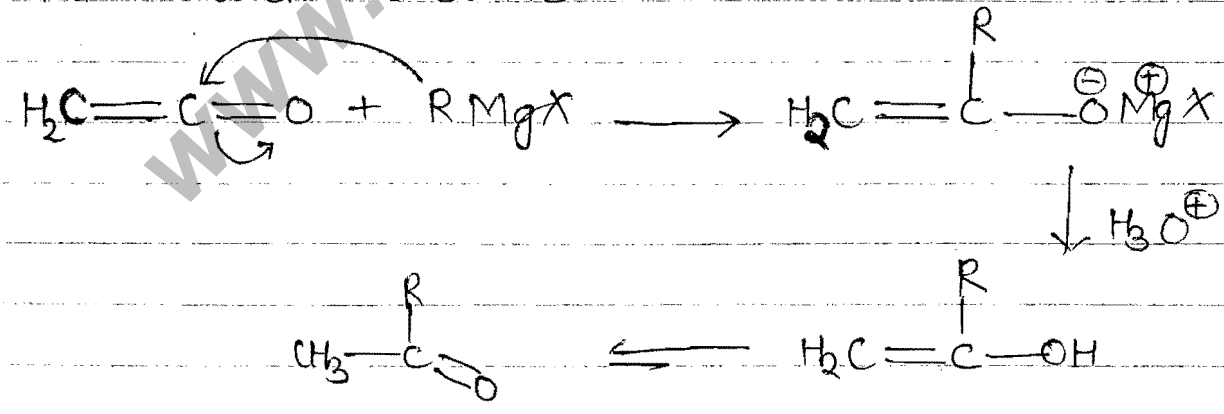


2014 GATE

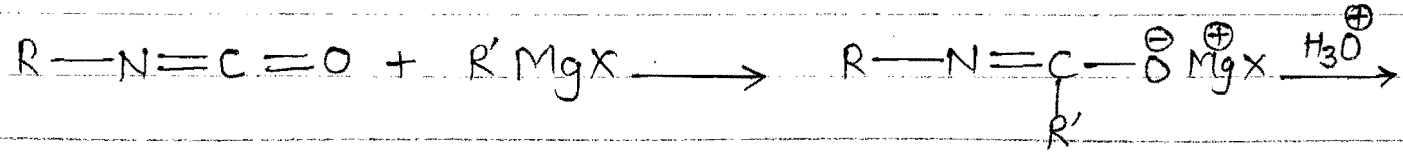


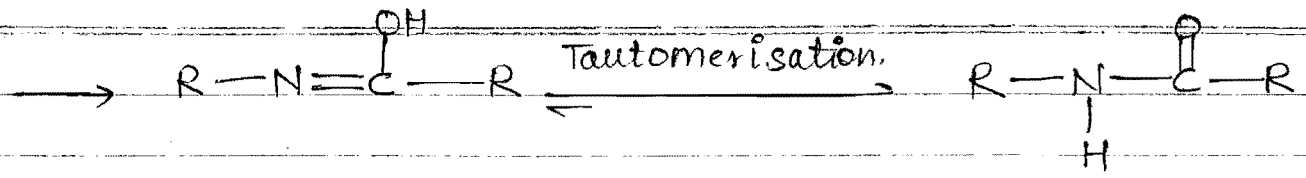


Rxn. with Ketene

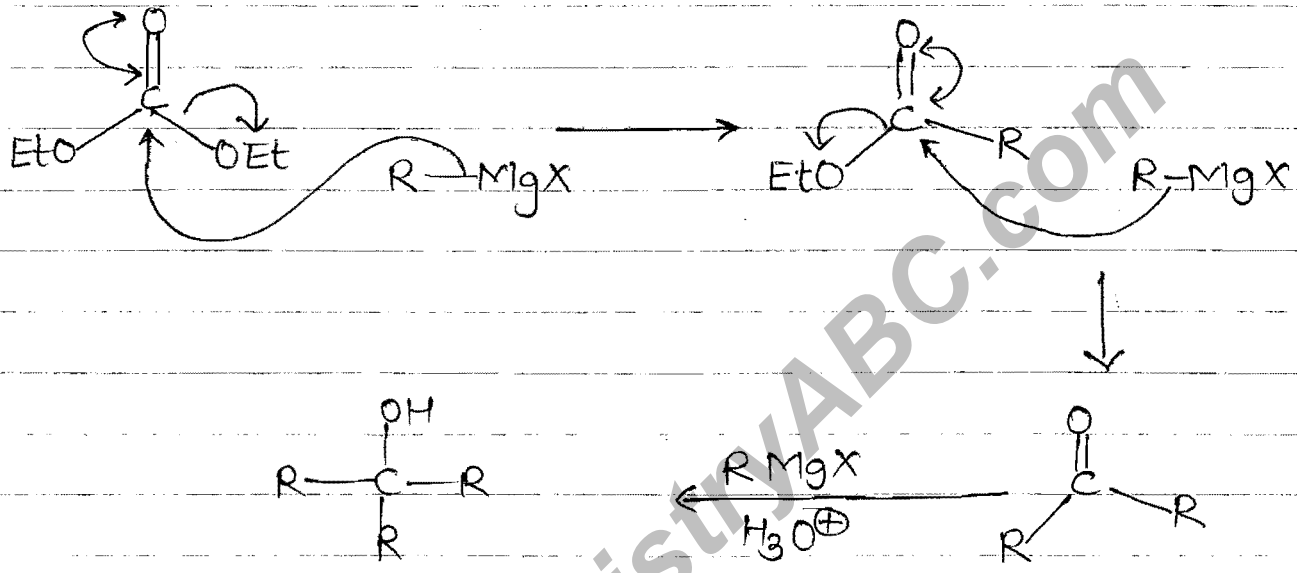


Rxn. with Isocyanate:-





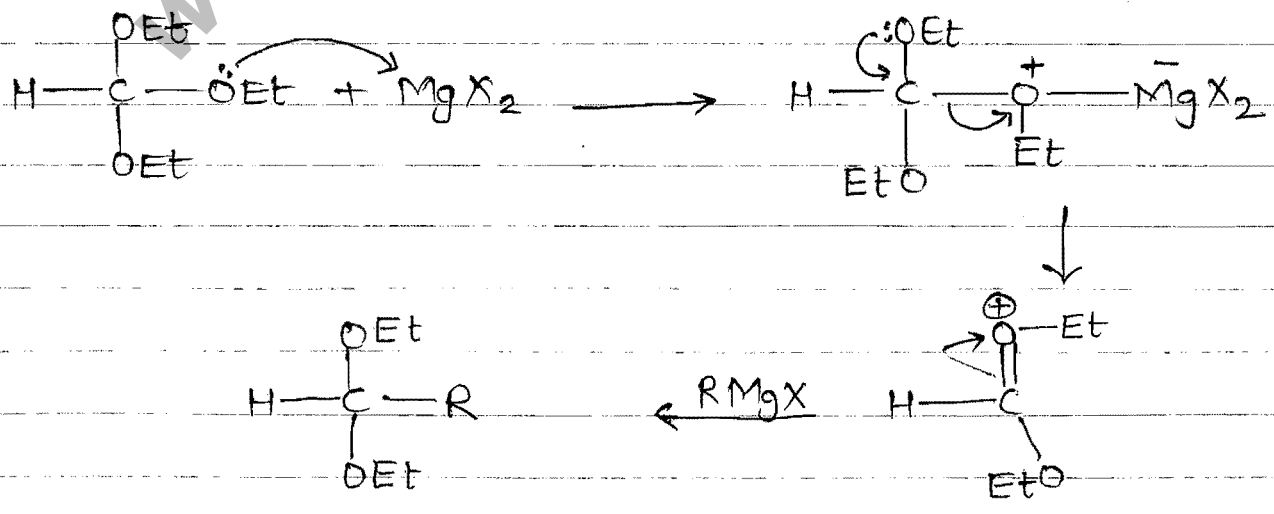
Rxn. with Carbonate:-



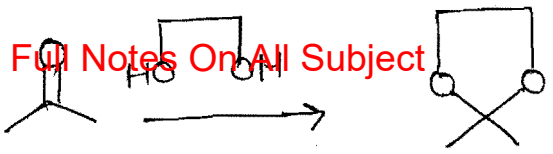
Rxn. with ortho ester:-

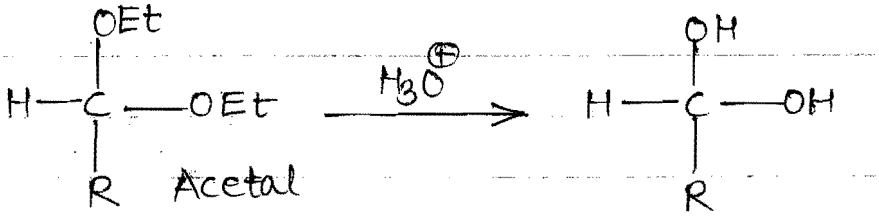
RMgX doesn't react with ortho ester directly but Grignard reagent exist in Schlenck equilibria so MgX_2 reacts with ortho ester.

Lewis Acid.



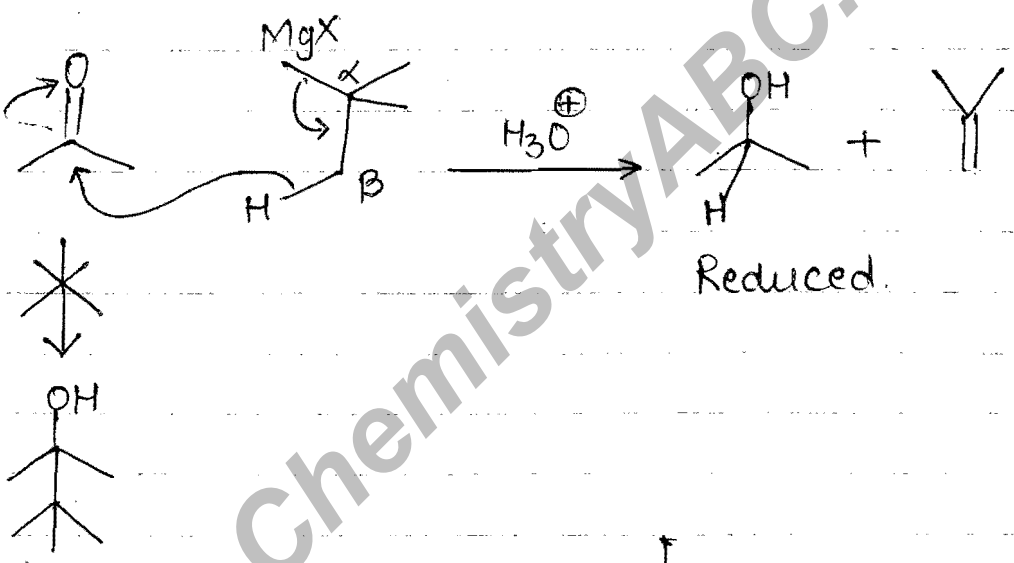
Acetal

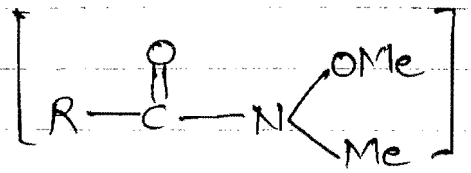




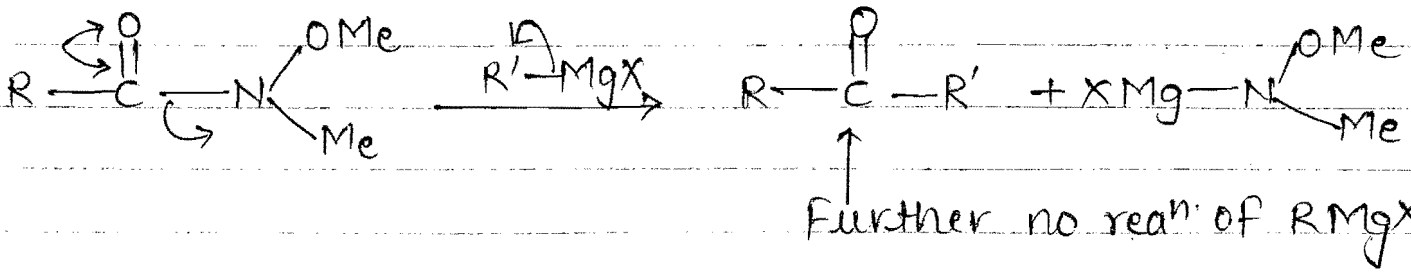
Bulky Grignard reagent possesing β-H atom can act as a reducing agent.

V. Imp

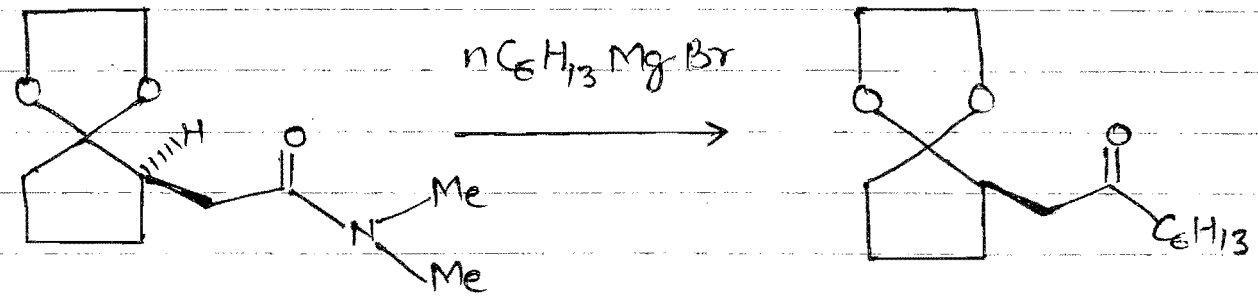


Rxn. with Weinreb Amide 

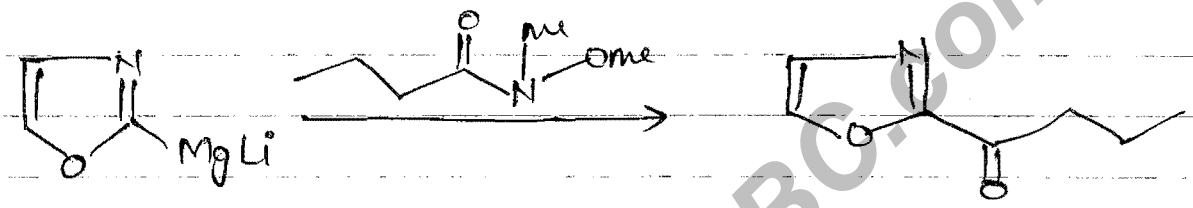
Grignard reagent gives only mono addⁿ. with weinreb amide.



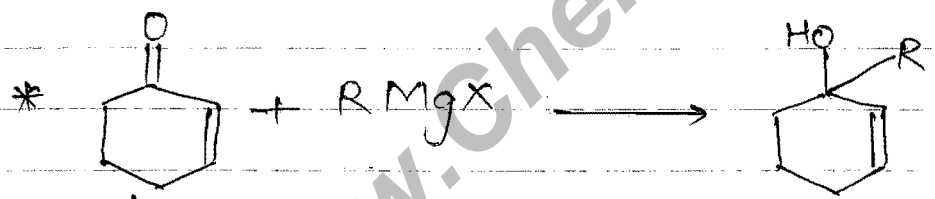
Ex.



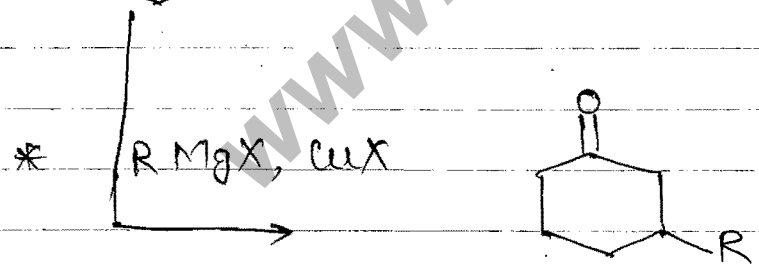
Ex.



Grignard reagent gives direct addⁿ. with α,β-unsaturated carbonyl compound, but in the presence of CuX or Any Lewis acid, Grignard reagent gives 1,4 addⁿ.

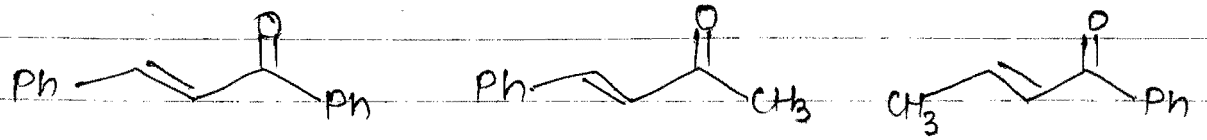


Direct addⁿ.



Michael Addⁿ.

But in the following type α,β - unsaturated comp. Grignard Reagent gives 1,4 addition even in the absence of CuX.

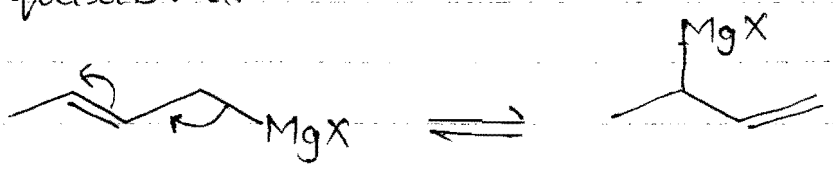


1,4 addⁿ. even absence of CuX.

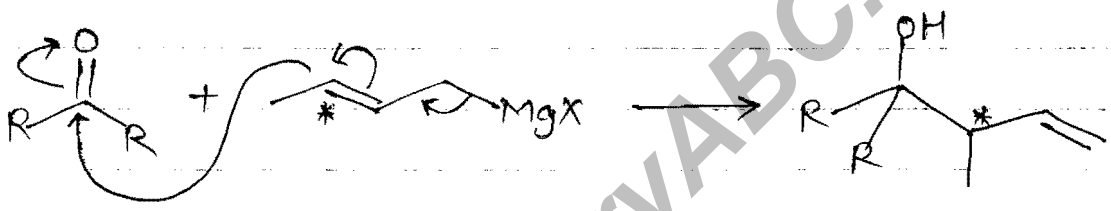
Abnormal Behaviour of Grignard Reagent:-

Allylic grignard reagent, gives addⁿ. Rxn. with carbonyl with allylic shifting.

Allylic grignard reagent exist in following Equilibria.

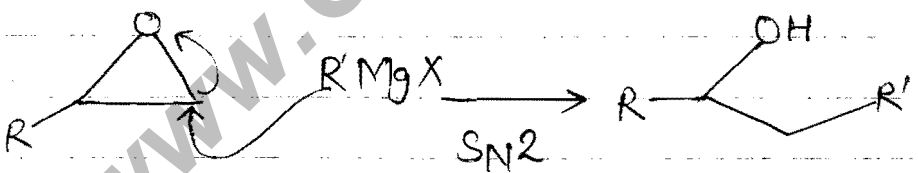


Ex.

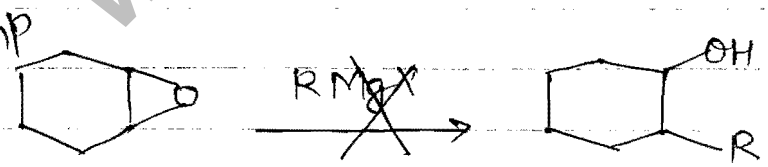


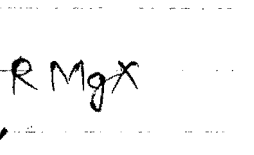
Rxn. with Epoxide Ring:-

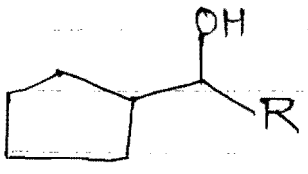
Grignard reagent exist in schlenk equilibria, so there is competetion for ring opening of epoxide via S_N1 or S_N2 mech.



V. imp

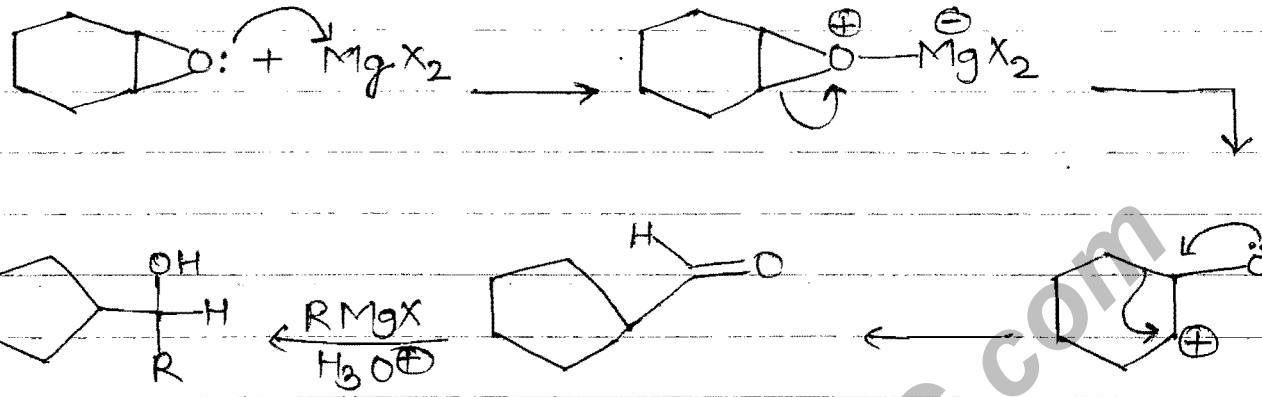






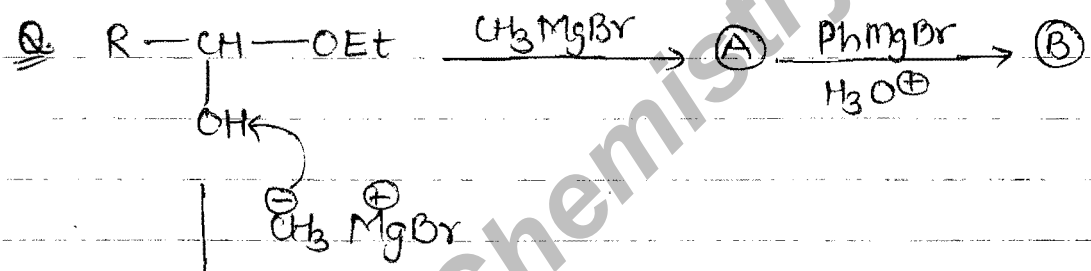
← This prod. is due to schlenk eqᵐ. Since Gilmam does not exist in Schlenk eqᵐ. so that will not form this prod.

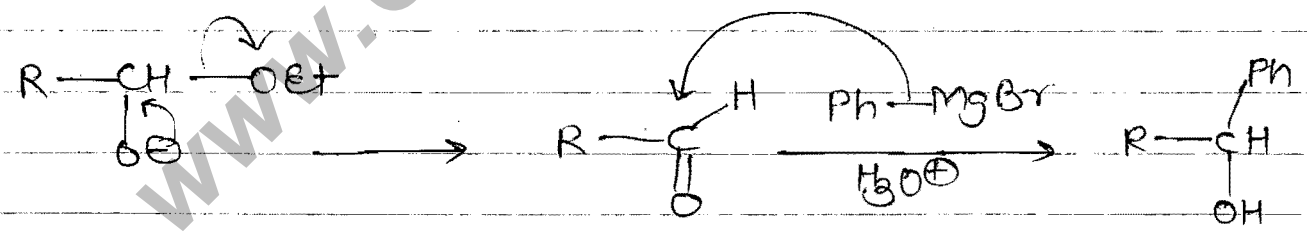
Mechanism.



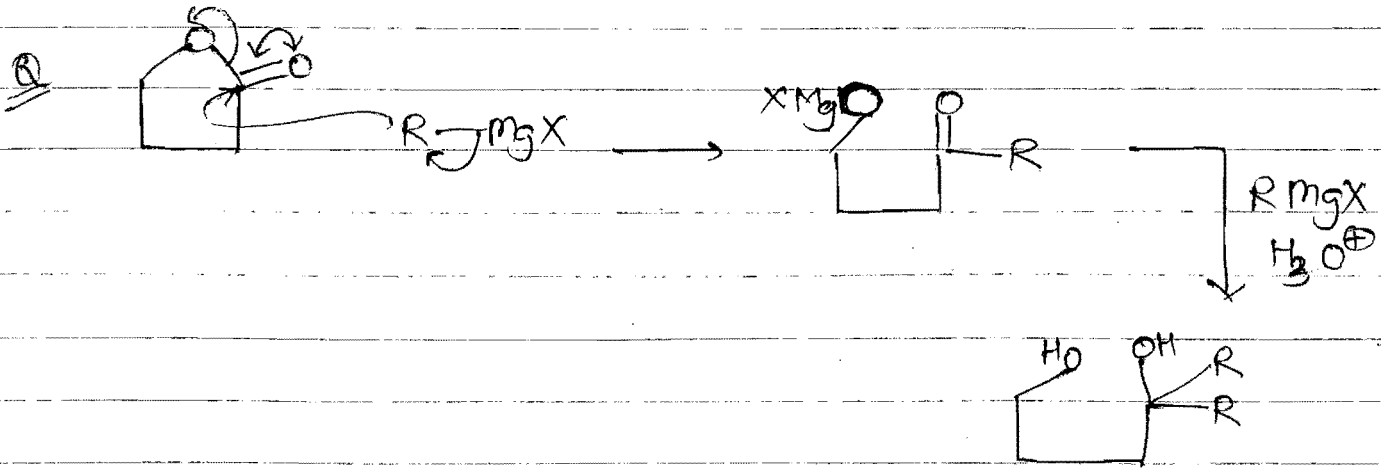
Positive charge on ring ⇒ Demjanov Ring Contraction.

Q.





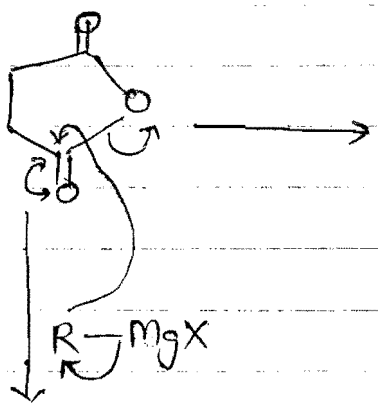
Q

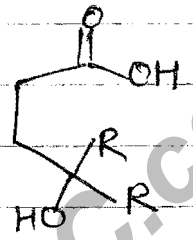


Q $R-MgX + O=C=O \xrightarrow{H_3O^{\oplus}} R-\underset{\underset{O}{\|}}{C}-OH$

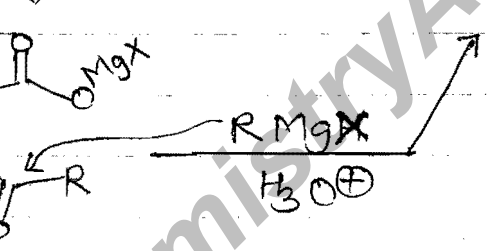
Q $RMgX$ (excess) + $EtO-\underset{\underset{O}{\|}}{C}-OEt \longrightarrow R-\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}-R$

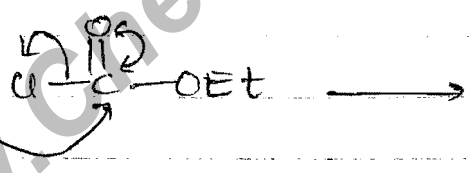
Q $RMgX$ +



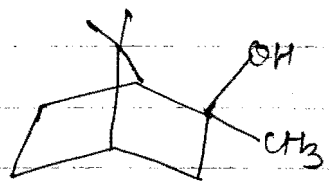


Mech.

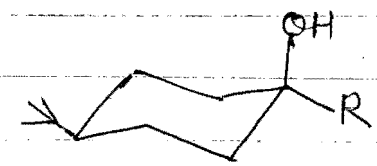


Q $RMgX$ +  $\longrightarrow$ $R-\underset{\underset{O}{\|}}{C}-OEt$

1 eq.

Q  CH_3MgX 

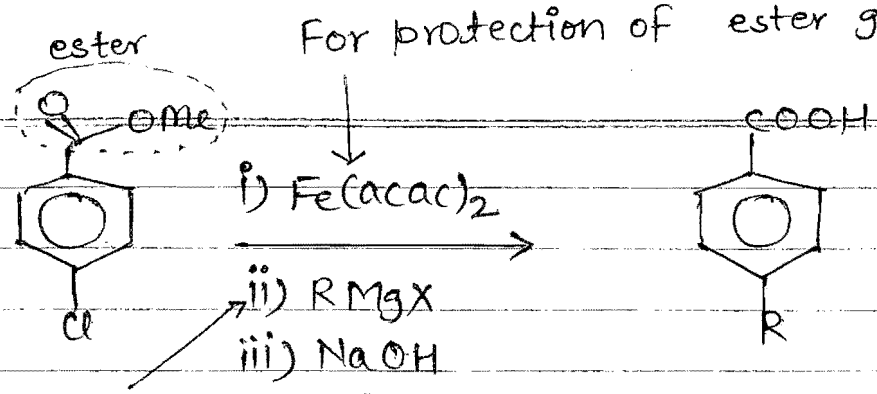
Endo attack

Q  $RMgX$ 

Equatorial attack

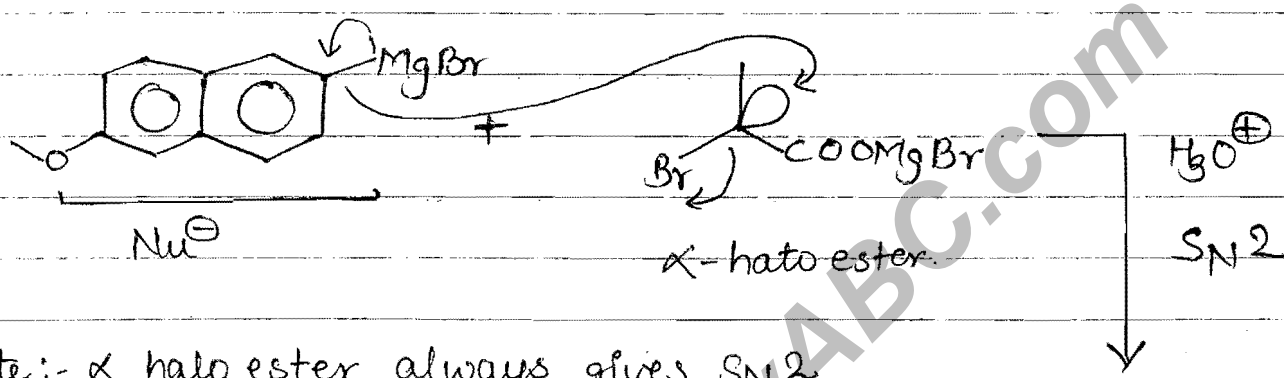
For protection of ester group.

Q



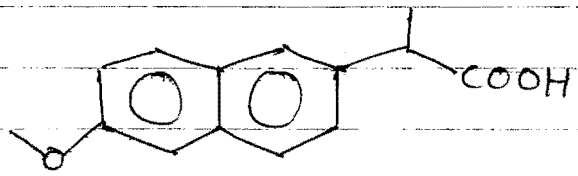
Nucleophilic substitution ↑ Deprotection of ester group.

Q



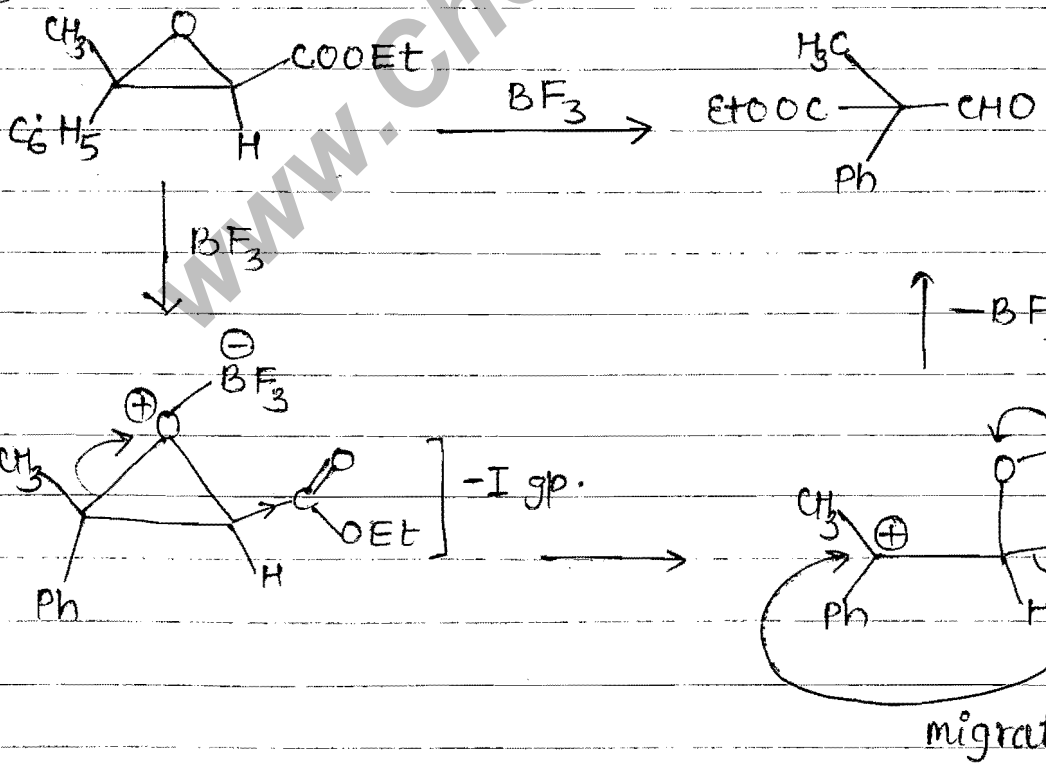
Imp.

Note:- α halo ester always gives SN2 not SN1 mechanism.



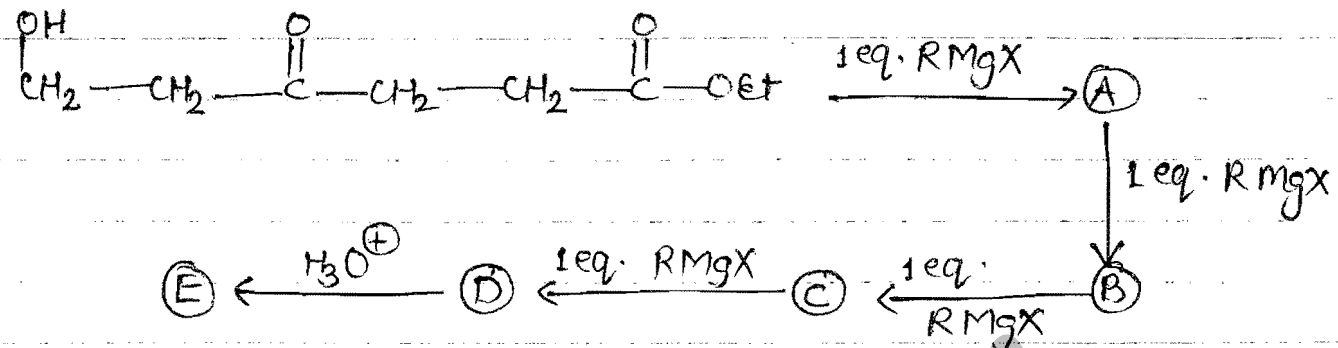
Imp.

Q

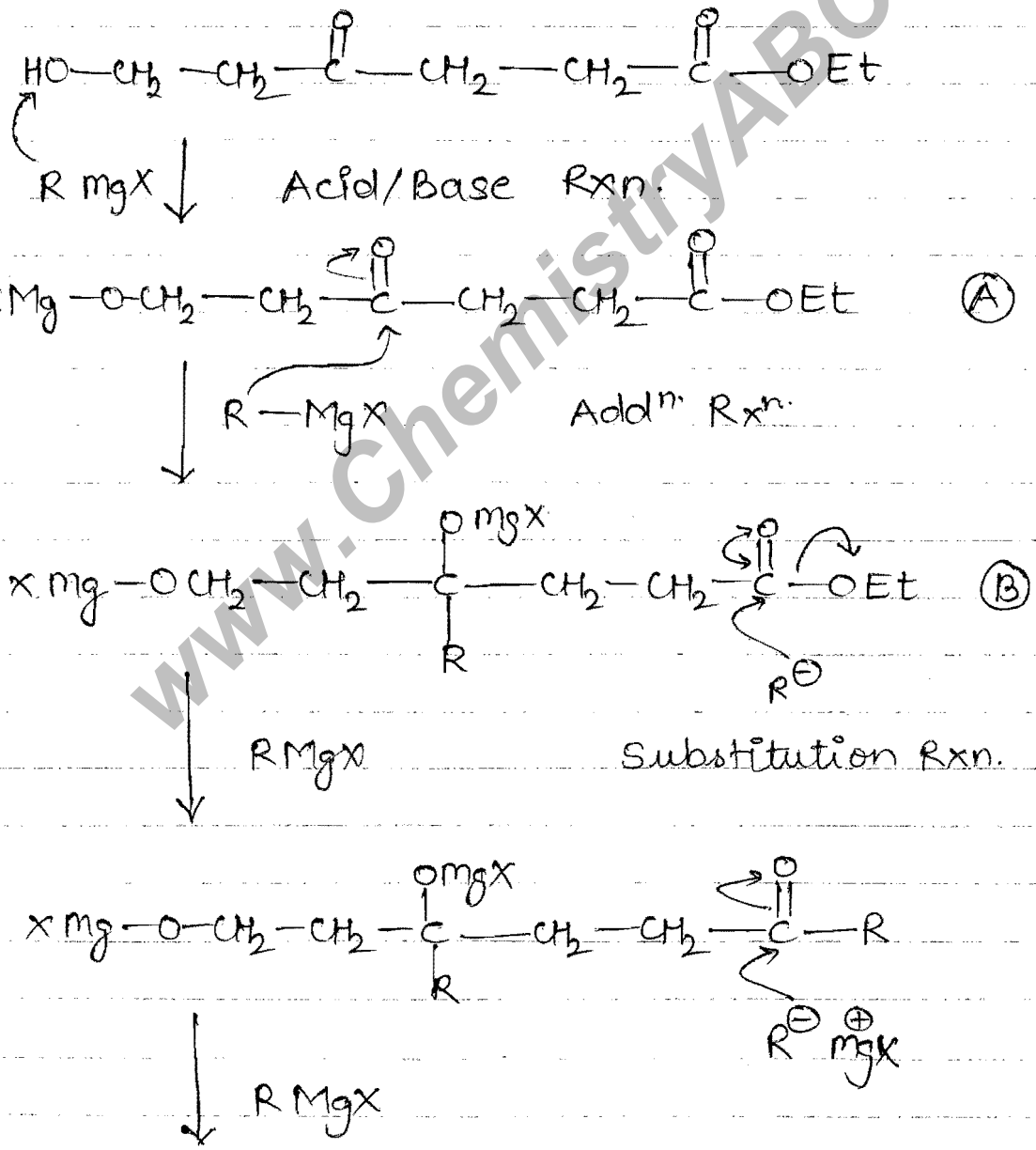


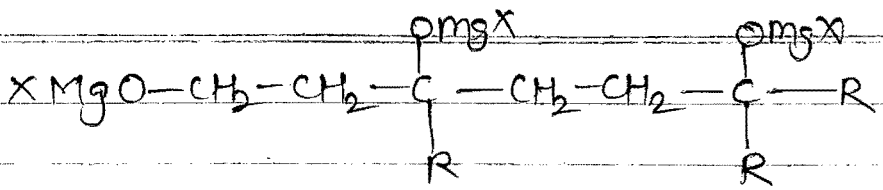
V.V. imp.

Q

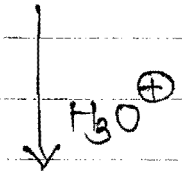


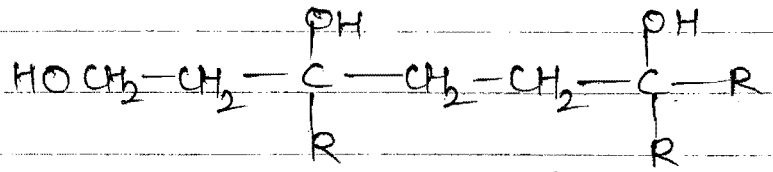
Acid/base Reaⁿ. > Addⁿ. Rxn. > Substitution Rxn. > Elimination Rxn.



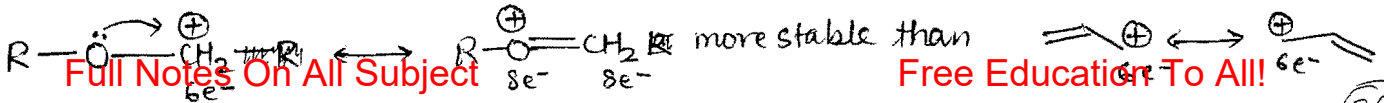


(D)





(E)

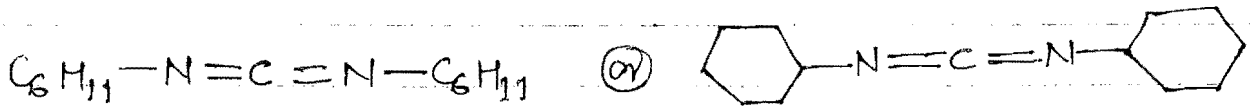


Substituted carbocation.

DICYCLOHEXYLCARBODIIMIDE

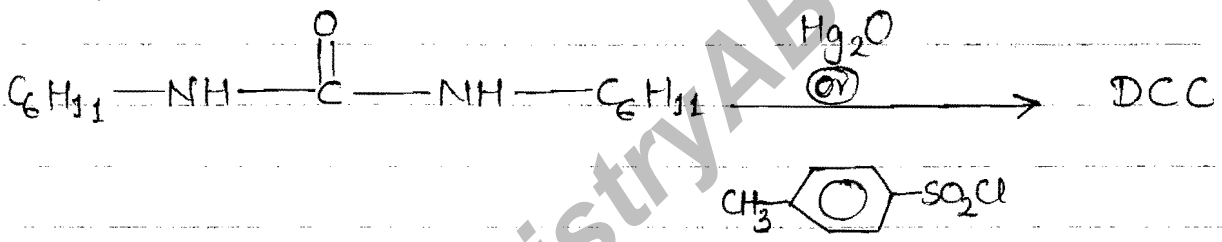
DCC

पानी का प्यासा

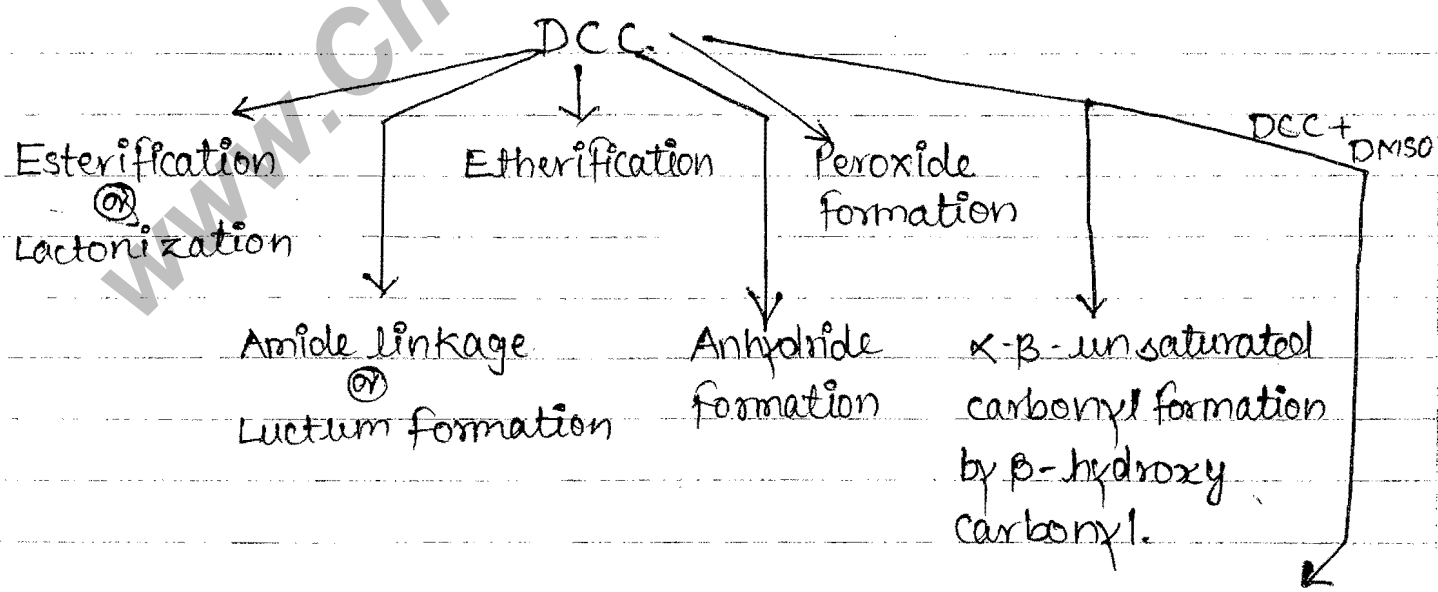


DCC is dehydrating reagent (H_2O removal). DCC stored under anhydrous condition.

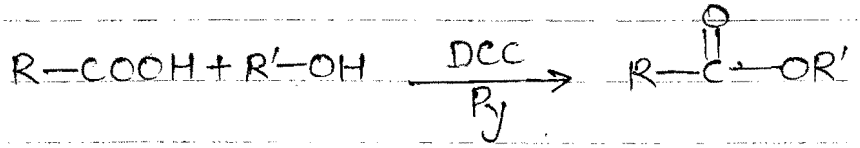
Preparation of DCC :-

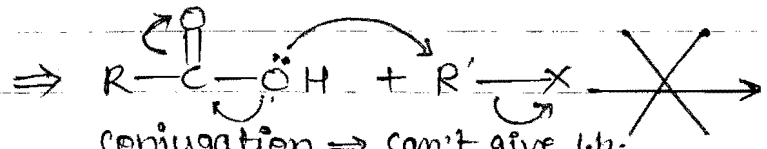


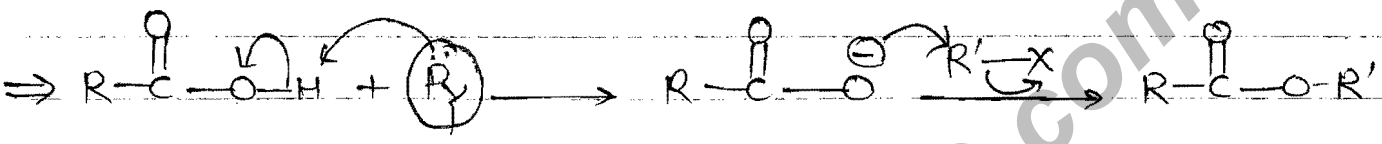
Applications of DCC ⇒ Thirsty DCC



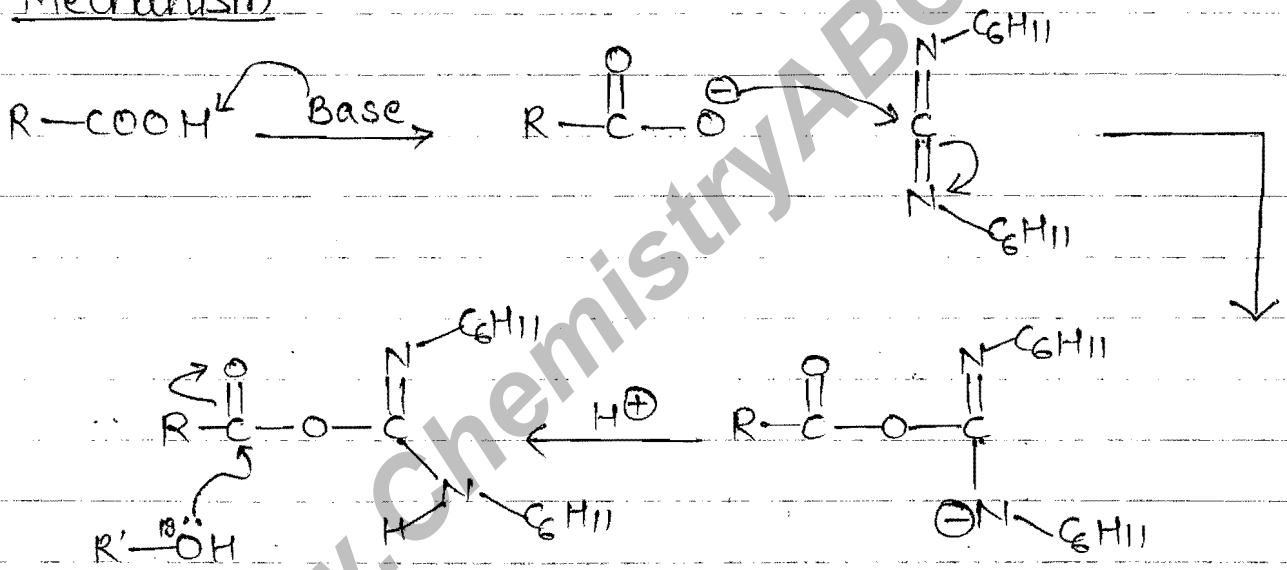
Moffat oxidation
(oxidation of alcohol by DCC in the +nce of DMSO)

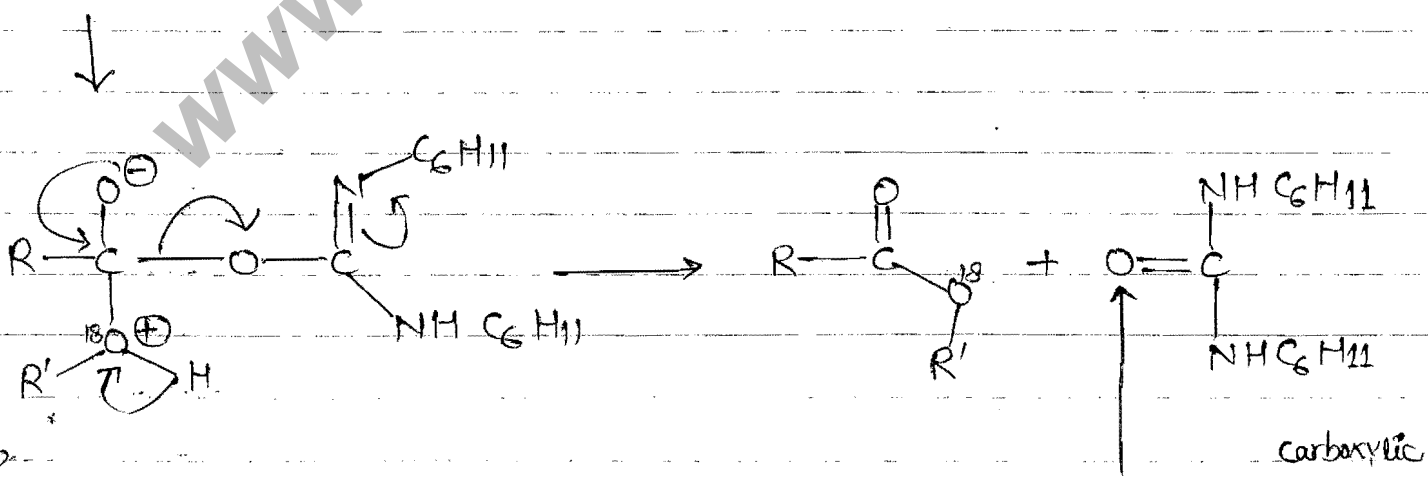






Mechanism

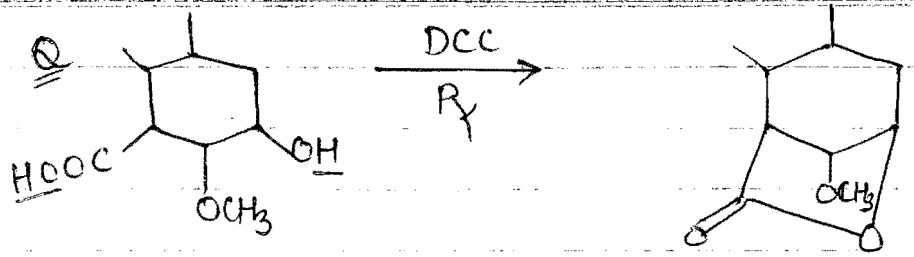




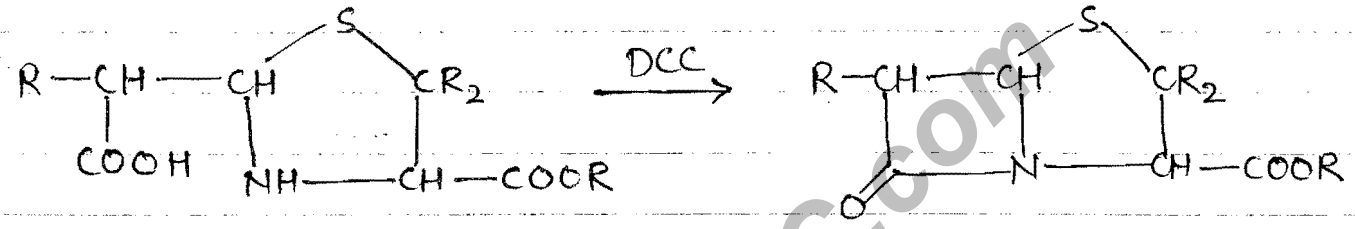
gmp

Here OH of Acid & H of alcohol undergo dehydration.

carboxylic oxygen of Acid.

Q 

Lactone formation.

Q 

Lactone formation

Q $R-OH \xrightarrow{DCC} R-O-R$

Q $ArOH + MeOH \xrightarrow{DCC} Ar-O-Me$

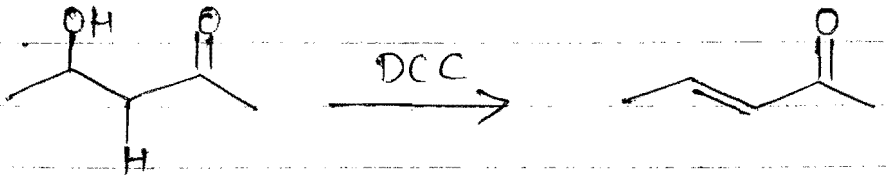
Q $R-COOH \xrightarrow{DCC} R-C(=O)-O-C(=O)-R$

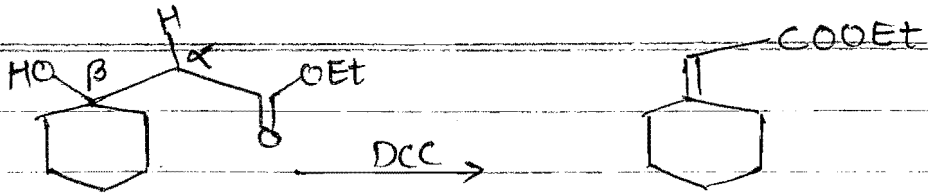
Imp Q $R-COOH \xrightarrow[H_2O_2]{DCC} RCOOOOR$ Peroxide

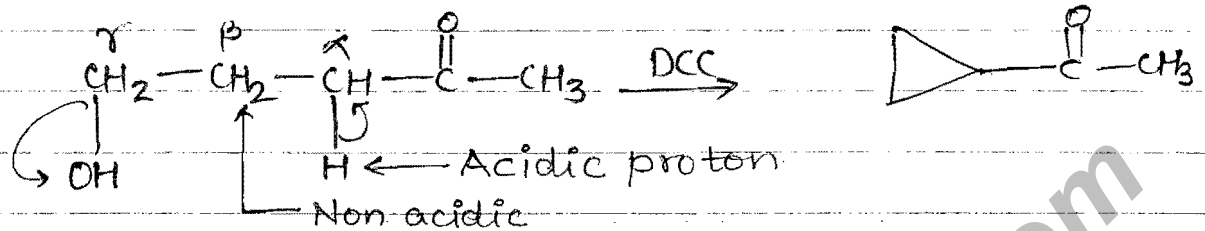
$R-COOH \xrightarrow{H_2O_2} R-C(=O)-O-OH$ Per acid

$R-C(=O)-O-OH \xrightarrow{DCC} R-C(=O)-O-O-C(=O)-R$ Peroxide

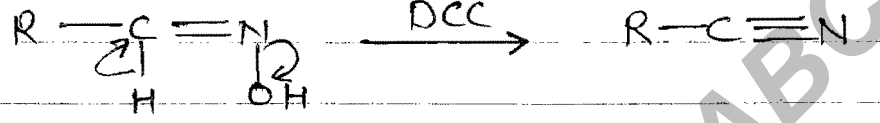
Q $Ar-SH + MeOH \xrightarrow{DCC} Ar-S-Me$

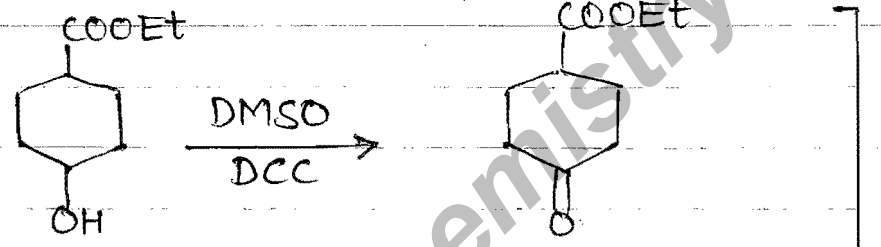
Q 

Q 

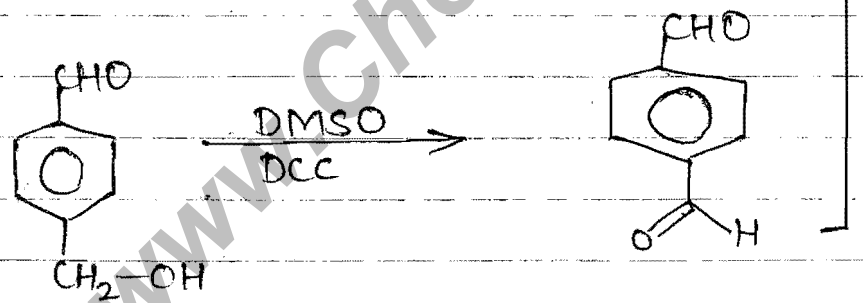
Imp. Q 

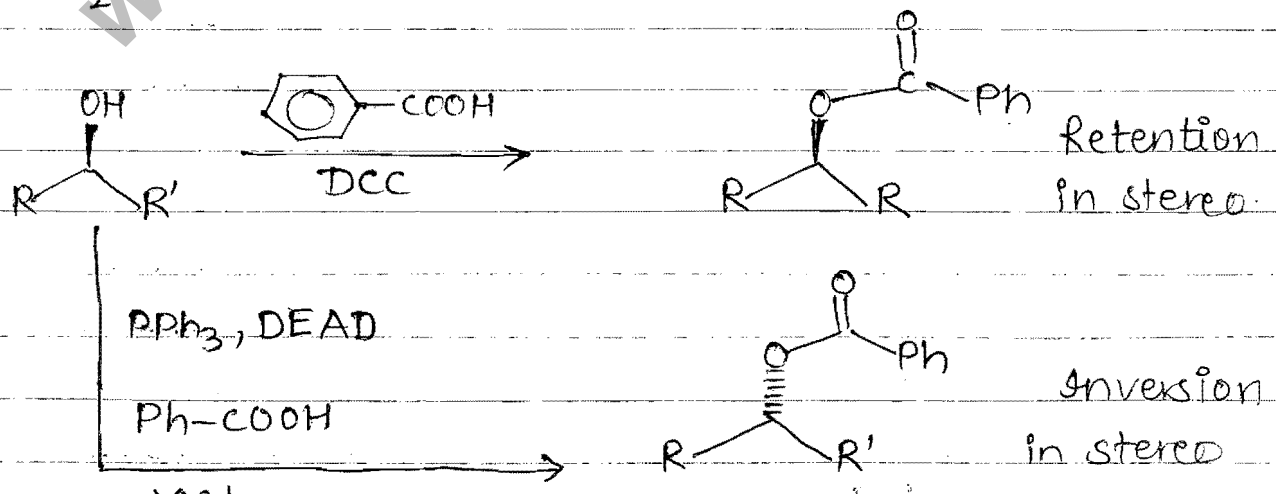
γ-hydroxy ketone gives cyclopropyl ketone

Q 

Q 

Moffut Oxidation

Q 

Q 

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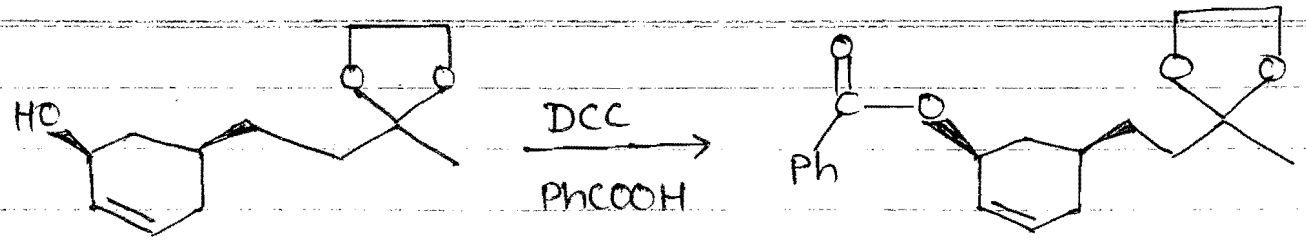

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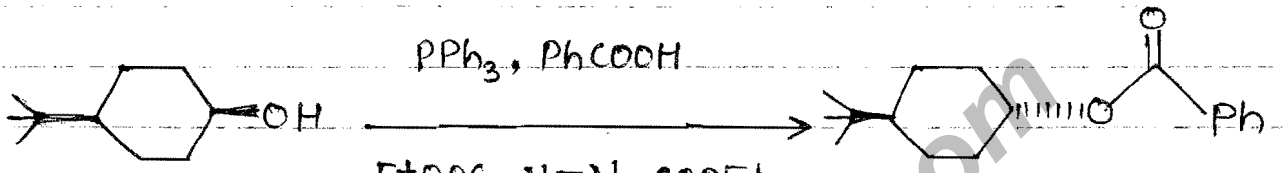
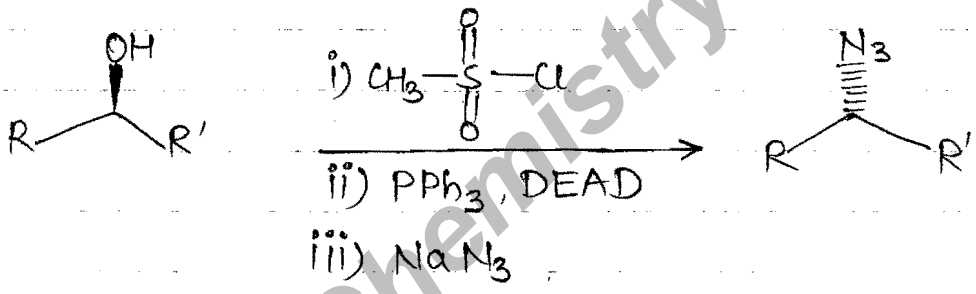


Mitsunobu

* DEAD is light ($h\bar{\nu}$) sensitive

*



gmp.

TRIBUTYL TIN HYDRIDE

Bu_3SnH

Bu_3SnH is very specific reagent for the reduction of C—X bond to C—H bond.

Preparation :-

$$n\text{-}Bu_3SnCl + LiAlH_4 \longrightarrow Bu_3SnH$$

Applications:-

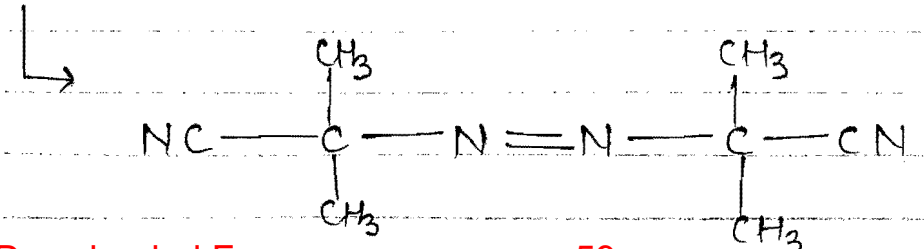
Bu_3SnH

- M. gmp. R—X → R—H
- M. gmp. ∞ Formation of 5-memb. ring
- $R\text{-}NO_2$ → R—H
- C—C coupling
- Reduction of Carbonyl

Reduction of C—X bond to C—H bond:-

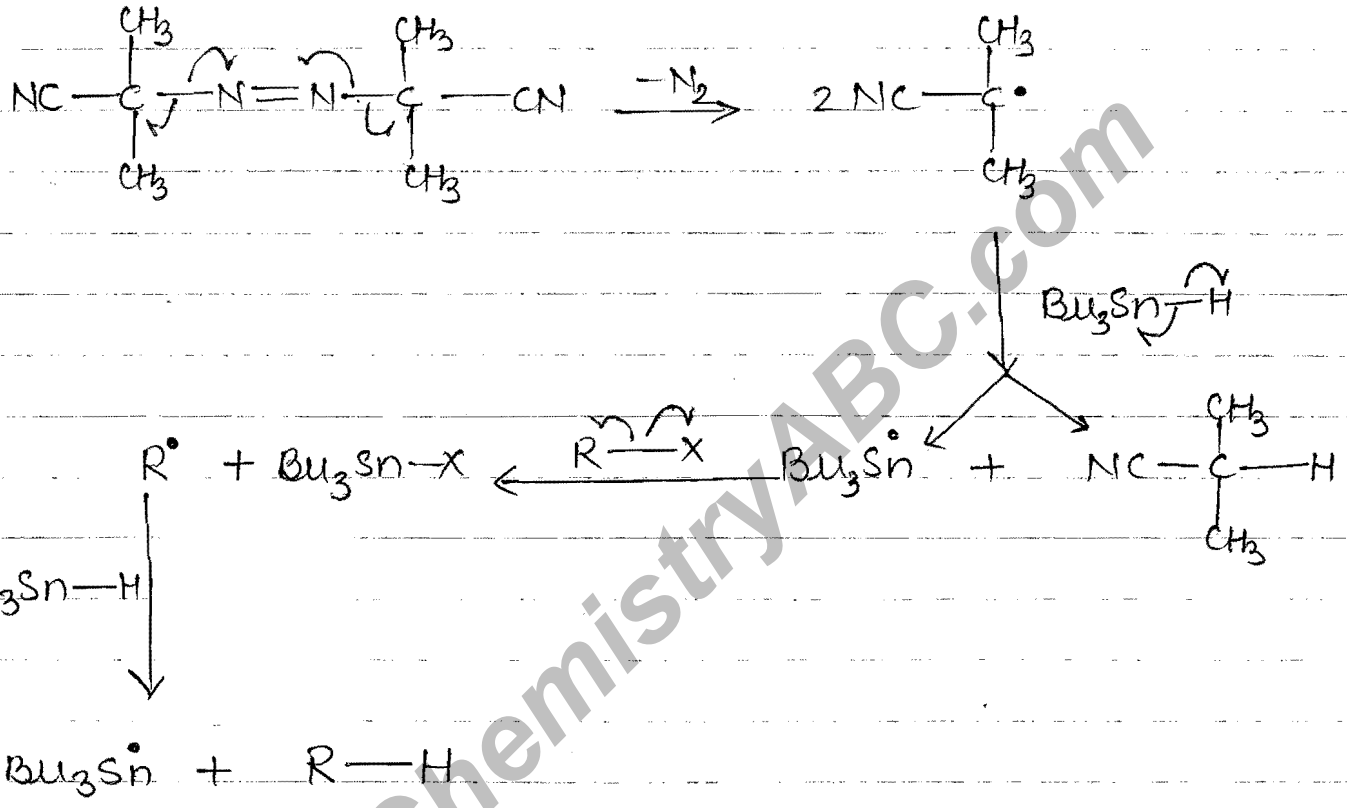
$$R\text{—}X \xrightarrow[AIBN]{Bu_3SnH} R\text{—}H$$

AIBN ⇒ Azabis isobutyro Nitrile



Reaction takes place by free radical Mechanism:-

Mechanism:-



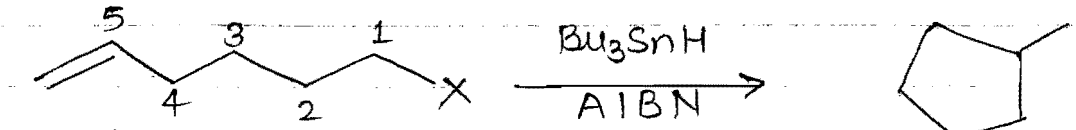
Some times intramolecular free radical add^{n} rxn. take place and 5-memb. ring formation occurs. When Alkene tnt at 5th position w.r.t. halogen, then In the tnce of Bu_3SnH/AIBN, 5 memb. ring form via intramolecular free radical mechanism. The formation of 5-memb. ring depends upon two factors - i) concentration of Bu_3SnH.

ii) Steric factor.

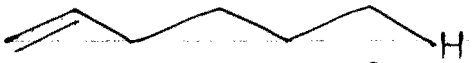
If conc. of Bu_3SnH is high (or) Bu_3SnH is given in excess amount and sterically hindrance tnt @ alkene then no 5 memb. ring form. In normal condition Bu_3SnH forms 5-memb. ring.

5 Memb. Ring formation

Bu_3SnH

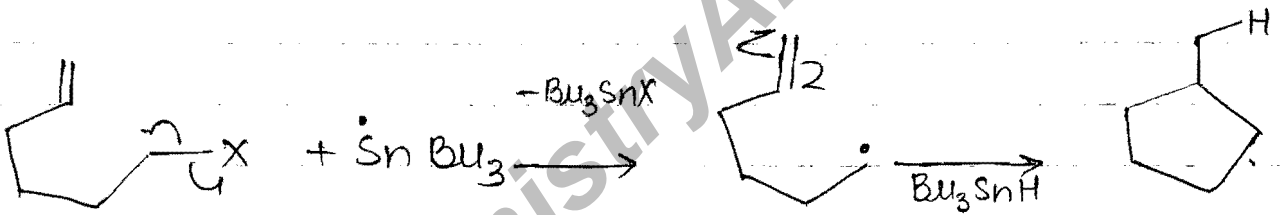


Excess Bu_3SnH
AIBN



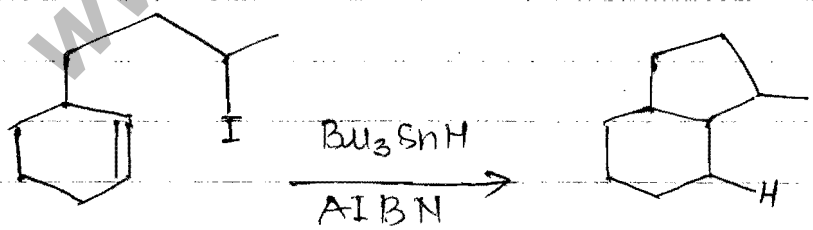
No ring formation.

Mechanism :-



If more conc. of Bu_3SnH then it react (provides H° Frequently) so no breaking of double bond ⇒ No 5-memb. ring formation.

Q



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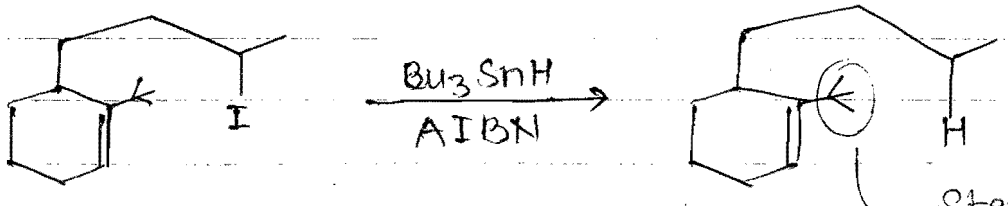

Imp.

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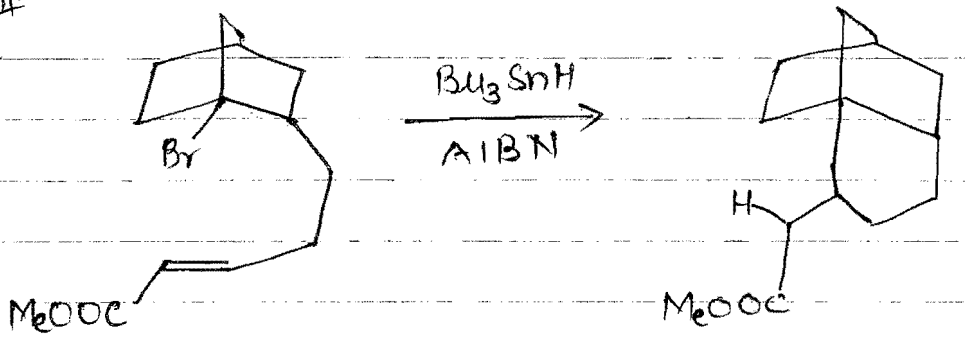

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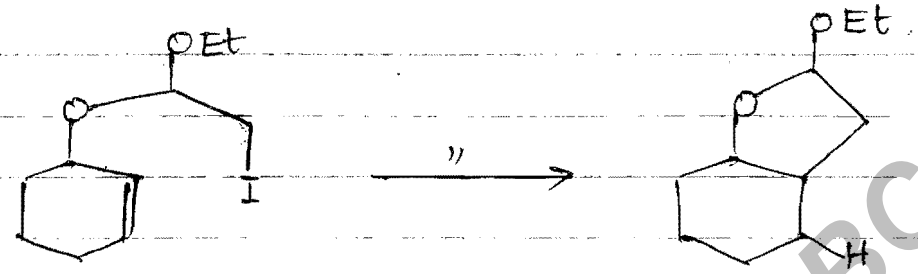

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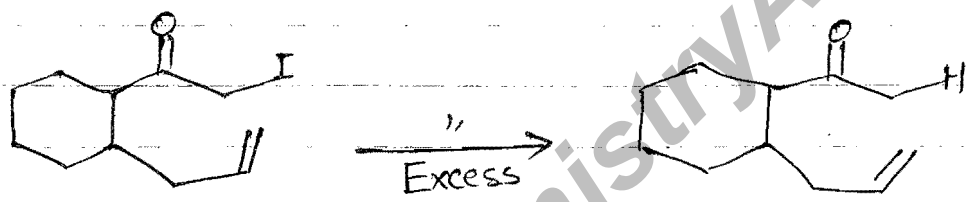

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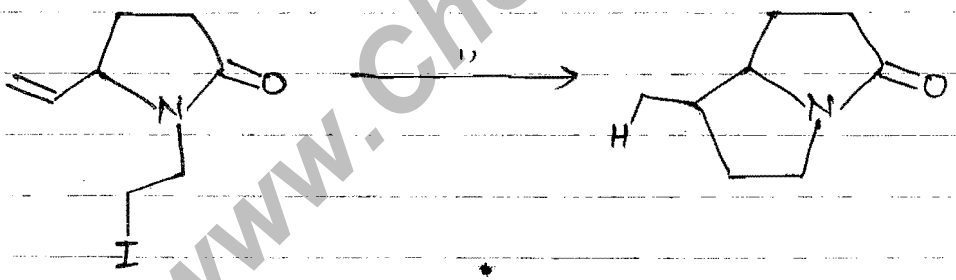

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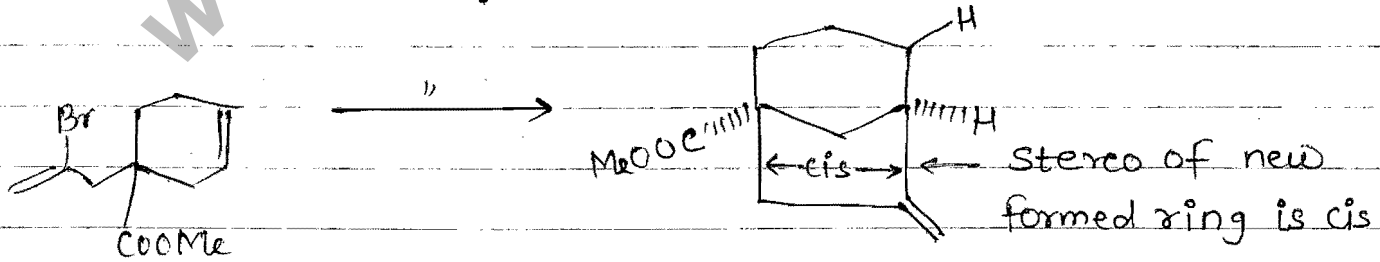

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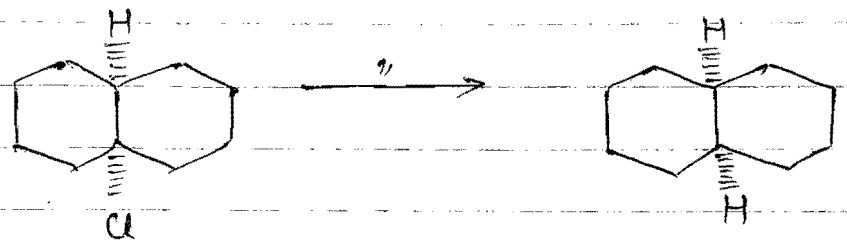

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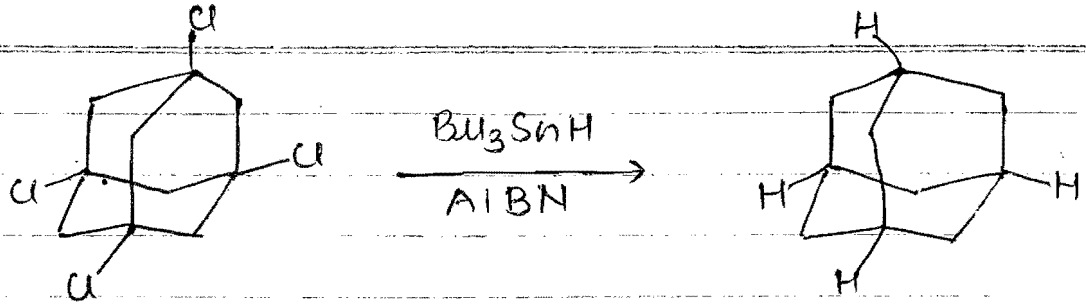

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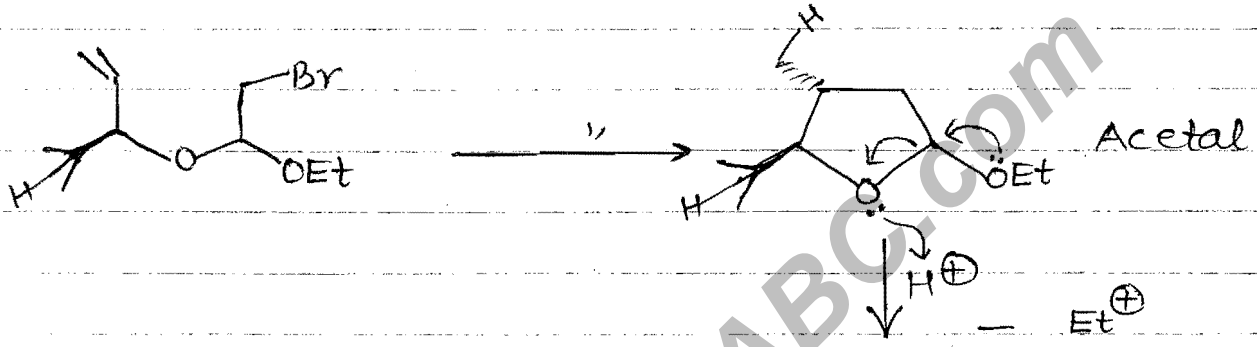
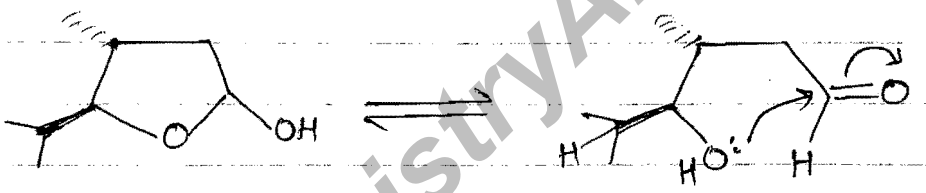
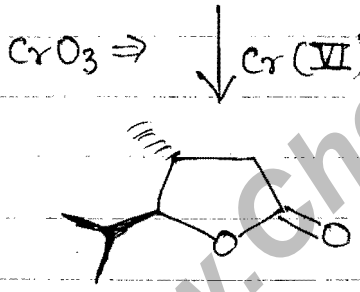
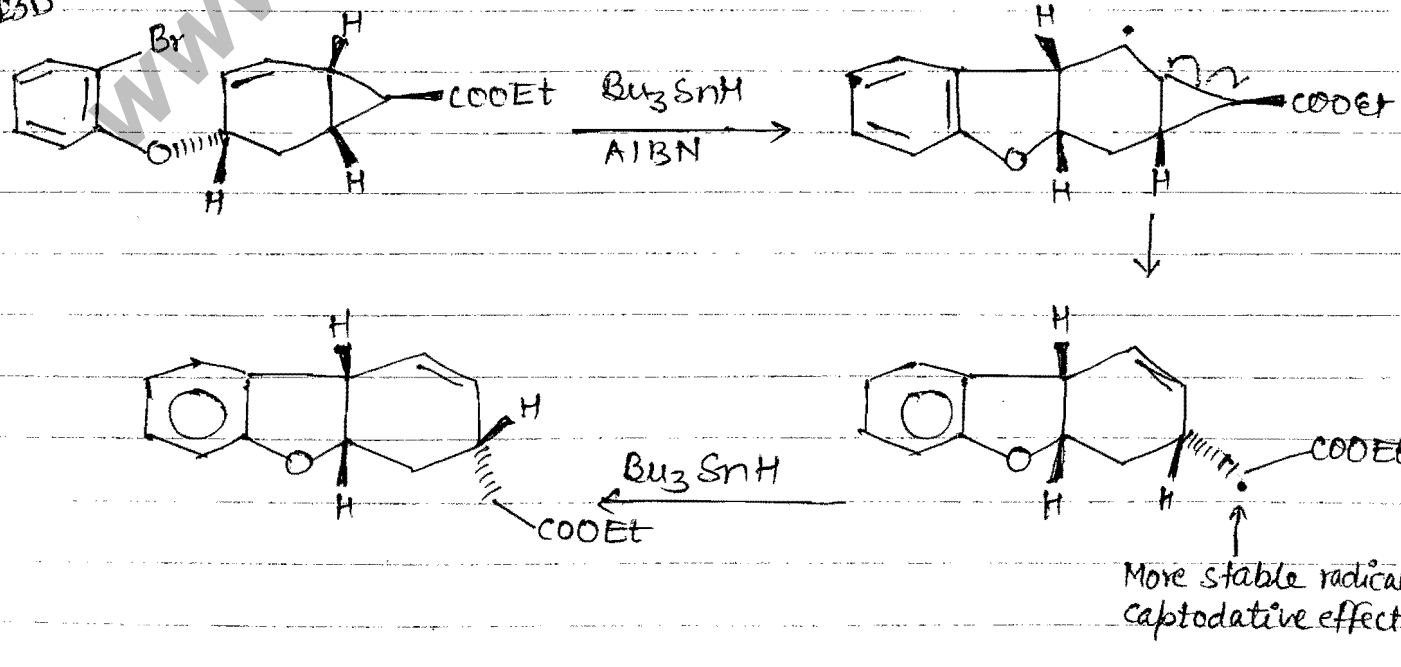




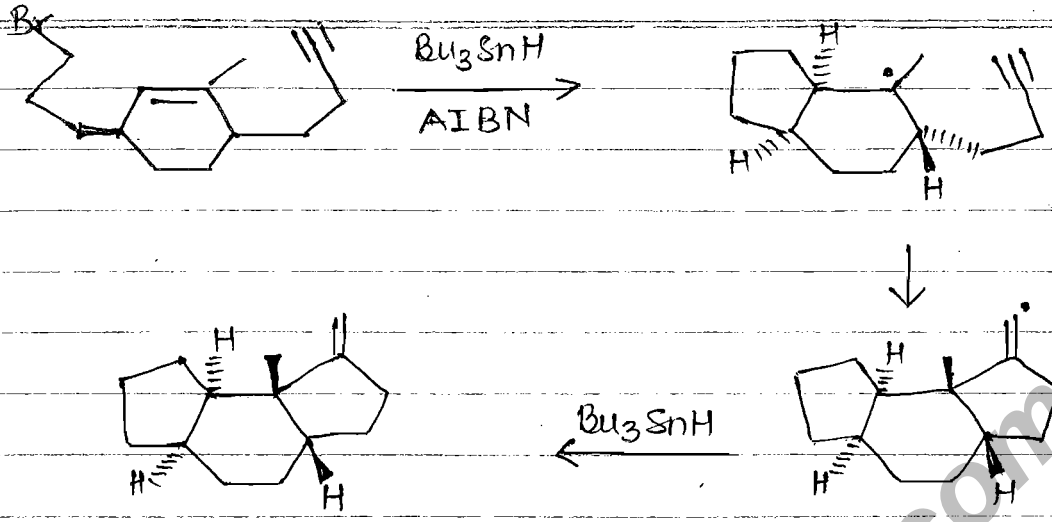


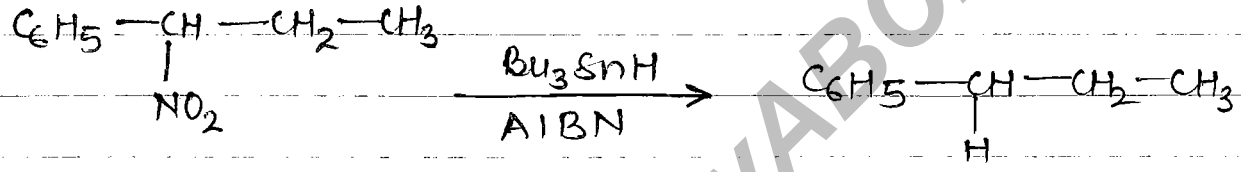
2013D

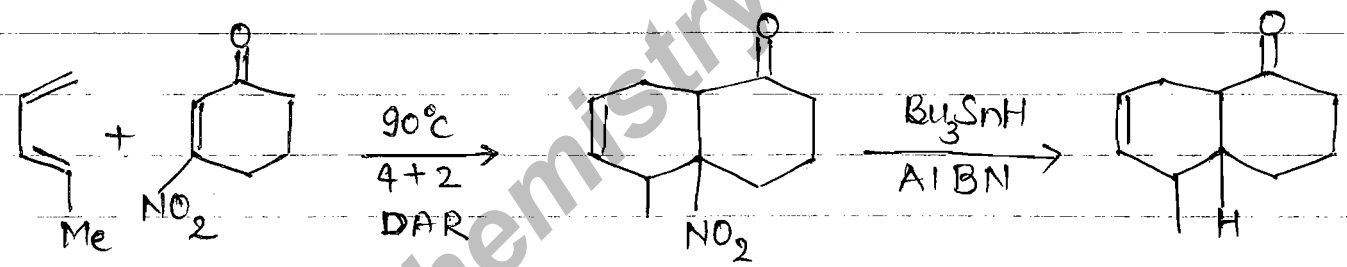
Q



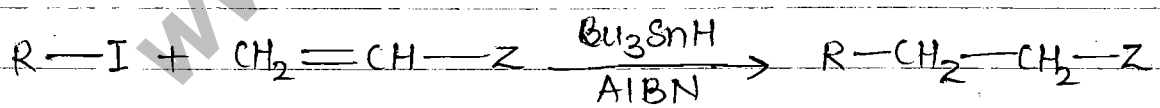
2014J

Q. 

Q 

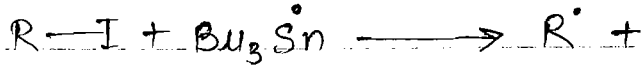
Q 

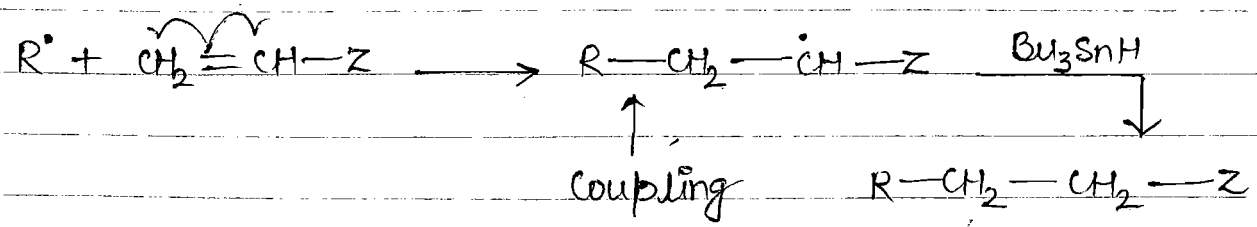
Dehalogenation followed by intermolecular C–C coupling also takes place by tributyl tin hydride.

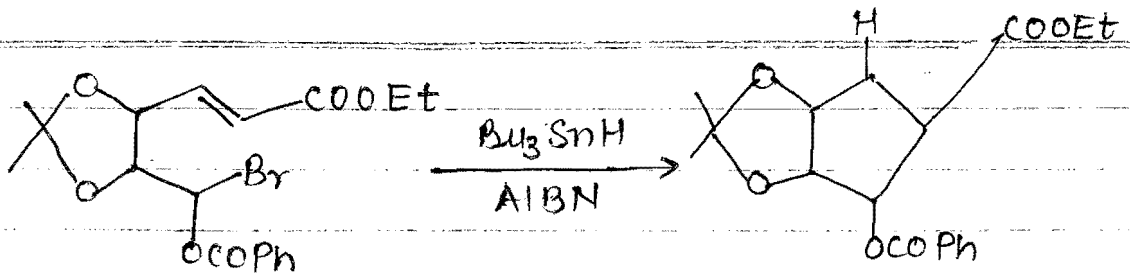


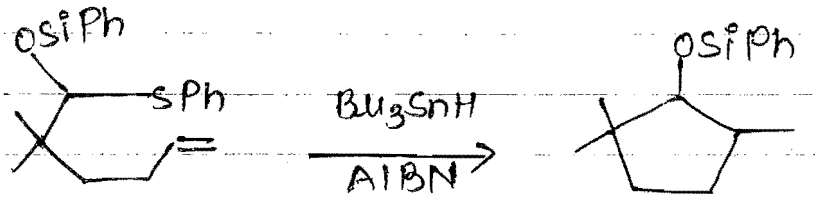
Z = –CN, –CHO, –COR, –COOEt

Mechanism:-

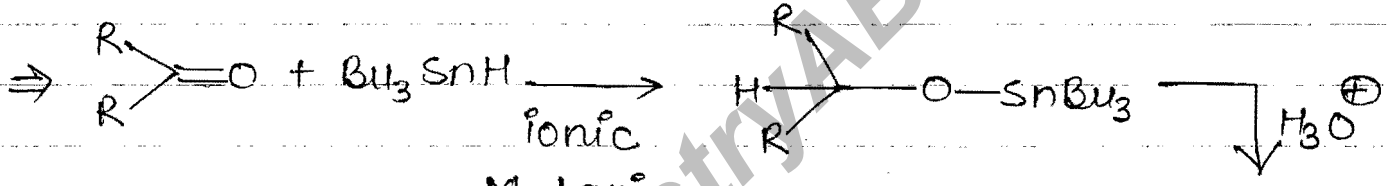


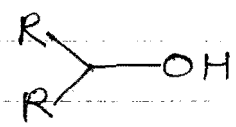


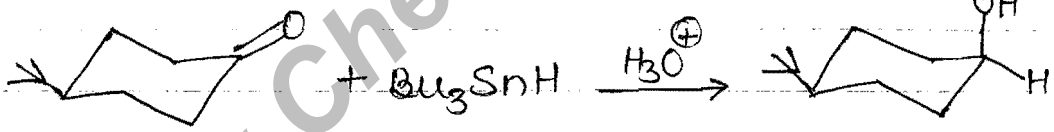
Q 

Imp. Q 

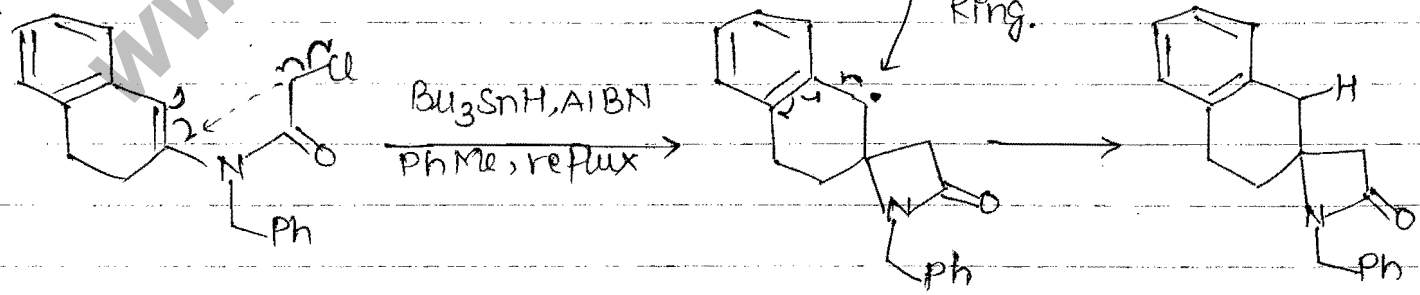
Reduction of Carbonyl.

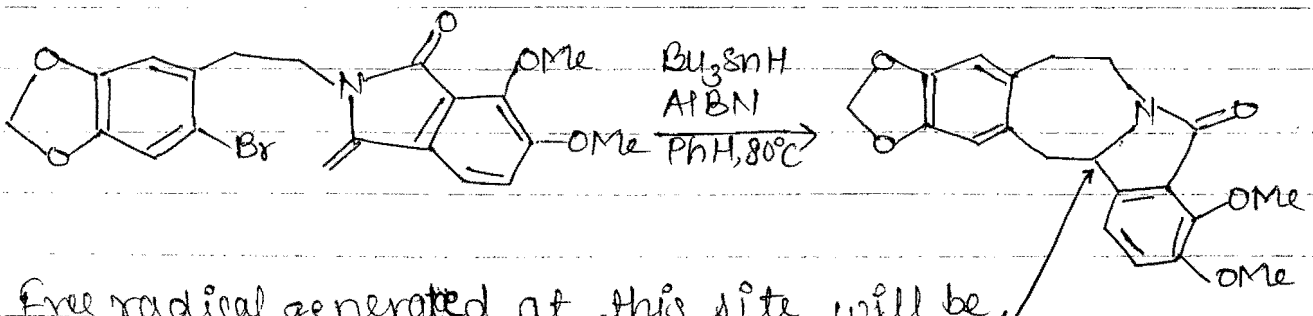




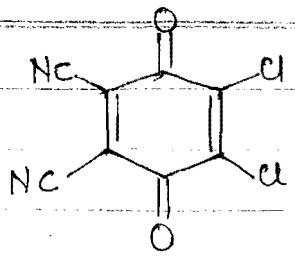


Equatorial Attack

Imp. 

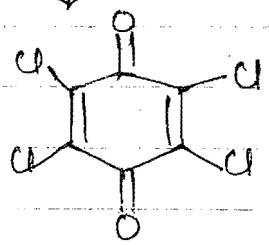
Imp. 

Free radical generated at this site will be stabilized by benzene ring.

DDQ 

Dichloro dicyano quinone

Chloronil also works as DDQ



DDQ is yellow solid.

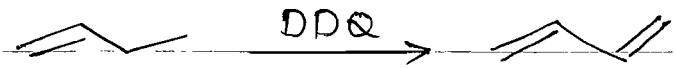
Applications of DDQ:-

- Unsaturation
- Aromatization
- Oxidation of Alco.
- Cyclization
- Salt formation
- Insertion of Oxygen.

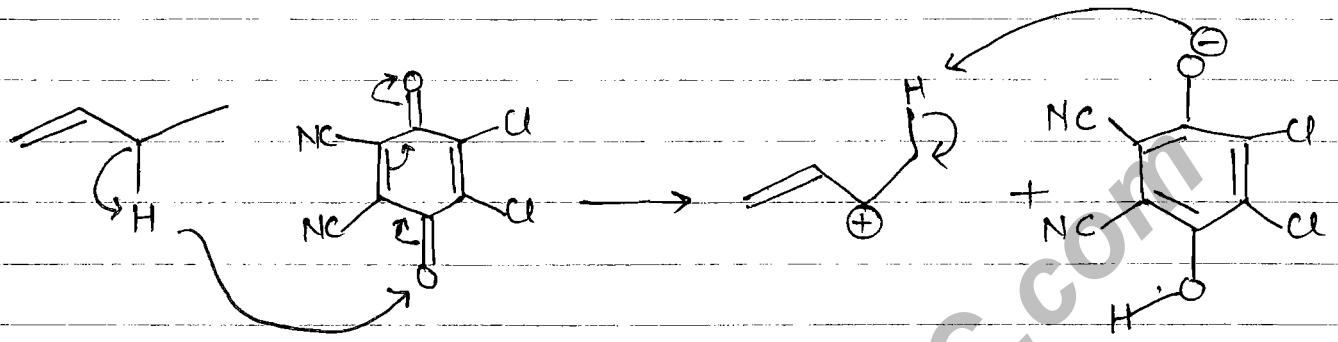
When DDQ react with the comp. having Allylic or benzylic 'H' then first of all DDQ abstract hydride ($H^{\ominus}$) from allylic position and then proton ($H^{\oplus}$) abstract. In this rxn. carbocation form as an intermediate, so if rearrangement possible then rearrange carbocation. DDQ used as a Dehydrogenating agent.

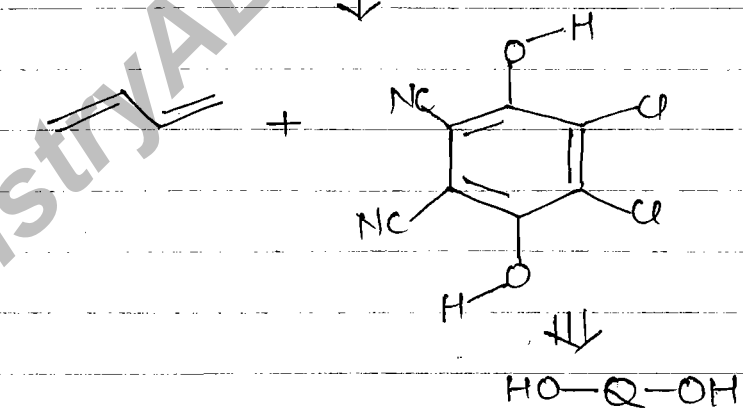
Pd/C @ S @ Se also used for dehydrogenation

Pd/C/H_2 is ~~dehydrating~~ Hydrogenating agent.

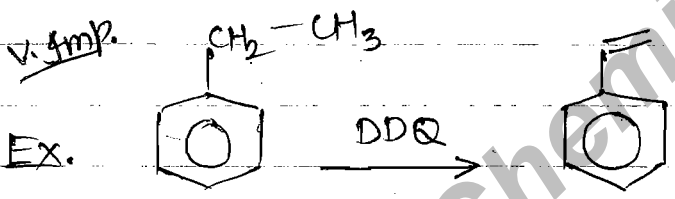
Ex. 

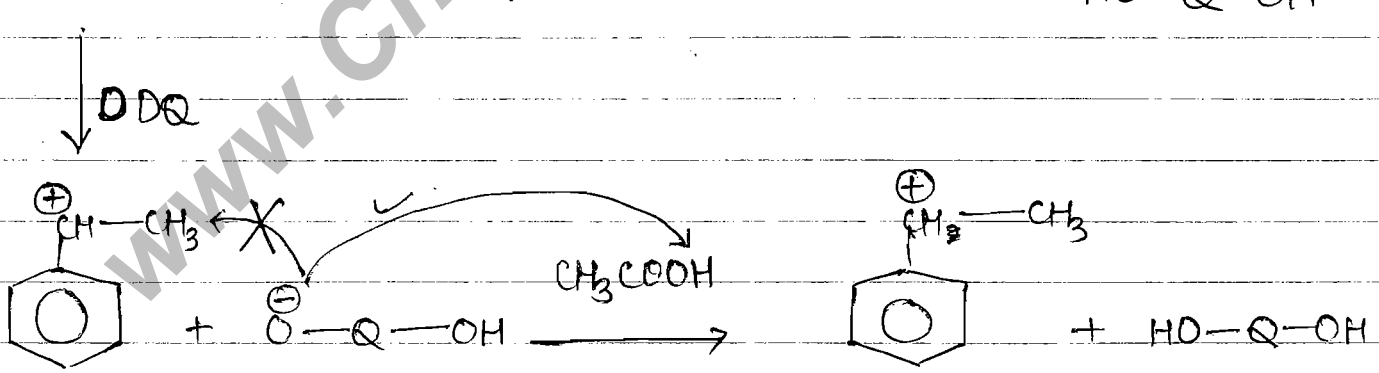
Mechanism

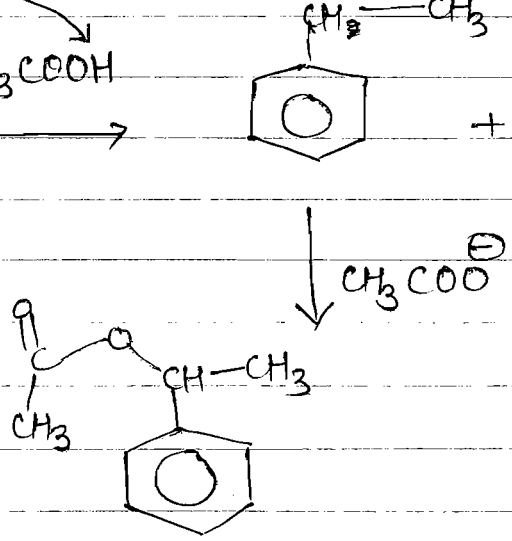


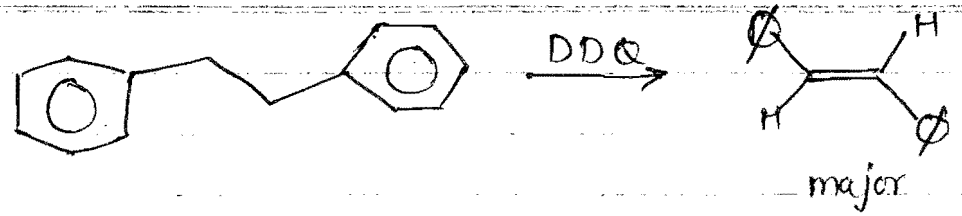


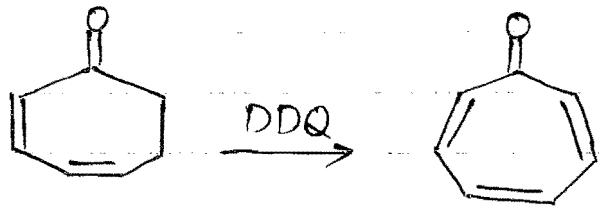
v. imp.

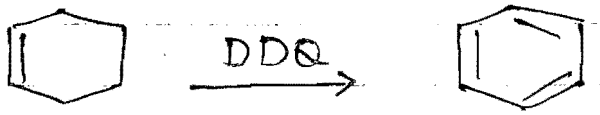
Ex. 

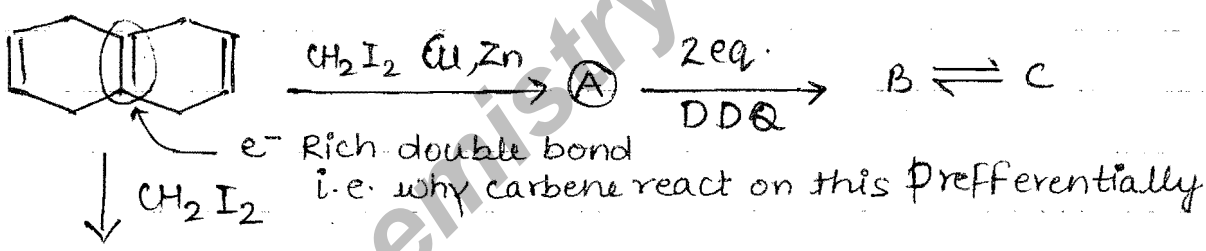


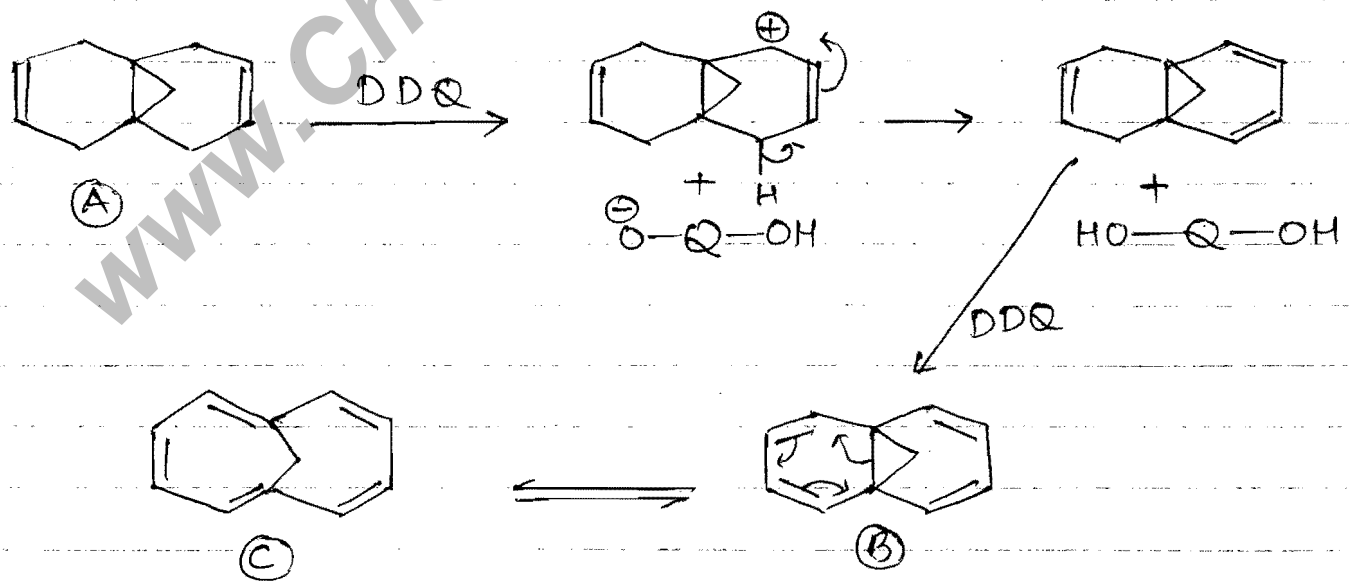


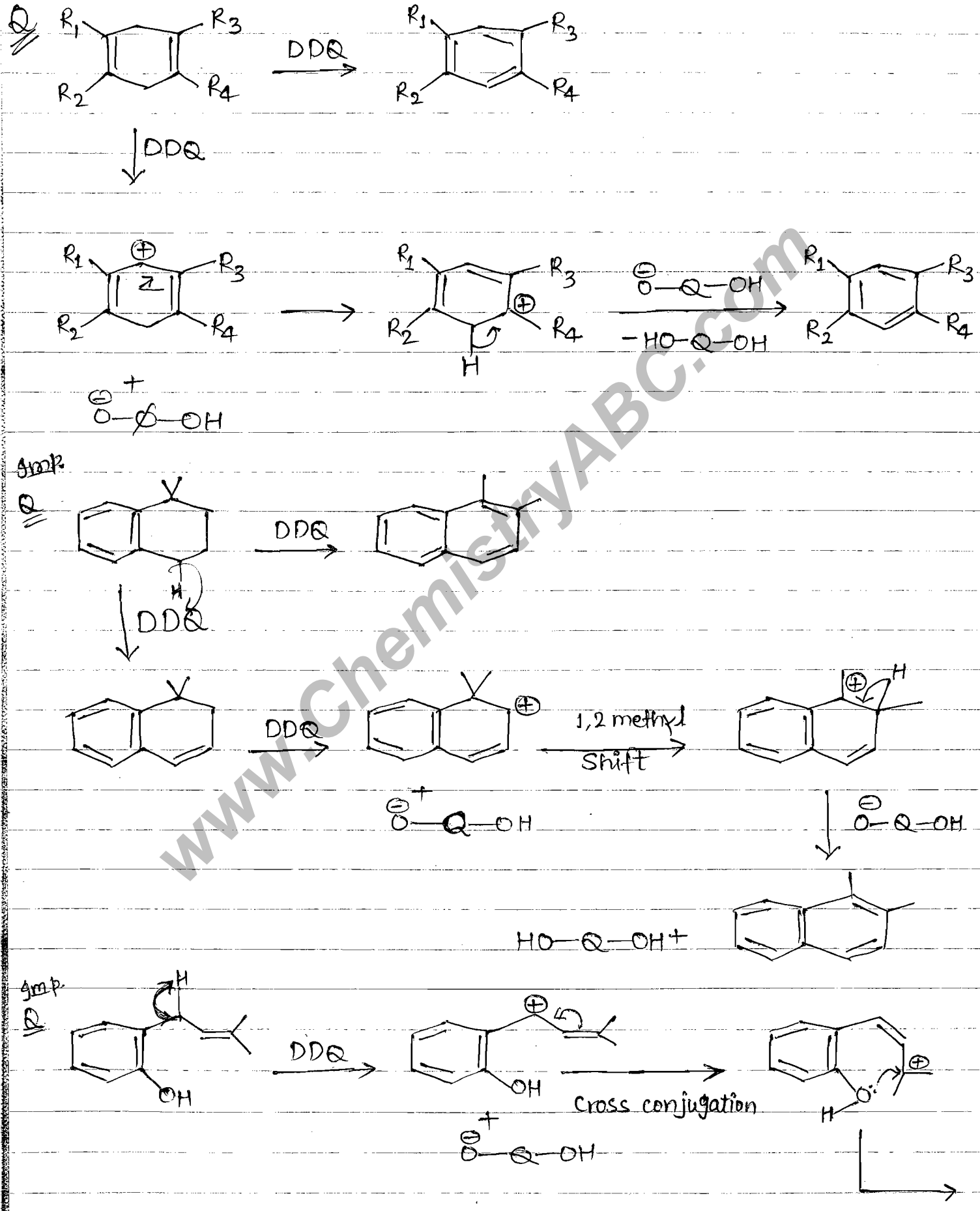
Q 

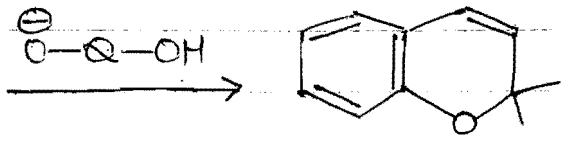
Q 

Q 

Imp. Q 







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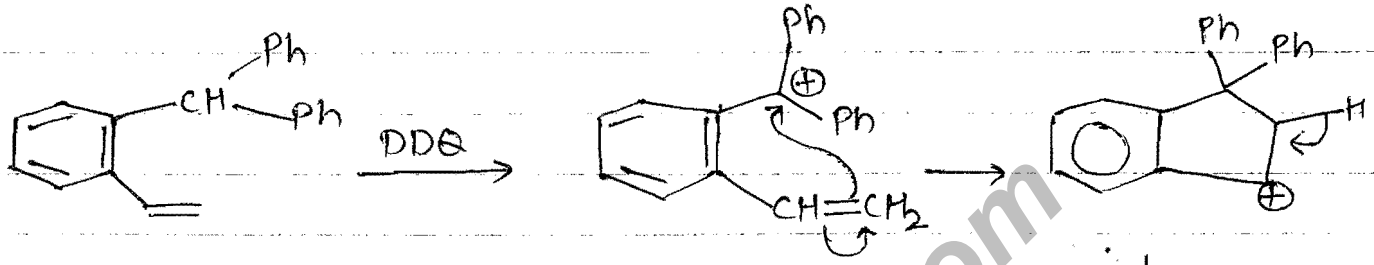

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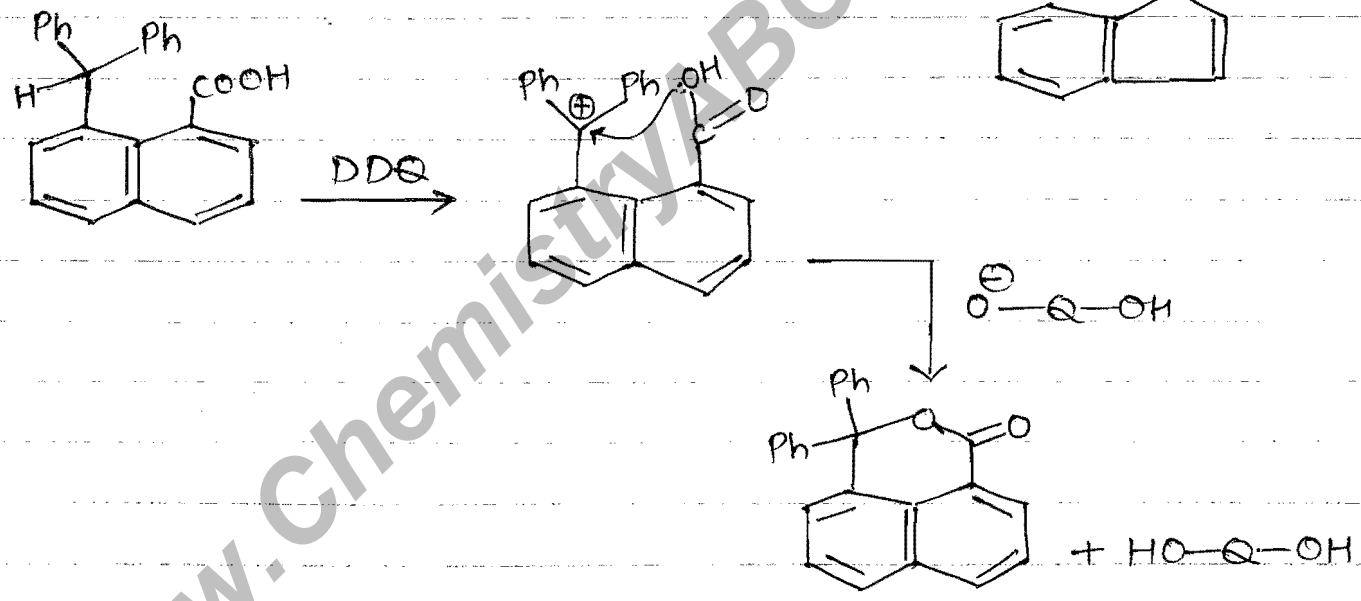

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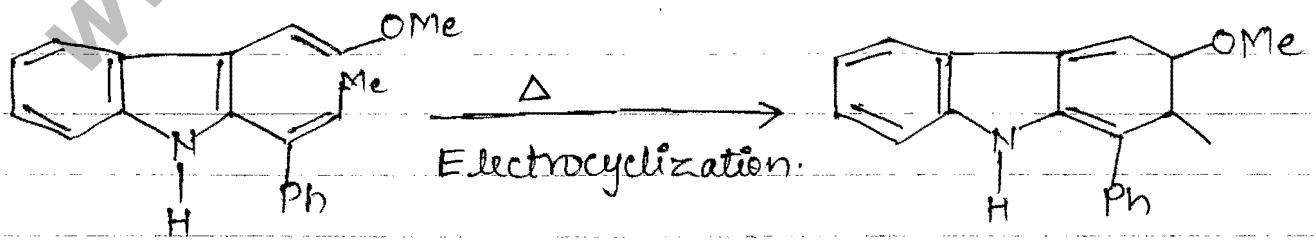

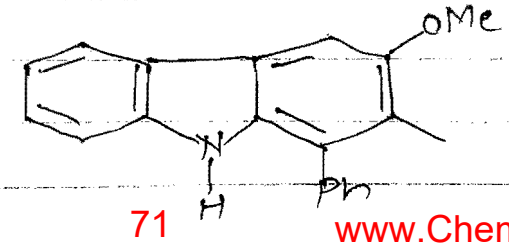

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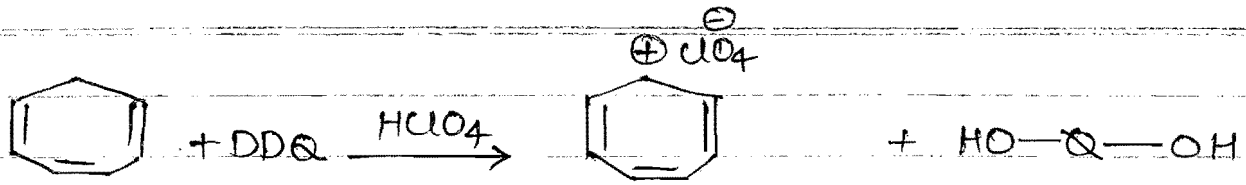
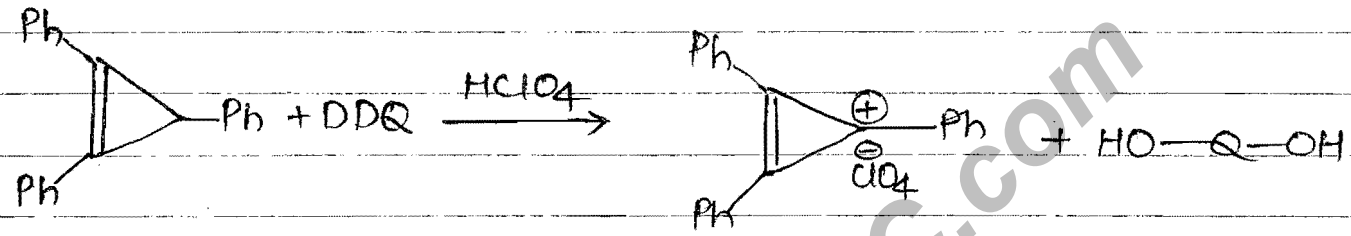


Quasiaromatic (Salt)

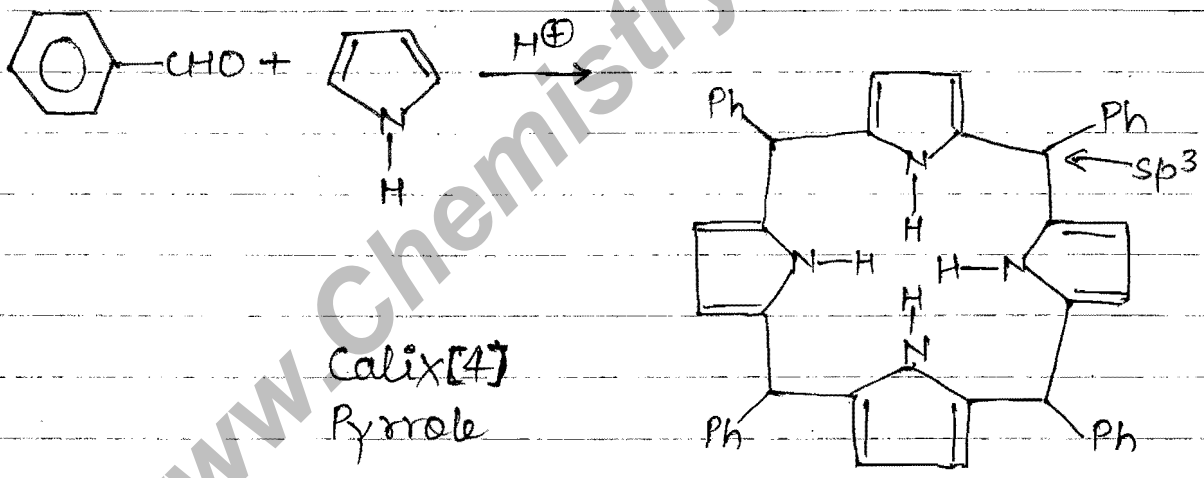
Q



Quasiaromatic (Salt)

V. Imp.

Q

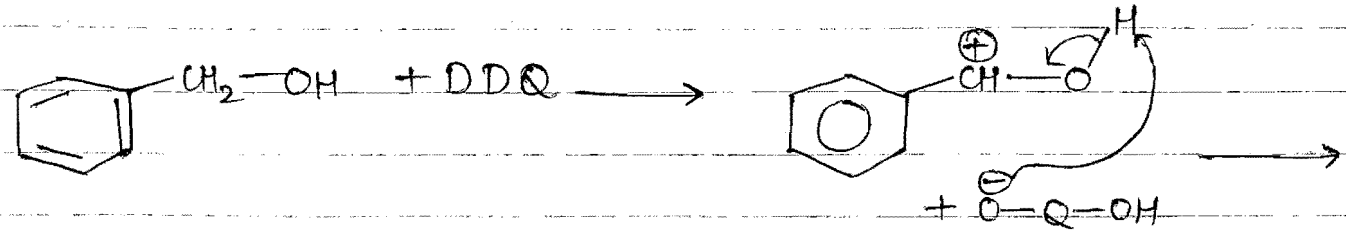


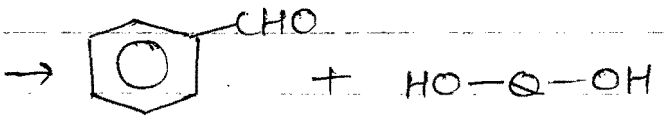
Calix[4] Pyrrole

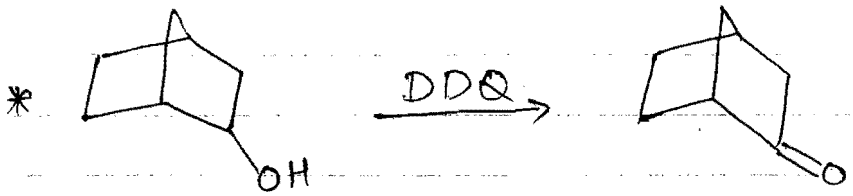
DDQ

Porphyrine (Aromatic)

Oxidation of alcohol:-

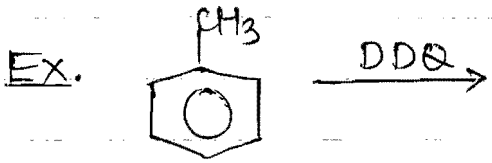




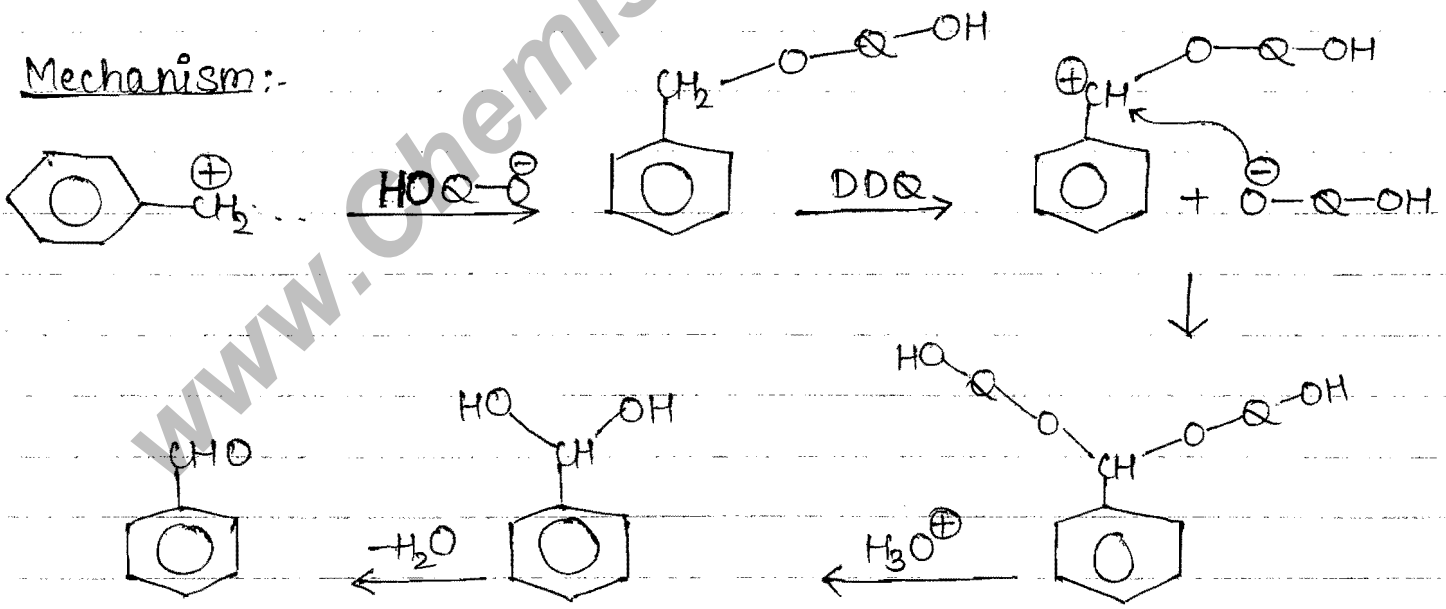


If dehydrogeration is not possible then allylic or benzyllic position oxidised in to carbonyl.

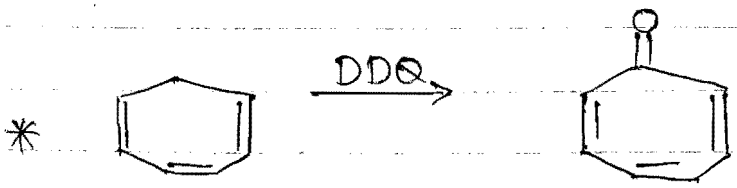
Ex.



Mechanism:-



Note:- If dehydrogen ation is not possible then such mech. proceed.



HYDRATION (or) Addⁿ of Water

Direct addⁿ. Hydroboration Oxymercuration demercuration

Direct addition of Water:-

Direct addⁿ of water on alkene takes place very-very hardly.

Ex. $R-CH=CH_2 + H_2O \longrightarrow R-\overset{\oplus}{C}H-CH_3 \xrightarrow{\ominus OH} R-CH(OH)-CH_3$

* In assymitric alkene, electrophile attack at more e^- rich carbon. In direct addⁿ carbocation is formed as intermediate, so if rearrangement possible then rearrange carbocation.

~~Sto~~ since direct addⁿ is very Hard so two new methods developed - 1) Hydroboration 2) Oxymer- - - demer-

HYDROBORATION :-

Ex. $R-CH=CH_2 \xrightarrow{BH_3/H_2O_2/\ominus OH} R-CH(H)-CH_2(OH)$

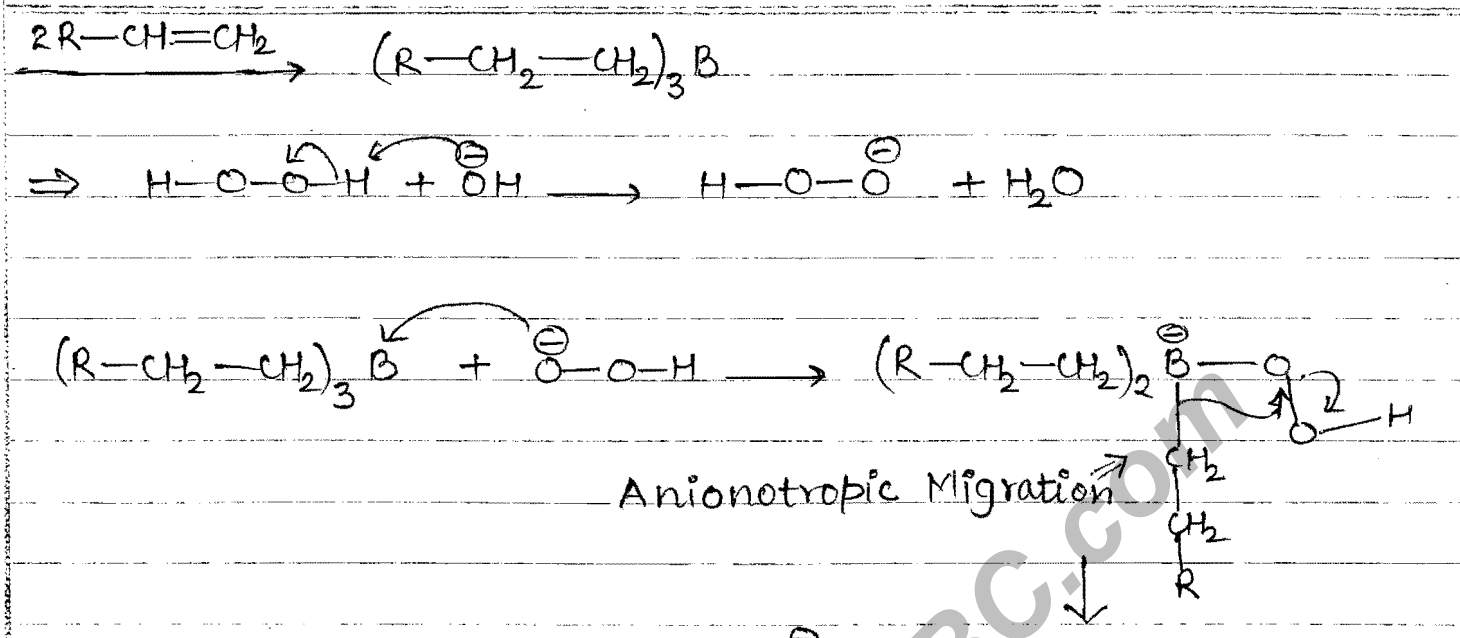
Mechanism:-

$R-CH=CH_2$ + $H-BH_2$ → $R-CH(H)-CH_2$ ⋯ BH_2 (T.S.)

Syn addition

Marconicov addⁿ of BH_3

$R-CH(H)-CH_2(BH_2)$



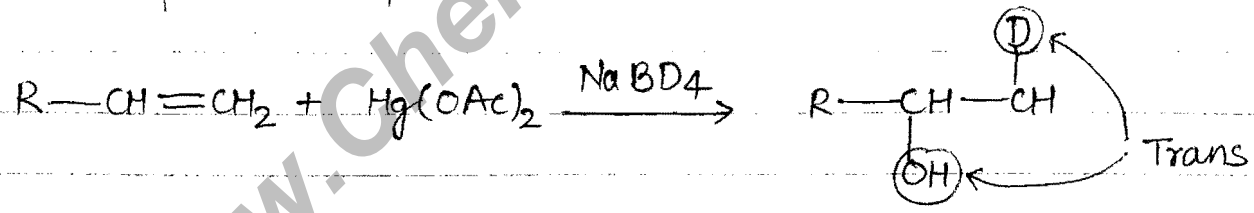
Key points of Hydroboration:-

* No true carbocation form
* No rearrangement
* 4 memb. T.S. form
* Addition of BH_3 take place acc. to Markonicoff Rule.
* Syn addn. take place.
* Boron to oxygen migration (Anionotropic migration)
* Addn. of H_2O takes place acc. to Antimarkonicoff Rule.

OXYMERCURATION - DEMERCURATION

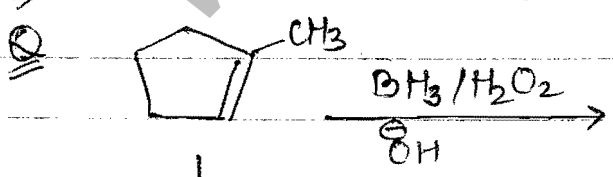
Key points:-

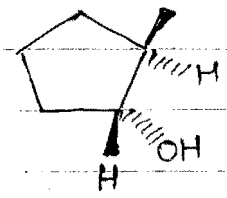
* No true carbocation form.
* No rearrangement take place
* only 3 memb. T.S. form.
* Addn. of H_2O takes place acc. to Markonicoff Rule.
* Anti product form means H & OH trans.



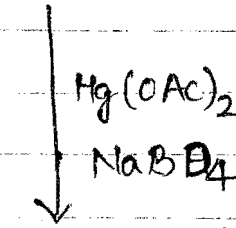
Anti product.

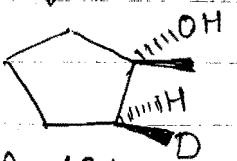
v. imp.



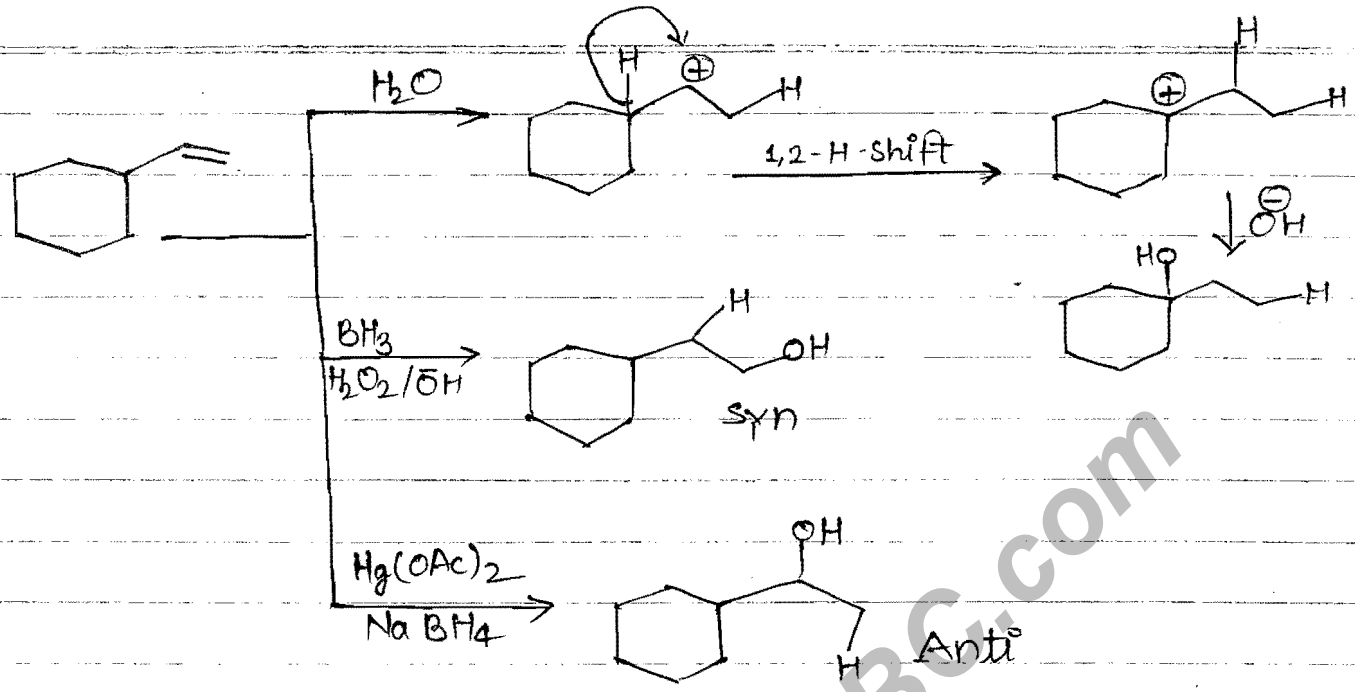


Syn prod.
Antimarconicoff pdt.





Anti pdt Markonicoff pdt



ORGANOBORANEs & BORANEs

Organic comp. + borane → Organoborane —(Desired Reagent)→ Desired pdt.

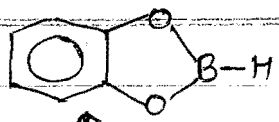
alkene / Alkyne.

$(R-CH_2CH_2)_3B$
Organoborane

- $H_2O_2/\bar{O}H$ → $R-CH_2-CH_2-OH$ (Alcohol)
- CH_3COOH → $R-CH_2-CH_2-H$ (Alkane)
- $X_2/\bar{O}H$ → $R-CH_2-CH_2-X$ (Haloalkane)
- $AgNO_3/\ominus OH$ → $R-CH_2-CH_2-CH_2-CH_2-R$ (dimerization)
- $NH_4Cl, NaOCl$ → $R-CH_2-CH_2-NH_2$ (Amine)

TYPES of BORANES

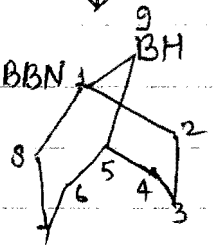
Catecol Borane



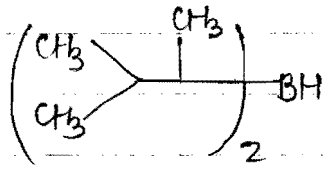
BH_3 (B_2H_6)

$BF_3 \cdot OEt_2 + NaBH_4$

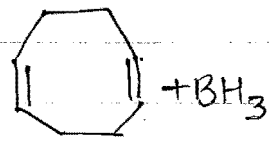
9-BBN



Disamyl Borane

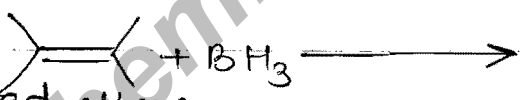


$BH_3 \cdot SMe_2$
Camercially available

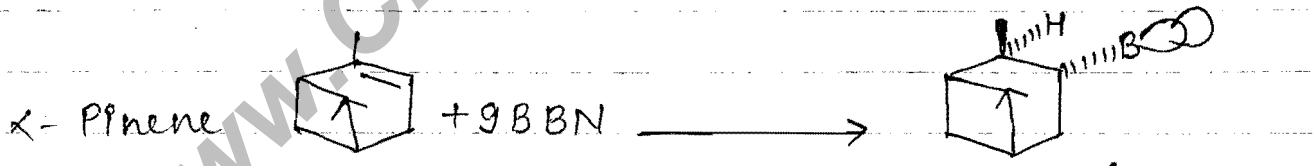


Trisubstituted Alkene

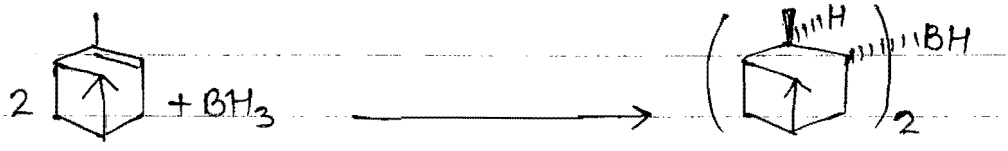
Thexyl borane



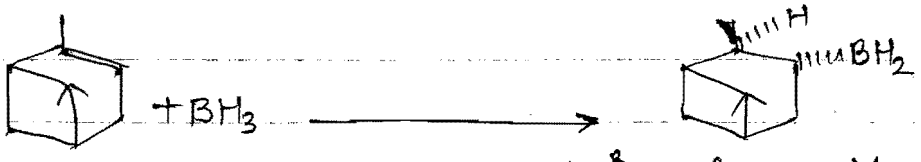
Tetrasubstituted alkene



Alpine borane



di-isocamphenyl borane $(IPC)_2BH$

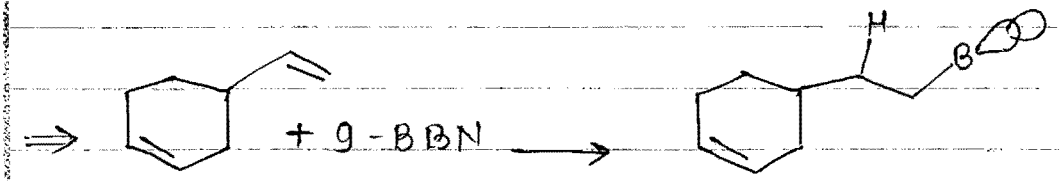


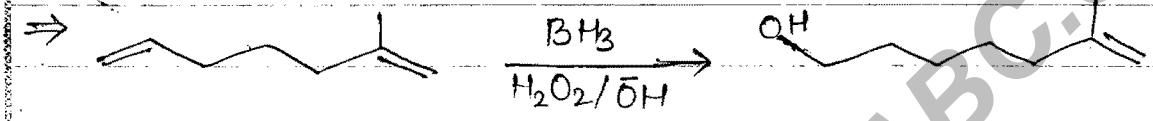
mono-isocamphenyl borane

$(IPC)BH_2$

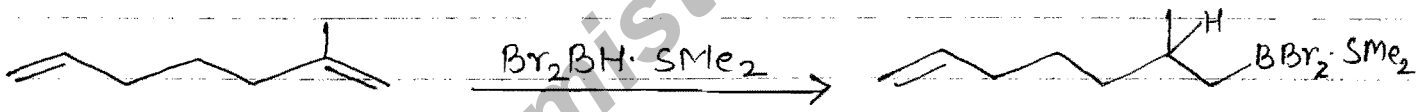
Reactivity of Boranes towards Alkene:

* Less substituted (Less sterically Hindered) Alkene is more reactive than more sterically hindered Alkene.



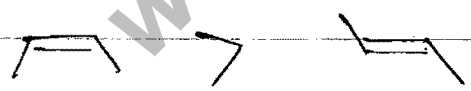


* But there is one exception, Halogenated Borane ($Br_2BH{\cdot}SMe_2$) react at more substituted alkene.



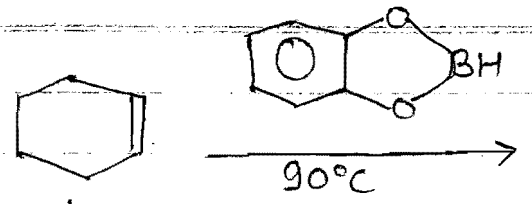
* Terminal alkene is more reactive than internal alkene.

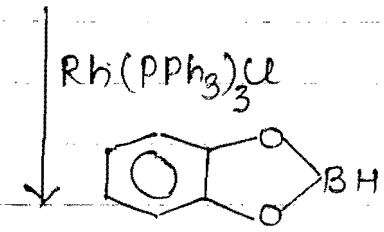
* 'Z' alkene is more reactive than 'E' alkene.



Reactions of Alkene with different Boranes:-

⇒ Cathecol Boranes:- Cathecol borane is less reactive and required high temperature but in the +nce of catalyst, more commonly Rh complex, reactivity and selectivity increased of cathecol Boranes.



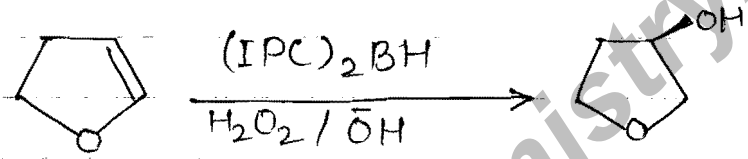


(P)

Prod. in less time

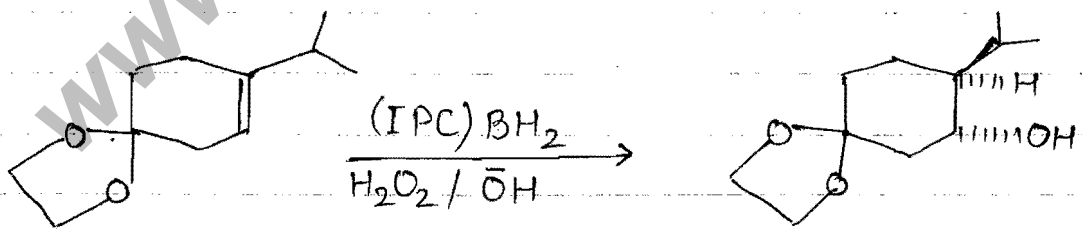
Diisocamphenyl Borane $(IPC)_2BH$

Most effective for cis disubstituted Alkene.

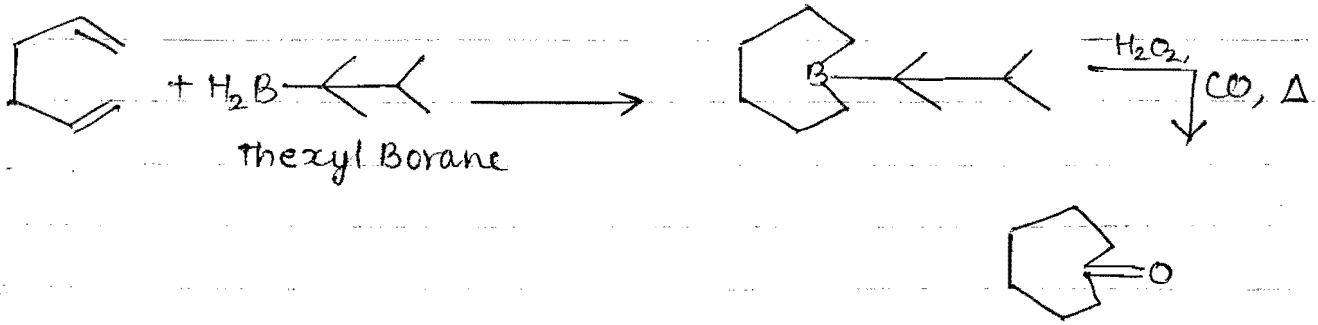


Mono isocamphenyl Borane $(IPC)BH_2$

Most effective for trans or trisubstituted Alkene.

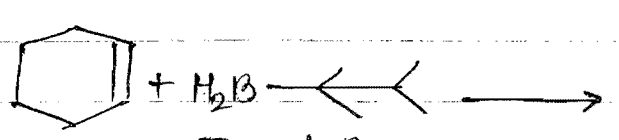


Q

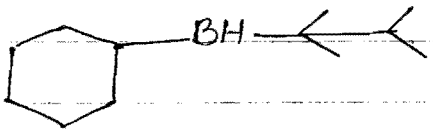


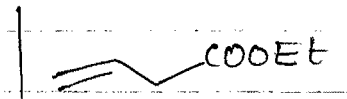
CSIR: If, among 4 options one option having charged spp. then reject that one, generally charged spp. is intermediate not pdt. If mech. possible then, proceed and make neutral pdt; If cyclization/aromaticity, Hydrogen bonding / ABMO stability possible then make that product.

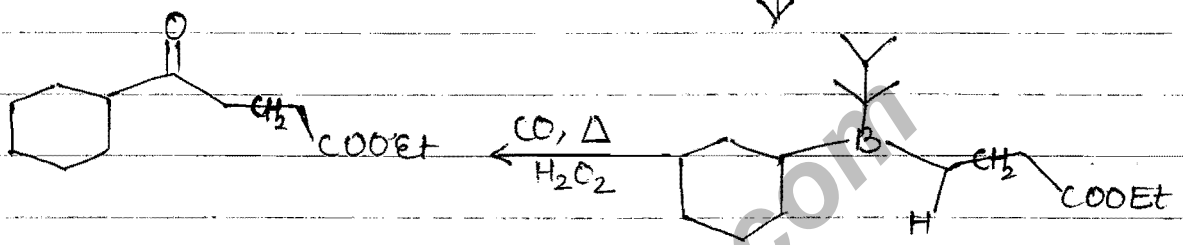
Q



Thexyl Borane







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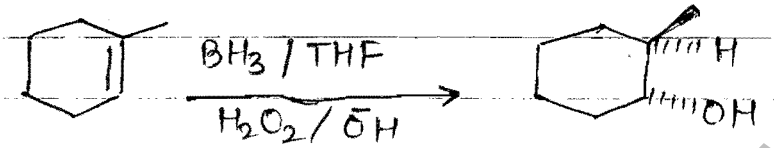

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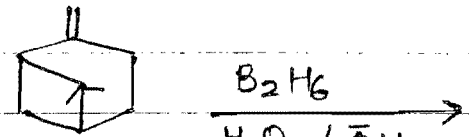

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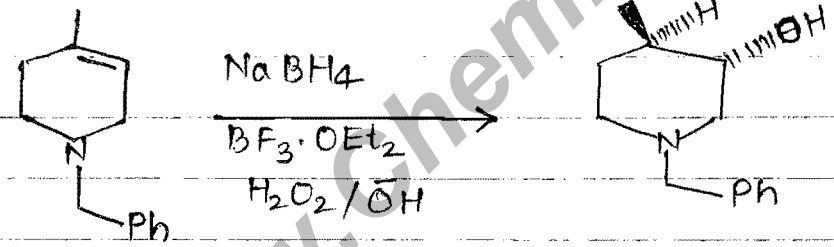

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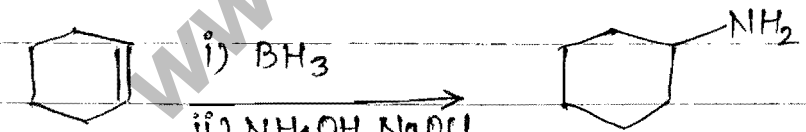

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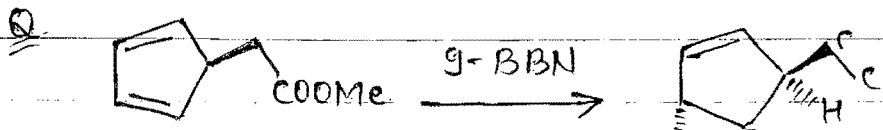
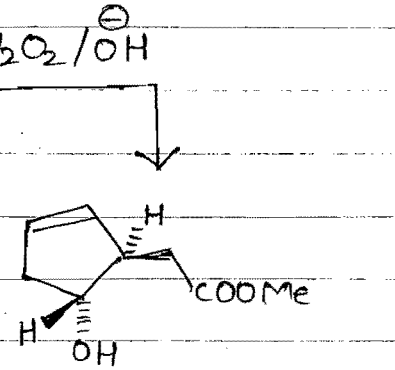
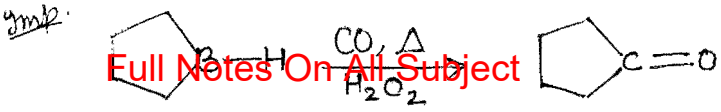
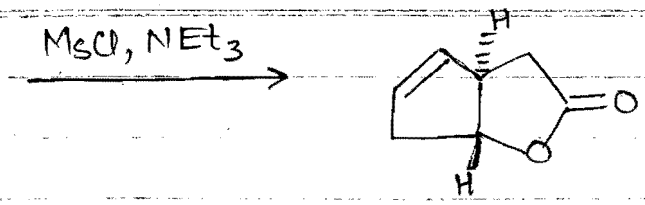


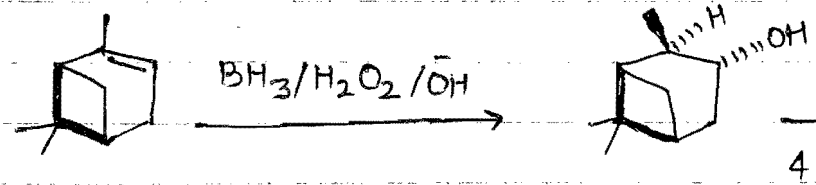
Allylic cation more stable

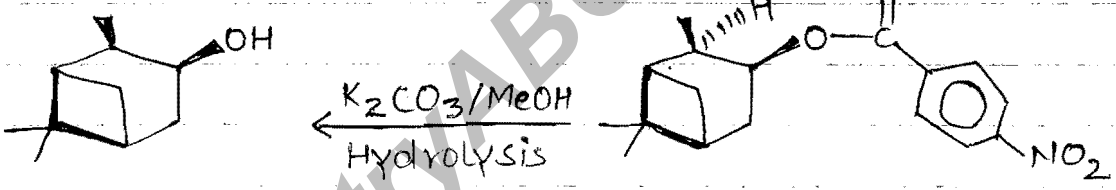




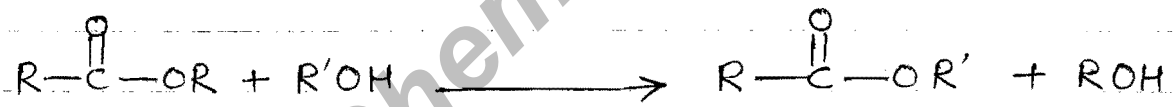


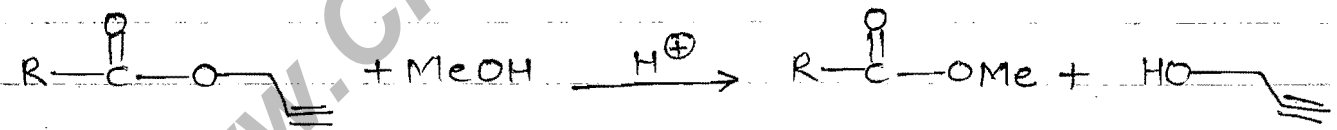
NET Q

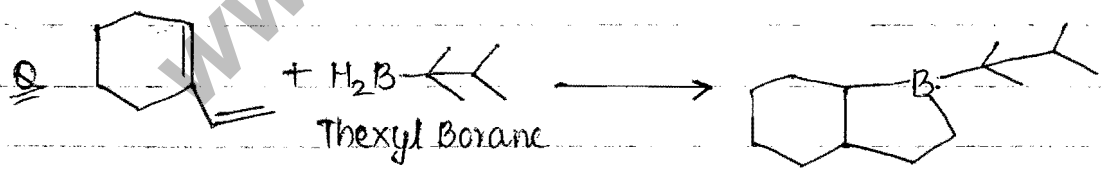


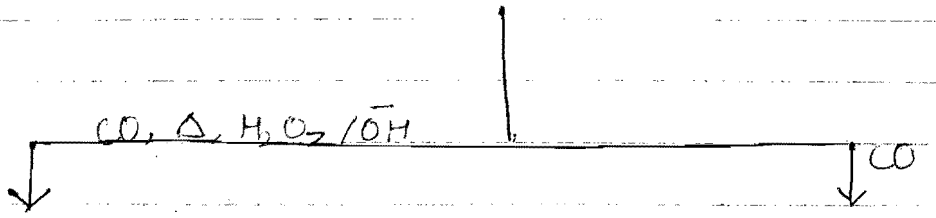


Trans Esterification





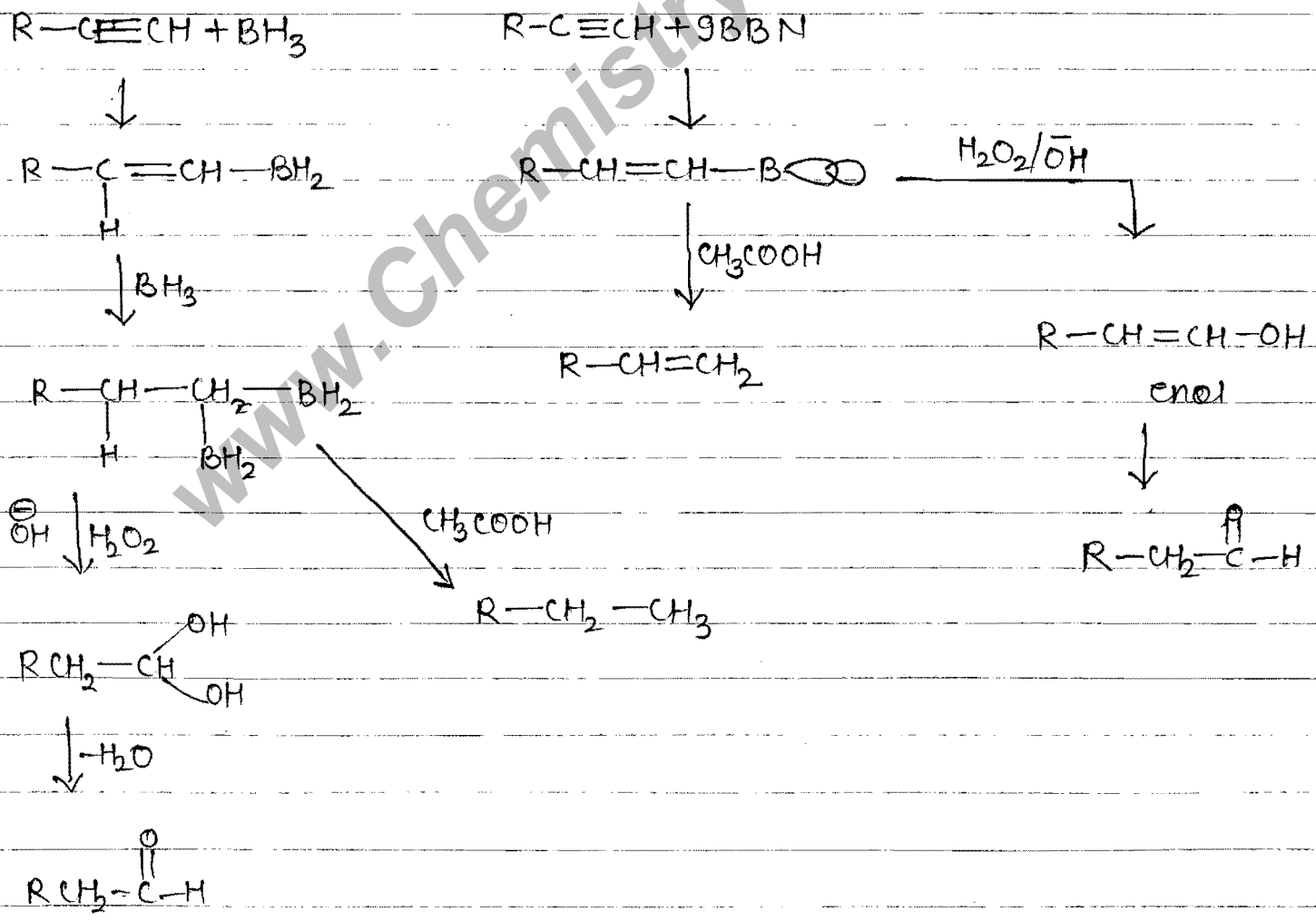




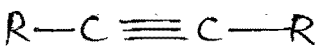
Reactions of Borane with Alkyne:-

Alkyne

- Terminal
  - Borane
    - Smaller Borane (BH_3) → diboration
    - Bulky Borane (9-BBN, Thexyl) → Monoboration
- Internal Alkyne

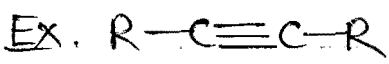


Internal Alkyne

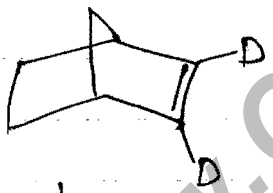


Borane

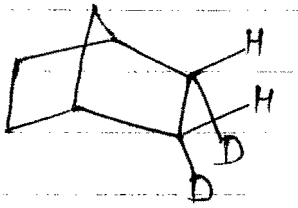
Small Borane ⇓ Diboration

Ex. 

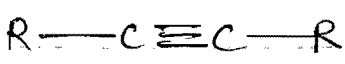
BH_3
CH_3COOH

Ex. 

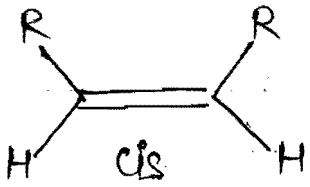
BH_3
CH_3COOH



Bulky Borane ⇓ Monoboration.

Imp. Ex. 

9-BBN
CH_3COOH



Alkene.

imp

Chemoselectivity of BH_3 :-

BH_3 is the best reducing agent for carboxylic acid to form alcohol.

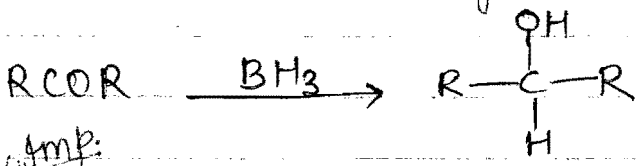
Functional Group	$\xrightarrow{BH_3}$	Product
1) carboxylic acid	$\xrightarrow{BH_3}$	Alcohol.
2) Carbonyl	$\xrightarrow{''}$	Alco.
3) $R-C\equiv N$	$\xrightarrow{''}$	$R-CH_2-NH_2$
V.V Imp. 4) $R-\overset{O}{\overset{\|}{C}}-N(R)(R)$	$\xrightarrow{''}$	$R-CH_2-N(R)(R)$ (amine)
5) Anhydride	$\xrightarrow{''}$	Alco.
6) Epoxide	$\xrightarrow{''}$	Alco.
7) Ester	$\xrightarrow{''}$	Alco.

BH_3 don't reduce following groups. $R-\overset{O}{\overset{\|}{C}}-Cl$, $R-NO_2$, $R-X$.

Reactivity order of BH_3

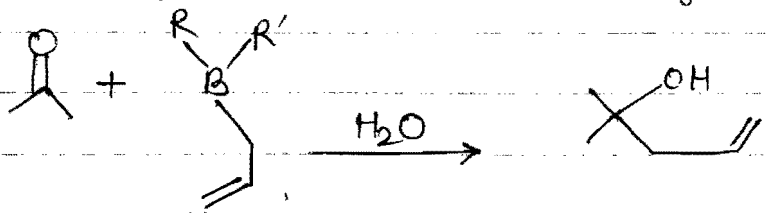
* Carboxylic acid > Alkene > $R-CHO$ > $R-\overset{O}{\overset{\|}{C}}-R$ > Cyanide > epoxide > ester.

Rxn. with Carbonyl:

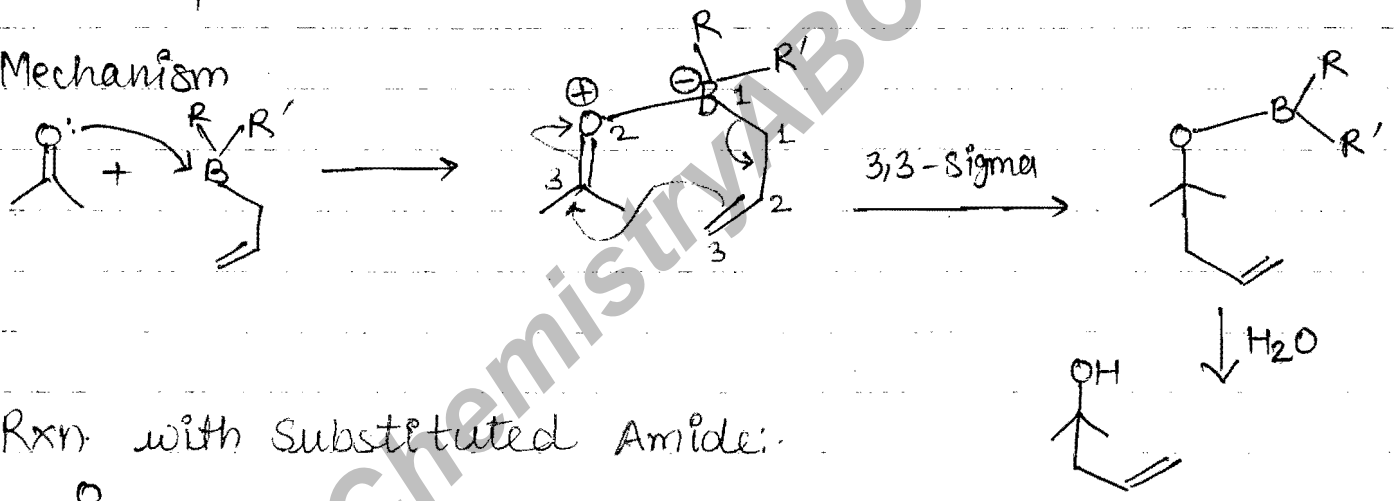


V.V.Imp:

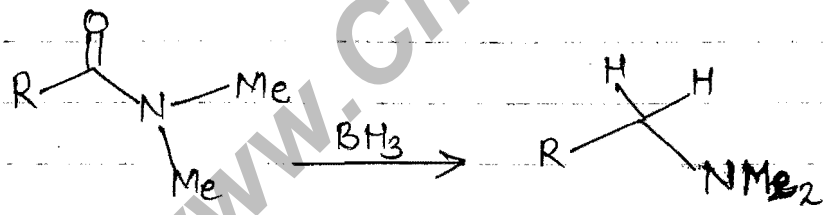
Rxn. of Carbonyl with allylic Borane

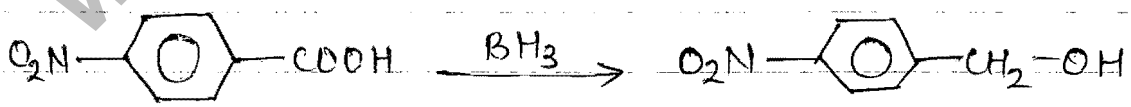


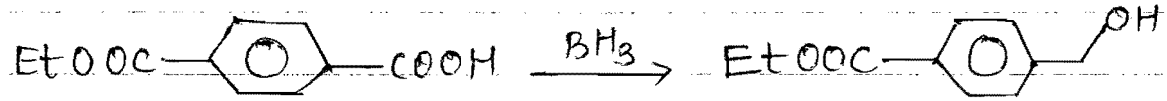
Mechanism

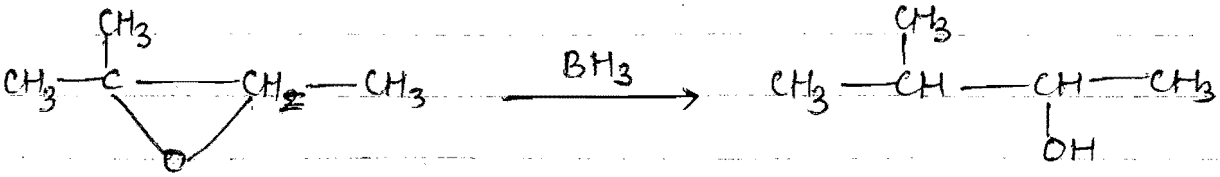


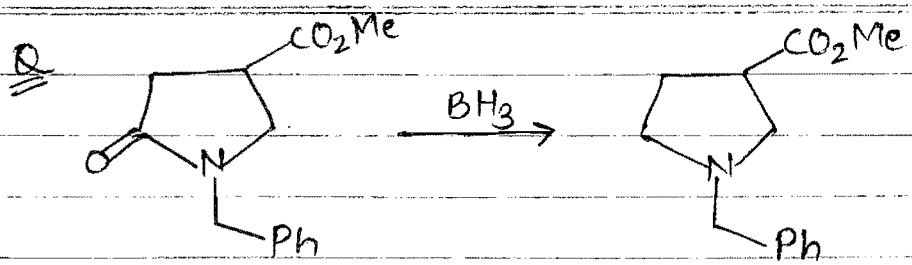
Rxn. with Substituted Amide:



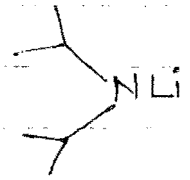
Q 

Q 

Q 



LITHIUM DI ISOPROPYL AMIDE ⇒ LDA



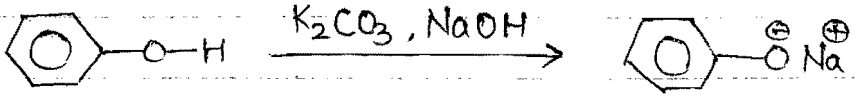
* LDA is a STROG BASE
* LDA Rxn. take place at two temp.
* Generally THF solvent used.
* LDA is non Nucleophilic.
* LDA Rxn. are kinetically controlled (Low temp)
* LDA can abstract less acidic proton as well as strong acidic proton.
* LDA abstract proton from less sterically hindered side, because it is bulky Base.

Base (Acc. to Abstraction of Acidic 'H')

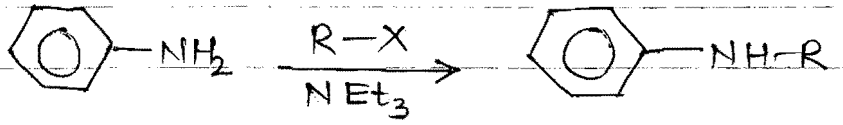
- Weak Base: K_2CO_3, $NaHCO_3$ (R.T.)
- Strong Base: LDA, BuLi, NaH, KH, $NaNH_2$, NaOH (L.T.) ⇒ Low temp.

Base (Acc. to abstraction of Alcoholic 'H')

- Weak Base: NaOH
- Strong Base: LDA, NaH, KH, $NaNH_2$

⇒ 

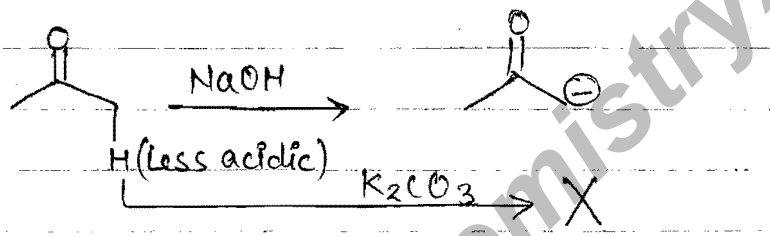
For the abstraction of Amine proton, Generally triethyl amine, NaH, NEt_3 etc. are used.

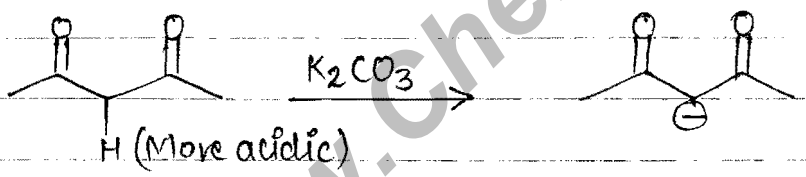


Base (Acc. to enolate formation)

Weak Base
NaOH, KOBu^t (High temp.)

Strong Base
LDA, $NaNH_2$ (Low temp.)





Choice of Base depends upon the nature of substrate.

Formation of enolate:-

Enolate

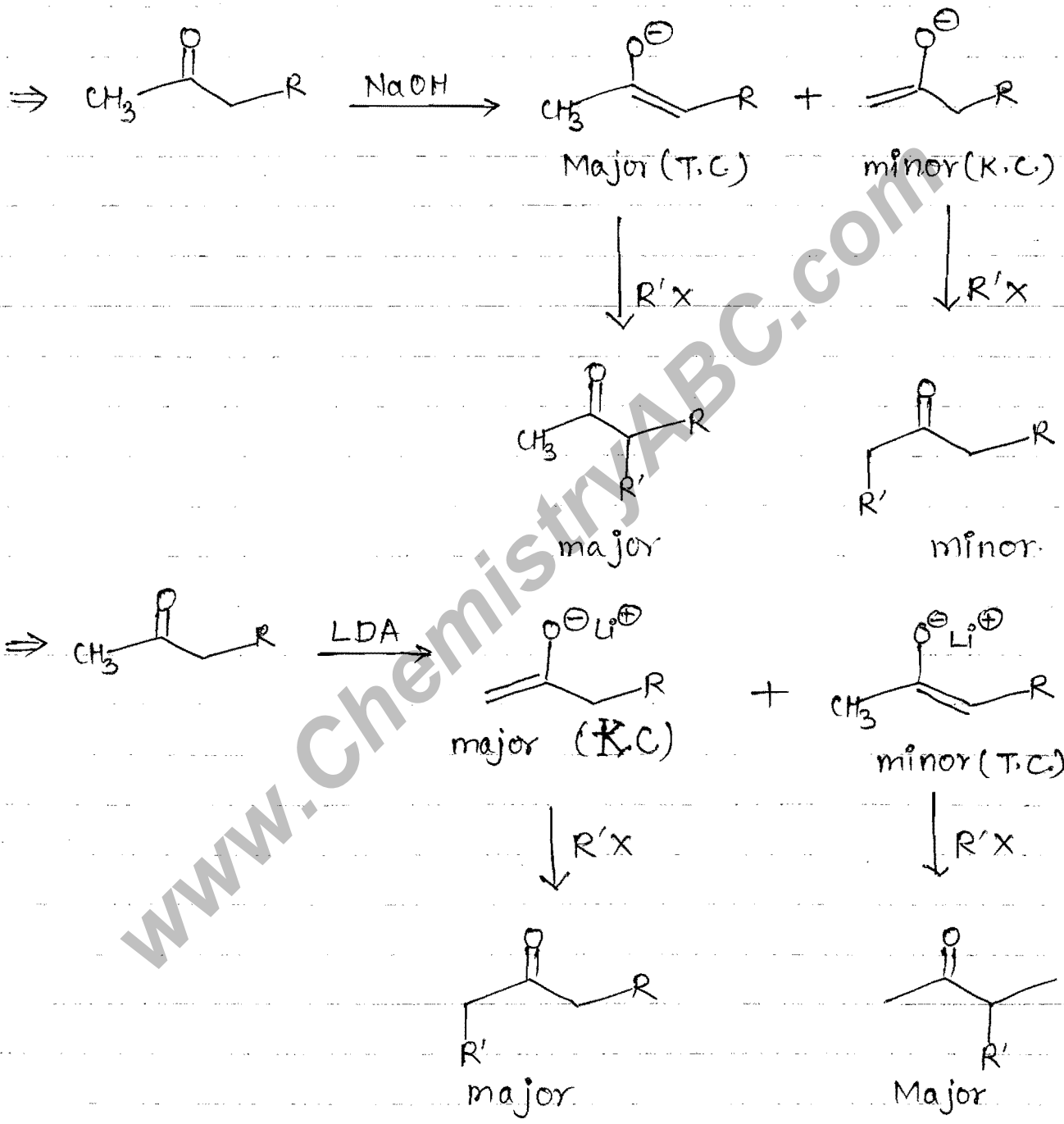
Kinetically controlled
(Less substituted)
enolate

↑ Strong Base (LDA, $NaNH_2$)

Thermally controlled
(More substituted enolate

NaOH,
t_{BuOK} ↑ Weak Base

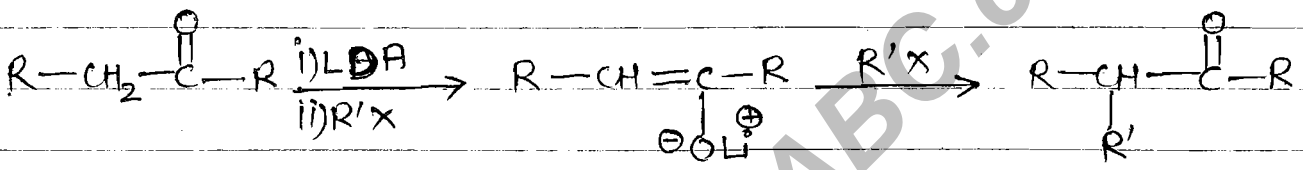
Enolate behave as Nucleophile; giving nucleophilic addⁿ, and nucleophilic substitution Rxn.

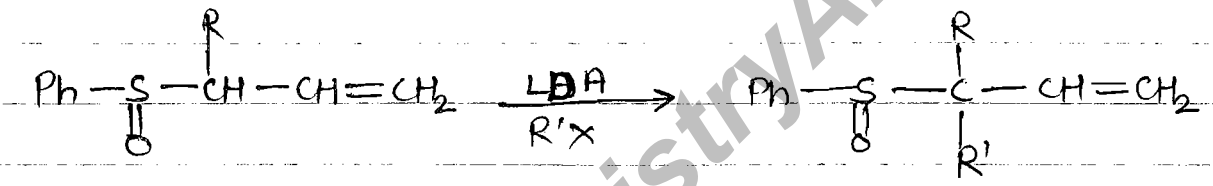


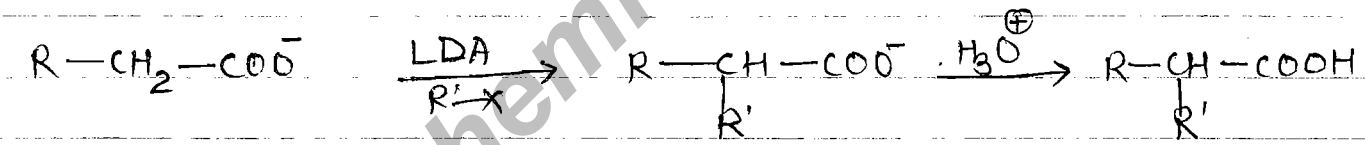
LDA abstracts $H^{\oplus}$ from α position to carbonyl or allylic position of Alkene $\Rightarrow$ Abstraction of Acidic proton.

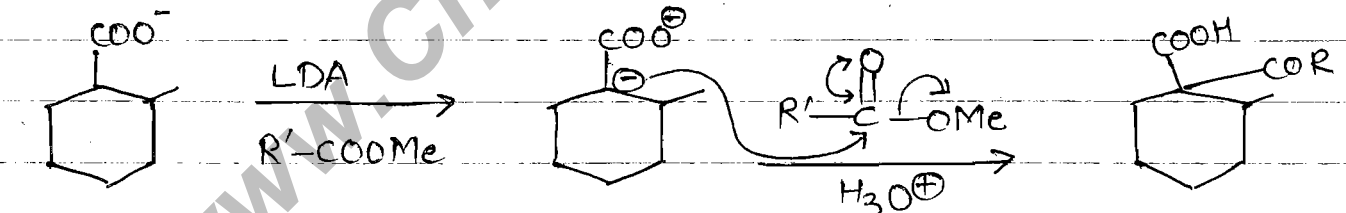
Applications of LDA

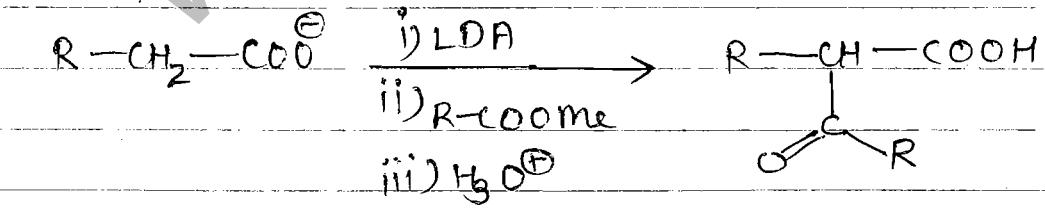
- Acid Base Rxn.
- enolate ($Nu^{\ominus}$)
  - Nucleophilic Substitution
  - Nucleophilic Addⁿ.

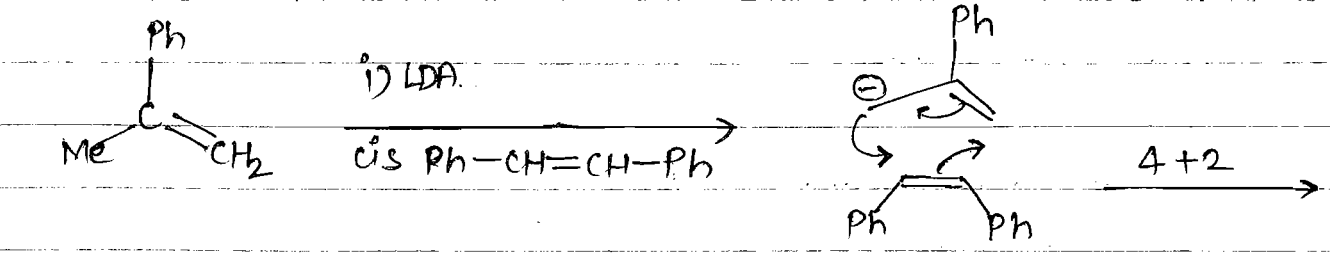
Q 

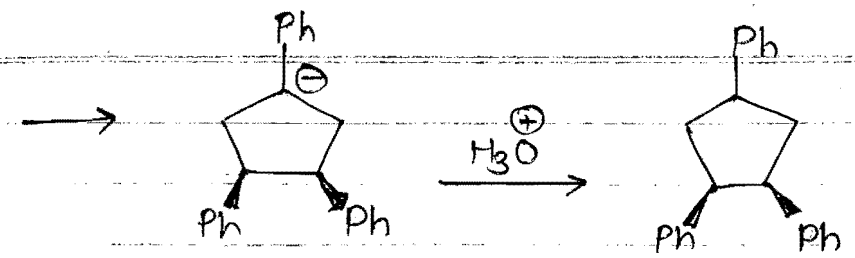
Q 

Q 

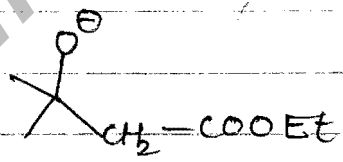
Q 

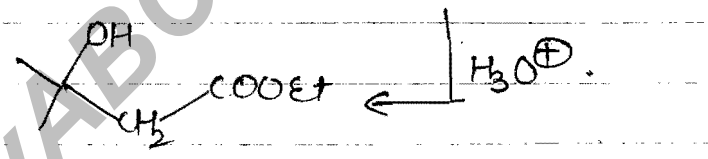
Q 

Q 

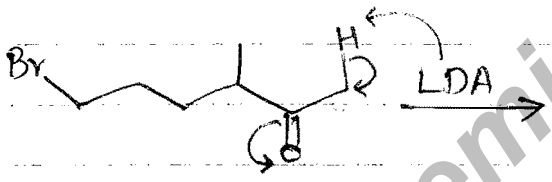


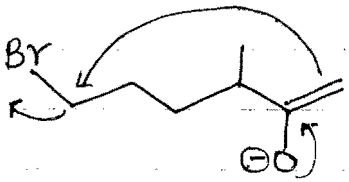
Q $CH_3-COOEt$ i) LDA ii) >=O iii) $H_3O^{\oplus}$ $\ominus CH_2-COOEt$ >=O

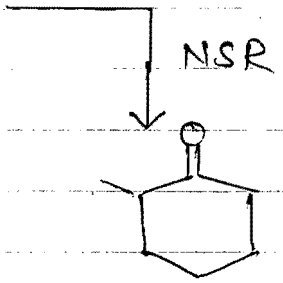


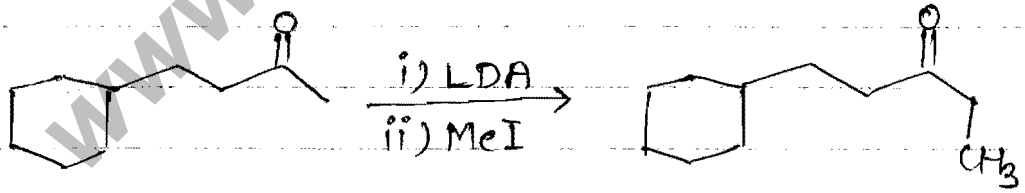


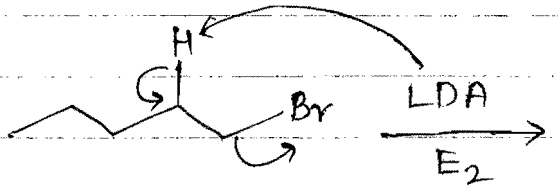
β- Hydroxy ester

Q 

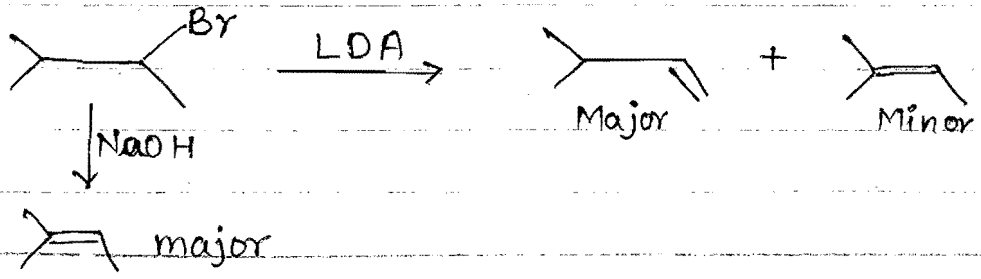


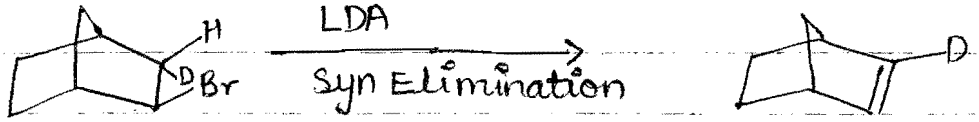


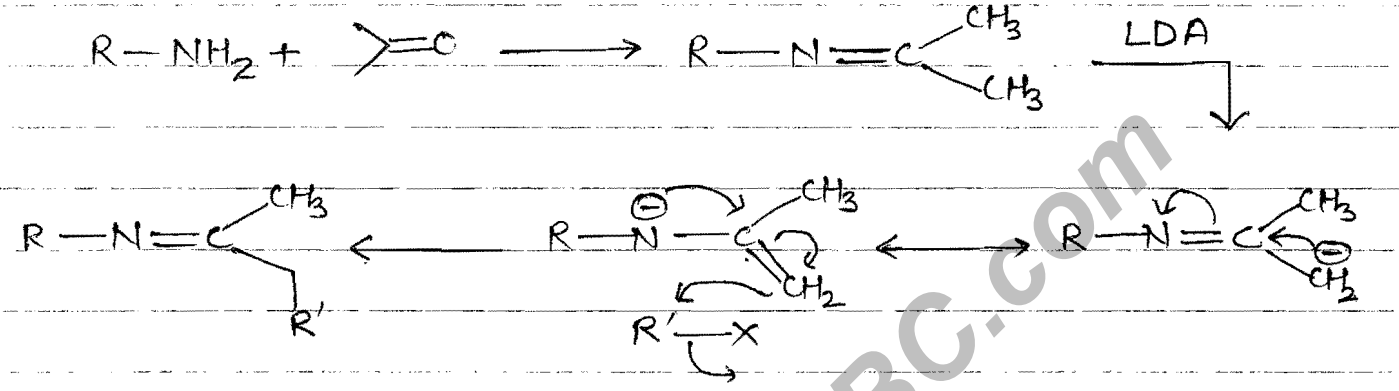
Q 

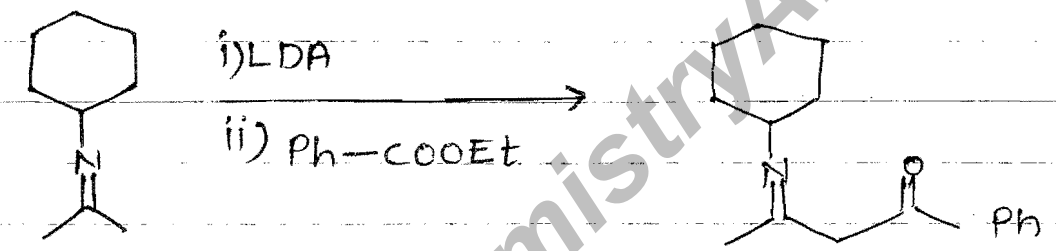
Q 

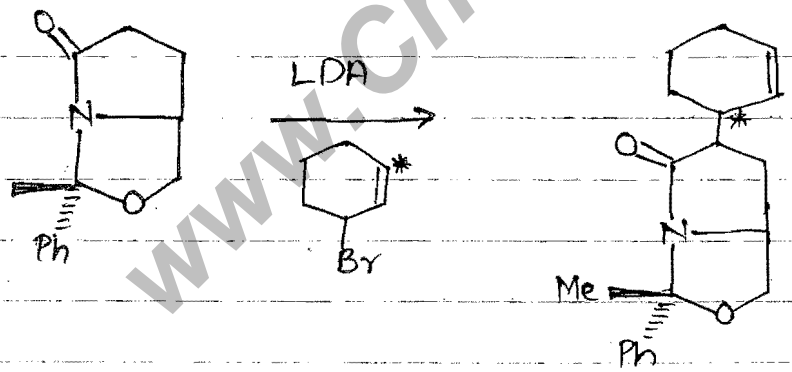
Elimination

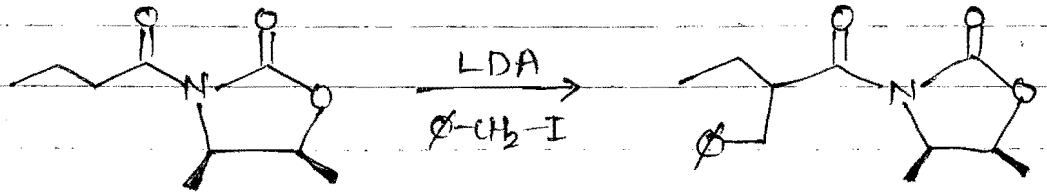
⇒ 

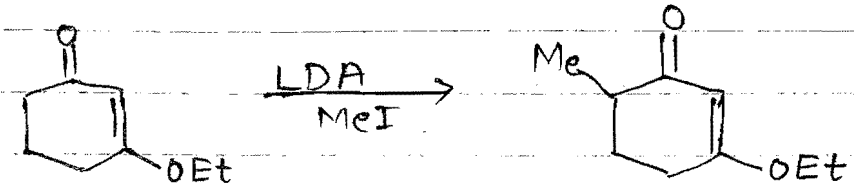
Q 

Q 

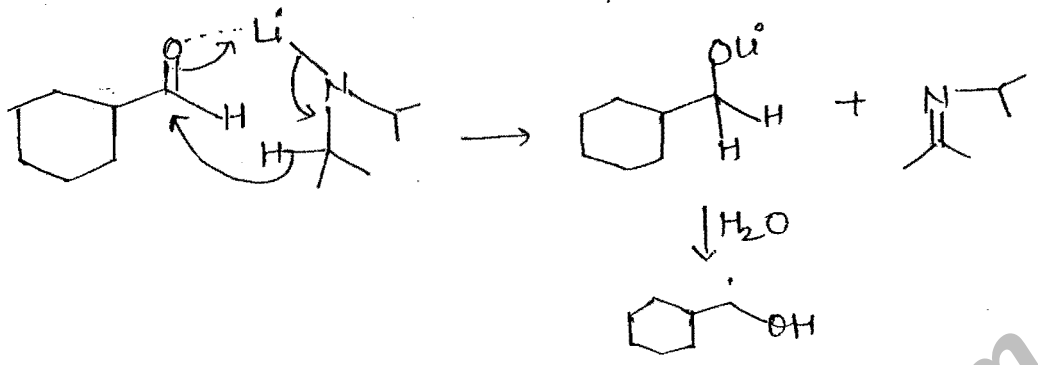
Q 

Q 

Q 

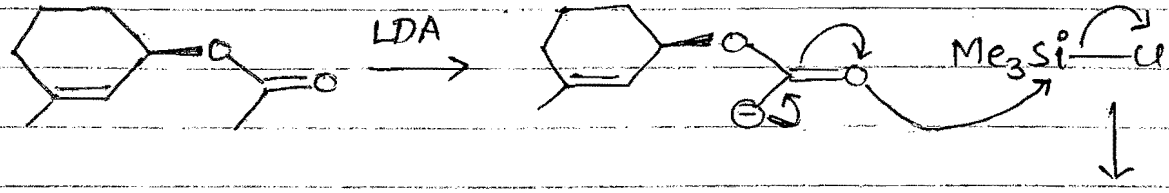
Q 

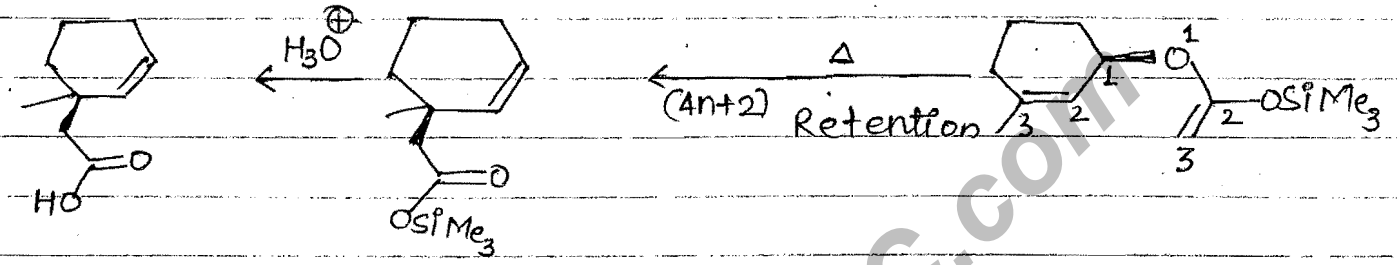
LDA can also transfer hydride ion ($H^{\ominus}$) just like MPV Redn



Imp.

Q





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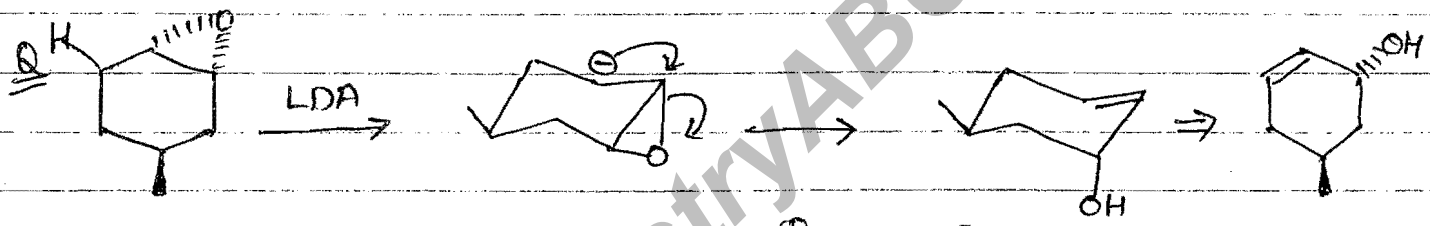


Q BOC—NH—CH(CH$_2$Ph)—COOH (Protecting Group) 3LDA → BOC N$^{\ominus}$Li$^{\oplus}$ CH(CH$_2$Ph)—COO$^{\ominus}$Li$^{\oplus}$

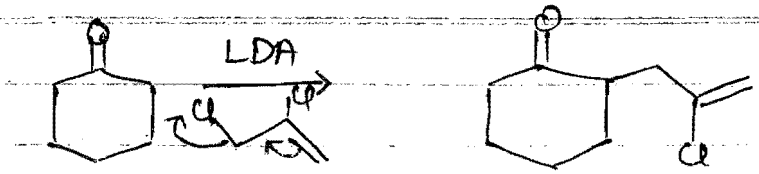
Ph—CH$_2$—Br

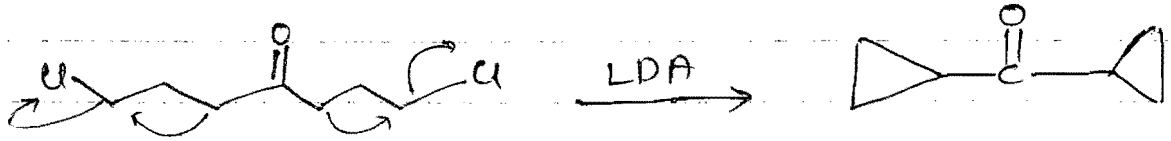
BOC—N(H)—CH(CH$_2$Ph)—COOH $\xleftarrow{H_3O^{\oplus}}$ BOC N$^{\ominus}$Li$^{\oplus}$ CH(CH$_2$Ph)—COO$^{\ominus}$Li$^{\oplus}$

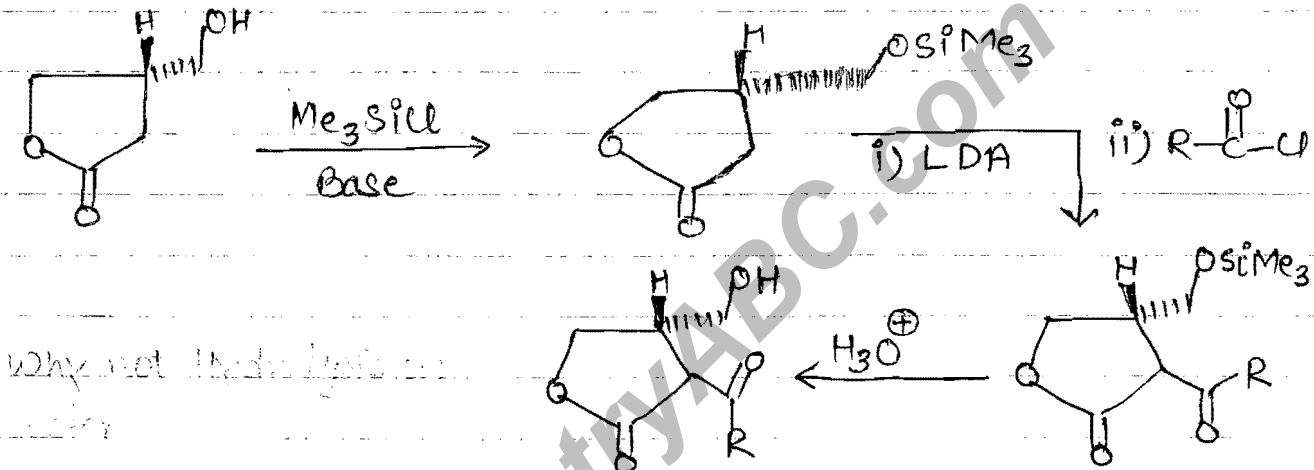
$\Rightarrow$ $R-NH_2$ + di ^tBu Anhydride → R—NH—C(=O)—O—BOC

R NHBOC $\xrightarrow{CF_3COOH}$ $R-NH_2$

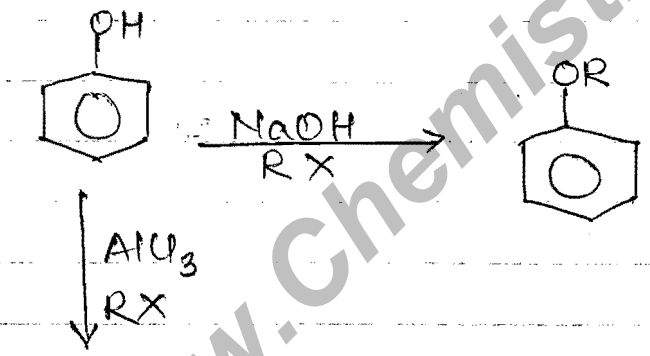
Best for deprotection of BOC

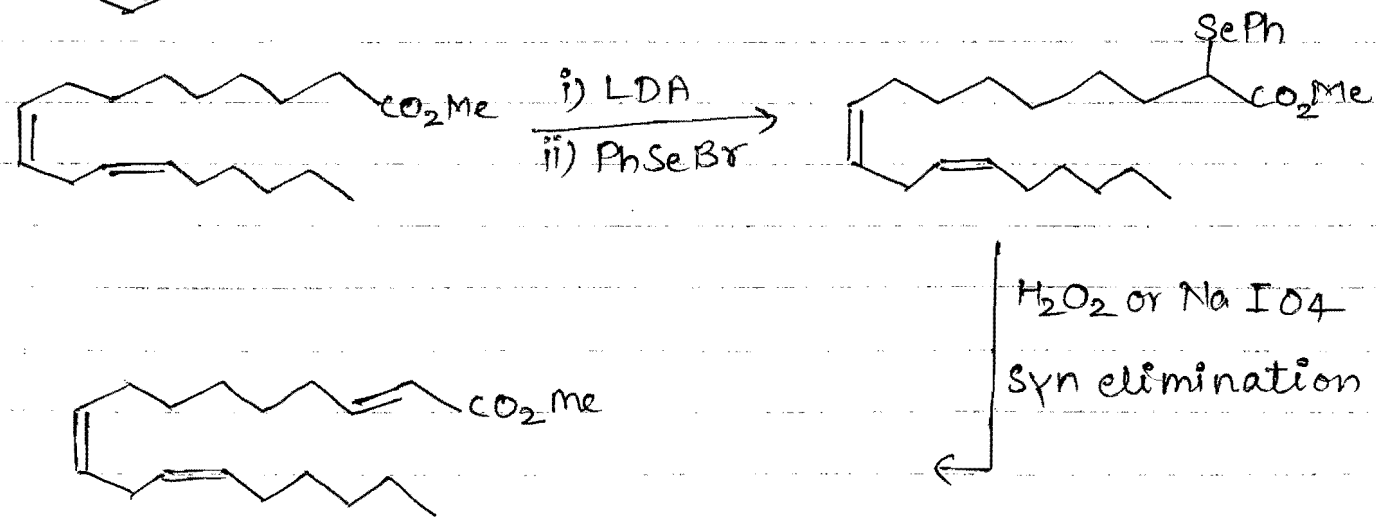
Q 

Q 

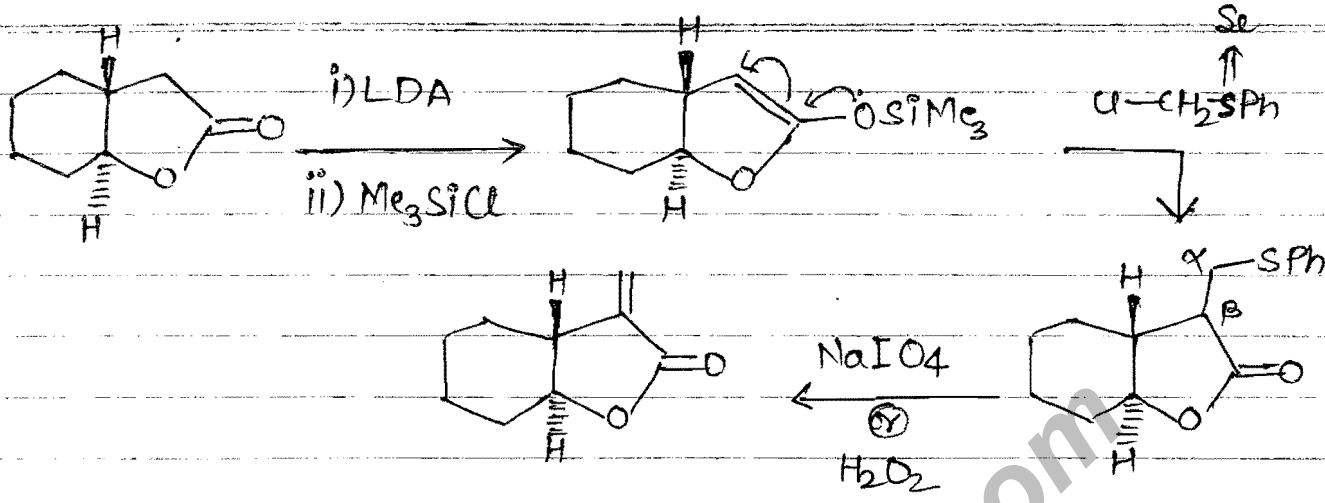
Q 

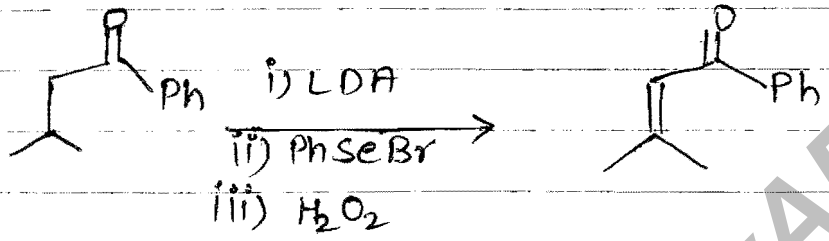
Why not Nucleophilic ...

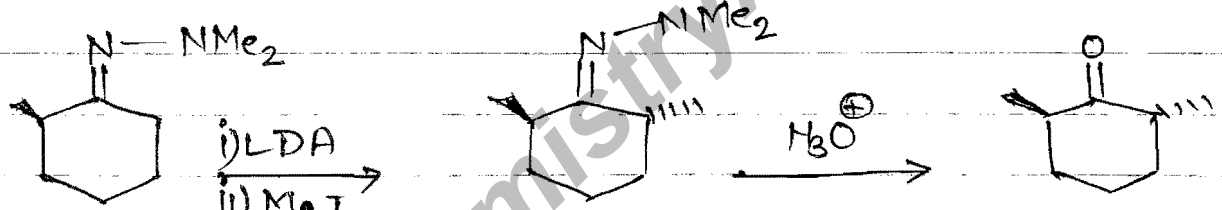
⇒ 

Q. 

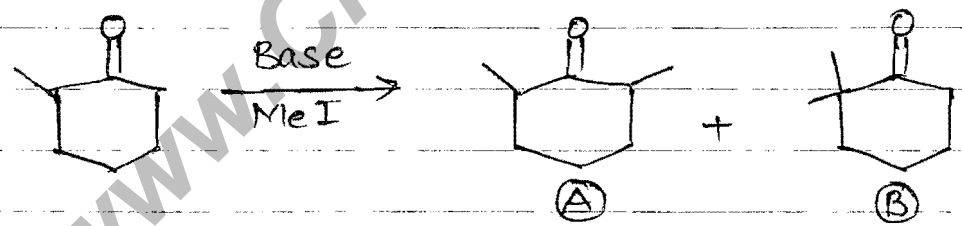
$Cl-CH_2SePh$ (or) $Cl-CH_2SPh$
Same function.

Q 

Q 

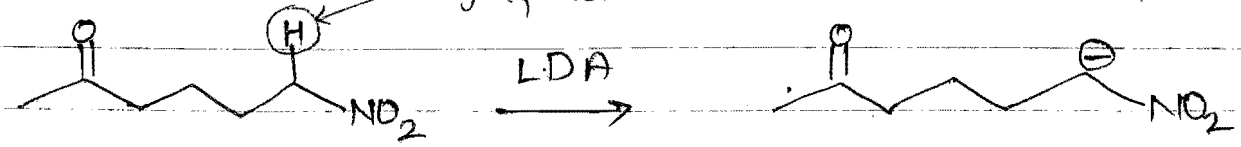
Q 

V.imp

Q 

Base	Major	Minor
LDA or $\bar{N}H_2$	A	B
NaOEt or $\bar{O}H$	B	A
(or) $t_{BuO}K$		

Highly acidic H ⇒ abstraction by any Base

Q 

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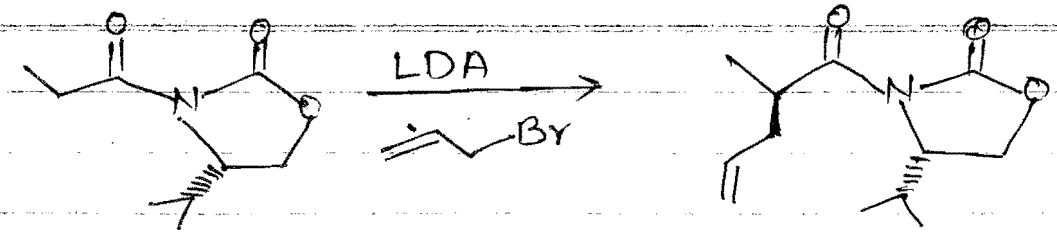

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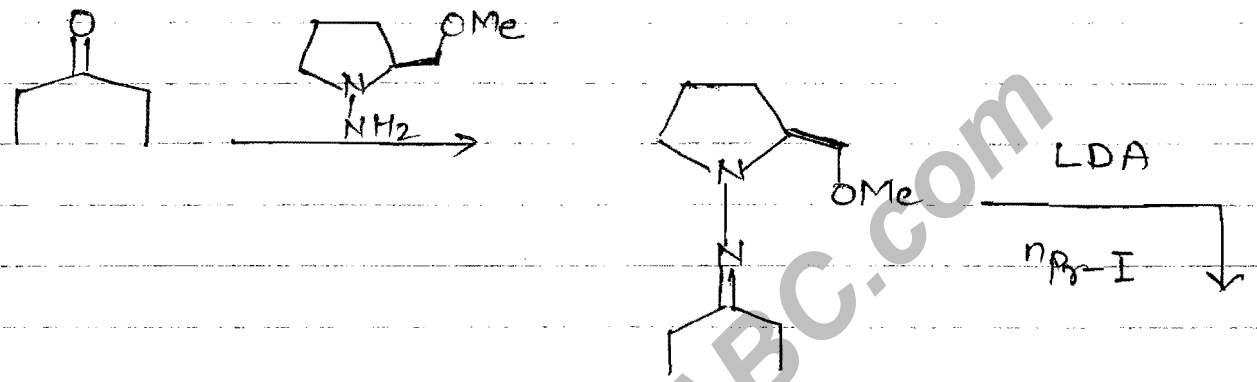

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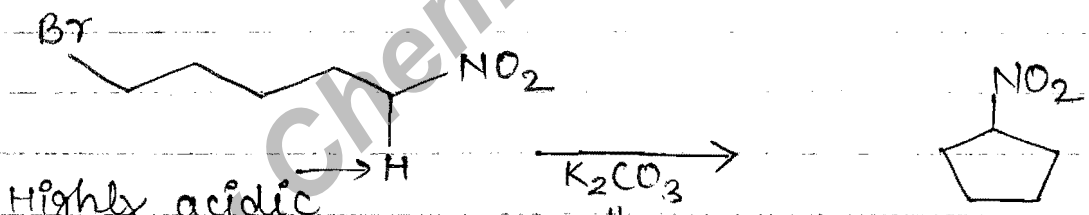
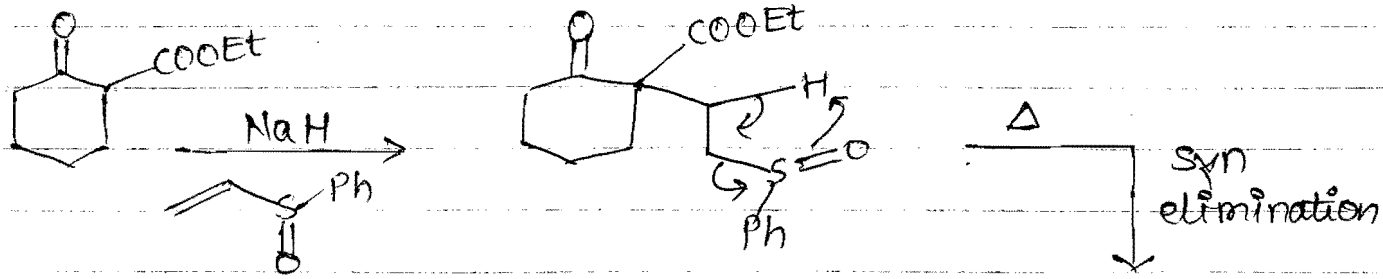


Highly acidic ⇓ Mild Base can also abstract.

⇓ Mild Base

Q



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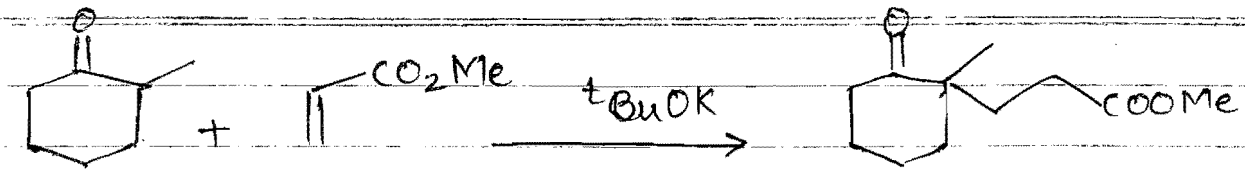

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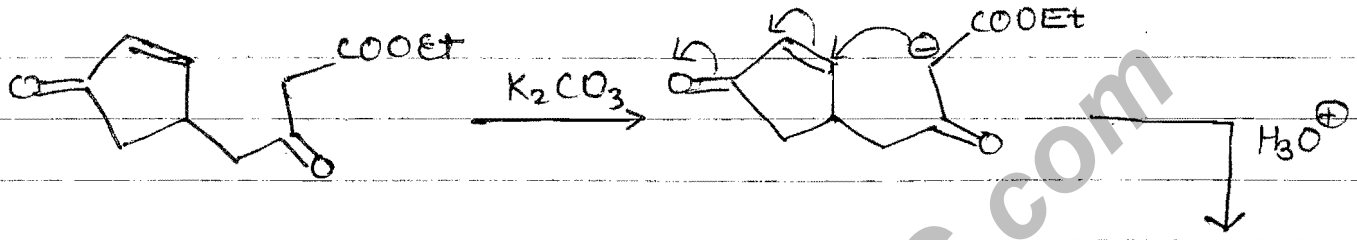
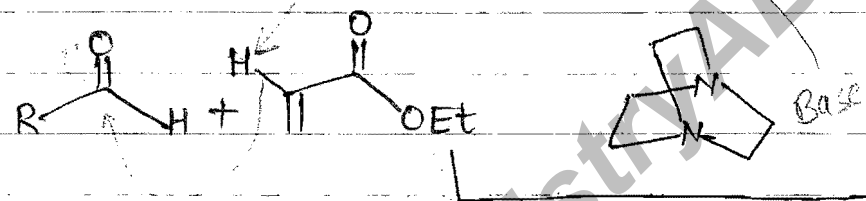
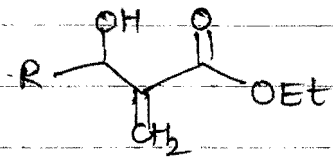


2014
V.V.Imp.
Q



DABCO
1,4 diazobicyclo[2.2.2] octane

Baylis Hilman Rxn. →



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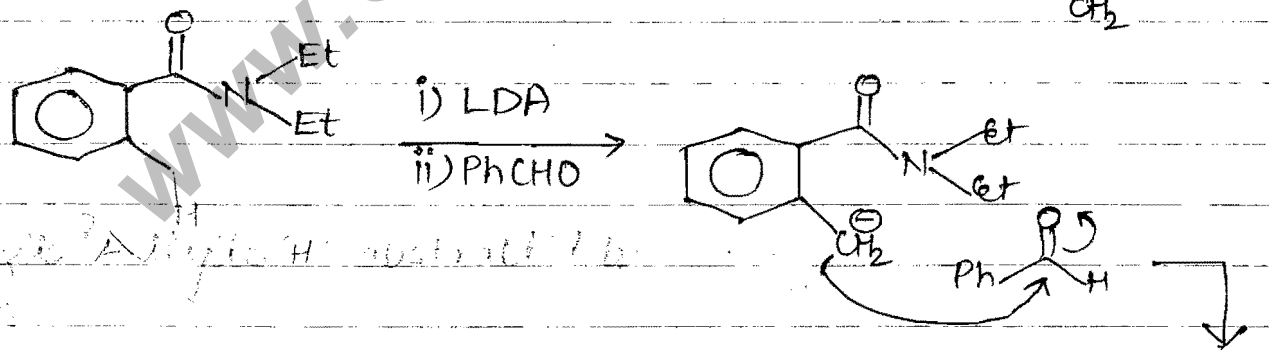
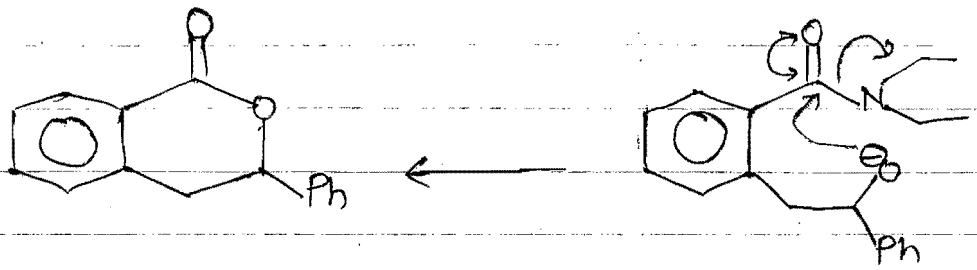
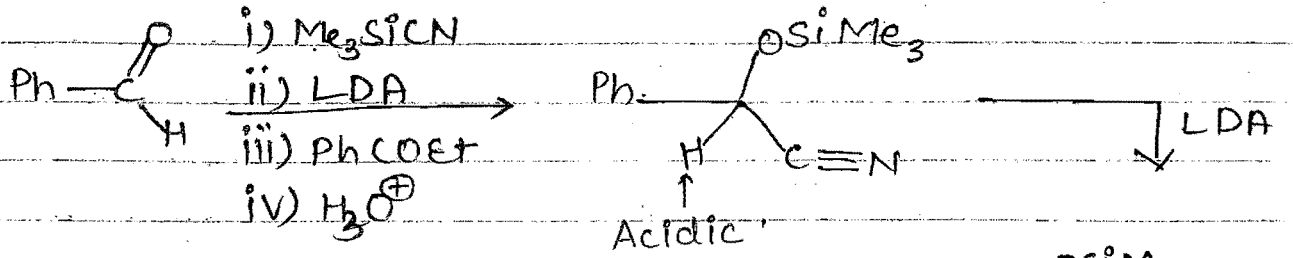
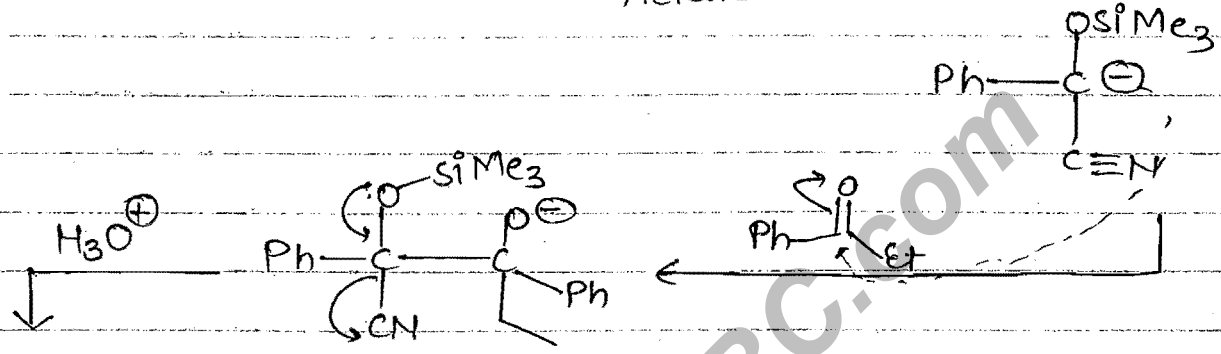


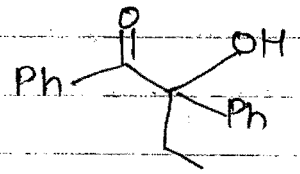


Imp.

Q

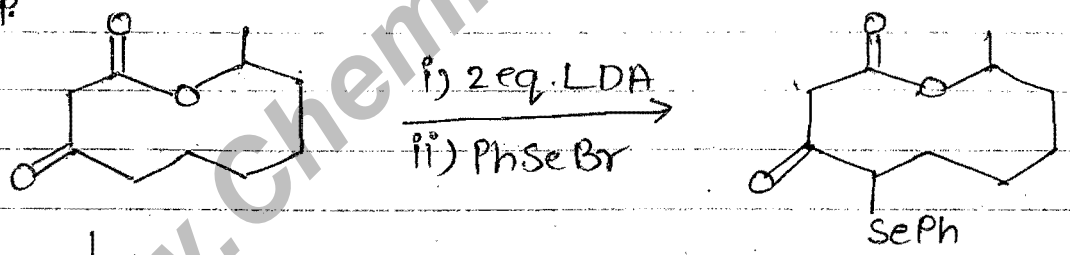


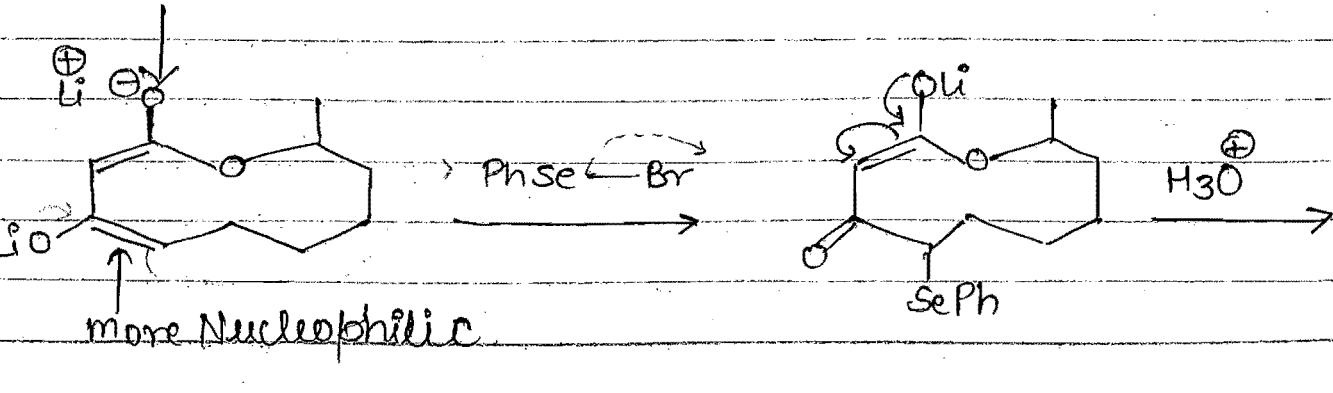


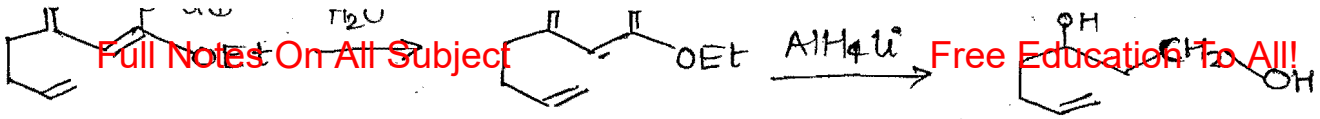


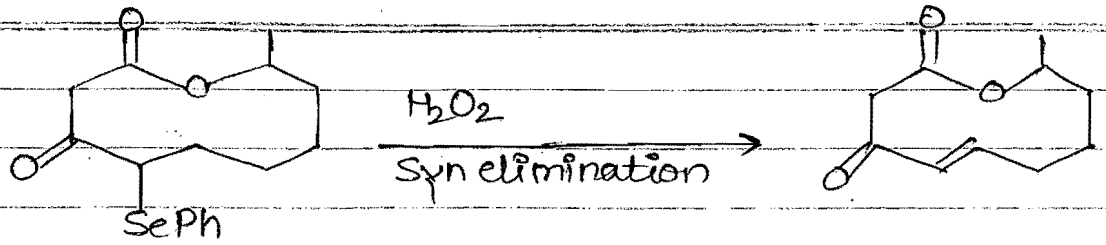
V.V.Imp

Q.



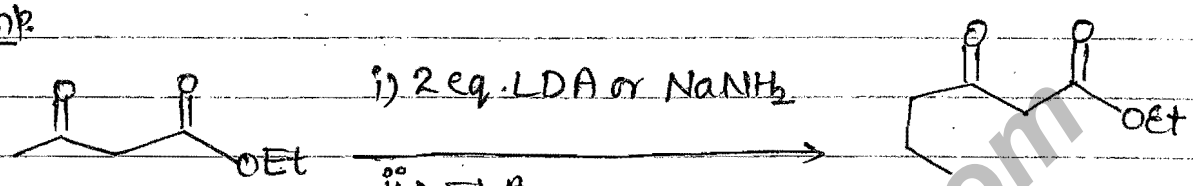






V.V. Imp.

Q



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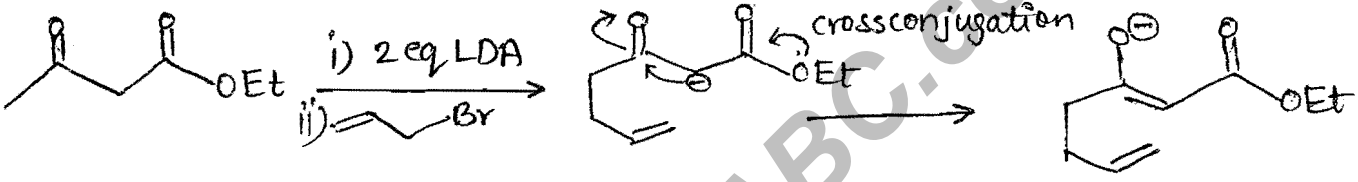
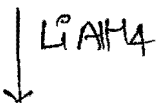
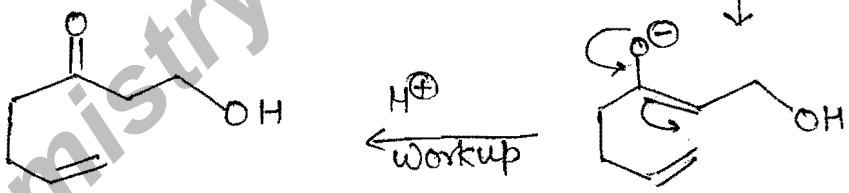


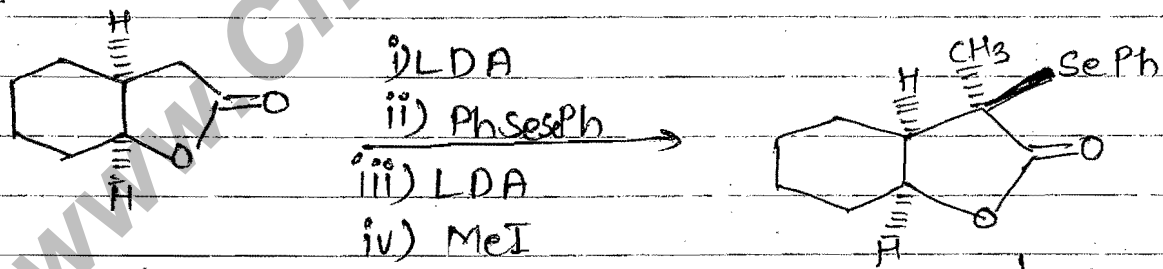


Further no rxn. of $LiAlH_4$ on carbonyl becoz it becomes inactive in water

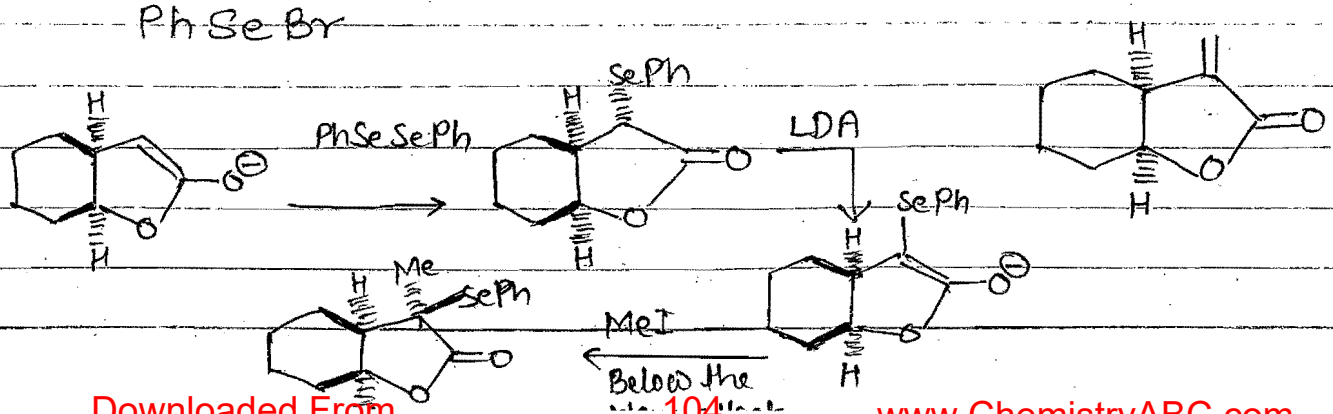


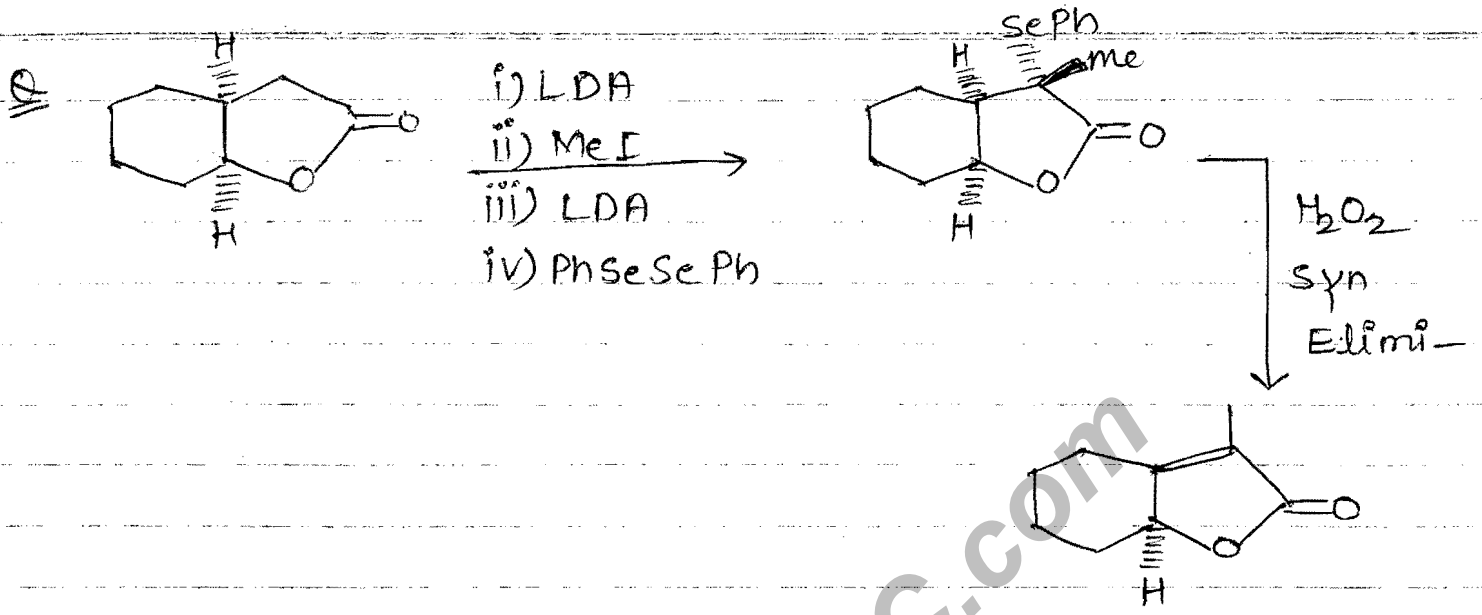
2014
V.V. Imp.

Q

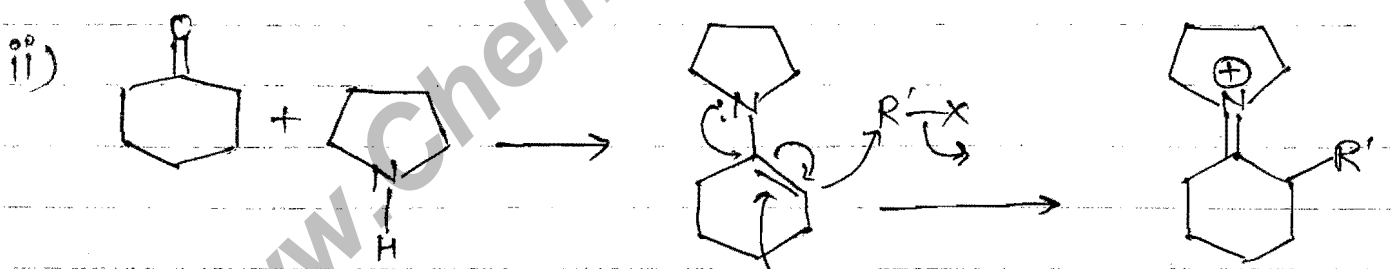


PhSe SePh just like PhSeBr

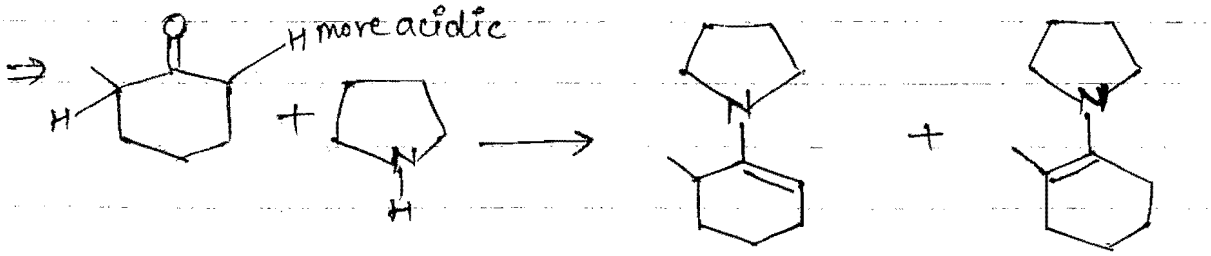


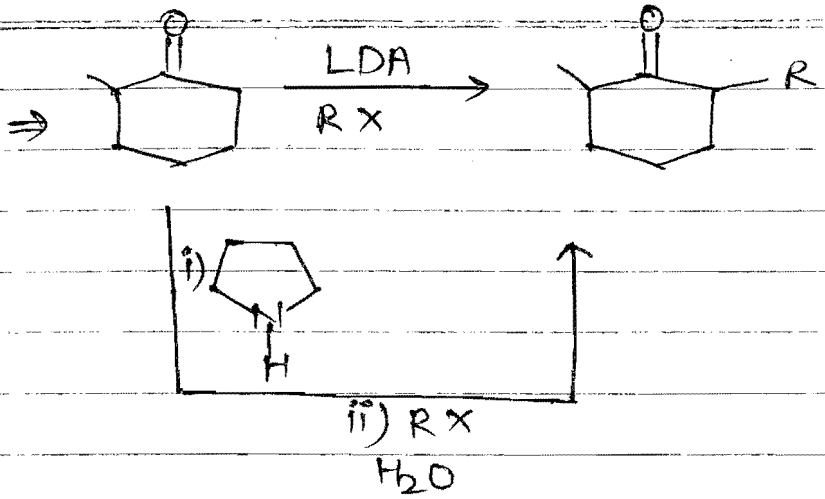


Which method is better for Alkylation:-

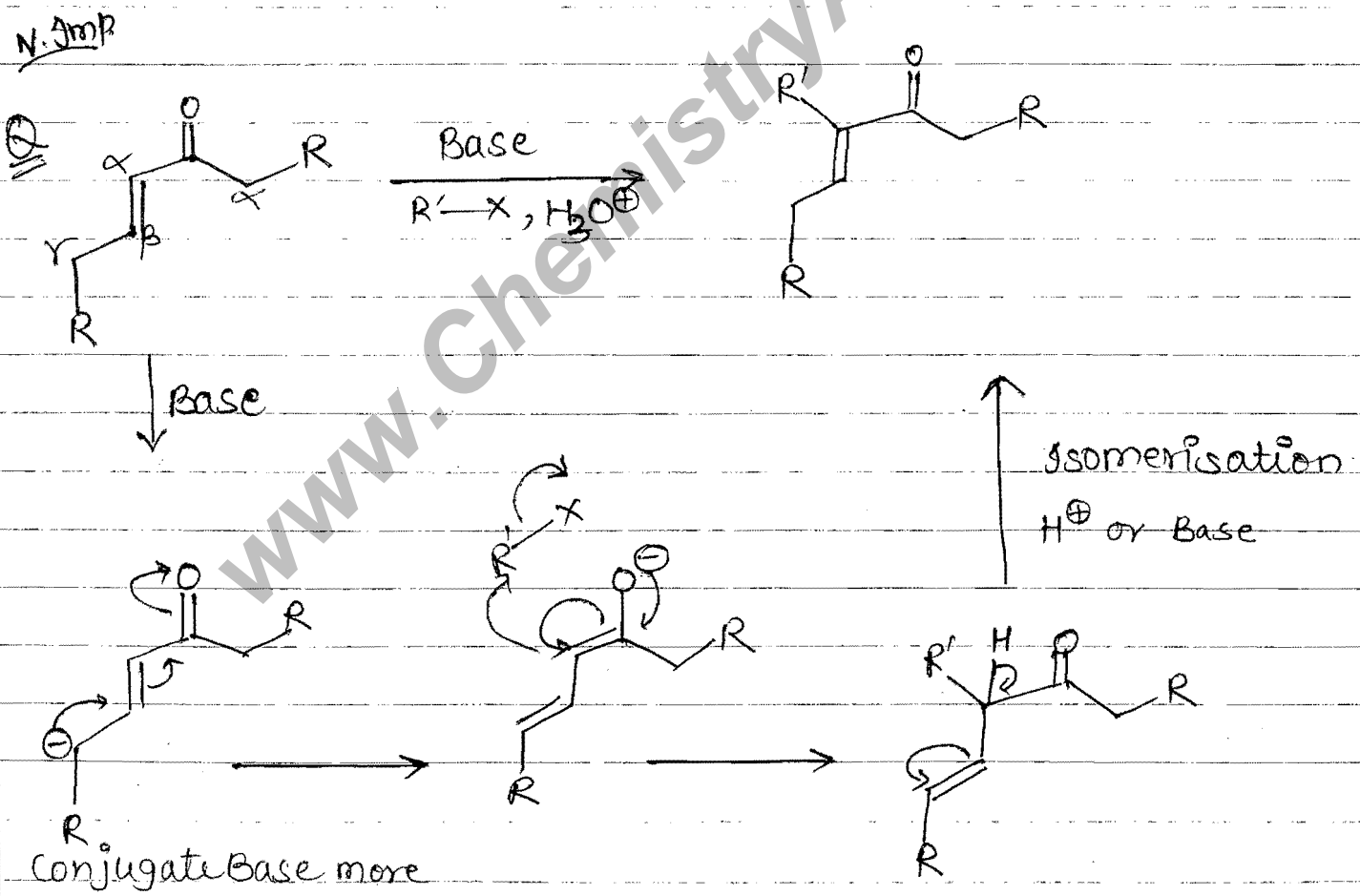


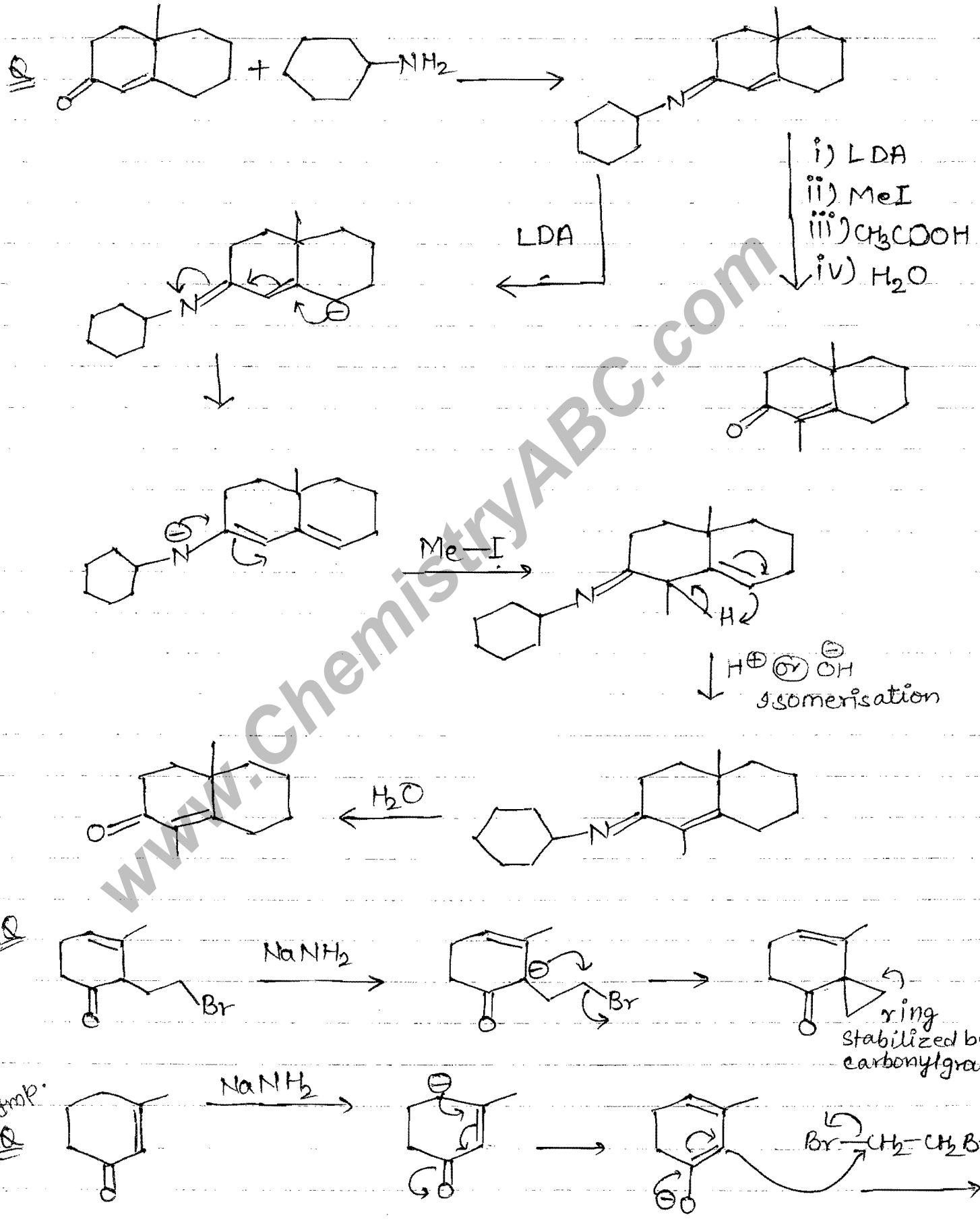
ii) method is better than i)

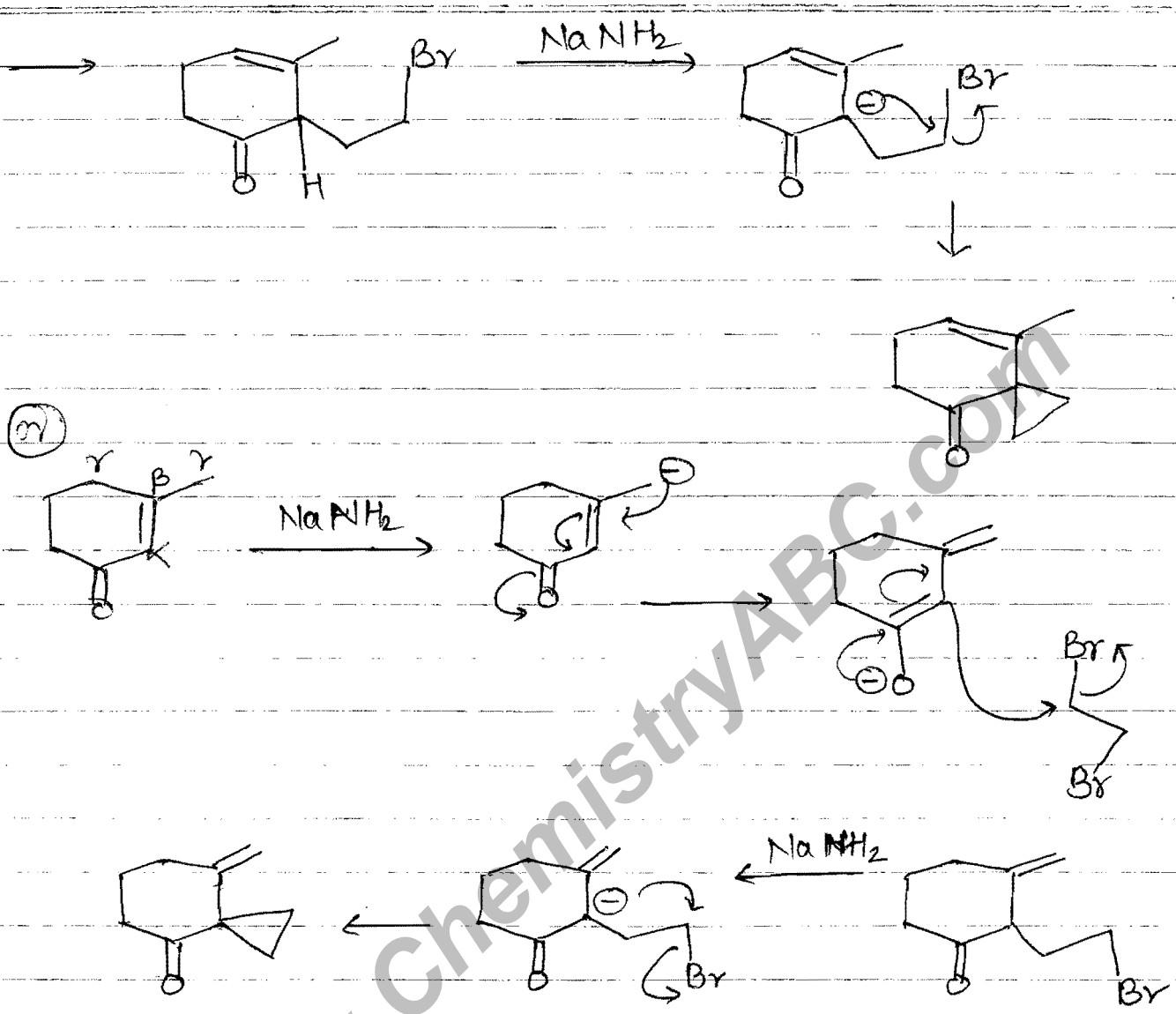




Rxn of α,β- unsaturated carbonyl comp. With Base :-

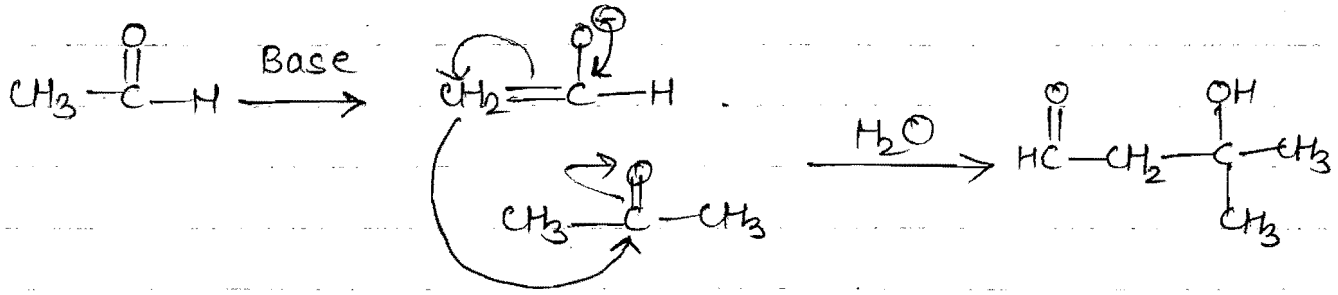


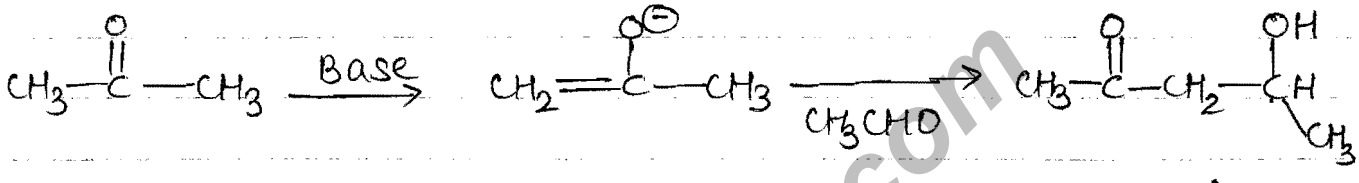


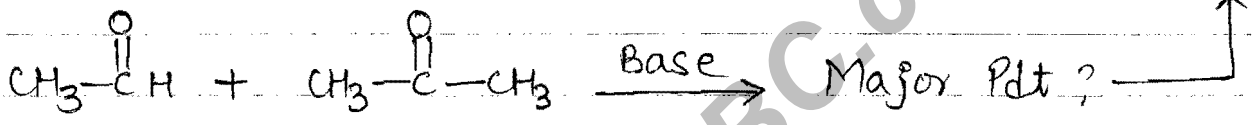


Direct Aldol Condensation:-

When in aldol condensation LDA use as a base then Kinetically controlled ete enolate form (less sterically Hind. proton abstraction) such type of aldol condensation k/a directly aldol condensation.

Ex. 

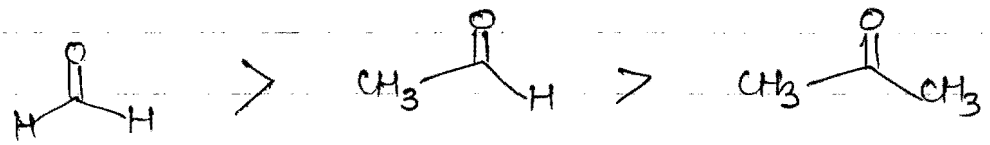
Ex. 

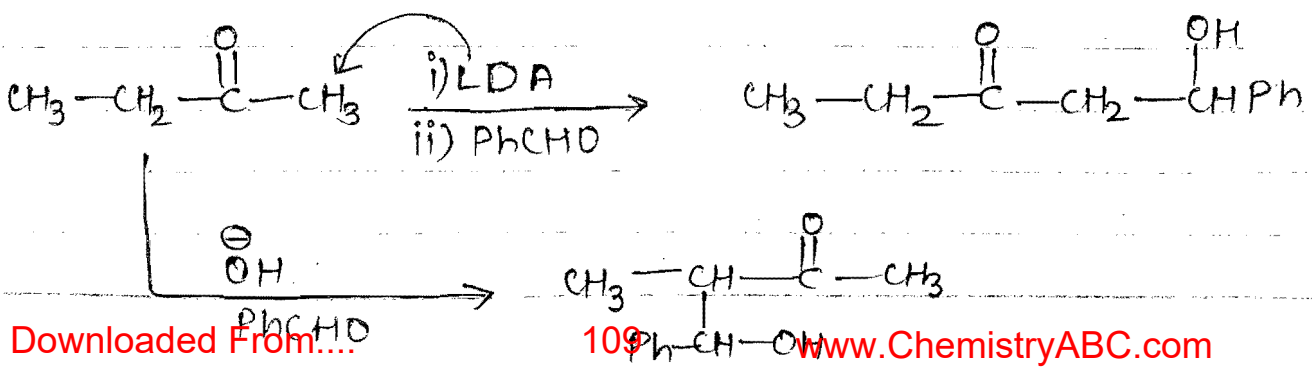
Q 

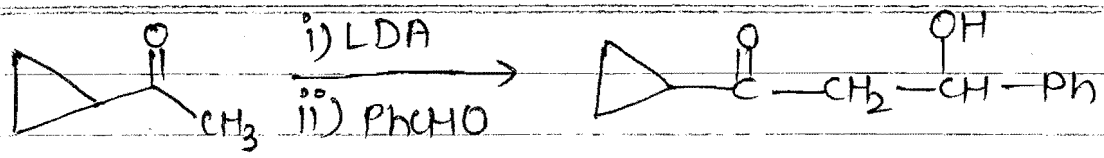
The spp which gives hardly Nucleophic addition Rxn, gives enolate i.e. ketonic enolate is more preffered than ald enolate.

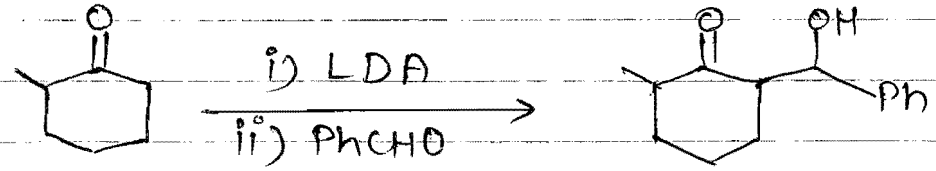
Q 

Q Write the correct order of Nucleophilic addn Rxn.



Q 

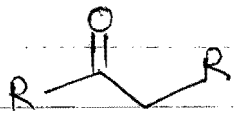
Q 

Q 

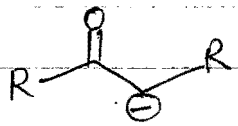
Most imp.

enolate

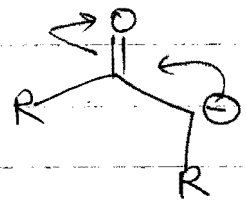
Z E

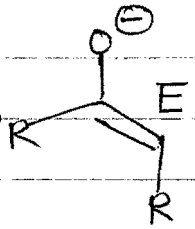


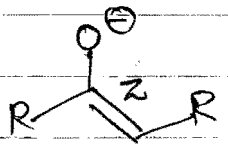
Base



Rotation

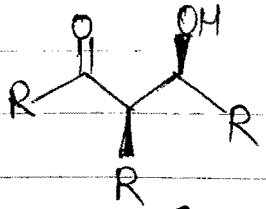






RCHO

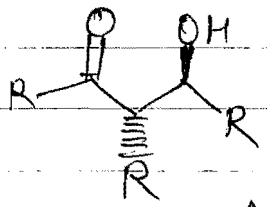
form Syn pdt



Syn.

RCHO

form Anti Product

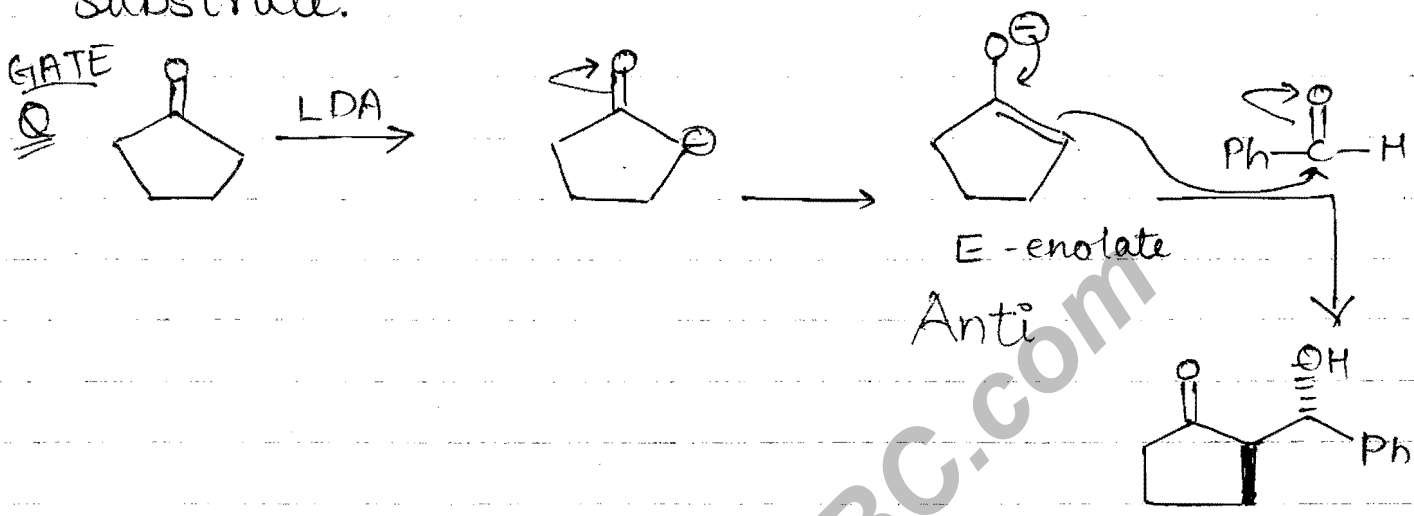


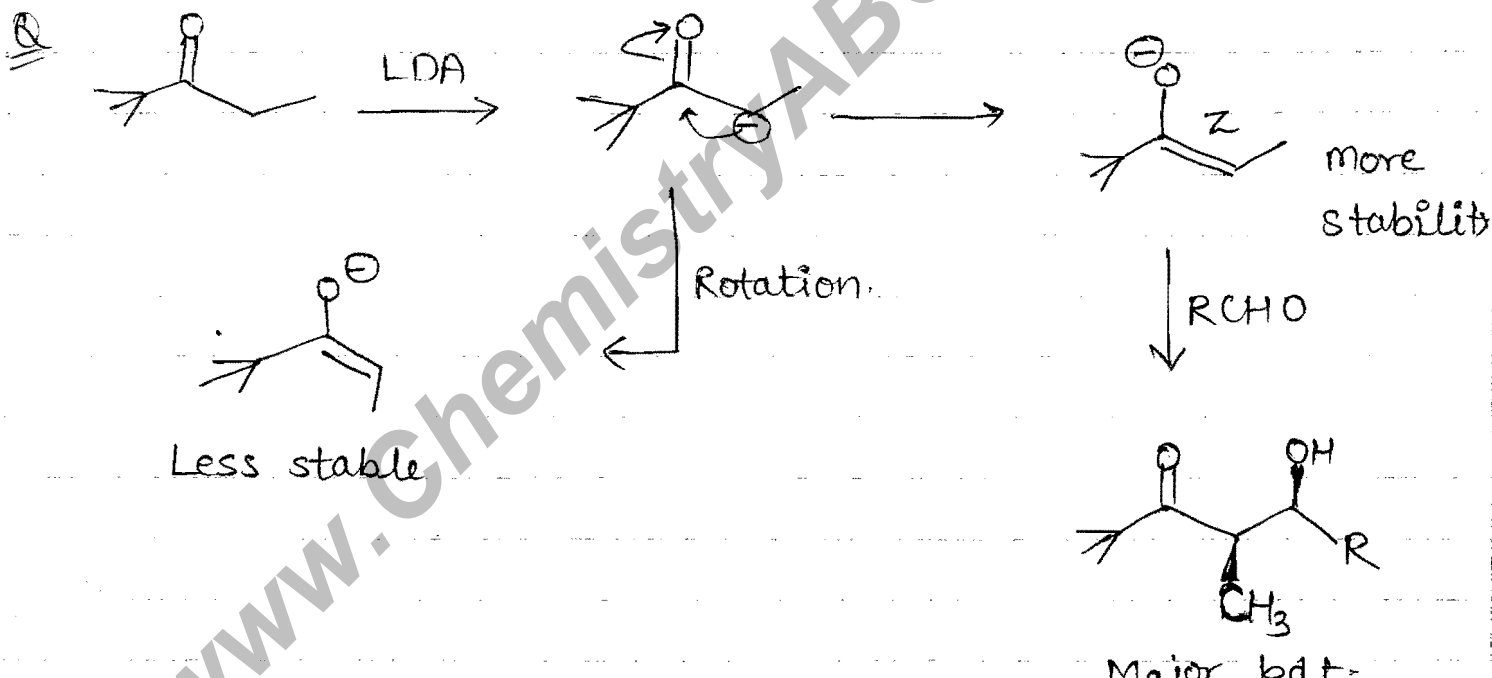
Anti

Z ⇒ Syn
E ⇒ Anti

The formation of enolate depends upon nature of substrate.

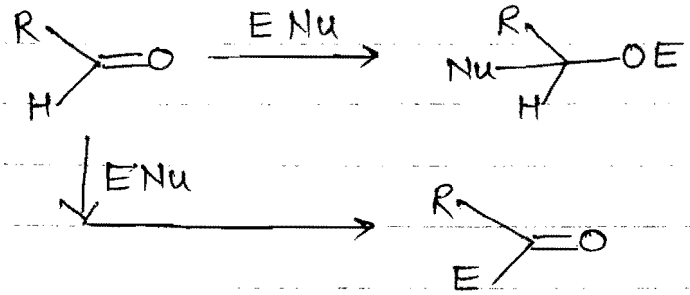
GATE



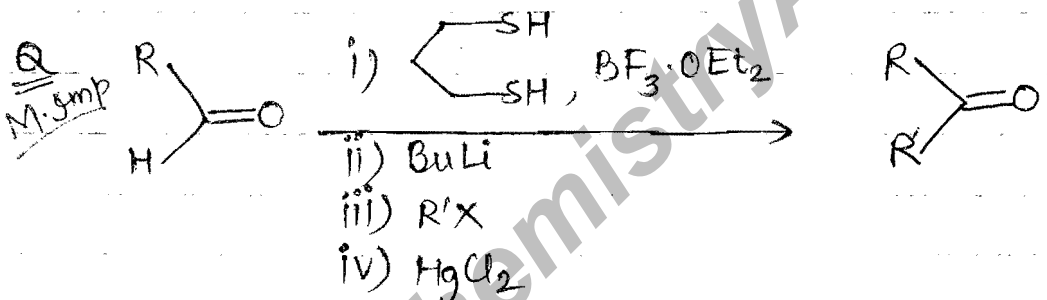


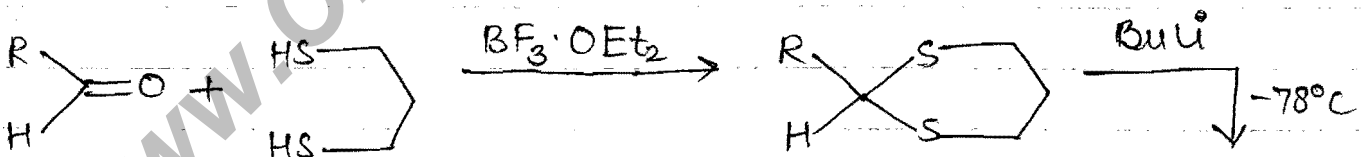
1,3 - DITHIANES

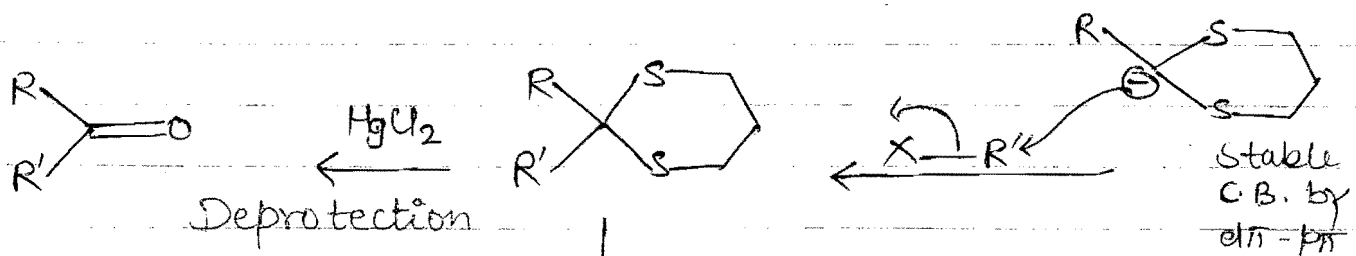
1,3-dithiane behave as umpolung reagent.

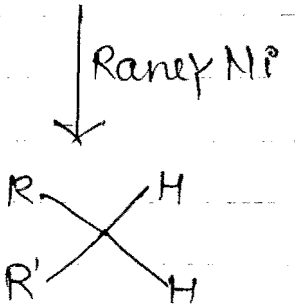


Q M.imp

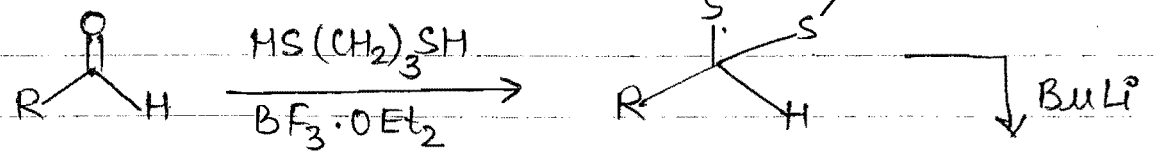


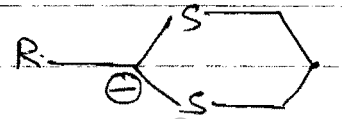






D

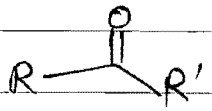


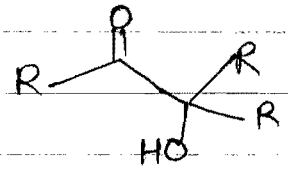


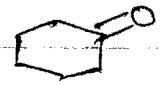
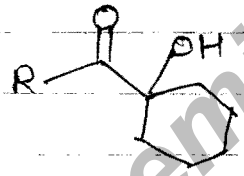
$Nu^{\ominus}$

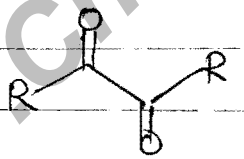
NSR (or)

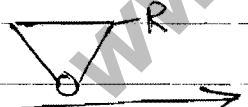
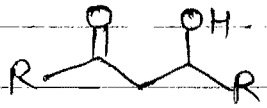
N.A·R

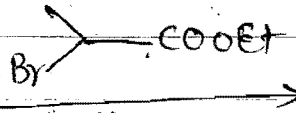
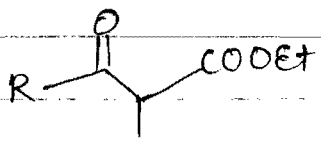
$R'X$, $HgCl_2$ →  Ketone

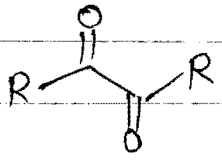
RCOR, $HgCl_2$ →  α-hydroxy carbonyl

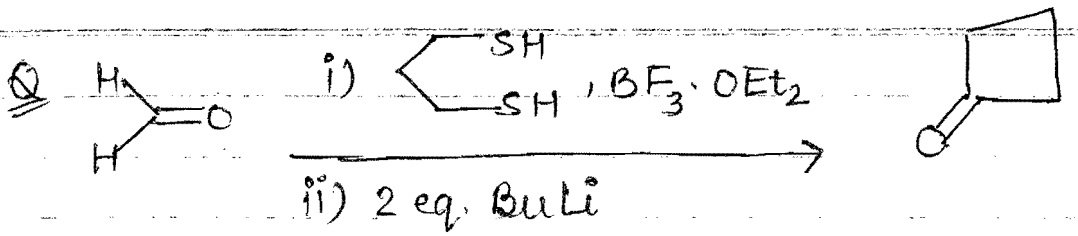
 , $HgCl_2$ → 

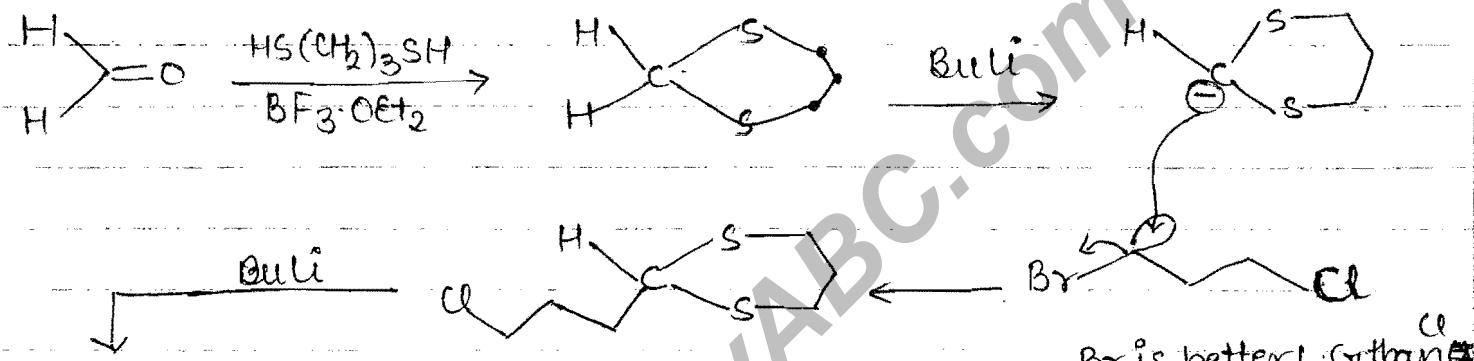
RCOOEt, $HgCl_2$ →  (1,2-diketone)

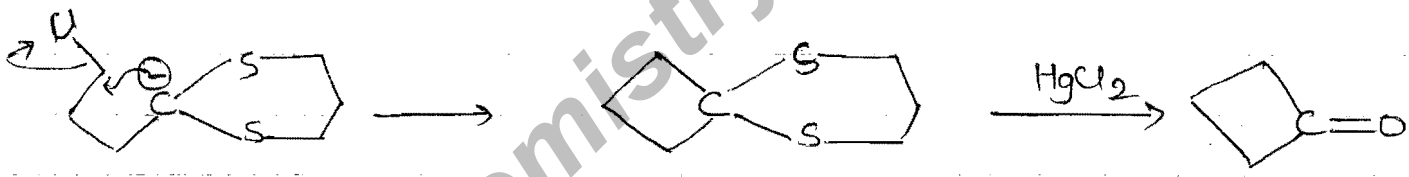
 , $HgCl_2$ →  β-hydroxy carbonyl

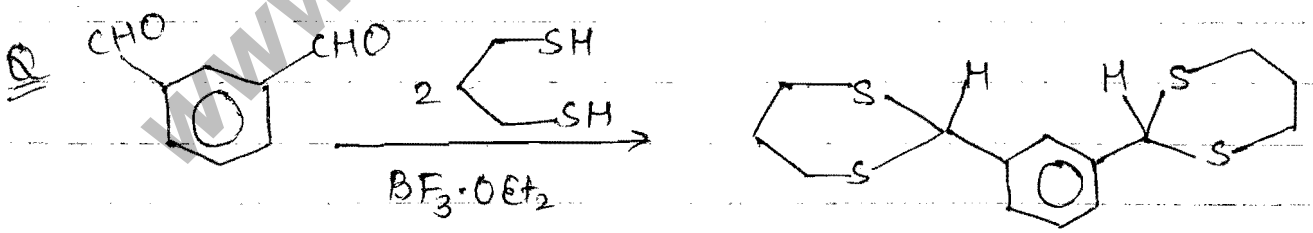
 , $HgCl_2$ →  β-keto ester

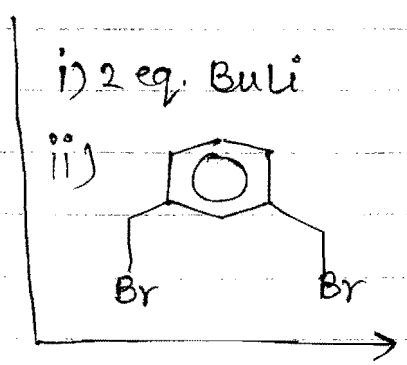
RCOCl, $HgCl_2$ → 

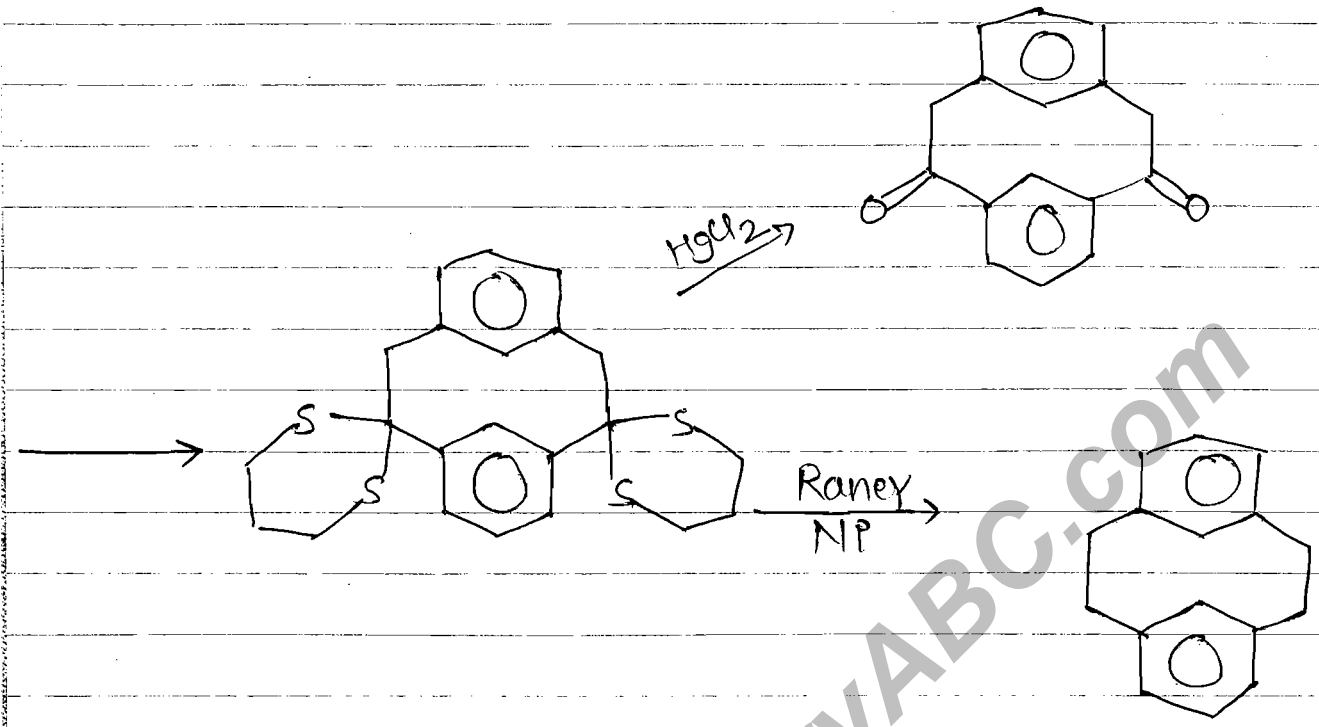
Q 





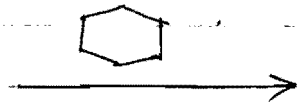
Q 





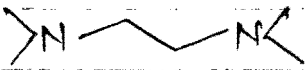
ORGANO LITHIUM (R-Li)

It exist in aggregation form



To reduce aggregation TMEDA is used

Tetramethylethylene diamine.

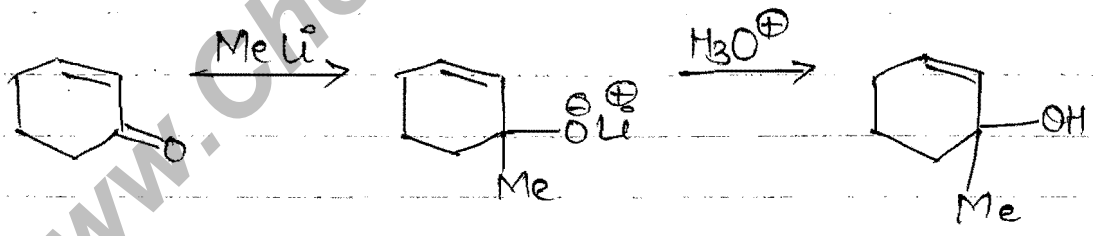


* Normally THF is used.
* Rxn. takes place at low temp.
* Solvent must be dry

Applications of R-Li

Organolithium gives 1-4 direct (1,2) addn rather than 1,4 addn

Ex.



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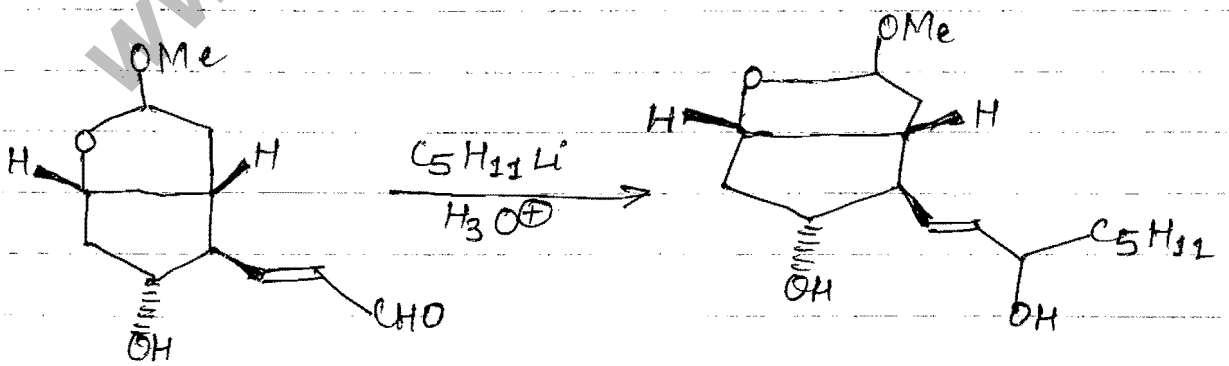
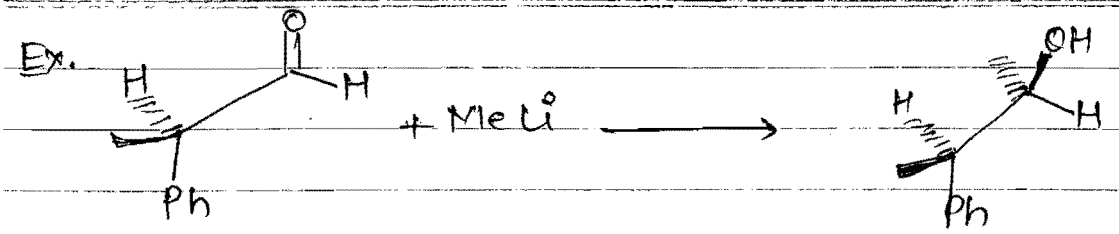
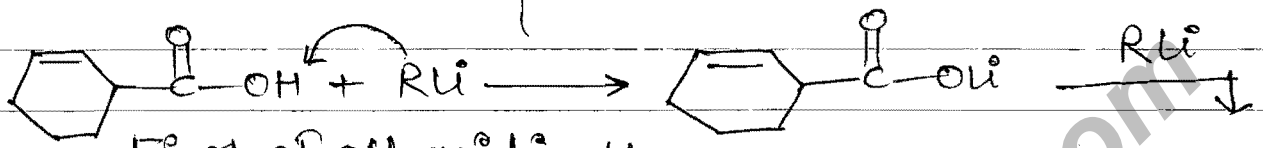


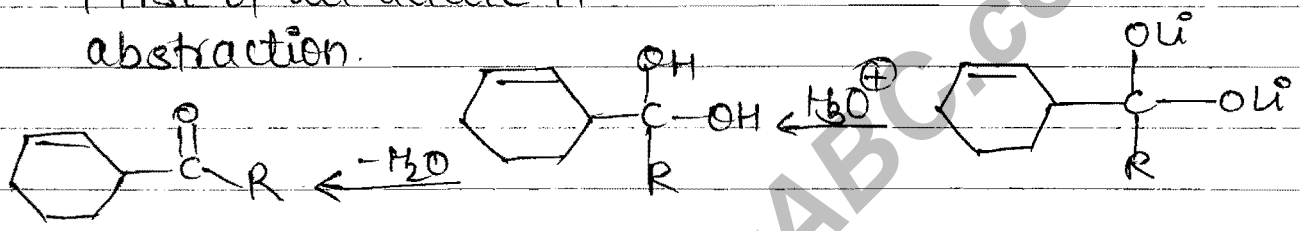
Ex.



Rxn. with carboxylic Acid:-



First of all acidic H abstraction.



$RLi + CO_2 \longrightarrow$ Ketone $R-\overset{O}{\overset{\|}{C}}-R$

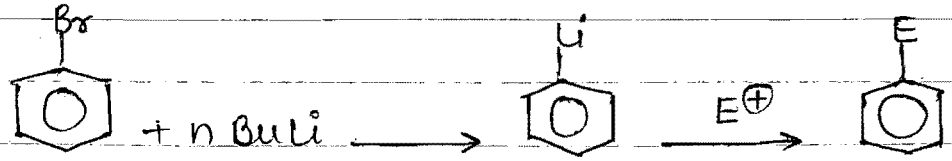
$RMgX + CO_2 \longrightarrow$ Acid. $R-\overset{O}{\overset{\|}{C}}-OH$

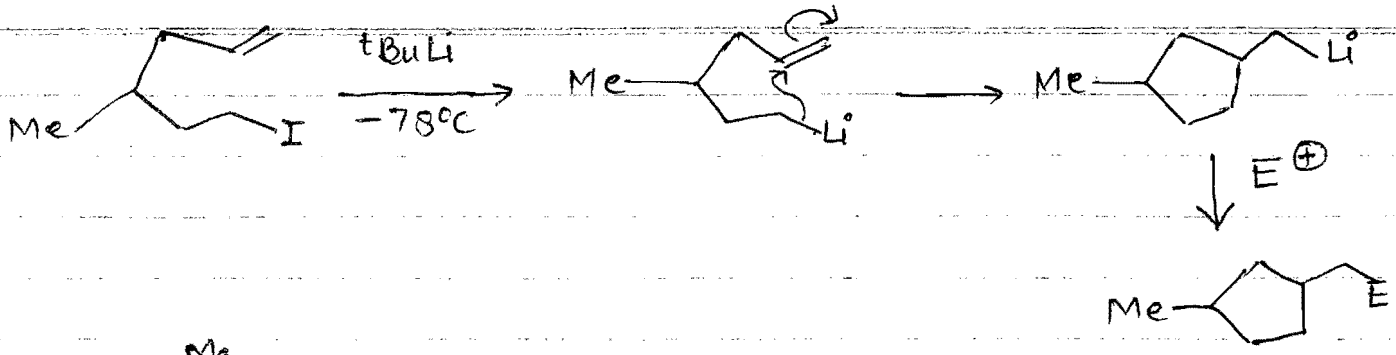
M. imp.

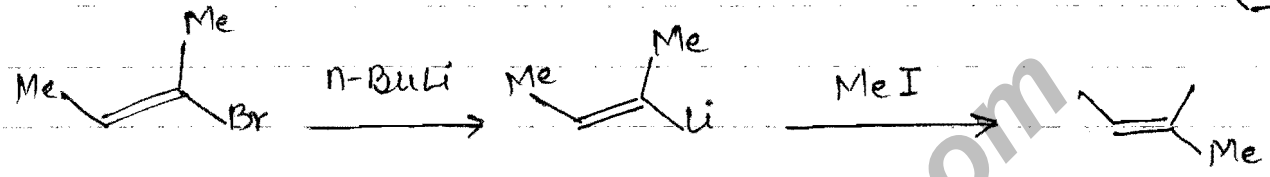
Rxn with Alkyl Halide:-

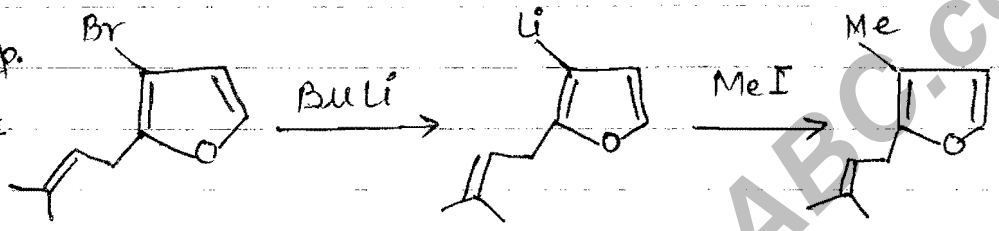
When organo lithium comp. react with alkyl halide then lithetion take place.

$R'-X + RLi \longrightarrow R'Li \xrightarrow{E^{\oplus}} R'-E$

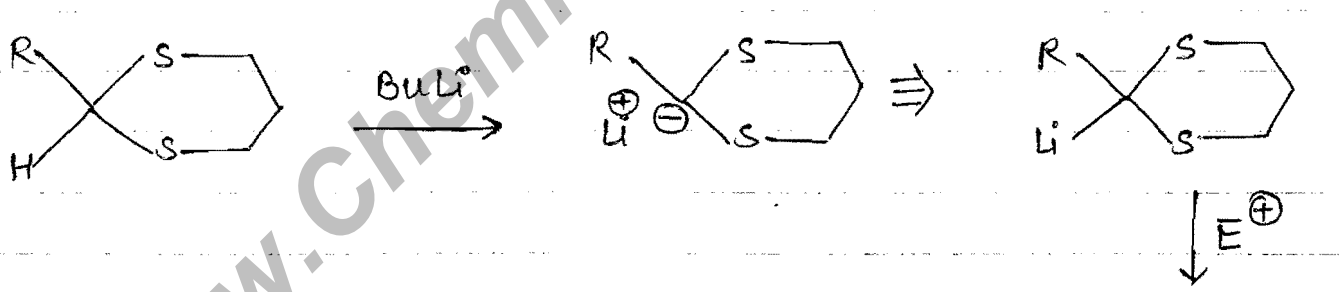


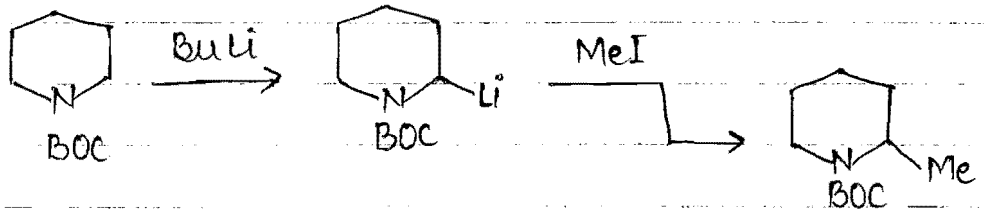
Q 

Q 

gmp. Q 

Formation of Sulfur/Nitrogen Ylide:-

Ex. 

Ex. 

v.v. gmp

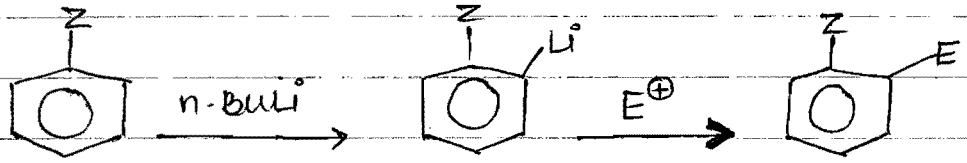
Complex Induced Proxomity Effect:- CIPE

Normal or 2° BuLi abstract directly proton from

 = BOC

aryl species, but an aryl species a substituent Z (Z = heteroatom containing spp.) must be +nt.

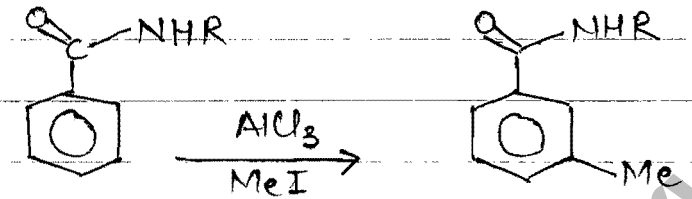
gmp.

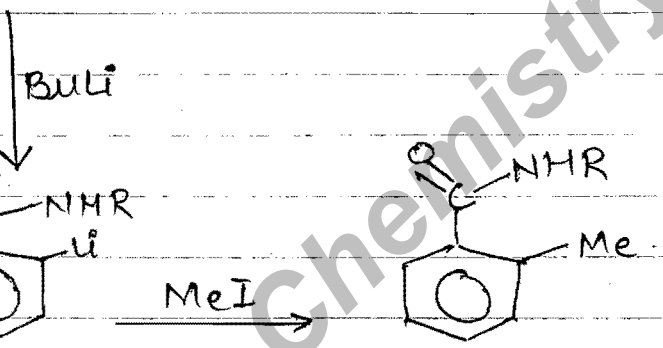


Z = SO_2NR, OCONR, $CONR_2$, OCH_2OMe, OMe

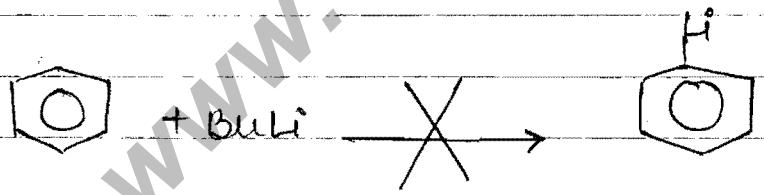
This effect is k/a CIPE.

Ex.



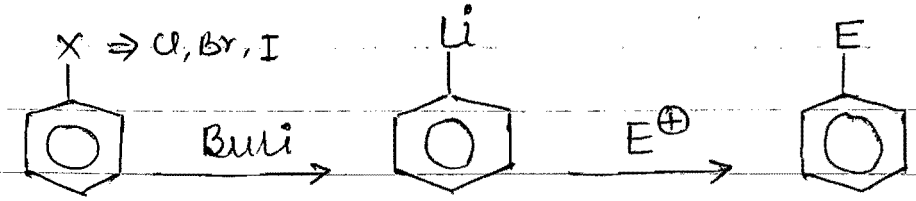


⇒

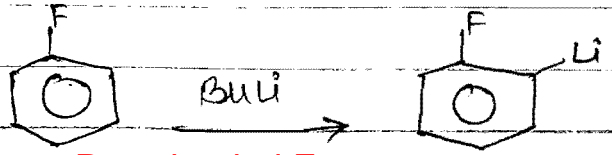


But when Z = Halogen (only I, Br, Cl) then directly replacement take place by replacement of Halogen. Lithetion

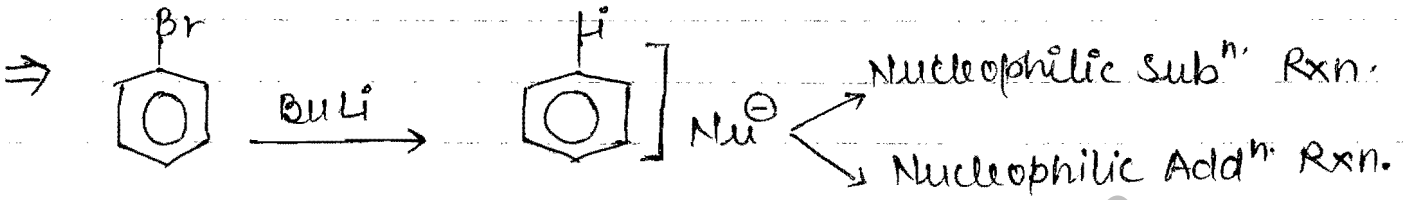
Ex.

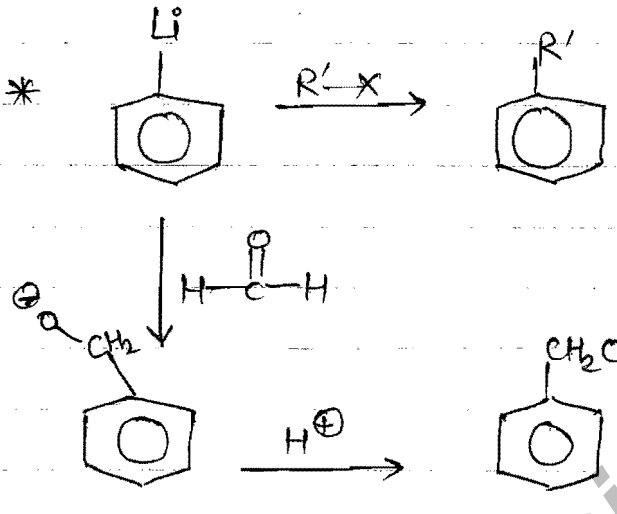


⇒

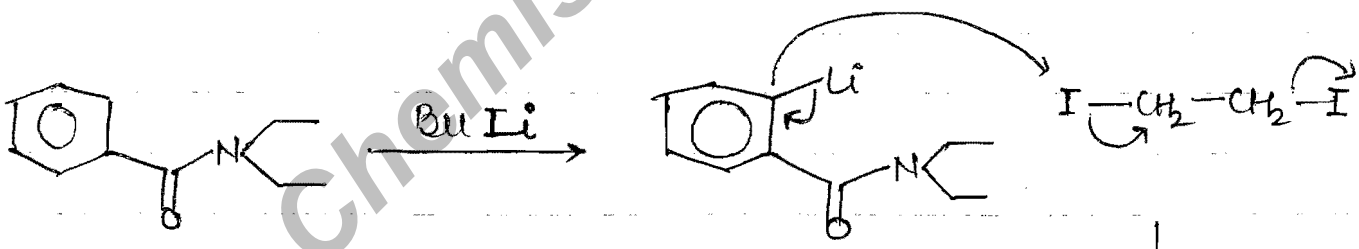


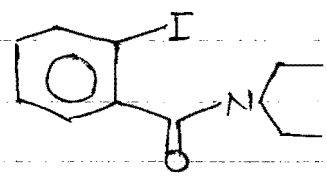
If in benzene ring Halogen and Z group, both +nt then Lithetion takes place at Halogen position.



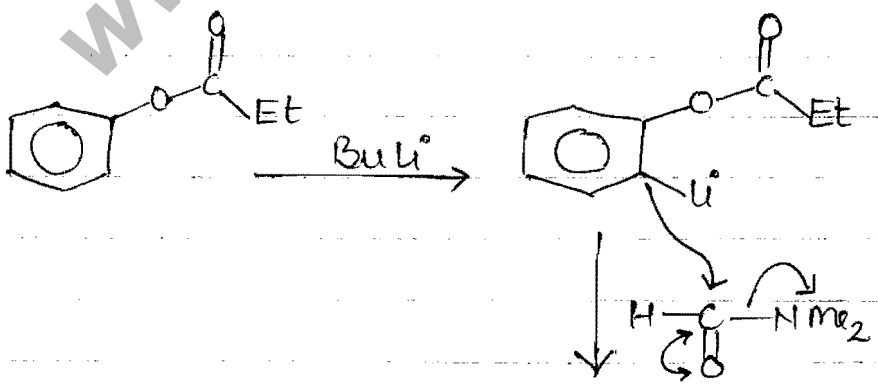


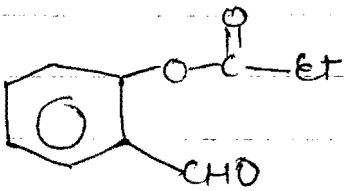
2014 Q

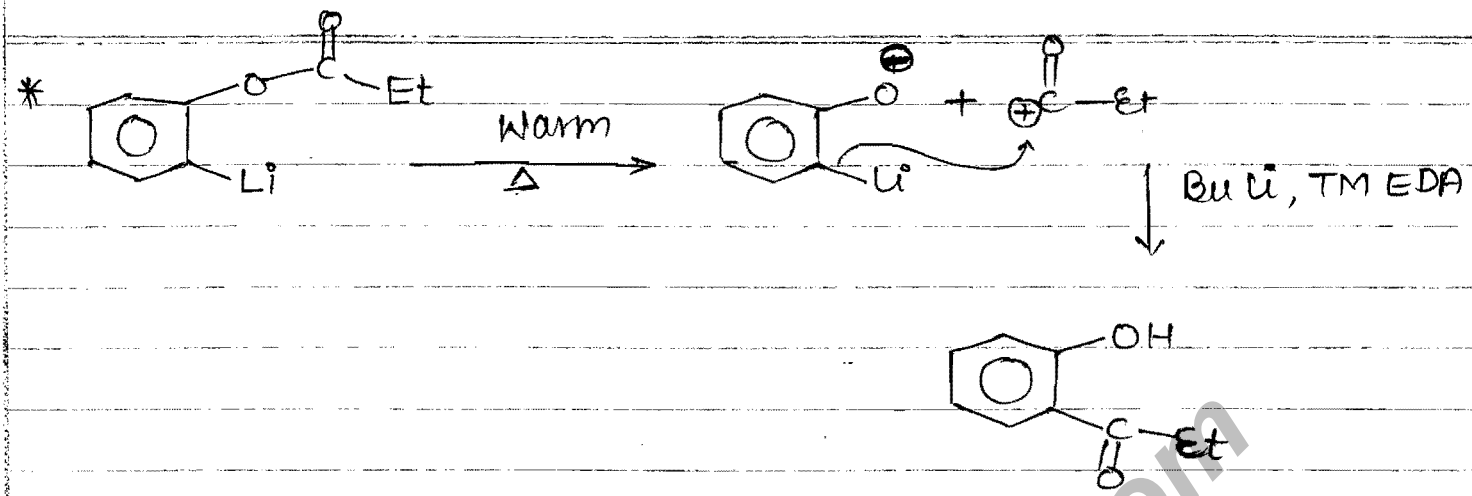




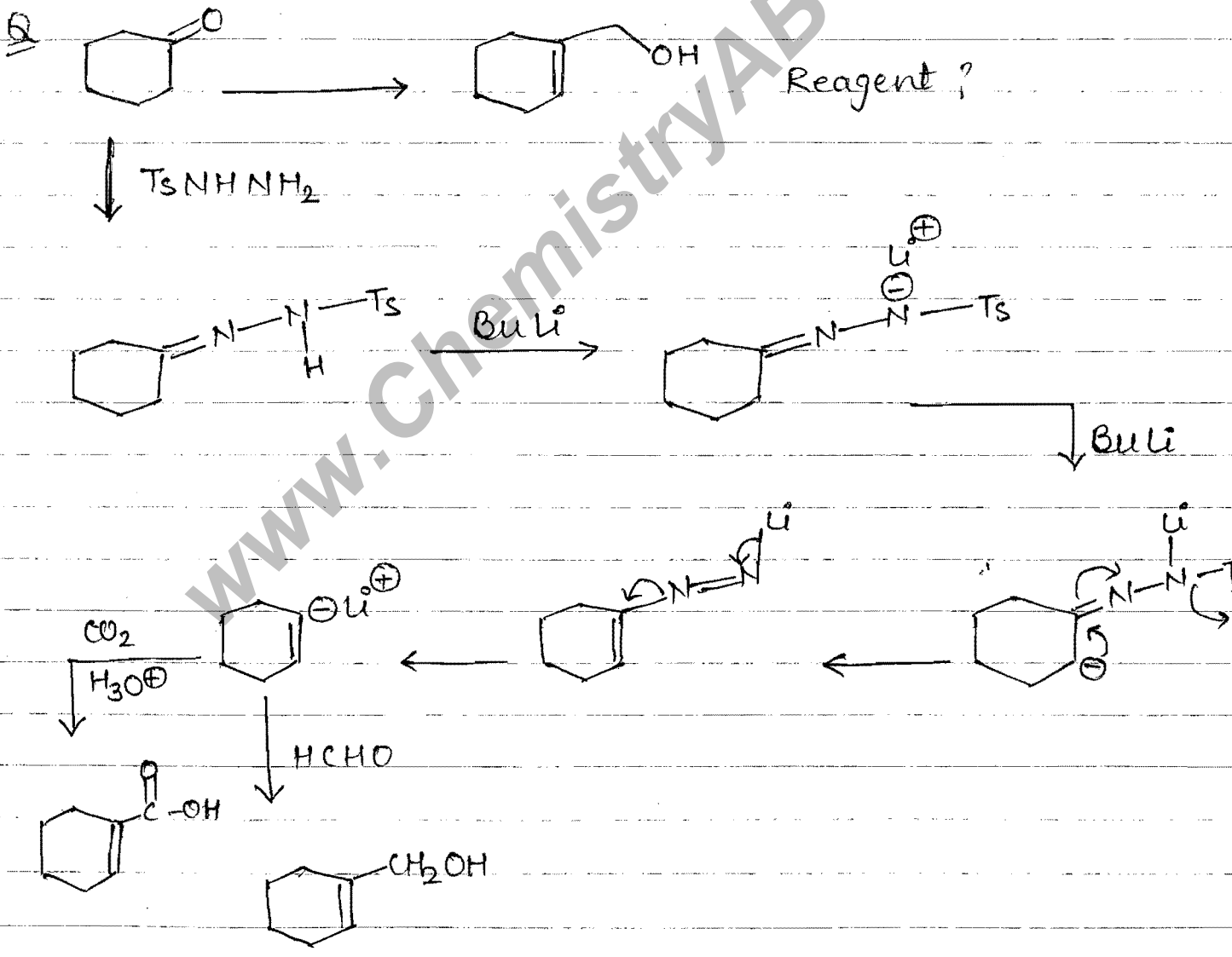
Q





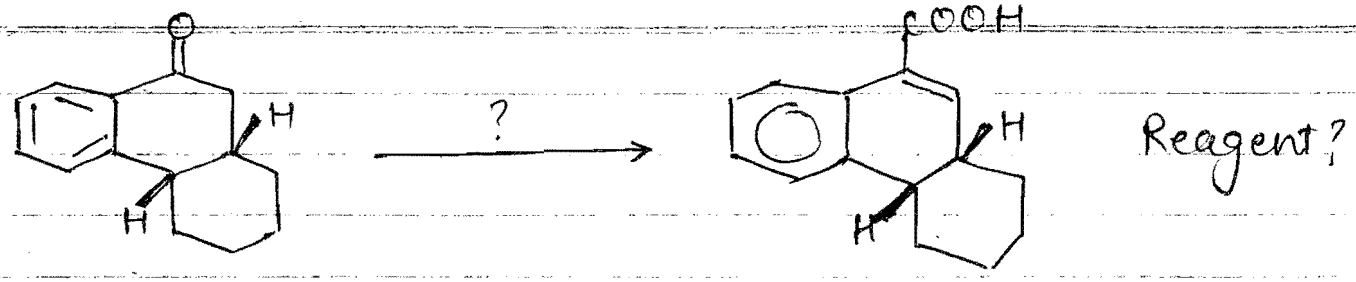


Use in Shapiro Rxn:-



NET 2014

Q



Reagent?

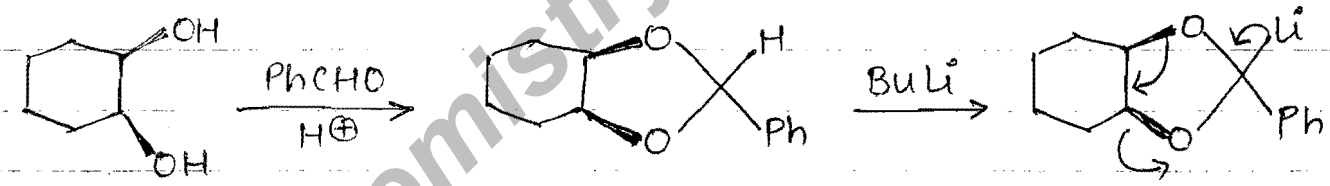
1) $TsNHNH_2$

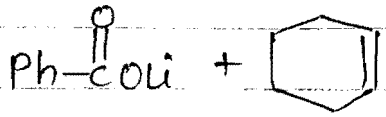
2) 2 eq. BuLi

3) CO_2

V. Imp.

Q





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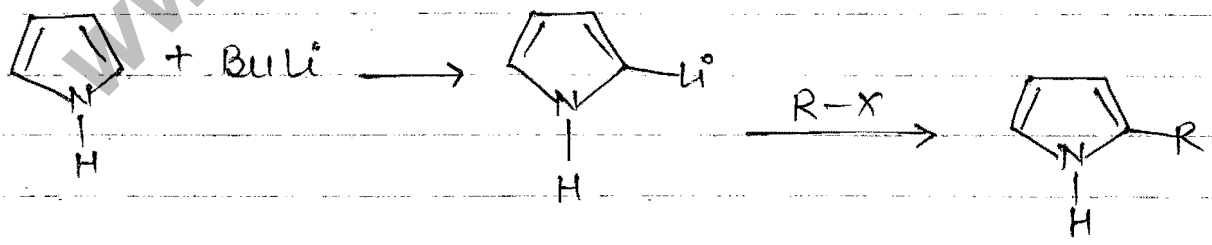


V.V.Imp.

HYDROGENOLYSIS

Bond cleavage by the hydrogen between carbon & more electronegative element in presence of catalyst is k/a hydrogenolysis. Hydrogenolysis is reductive cleavage.

$$C-Z \xrightarrow{\text{Catalyst}} \text{Hydrogenolysis } (CH + Z-H)$$

Hydrogenolysis

Imp. C–O | C–N | C–S | C–X | Imp. Cyclopropane C–C

Hydrogenolysis is a deprotection method.

Ex. $R-O-H \xrightarrow[Ph-CH_2-Br]{\text{Base}} R-O-CH_2-\bigcirc \xrightarrow{Pd/C/H_2} R-OH + \underset{Ph}{\overset{CH_3}{|}}$

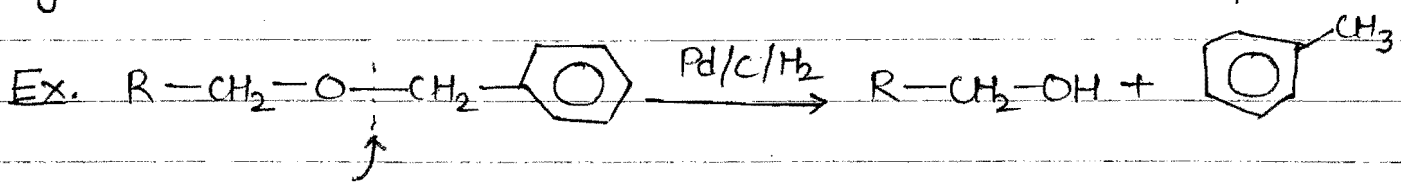
Hydrogenolysis of C–O bond

Imp. Ether | Ester | Alcohol | Imp. Carbomates

$R-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-Ph$ (Carbomate)

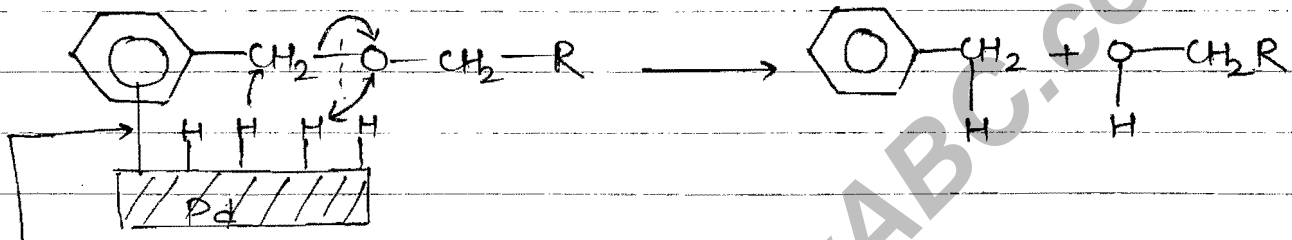
Hydrogenolysis of Ether:- Hydrogenolysis takes place via S_N2 mech. If benzyl gp tht in a comp. then hydrogenolysis take place easily.

Generally hydrogenolysis method used to remove benzyl group via deprotection method.

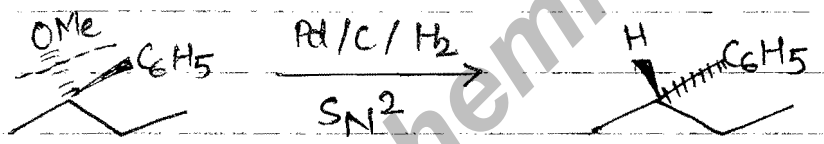
Ex. 

why this bond breaking.

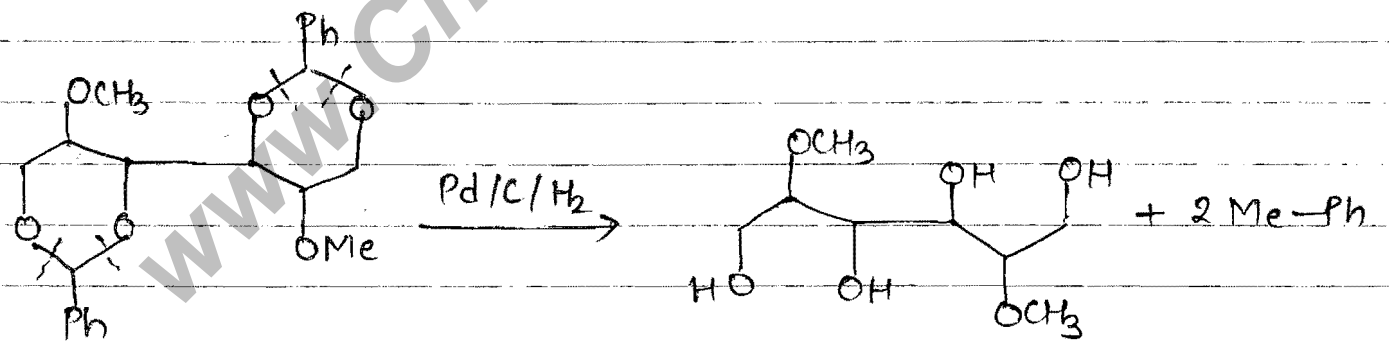
Explanation

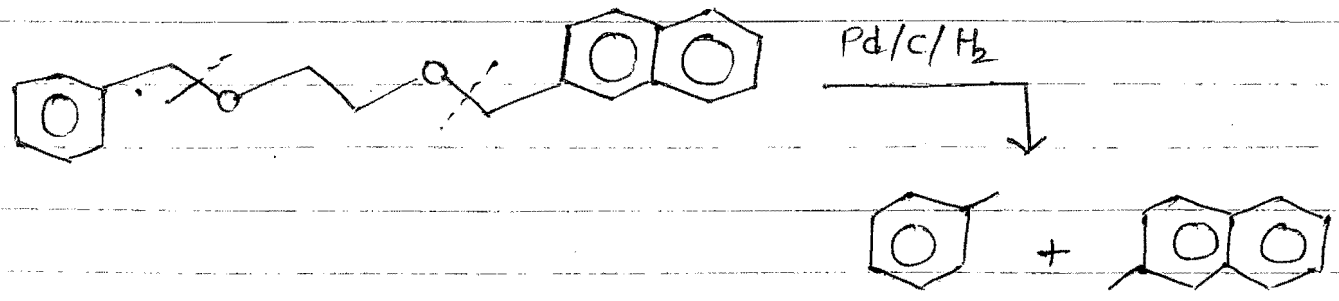


Electrostatic interaction b/w benzene & Pd/C

Q 

Stereo inverted.

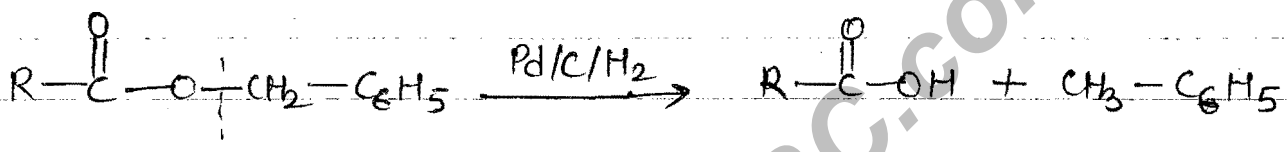
Q 

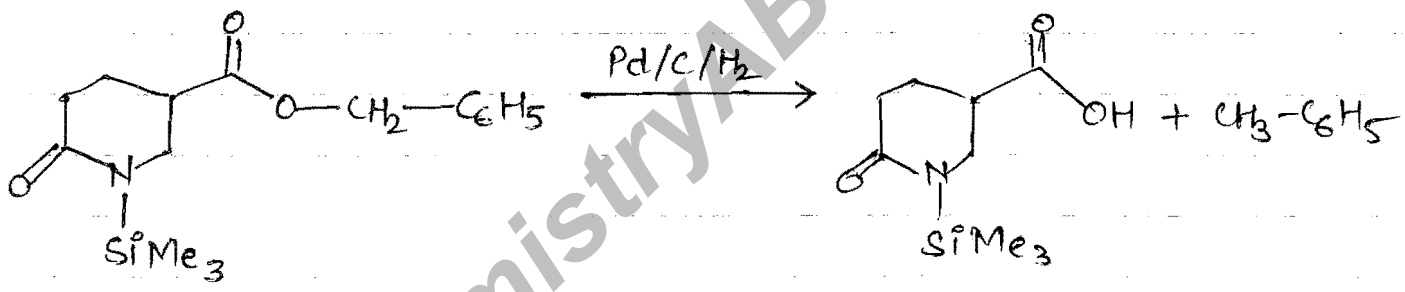
Q 

Hydrogenolysis of Allylic ether:-

In the case of allylic ether. Na & liq. NH_3 is used. because $Pd/C/H_2$ may be reduce C=C bond.

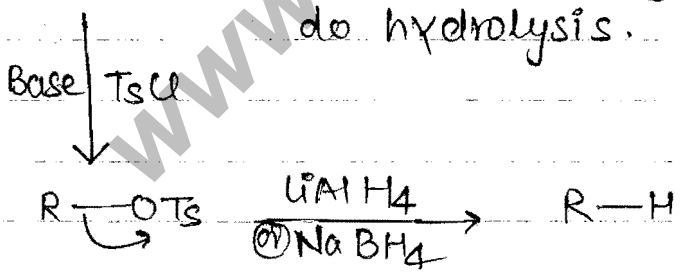
Hydrogenolysis of ester

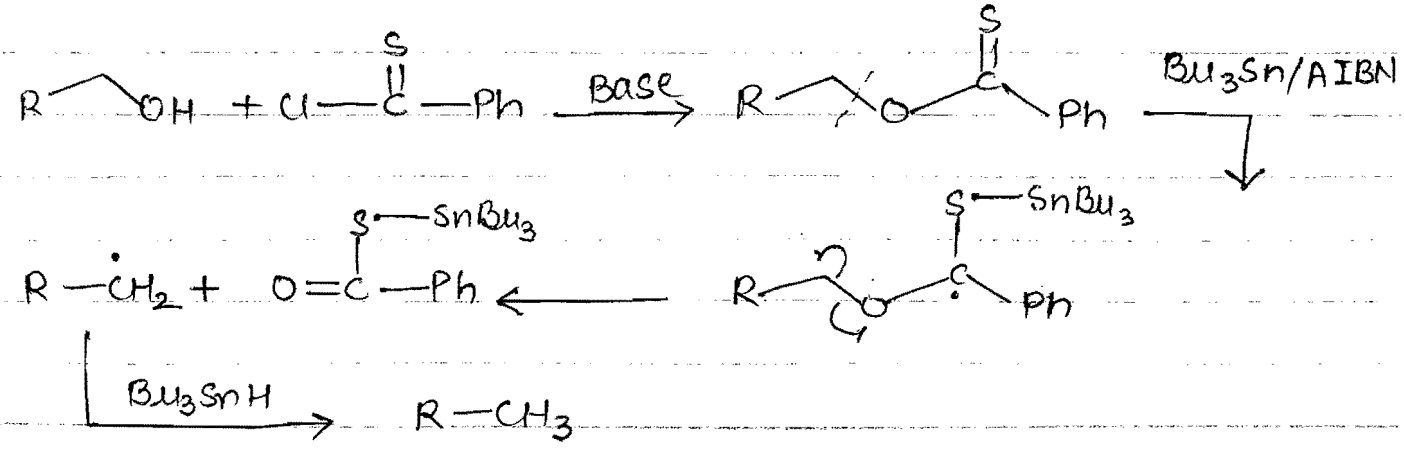
Q 

Q 

Hydrogenolysis of Alcohol:-

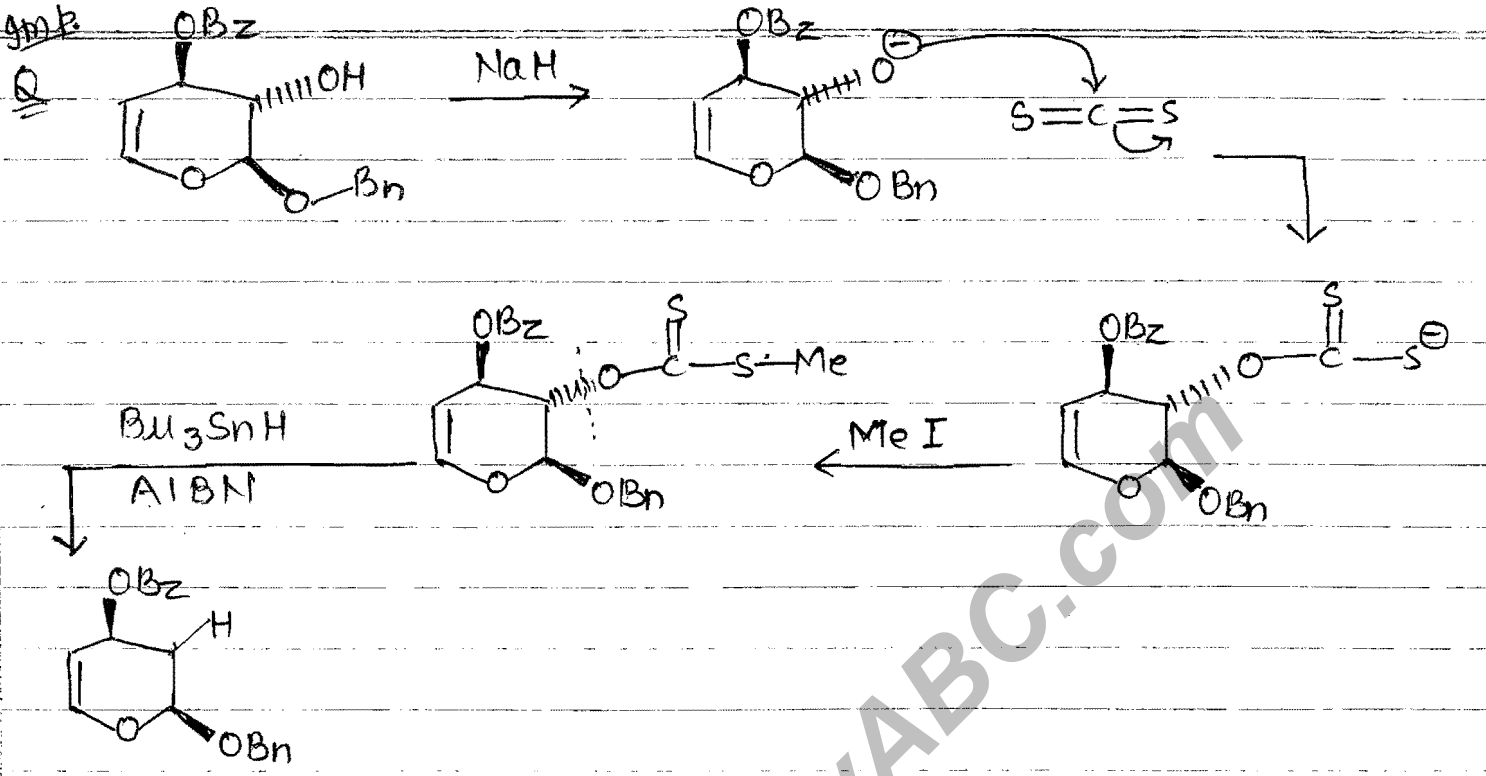
R—O—H No direct hydrolysis ; first of all make L.G. then do hydrolysis.



Q 

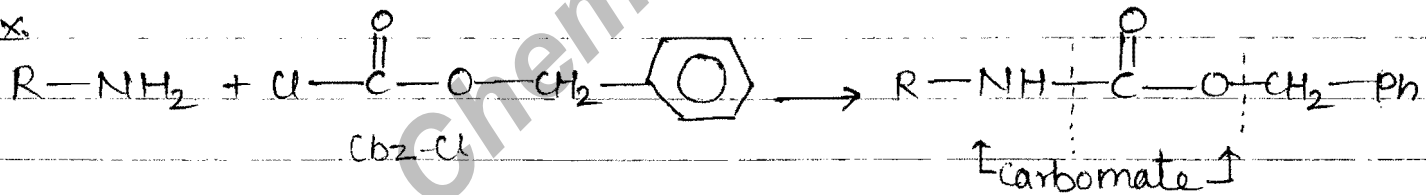
gmk

Q

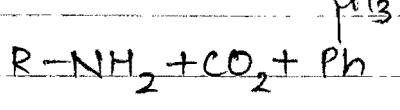


Hydrogenolysis of Carbomate:-

Ex.



$\xrightarrow{Pd/C/H_2}$



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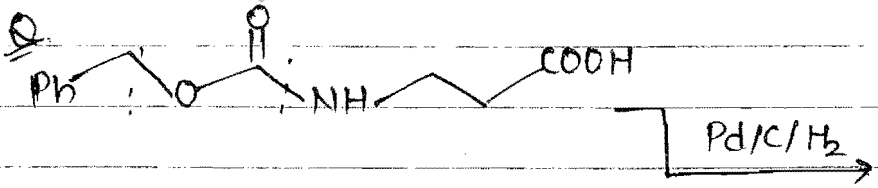
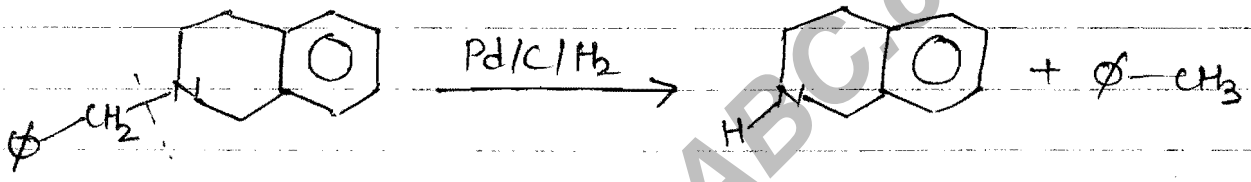


Hydrogenolysis of C—N Bond:-

The amine which are substituted with a benzyl group may be deprotected ~~via~~ by $Pd/C/H_2$ via Hydrogenolysis.

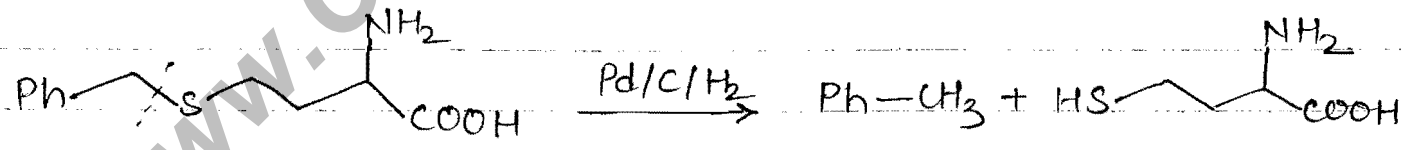
Ex. $C_6H_5-CH_2-N< \xrightarrow{Pd/C/H_2} C_6H_5-CH_3 + HN<$

$3° > 2° > 1°$

Q 

Q $C_6H_5-CH_2-\underset{\underset{Ph}{|}}{N}-CH_2-Ph \xrightarrow{Pd/C/H_2} 2\,Ph-CH_3 + H_2NPh$

Hydrogenolysis of C—S bond:-

Ex 

Hydrogenolysis of C—X bond:-

$R-X \xrightarrow{Bu_3SnH,\ AIBN} R-H$

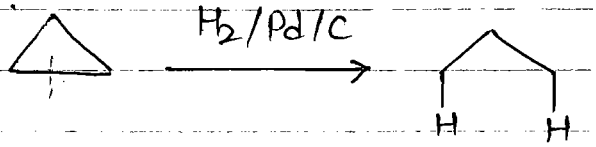
Rate of Hydrogenolysis.

C—X > C—O > C—S > C—N

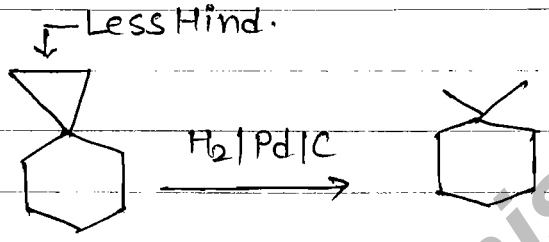
Hydrogenolysis of C—C bond ⇒ Cyclopropane Ring :-

In cyclopropane ring partially π-character are +nt, so in the +nce of Pd/C/H_2 hydrogenolysis take place becoz of ring strain. Least hindered bond will be break and gaminal dimethyl form

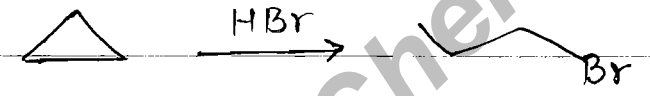
Ex.



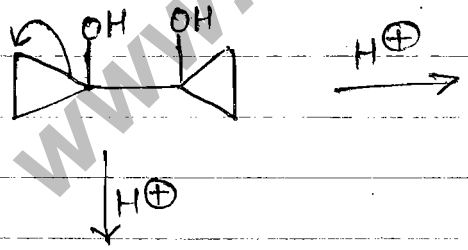
Ex.



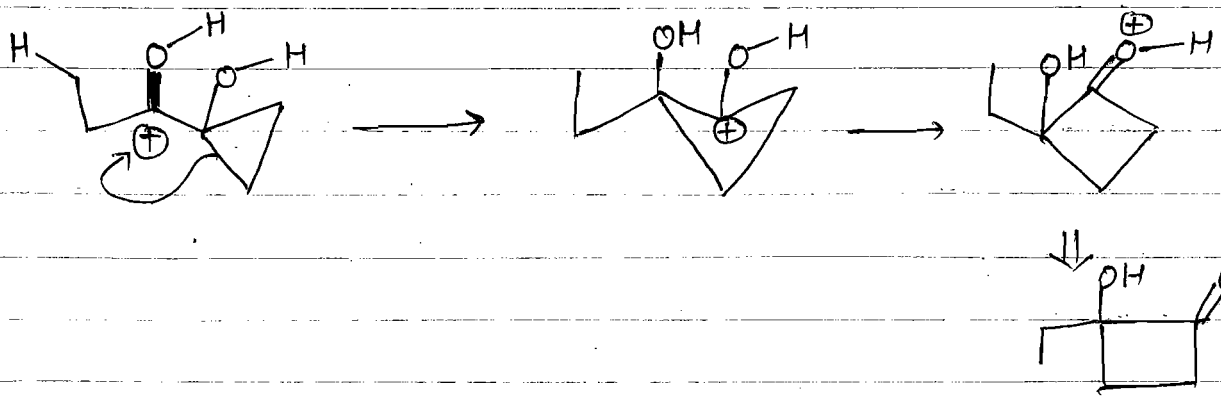
Ex.



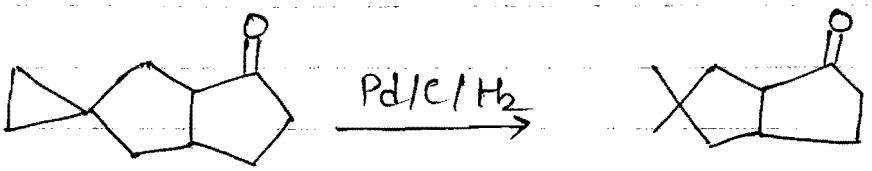
V.V.Imp 2014

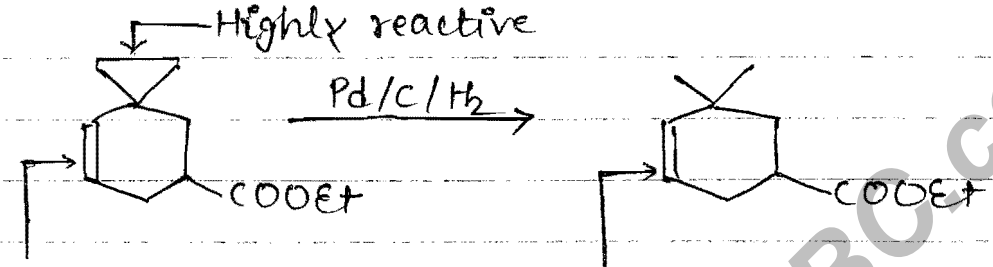


Not pinacol pinacol. becoz. cyclopropane ring is highly reactive, it react with $H^{\oplus}$.

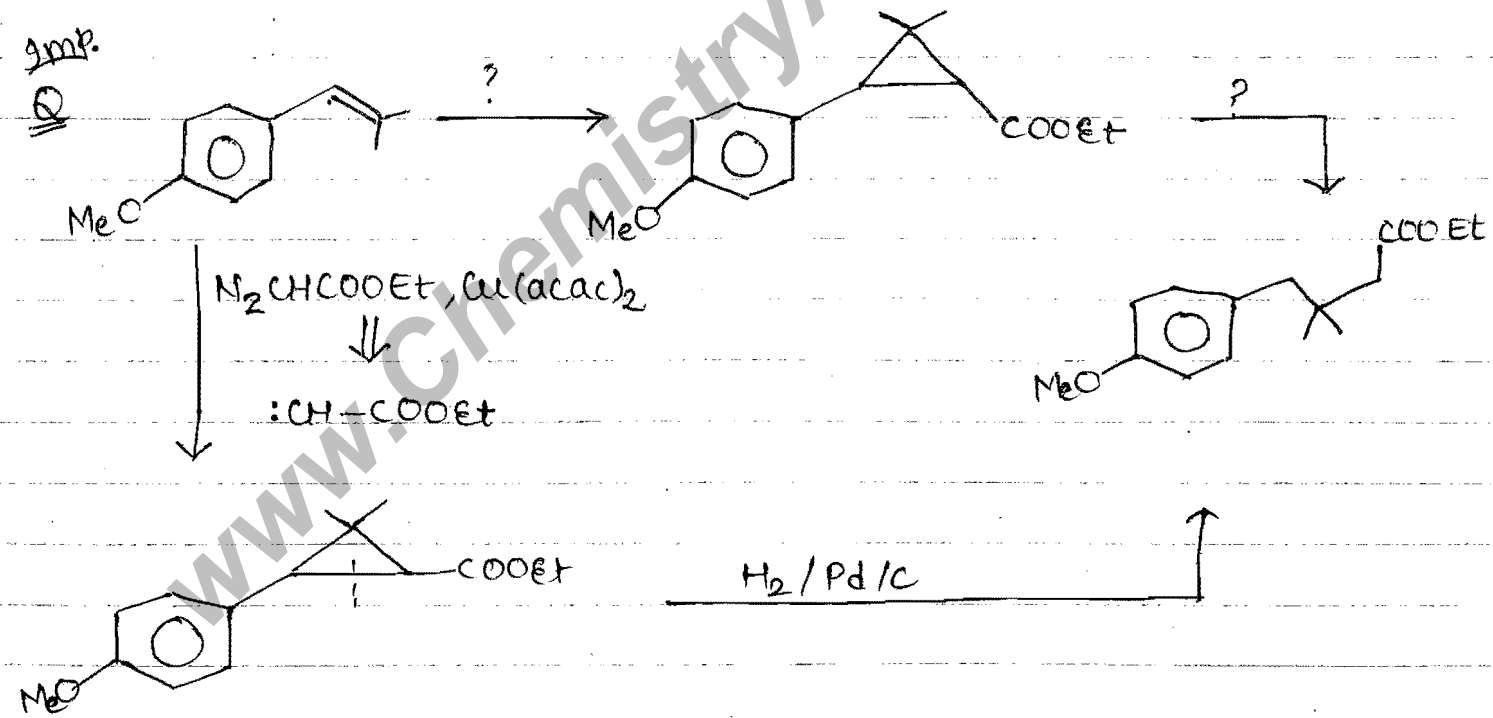


Hydrogendysis of cyclopropane ring take place very rapidly than C=C double bond.





Less reactive remain intact.

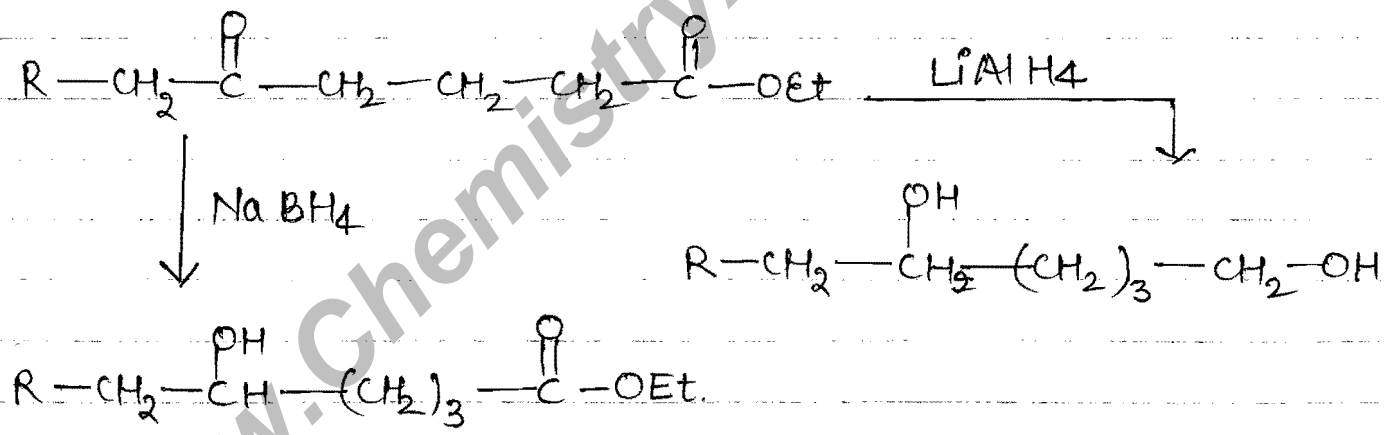


LITHIUM ALUMINIUM HYDRIDE

दारू का ठेकेदार ⇒ $LiAlH_4$

$LiAlH_4$ is a strong reducing agent, stored under anhydrous condition. In the ↑nce of moisture it becomes inactive, so always dry solvent used Normally protic polar solvent used. In $LiAlH_4$ Al—H bond is highly polar so $LiAlH_4$ is very reactive reagent. It is contractor of Alcohol.

Chemoselectivity of $LiAlH_4$:-



Functional Group	$LiAlH_4$	Product.
i) $R-\overset{O}{\overset{\|}{C}}-OR'$ (Ester)	⟶	$R-CH_2-OH + R'OH$ Alcohol.
ii) $R-\overset{O}{\overset{\|}{C}}-OH$ (Acid)	⟶	$R-CH_2-OH$ (Alcohol)
iii) $R-\overset{O}{\overset{\|}{C}}-R$ (carbonyl)	⟶	$R-\overset{OH}{\overset{\|}{C}}H-R$ (Alco.)
v. imp. iv) $R-\overset{O}{\overset{\|}{C}}-NHR$ (Amide)	⟶	$R-CH_2-NHR$ (Amine)

V. Imp.

v) $R-\underset{\underset{O}{\|}}{C}-NHR$ (Amide) $\xrightarrow[H_3O^{\oplus}]{LiAlH_4}$ RCHO (Carbonyl)

vi) $R-C\equiv N$ (Nitrile) $\xrightarrow{LiAlH_4}$ $R-CH_2-NH_2$ (Amine)

vii) $R-CH_2-NO_2$ (Nitro) $\xrightarrow{\quad " \quad}$ $R-CH_2-NH_2$ (Amine)

V. Imp.

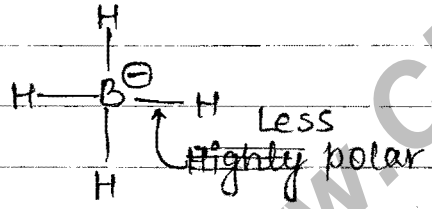
viii) $Ph-NO_2$ (Aromatic Nitro) $\xrightarrow{\quad " \quad}$ $Ph-N=N-Ph$

ix) $R-X$ (X = Halogen, OTs) $\xrightarrow{\quad " \quad}$ $R-H$

x) $R-N_3$ (Azide) $\xrightarrow{\quad " \quad}$ $R-NH_2$

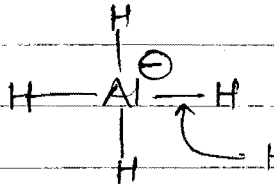
xi) Epoxide $\xrightarrow{\quad " \quad}$ Alcohol.

$\Rightarrow$ $NaBH_4$ ⇓



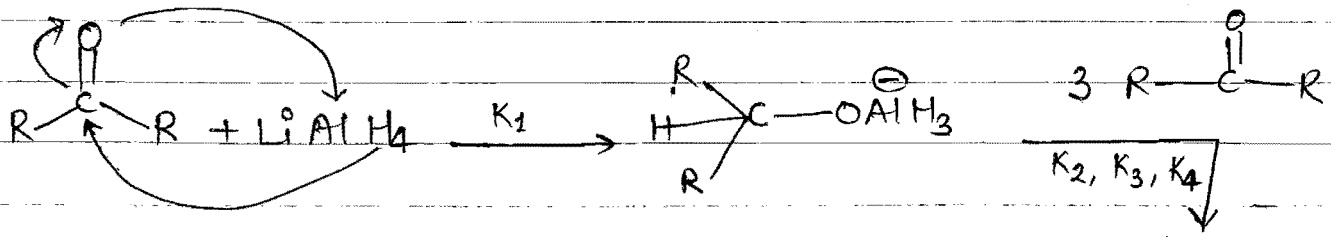
Less ~~Highly~~ polar

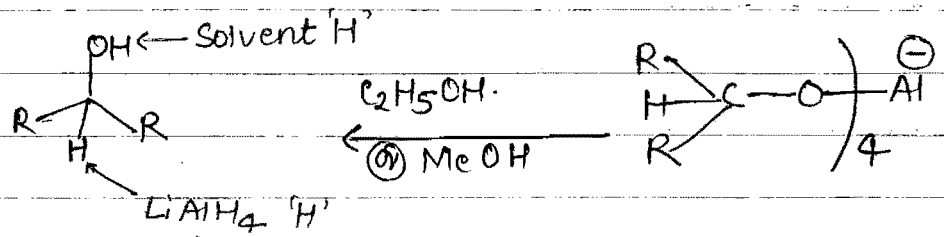
$LiAlH_4$ ⇓



Highly polar

Reduction of Carbonyl Compounds:-



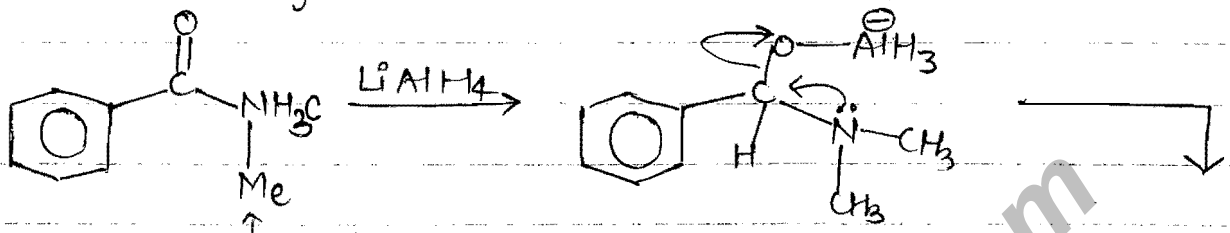


Rate constant order:- $k_1 > k_2 > k_3 > k_4$

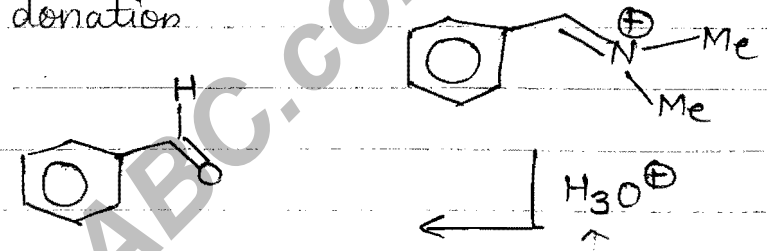
v. imp:

Reduction of Substituted Amide by $LiAlH_4$:-

Ex.

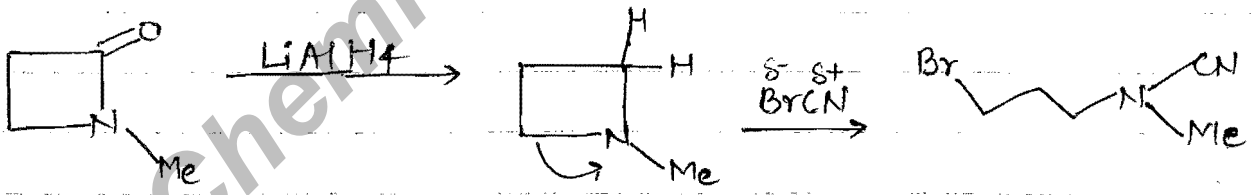


Methyl gps increasing the l.p. donation tendency of 'N'



In the +nce of H_2O, $LiAlH_4$ become inactive.

2014 Q.



v. imp:

⇒ $LiAlH_4$ (LAH) doesn't reduce C=C or C≡C bonds

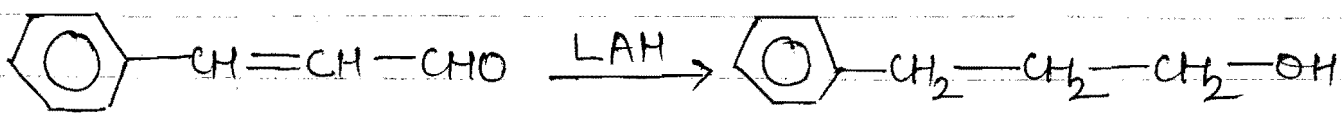
Ex. $CH_3-CH=CH-\underset{\underset{O}{\|}}{C}-H \xrightarrow{LAH} CH_3-CH=CH-CH_2-OH$

Ex. $CH_3-CH=CH-\underset{\underset{O}{\|}}{C}-R \xrightarrow{"} CH_3-CH=CH-\underset{\underset{OH}{|}}{CH}-R$

Ex. $R-C\equiv C-CHO \xrightarrow{"} R-C\equiv C-CH_2-OH$

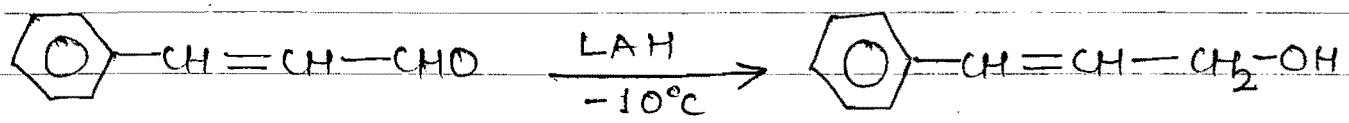
But $LiAlH_4$ reduce C=C bond in following cases -

v. imp

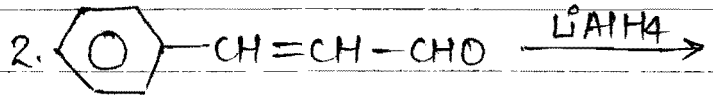


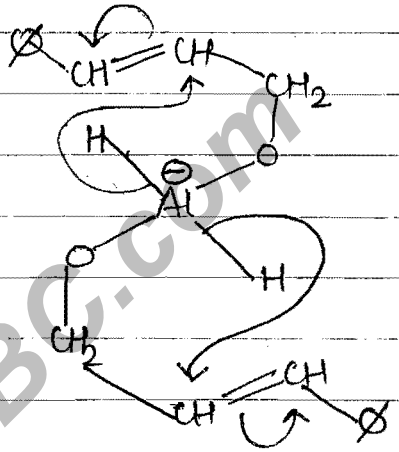
but at low temp. no reduction of C=C bond.

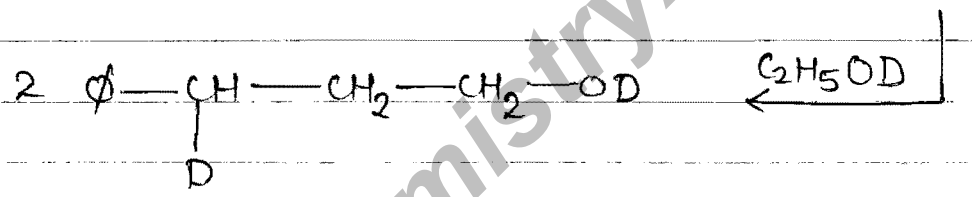
Ex.

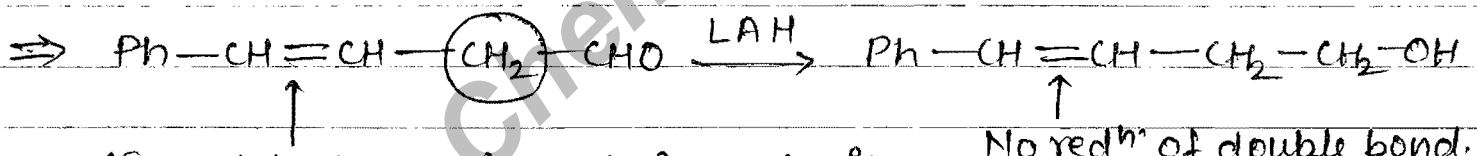


Mechanism

2. 



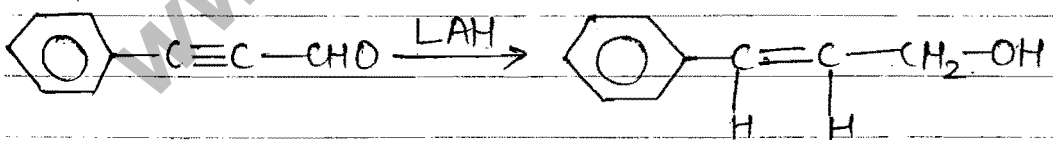




If double bond is not in conj with >C=O

No redⁿ of double bond.

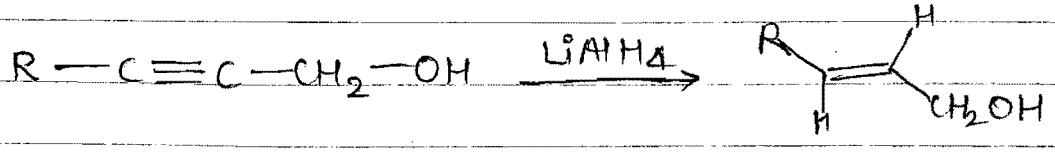
V. Imp.



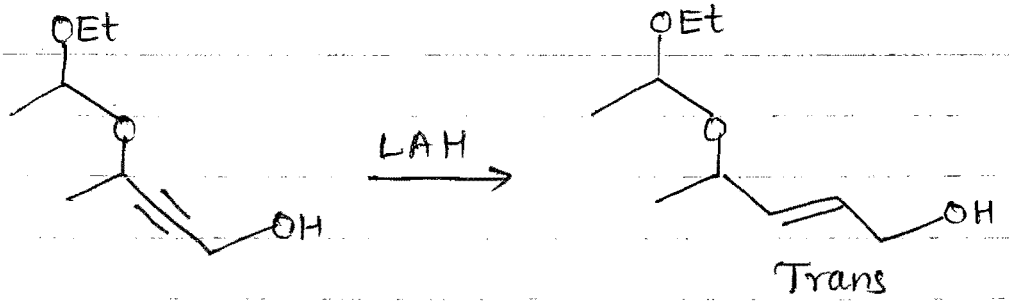
At low temp. no redⁿ of double or tripple bond.

V. V. Imp.

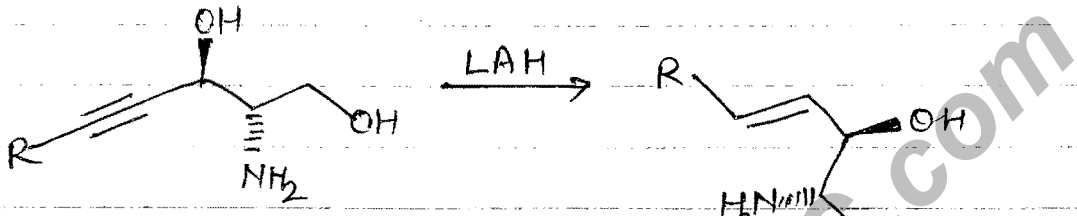
In the case of proparglic alco. LAH redue C≡C bond into trans Alkene.

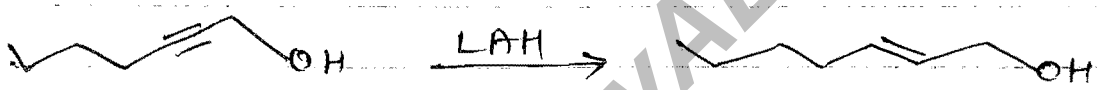


Trans

Q 

Trans

Q 

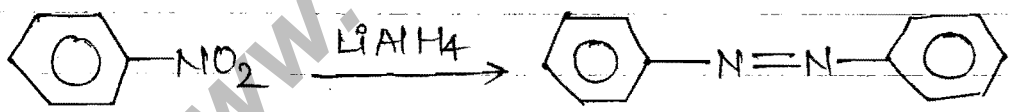
Q 

trans

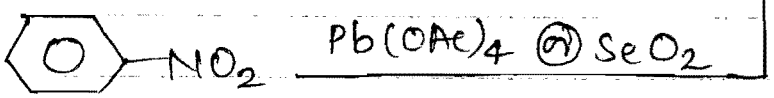
Redⁿ of Nitro comp by LAH:

$R-NO_2 \xrightarrow{LiAlH_4} R-NH_2$

↳ Aliphatic

* 

Zn/MeOH/$\overset{\ominus}{O}H$



V. Imp.

Derivative of $LiAlH_4$

$LiAlH_4$ + 3 eq. ^tBuOH ⟶ $LiAlH(O\,Bu^t)_3$

Strong reducing agent

Litheum tri tert. Butoxy Aluminium hydride.

mild reducing agent

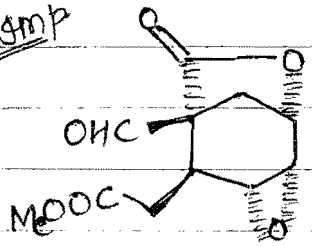
$RCHO + LiAlH(OBu^t)_3 \longrightarrow R-CH_2-OH$

$R-CO-R + \text{''} \longrightarrow R-\underset{OH}{CH}-R$

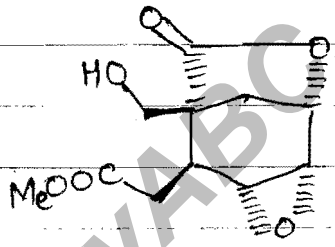
R–COOH, RCOOEt, epoxide ⟶ Very slow Reduction.

R–X, R–C≡N, $R-NO_2$ ⟶ No Reaction.

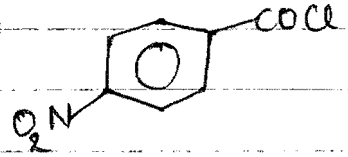
M. imp

Q 

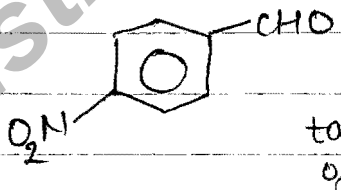
$LiAlH(OBu^t)_3$



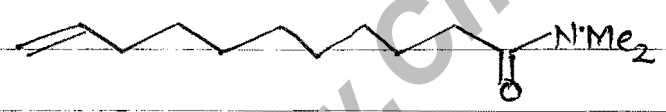
M. imp.

Q 

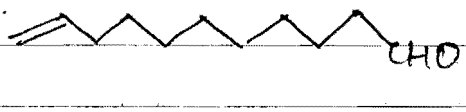
''



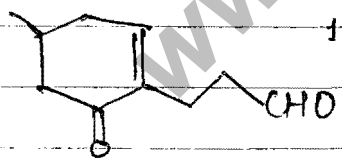
Further rxn. doesn't take place due to lack of Hydrogen of LAH.

Q 

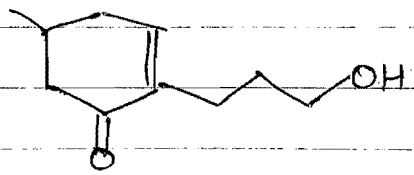
$LiAlH(OEt)_3$, $H_3O^{\oplus}$



V. imp.

Q 

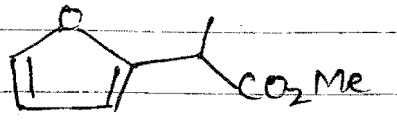
1 eq. $LiAlH(OBu^t)_3$



Q $R-CH_2-COOR \xrightarrow{LAH} R-CH_2-CH_2-OH + ROH$

Q 

LAH ⟶ $2\,R-CH_2-OH$

Q 

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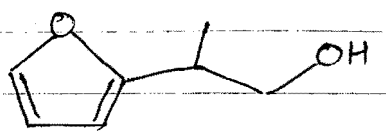
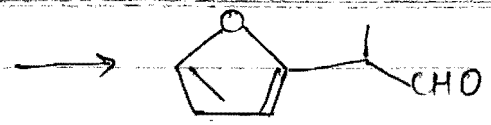
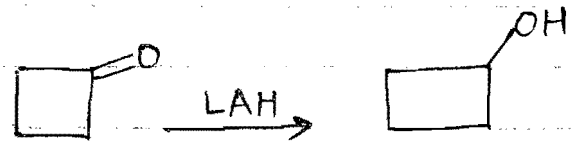
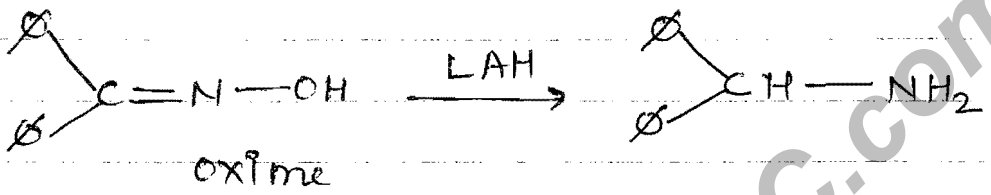


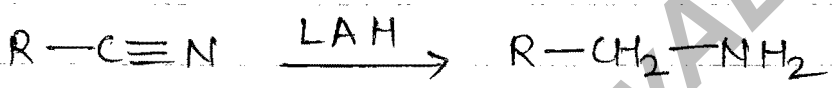
Cr(VI), [O]



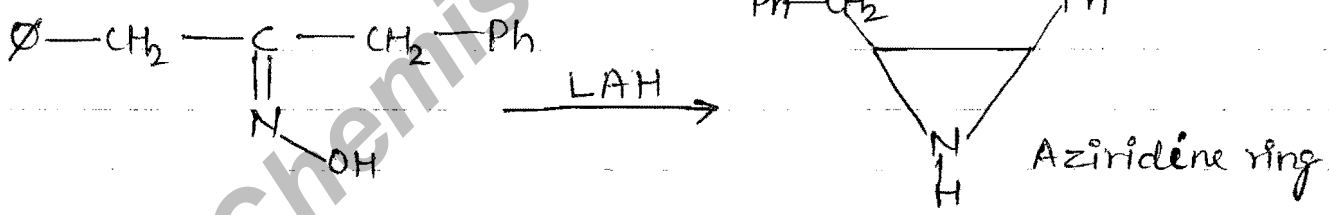
Q 

V. Imp.

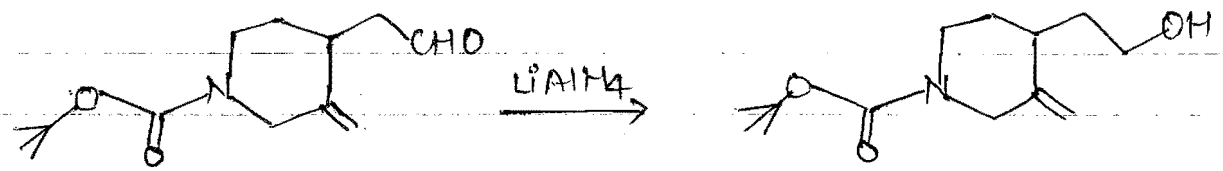
Q 

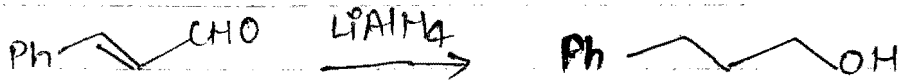
Q 

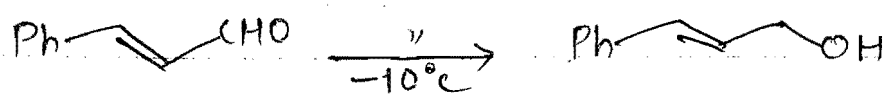
V. V. Imp

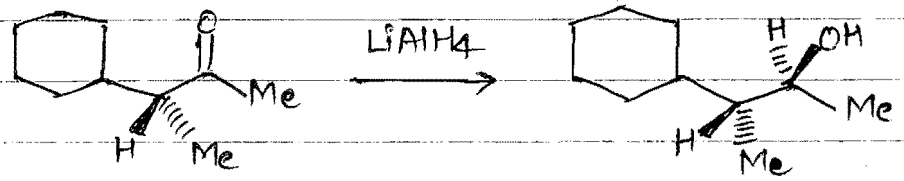
Q 

Mech.

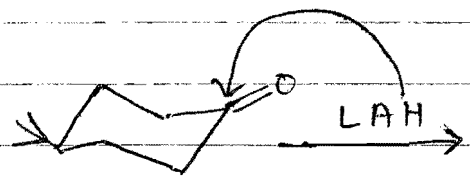
Q 

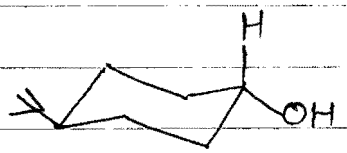
Q 

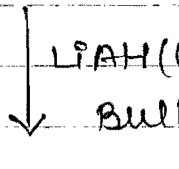
Q 

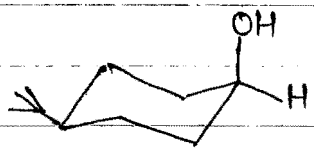
Q 

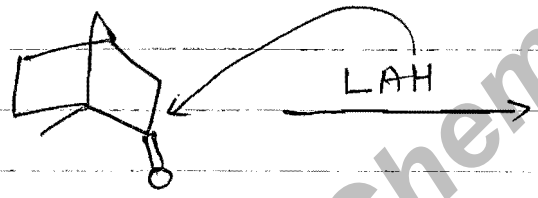
Cram's Rule

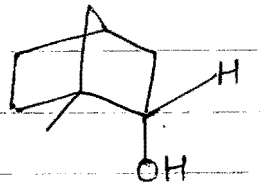
Imp. Q 

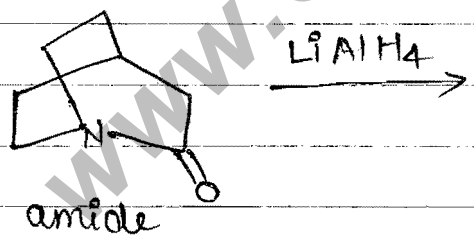


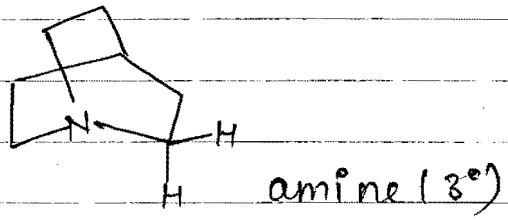


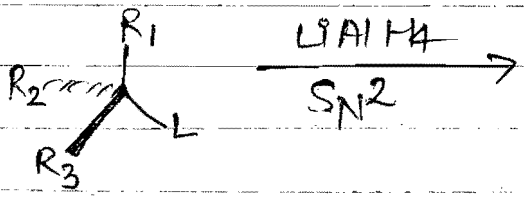


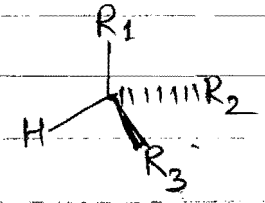
Q 

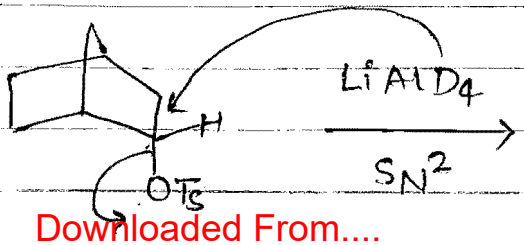


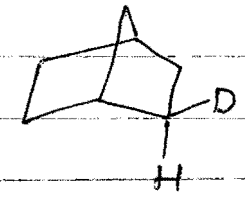
V. Imp. Q 



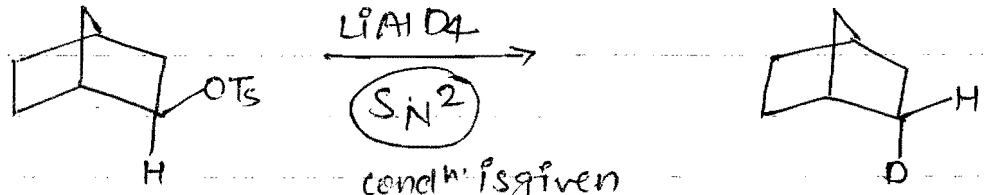
Q 



Q 

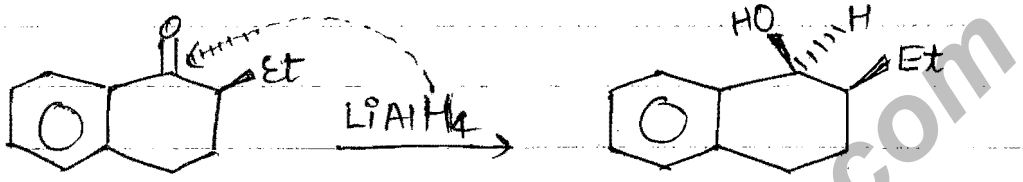


Q

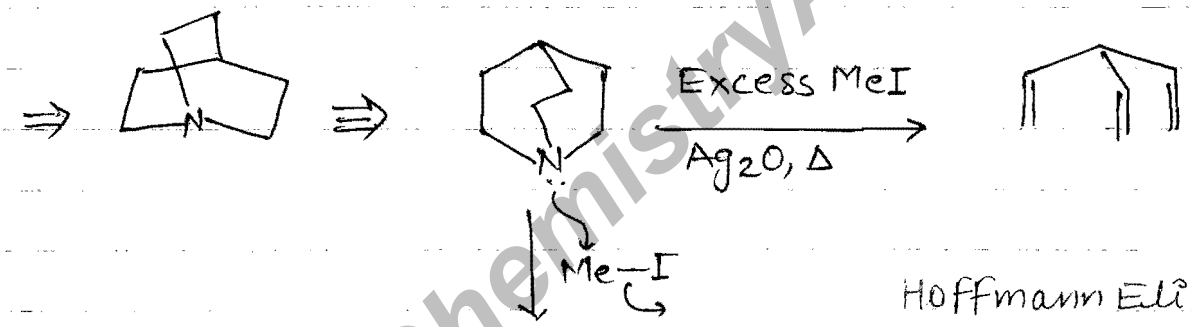


condⁿ is given
so don't use NGP

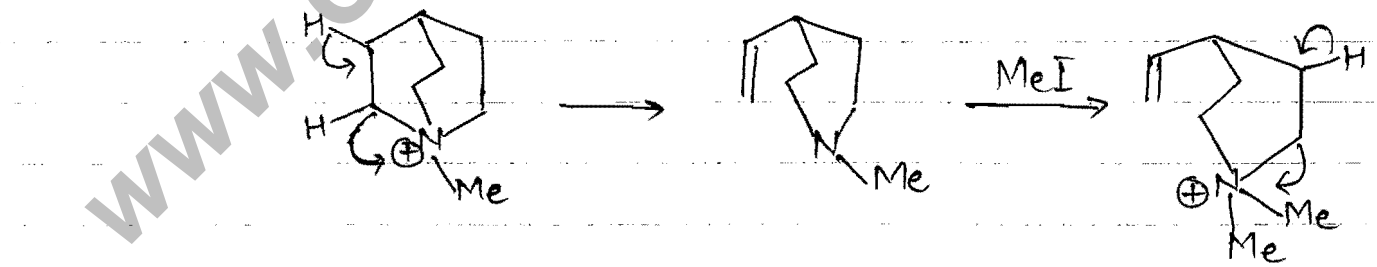
V. Imp.
Q

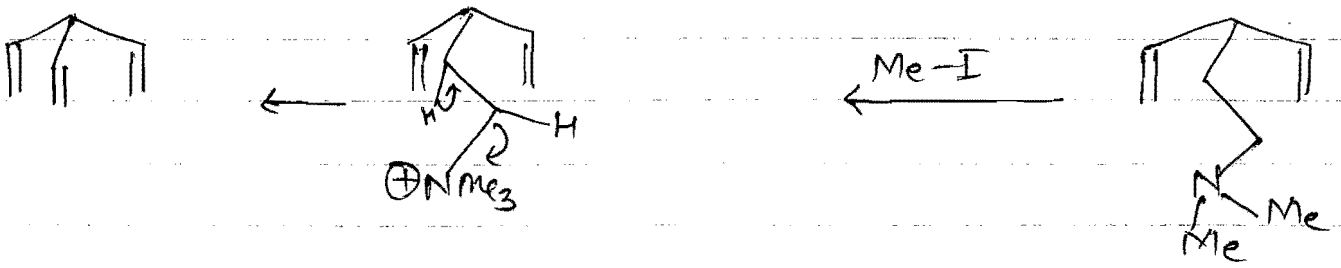


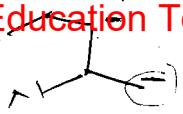
i) Rxn. is distereoselective
ii) $LiAlH_4$ attack from Re facial.



Hoffmann Elimination.

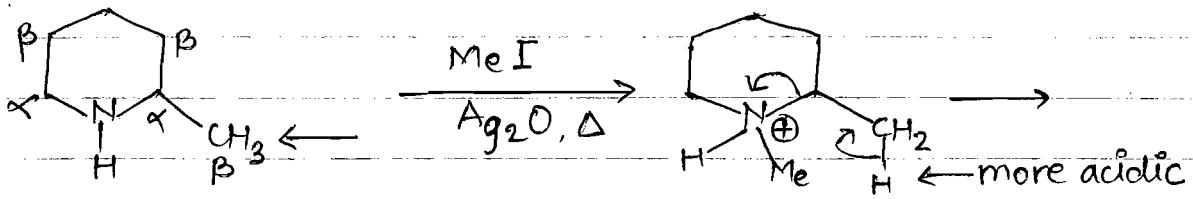






V. V. Imp.

When L.G. is $-\overset{\oplus}{N}R_3$ then more acidic β-proton is removed.



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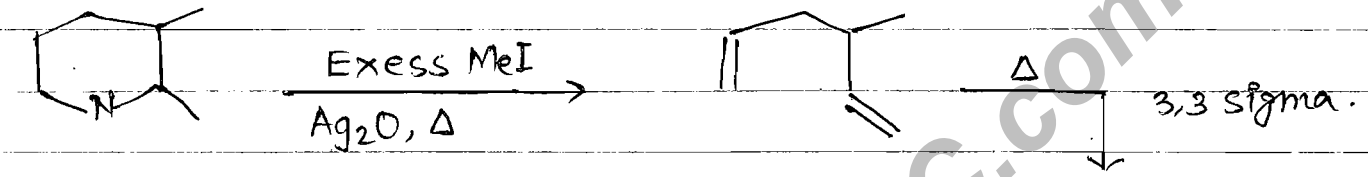

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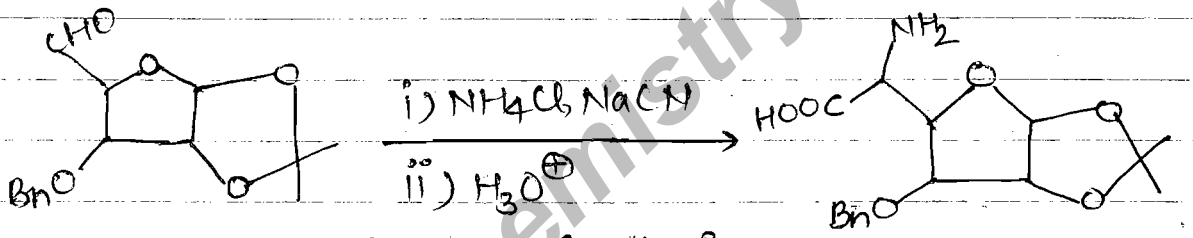
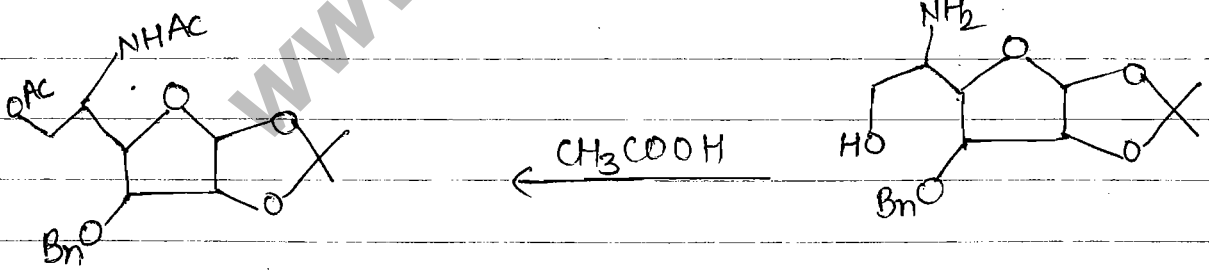


Stracker Synthesis of Amino acid

i) $LiAlH_4$
ii) CH_3COOH



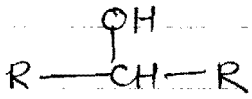
SODIUM BORO HYDRIDE ⇒ $NaBH_4$

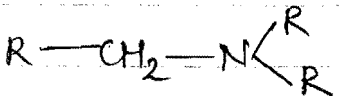
$NaBH_4$ is a reducing agent. Normally polar protic solvent ($EtOH$, $MeOH$) used. B–H bond is less polar.

Chemoselectivity of $NaBH_4$:-

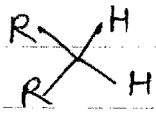
Functional Group. $\xrightarrow{NaBH_4}$ Product

1) $R-CHO \longrightarrow R-CH_2-OH$

2) $R-CO-R \longrightarrow$ 

imp. 3)  (iminium ion) $\longrightarrow$ 

4) $R-CH=N-R \longrightarrow R-CH_2-NHR$

imp. 5) $R_2C=N-NH-Ts \longrightarrow$  alkane

Tosyl hydrozone

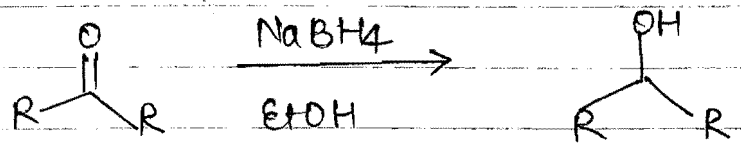
6) Ozonide $\longrightarrow$ Alcohol

7) $R-N_3 \longrightarrow R-NH_2$ (Amine)

8) $R\overset{+}{N_2}\,\overset{-}{B}F_4 \longrightarrow R-H$

Alkyl diazzonium boro fluorate

Reduction of Carbonyl comp. by $NaBH_4$:-

Ex. 

$K_1 > K_2 > K_3 > K_4$

$NaBH_4$ doesn't reduce C=C, C≡C bond

Ex. $CH_3-CH=CH-CHO \xrightarrow{NaBH_4} CH_3-CH=CH-CH_2-OH$

Ex. $Ph-CH=CH-CHO \xrightarrow{\quad " \quad} Ph-CH=CH-CH_2-OH$

Derivative of $NaBH_4$

$NaBH_4 \xrightarrow{3CH_3COOH} NaBH(OAc)_3$

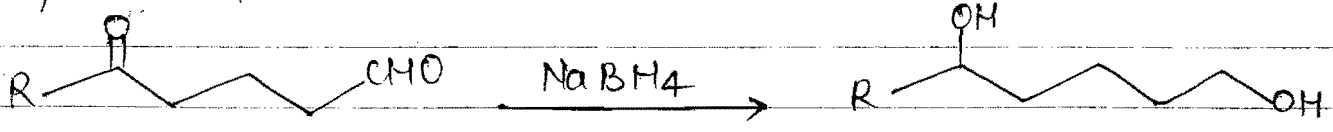
Triacetoxy sodium borohydride

Mild reducing agent.

$NaBH_3CN$

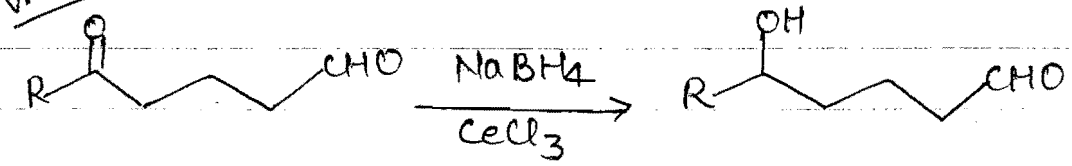
Cyno sod. borohydride

Redⁿ. of Ketonic Group in the +nce of Ald. gp. by $NaBH_4$:-



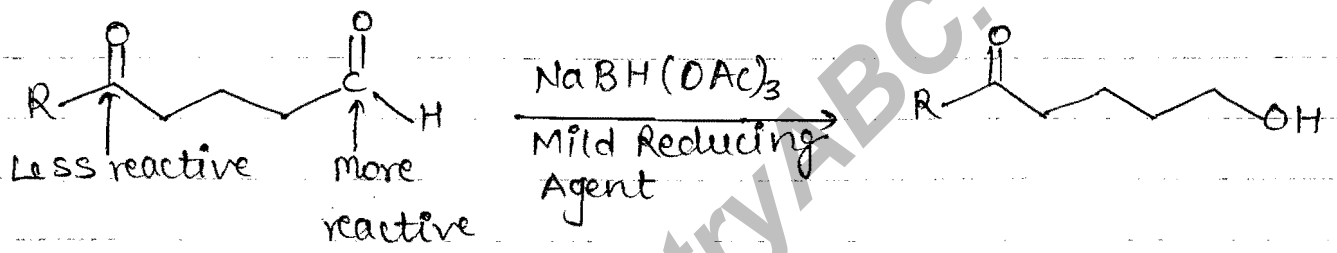
Selectivity ketonic gp. can be reduced by $NaBH_4$ in +nce of $CeCl_3$, becoz in the +nce of $CeCl_3$, carbon of ketonic gp. electrophilicity increases. This reduction ~~in~~ is K/a Luche's reduction.

V.V. Imp.

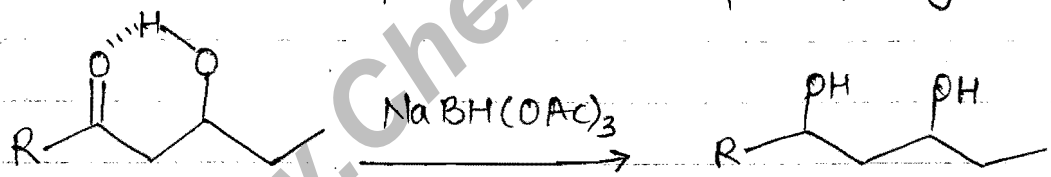


Reduction of Ald. group in the +nce of Ketonic gp:-

triacetoxy sod. boro hidride [$NaBH(OAc)_3$] reduced selectively ald. gp. in the +nce of Ketonic group.

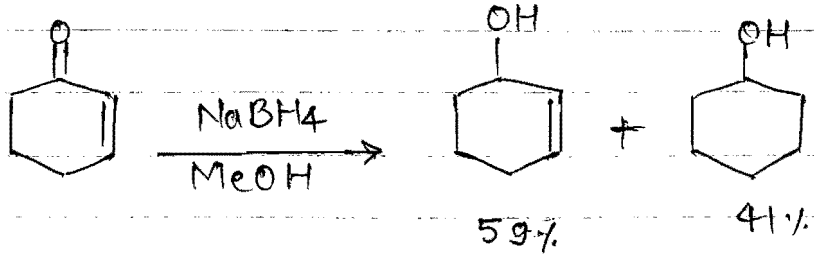


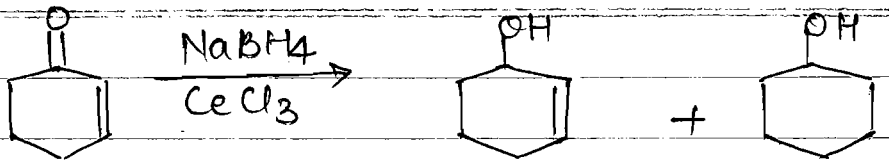
α & β hydroxy Ketone reduced by $NaBH(OAc)_3$ becoz electrophilicity increases by Hydrogen bonding.



* $NaBH_4$ gives 1,2 add^n. rather than 1,4 add^n.
* Mix. of pdt form (direct + Michael) but direct add^n. is major product.
* In the +nce of $CeCl_3$, direct add^n product yield can be increased.

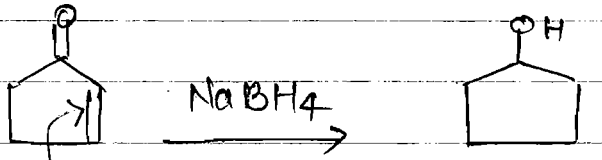
V.V. Imp.





99 % 1 %

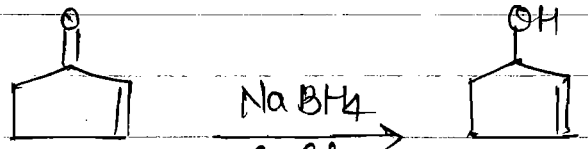
V.V. imp



ring strain

i.e. why C=C reduced.

100 %

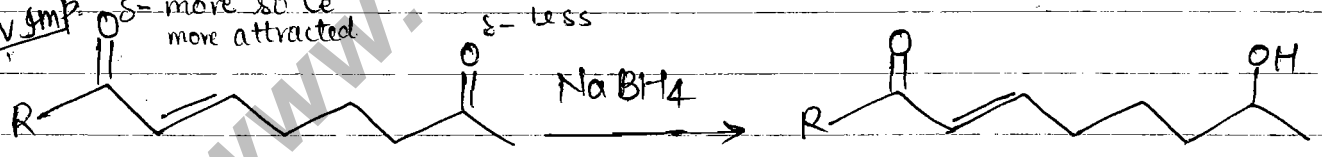


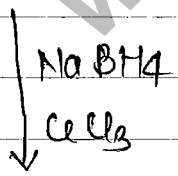
97 %

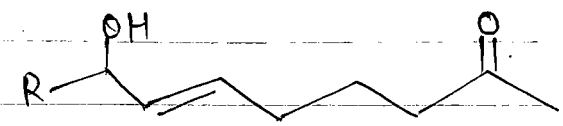
If in a comp. 2 type of carbonyl +nt, one is conjugate and another is non conj, then $NaBH_4$ reduce non conjugate carbonyl.

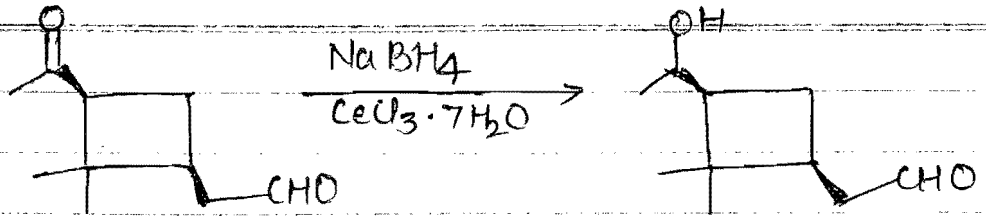
But in the +nce of $CeCl_3$ ~~non~~ conjugate >=O reduced.

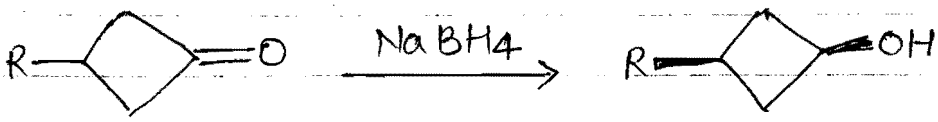
V.V imp. δ- more so Ce^{III} more attracted δ- less

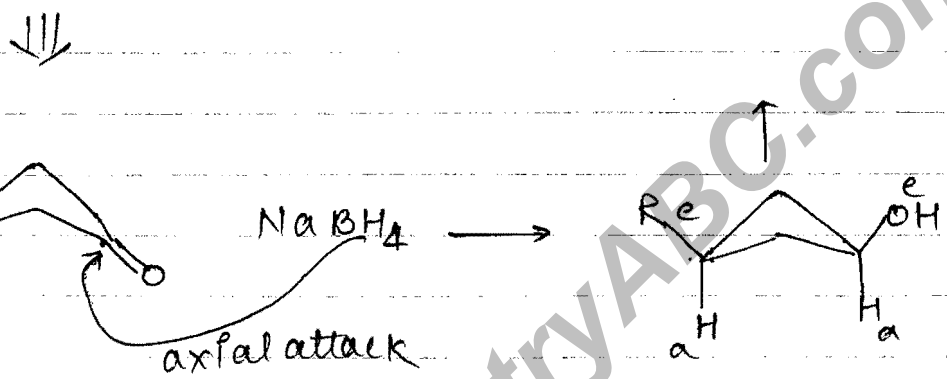


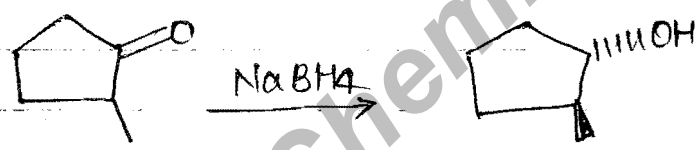


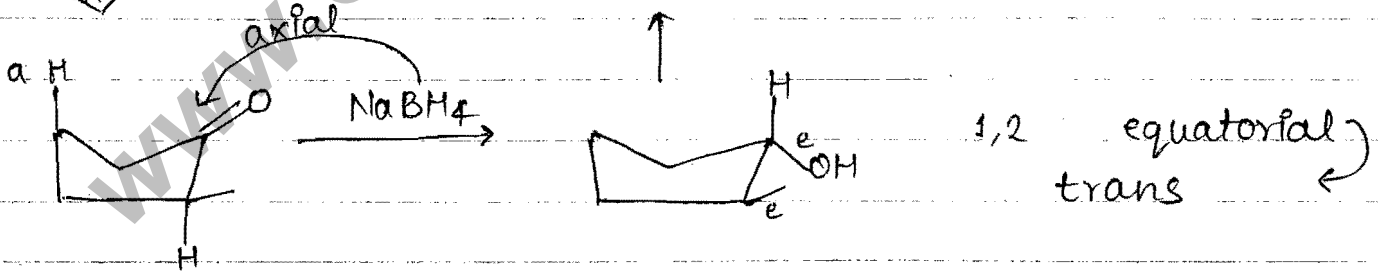


Q 

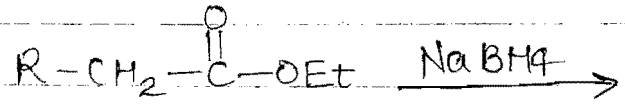
Q 



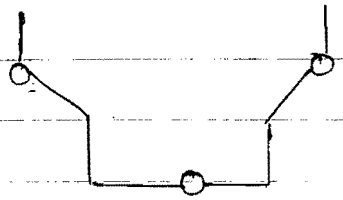
Q 



⇒ $NaBH_4$ doesn't reduce ester



but $NaBH_4$ reduce ester group in the +nce of LiCl in diglyne or in the +nce of I_2



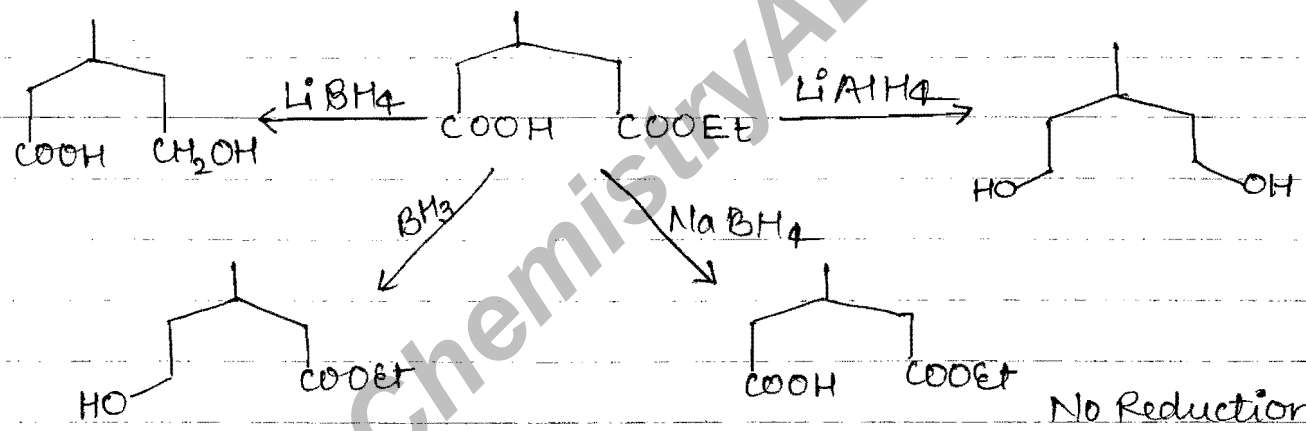
Diglyme

$$R-CH_2-COOEt \xrightarrow[\text{(or) } NaBH_4/I_2]{NaBH_4, LiCl, diglyme} R-CH_2-CH_2OH$$

V.V.Imp.

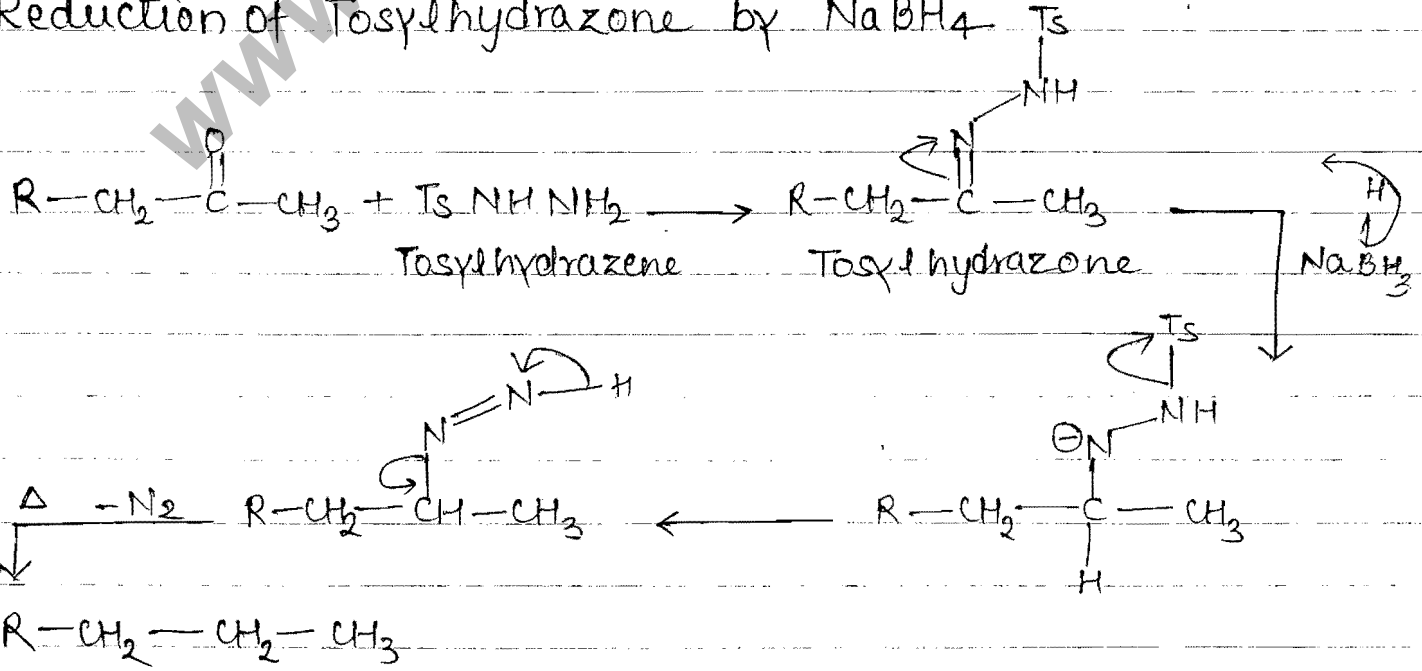
$LiBH_4$ also reduce ester group.

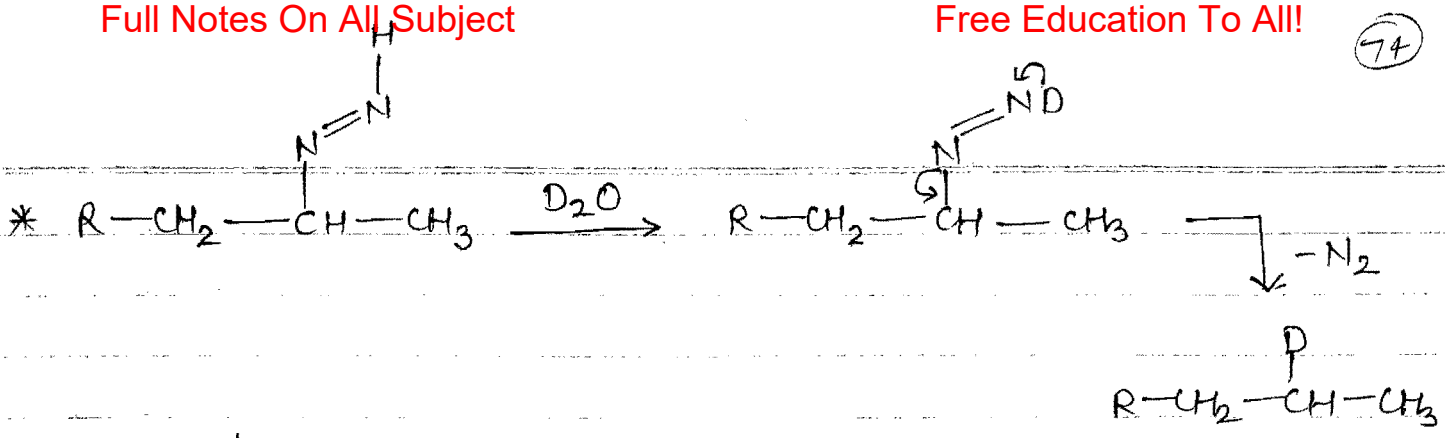
$$R-CH_2-COOEt \xrightarrow{LiBH_4} R-CH_2-CH_2-OH.$$



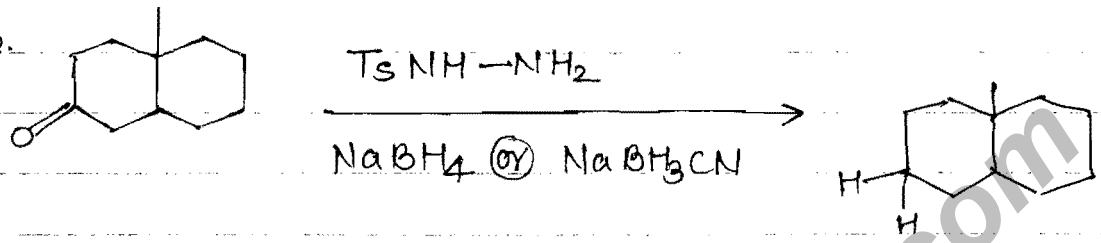
No Reduction.

Reduction of Tosylhydrazone by $NaBH_4$



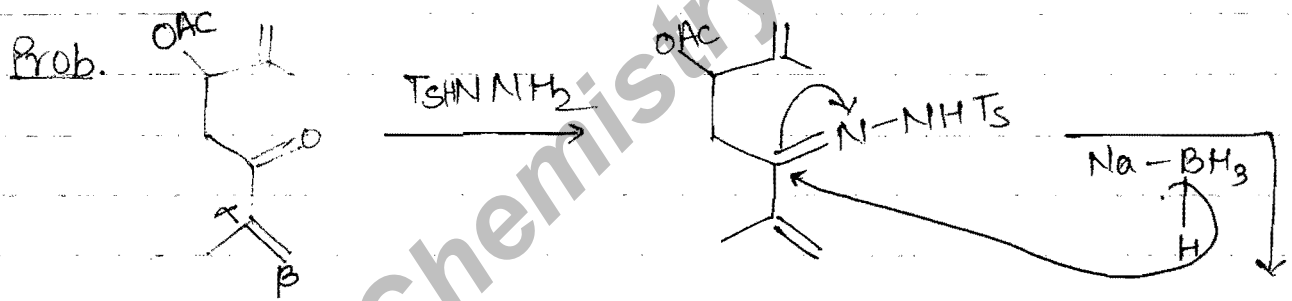


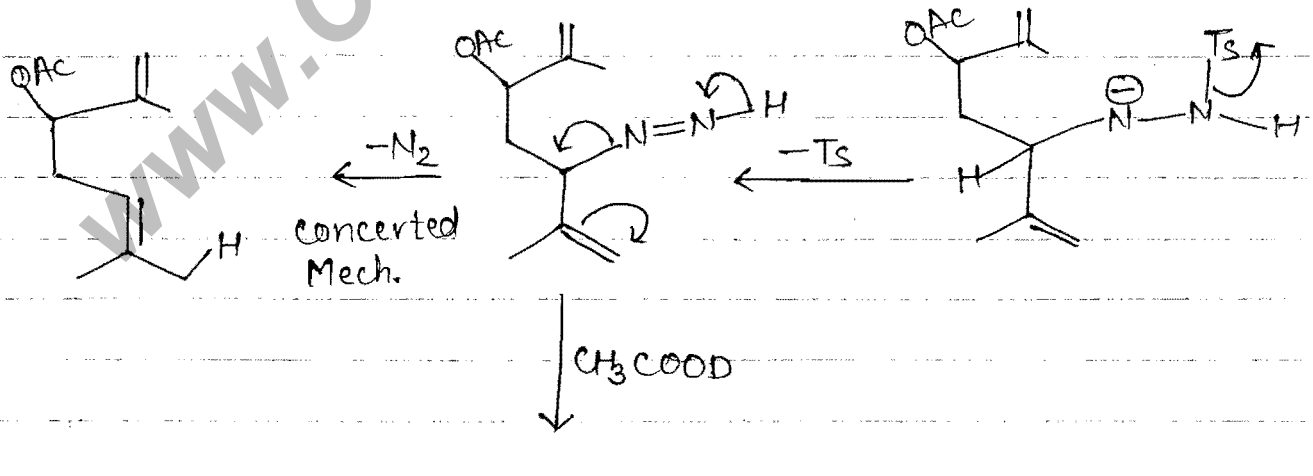
Prob.

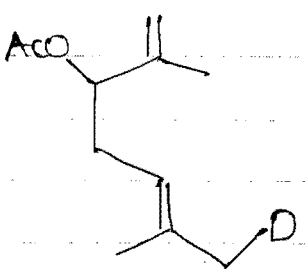


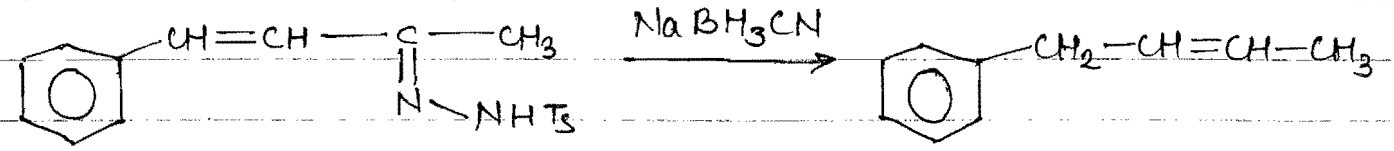
But when Ts NH–NH_2 react with α, β-unsaturated carbonyl comp., then α, β-unsaturated tosylhydrazone formed. ——— Migration of double bond will be takes place when it is react with $NaBH_4$

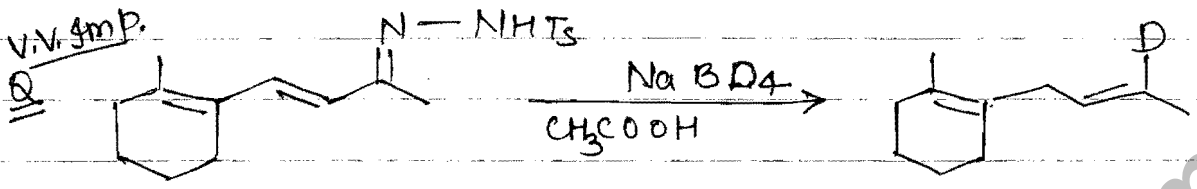
Prob.

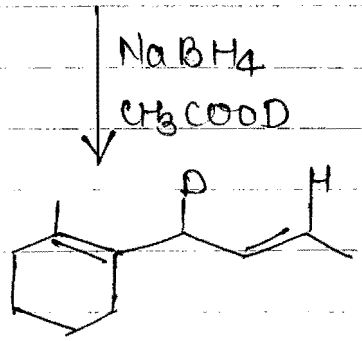






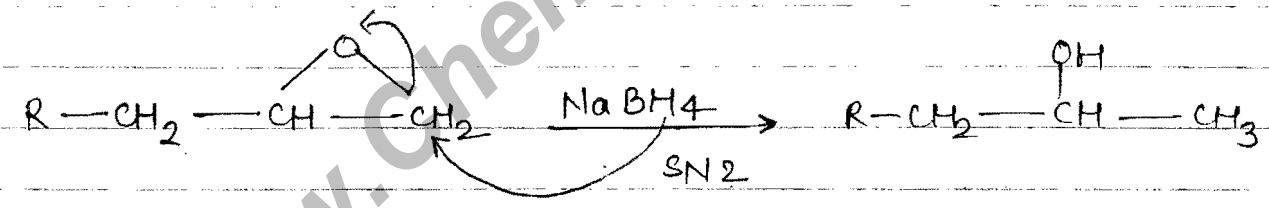
Q 

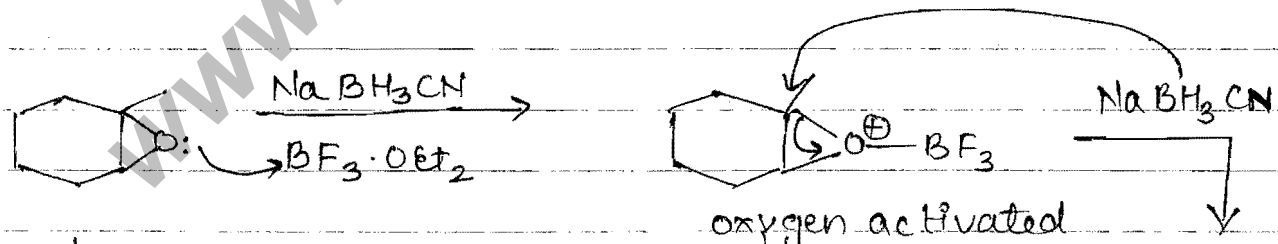
Q 

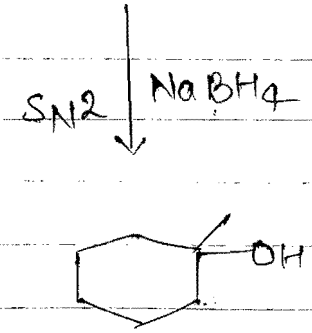


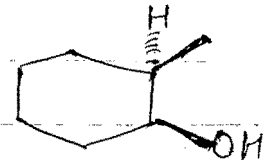
In the of

* $NaBH_4$ epoxide ring opening takes place from less hindered side.

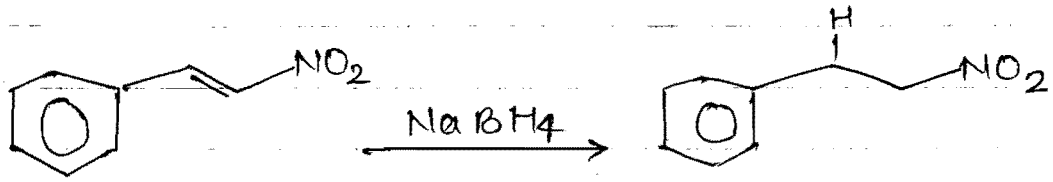
Q 

Q 

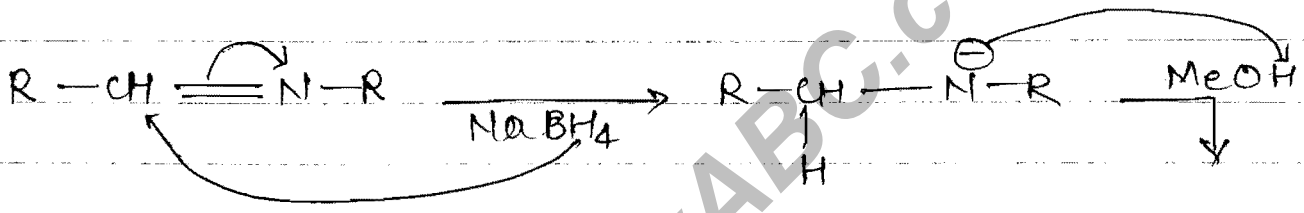




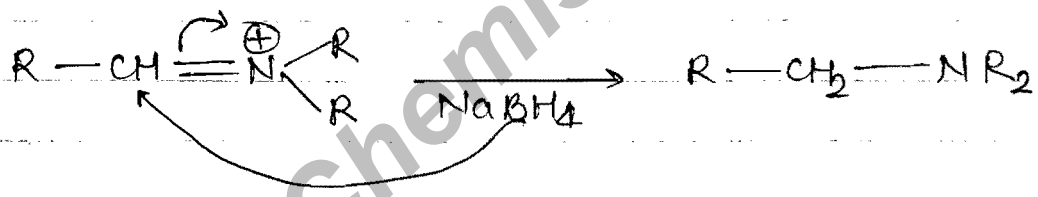
* $NaBH_4$ doesn't reduce Nitro group with α,β unsaturated Nitro comp.. $NaBH_4$ reduce c=c bond.



* $NaBH_4$ Reduce shif base (or) iminium ~~bond~~ salt.

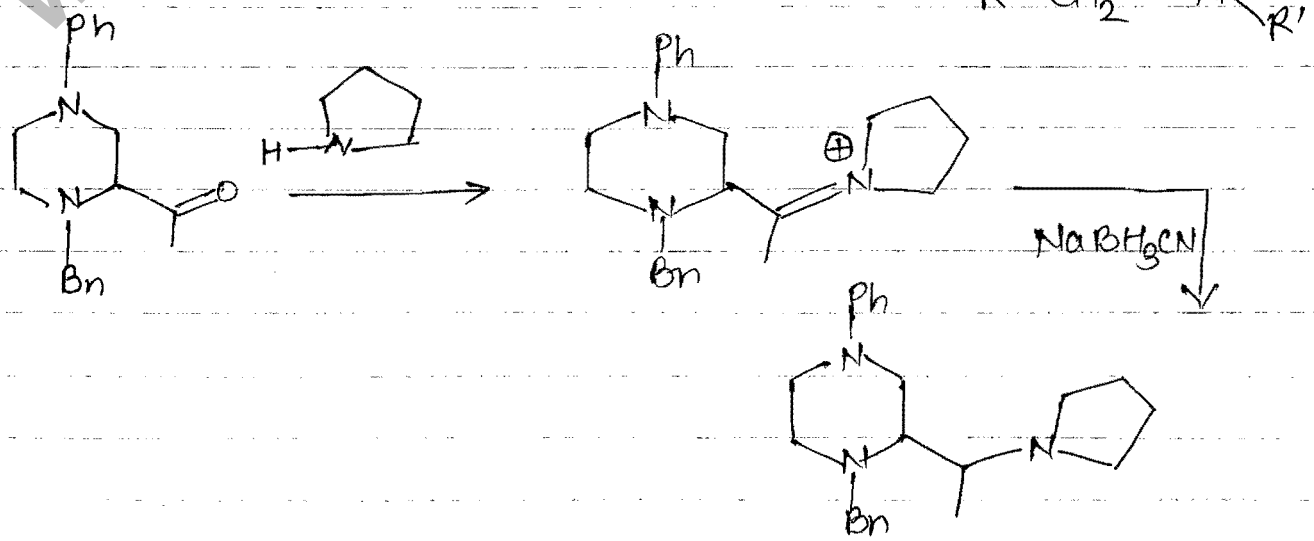
⇒ 

$R-CH_2-NH-R$

⇒ 

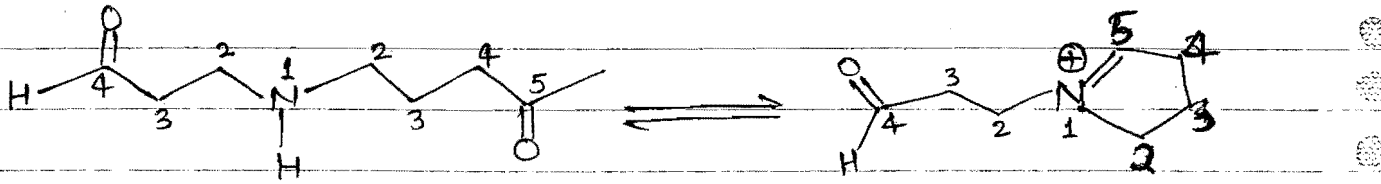
Q 

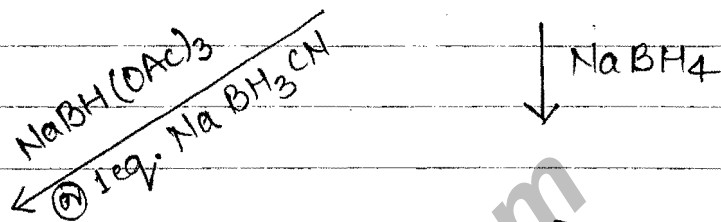
$R-CH_2-N(R)(R')$

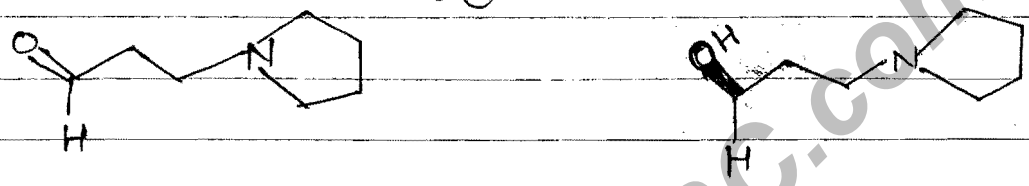
Q 

V. Imp.

Q







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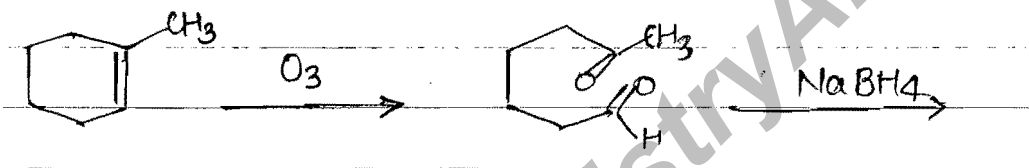

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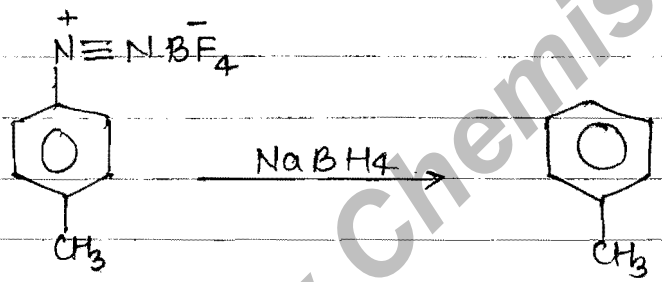

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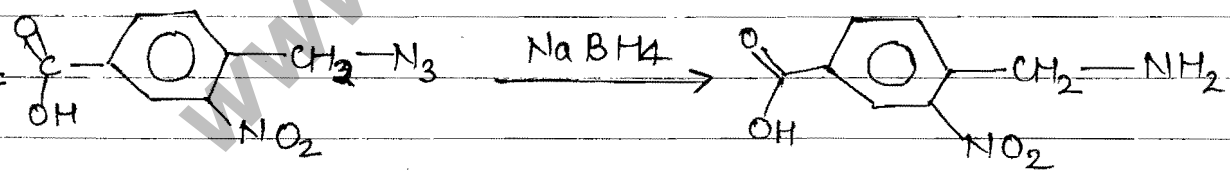
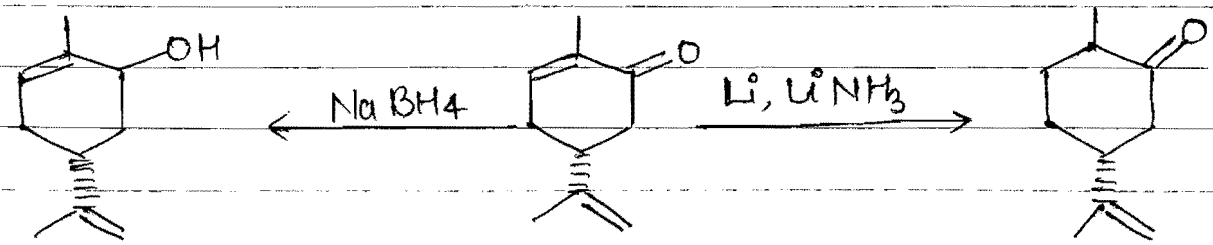
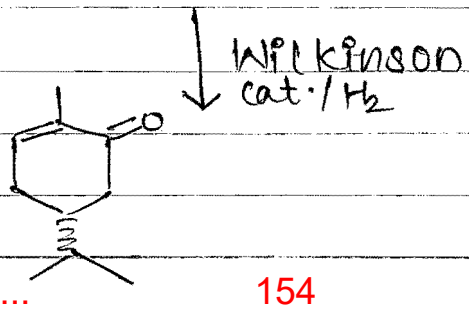


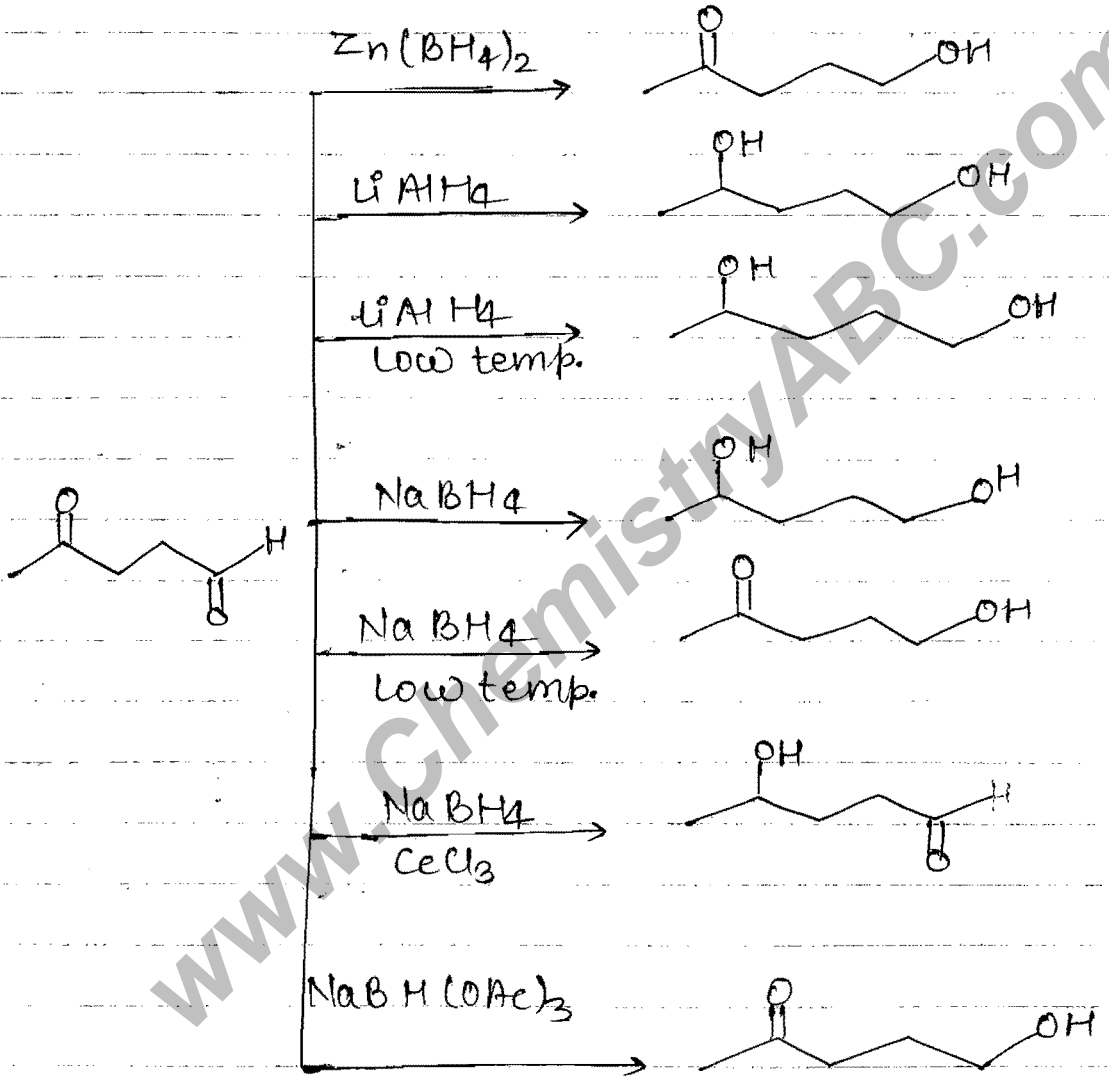




ZINC BOROHYDRIDE. $Zn(BH_4)_2$

for ald·gp.

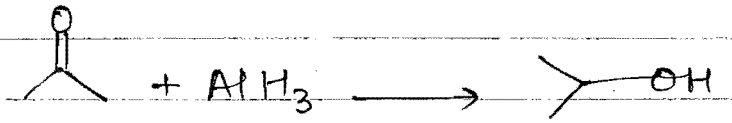
Zinc borohydride is highly selective, in the ⁺nce of keto group.

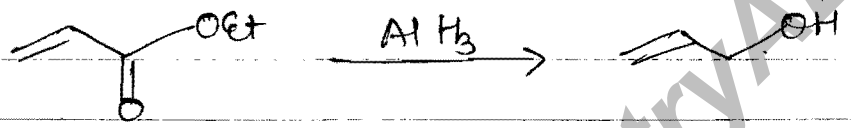


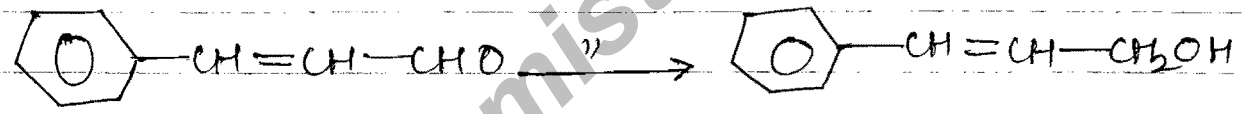
MIXED HYDRIDE (AlH_3) or Allen.

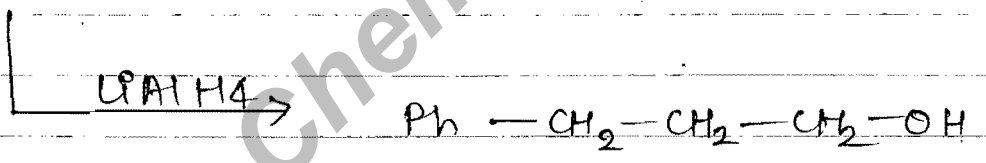
$LiAlH_4 + AlCl_3 \longrightarrow AlH_3$

Exist in polymeric form, & white solid form.





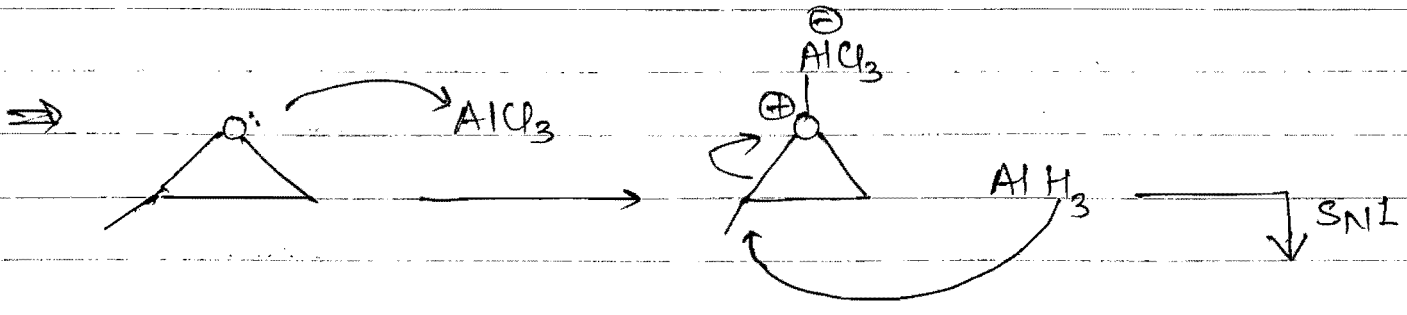




$R-X \xrightarrow{AlH_3}$ No Rxn.

$R-NO_2 \xrightarrow{"}$ "

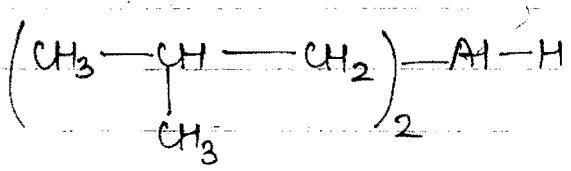
$R-OTs \xrightarrow{"}$ "



Contracter of Aldehyde

V.V. imp.

DIBAL-H



Diisobutyl alluminium hydride.

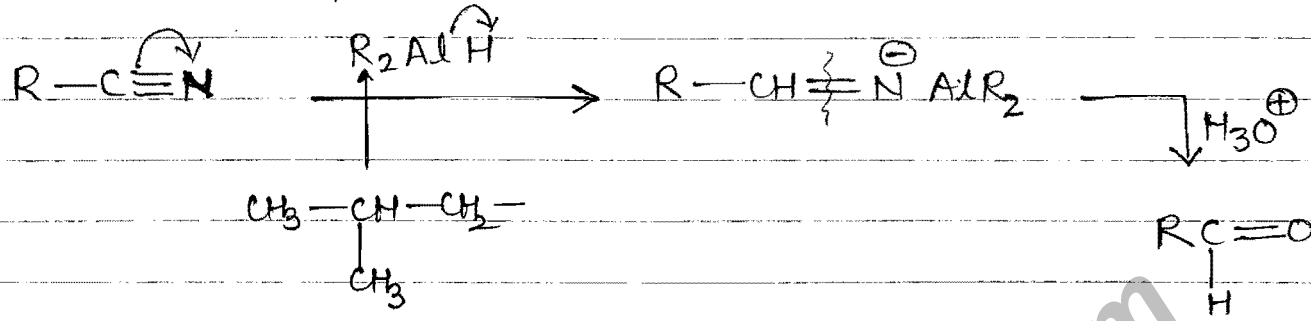
* DIBAL is a very selective reducing agent.
* It is a mild or weak reducing agen.
* It is a bulky reducing agent & contain a little amount of 'H' in the form of $H^{\ominus}$
* DIBAL is used most wildly for the ✱ reduction of R−C≡N into R−CHO.

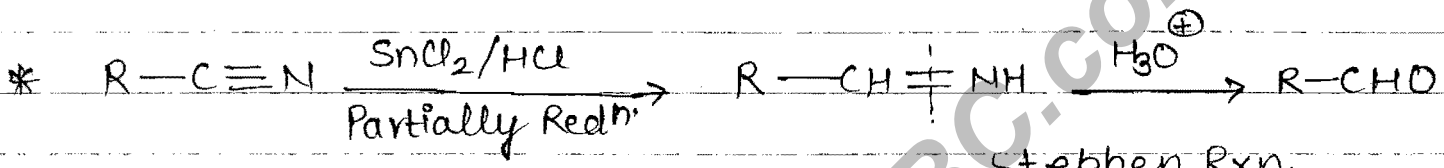
Chemoselectivity of DIBAL :-

Functional Group	DIBAL-H →	Product
imp. R−C≡N (Nitrile)	→	R−CHO
imp. Internal alkyne	→	Cis Alkene
imp. Ester	DIBAL-H → Low temp	Aldehyde
	DIBAL-H → High temp	Alcohol
Lactone	→	Aldehyde
Acid halide	→	Aldehyde

Lindlar catalyst ⇒ $Pd/CaCO_3/H_2$ ⓦ $Pd/BaSO_4/H_2$

Rxn. with Cyanide:-



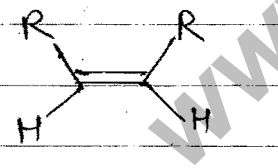


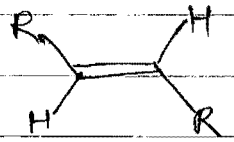
Rxn. with internal Alkyne:-

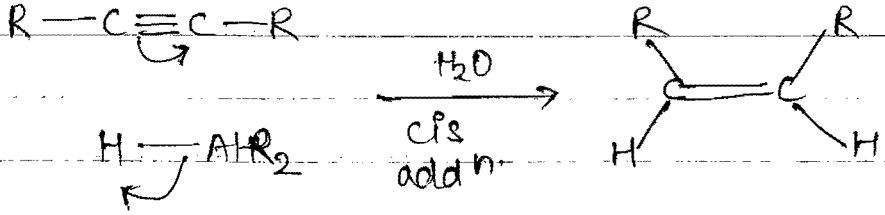
Internal alkyne
(R—C≡C—R)

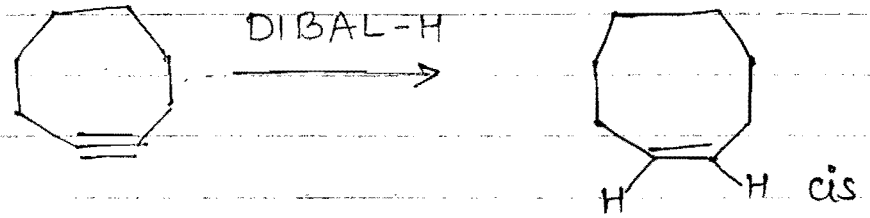
DIBAL—H
Lindlar cat.
→ cis alkene

Birch Red.
→ Trans alkene.

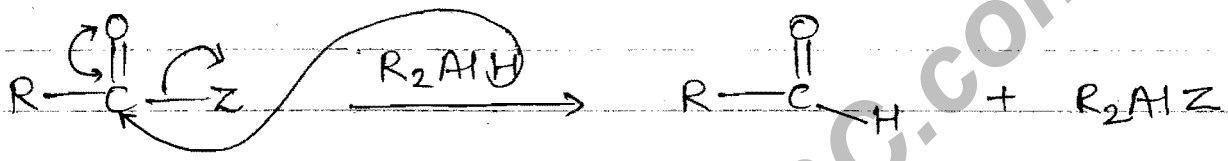






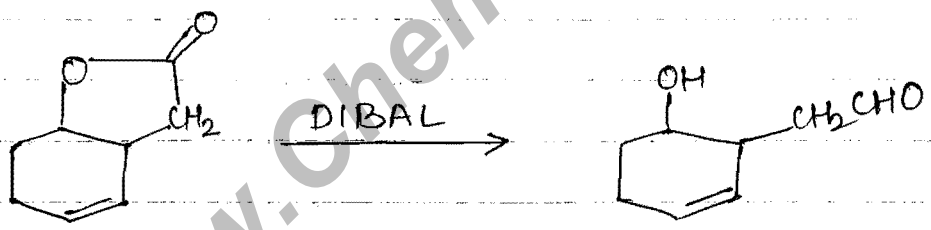
Q 

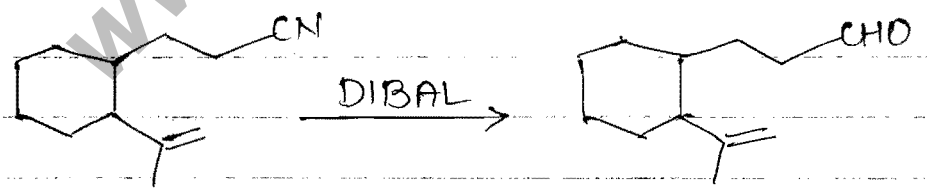
Rxn. with Ester:-

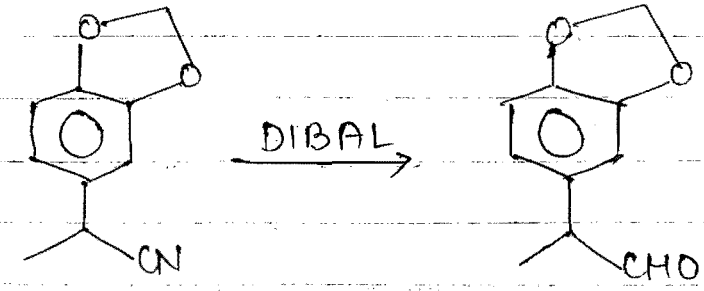


Z = -OEt
= -X

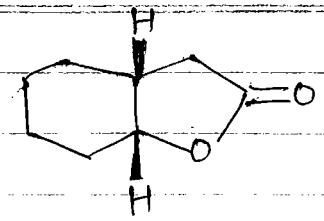
Further Redⁿ. doesn't take place becoz now no H^- remaining with DIBAL, but in the excess amount (with high temp.) Aldehyde further reduced into alcohol.

Q 

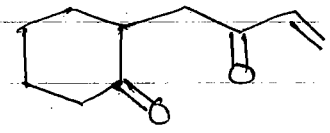
Q 

Q 

V. Imp.

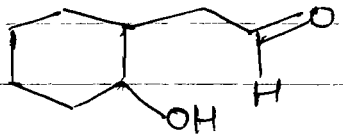
Q 

i) DIBAL
ii) $CH_2=CHMgBr$
iii) PCC

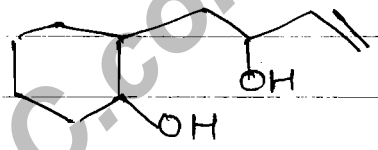


DIBAL

PCC oxidising agent.

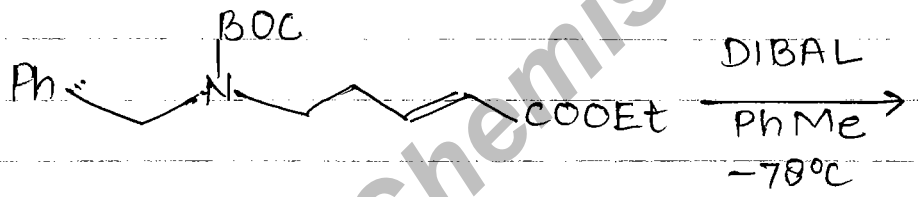


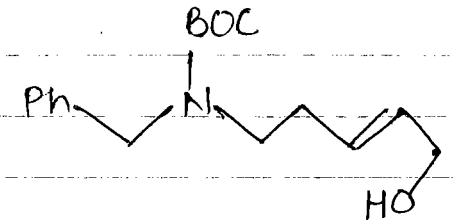
$CH_2=CHMgBr$



V.V. Imp.

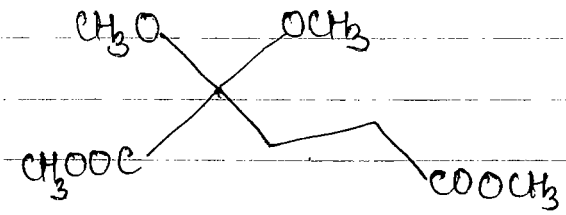
DIBAL has found considerable use for the selective Redⁿ. of α-β- unsaturated comp. to allylic alcohol.



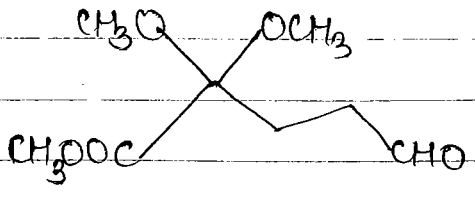


Allylic alco.

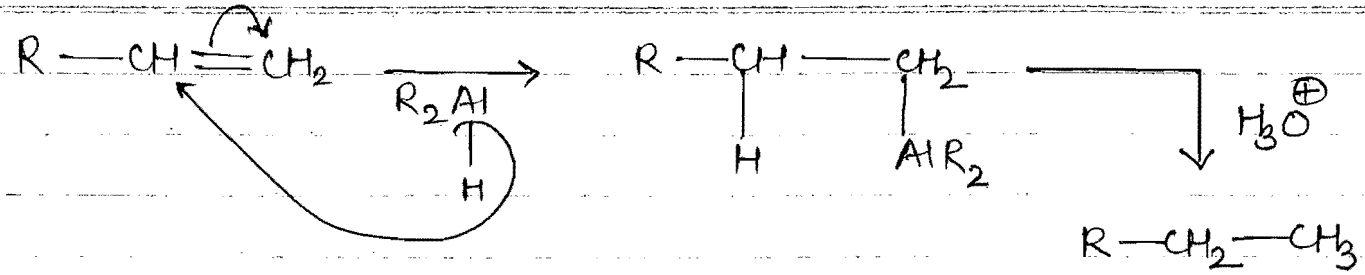
DIBAL attack at less sterically hindered group.

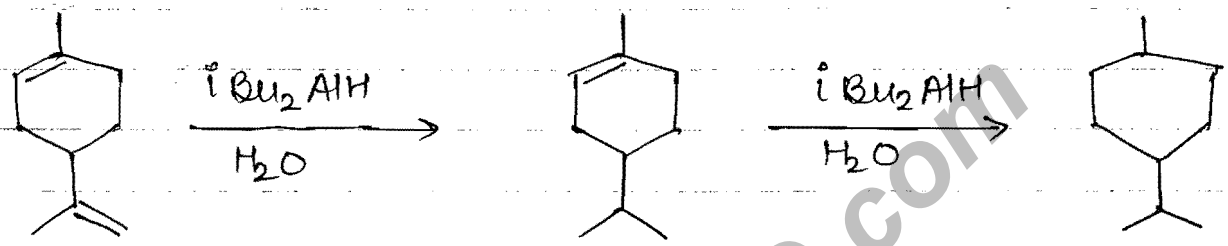


DIBAL (1 eq.)
DCM, −78°C

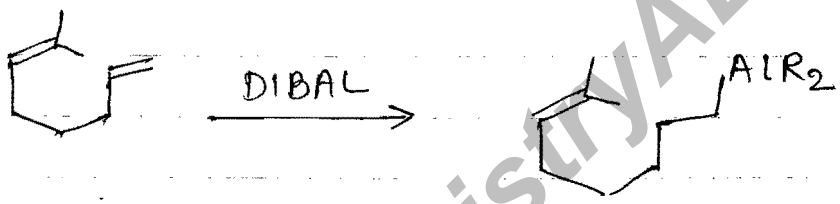


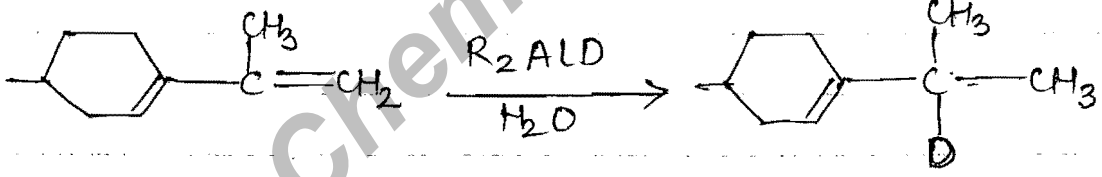
DIBAL also react with alkene & form alkane followed by acidic workup.

* 

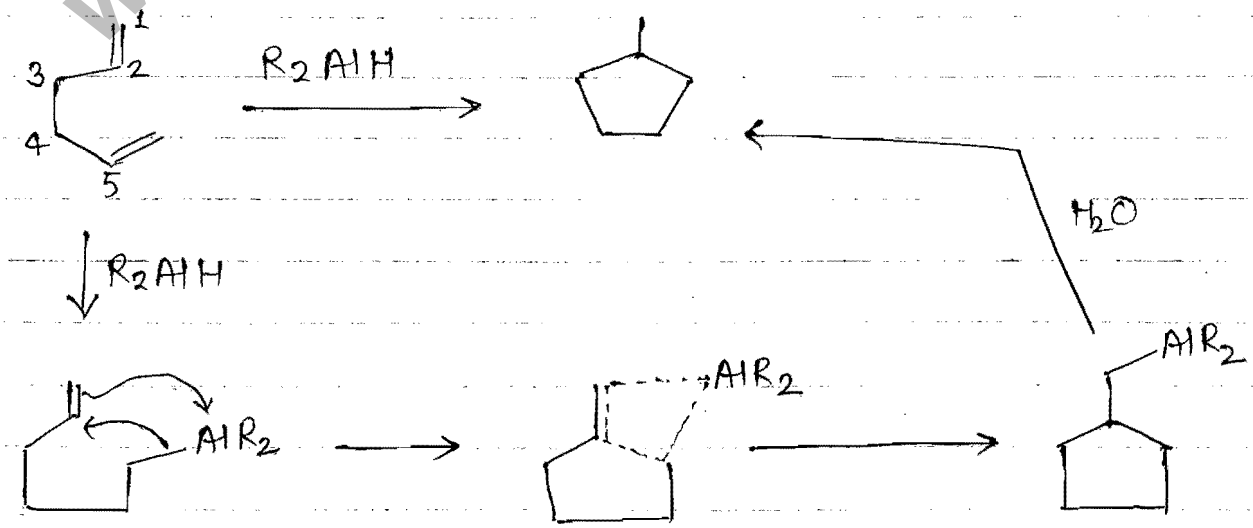
* 

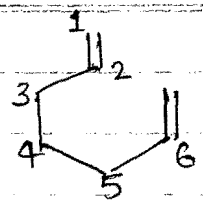
Less hind. Alkene reduced first.

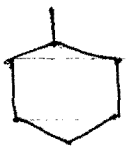
Q 

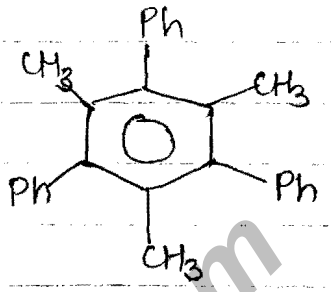
Q 

1,5 and 1,6 diene can be convert into 5 and 6 memb. cyclic comp.

* 

* 

$\xrightarrow{R_2AlH}$ 

* $C_6H_5-C\equiv C-CH_3 \xrightarrow[150^\circ]{i\,Bu_2AlH}$ 

* Acetylene $\xrightarrow[\Delta]{\text{Red hot Rod}}$ Benzene.

BASIC CHEMISTRY.

सामान्य रसायन विज्ञान

Rxn. of Alkyl halide with alco. KOH and aq. KOH.

$$R-CH_2-CH_2-X \xrightarrow[\text{N.S.R.}]{\text{aq. KOH}} R-CH_2-CH_2-OH$$

$$R-CH_2-CH_2-X \xrightarrow[\text{elimination}]{\text{alco. KOH}} R-CH=CH_2$$

Formation of Nitrocomp. by Alkyl Halide

$$R-CH_2-X \xrightarrow{KNO_2} R-CH_2-NO_2$$

$$R-CH_2-X \xrightarrow{AgNO_2} R-CH_2-ONO \quad (HSAB).$$

Formation of Cyanide by alkyl Halide

$$R-X \xrightarrow{KCN} R-CN \text{ (Cyanide)}.$$

$$\xrightarrow{AgCN} R-NC \text{ (isocyanide)}$$

Rxn. of PCl_3, PCl_5, $SOCl_2$, $SOBr_2$ with alco. ⓞr Oxygen containing comp.

$$R-CH_2-O-H \xrightarrow{PCl_3 \text{ ⓞr } PCl_5 \text{ ⓞr } SOCl_2} R-CH_2-Cl$$

* $SOCl_2$ is better than PCl_3; PCl_5

$R-CH_2-OH \xrightarrow{Red\ P + X_2} R-CH_2-X$

$R-CH_2-OH \xrightarrow{Red\ P + HI} R-CH_3$

Oxygen containing comp. $\xrightarrow{Red\ P + X_2}$ Alkyl Halide

$\downarrow$ Red. + HI

Alkane ← contractor of Alkane.

$R-CH_2-COOEt \xrightarrow{Red\ P + HI} R-CH_2-CH_3$

$R-CH_2-COOH \xrightarrow[\text{(a)}\ Br_2, PBr_3]{Red\ P / X_2} R-\underset{X}{CH}-COOH$ (HVZ Rxn.)

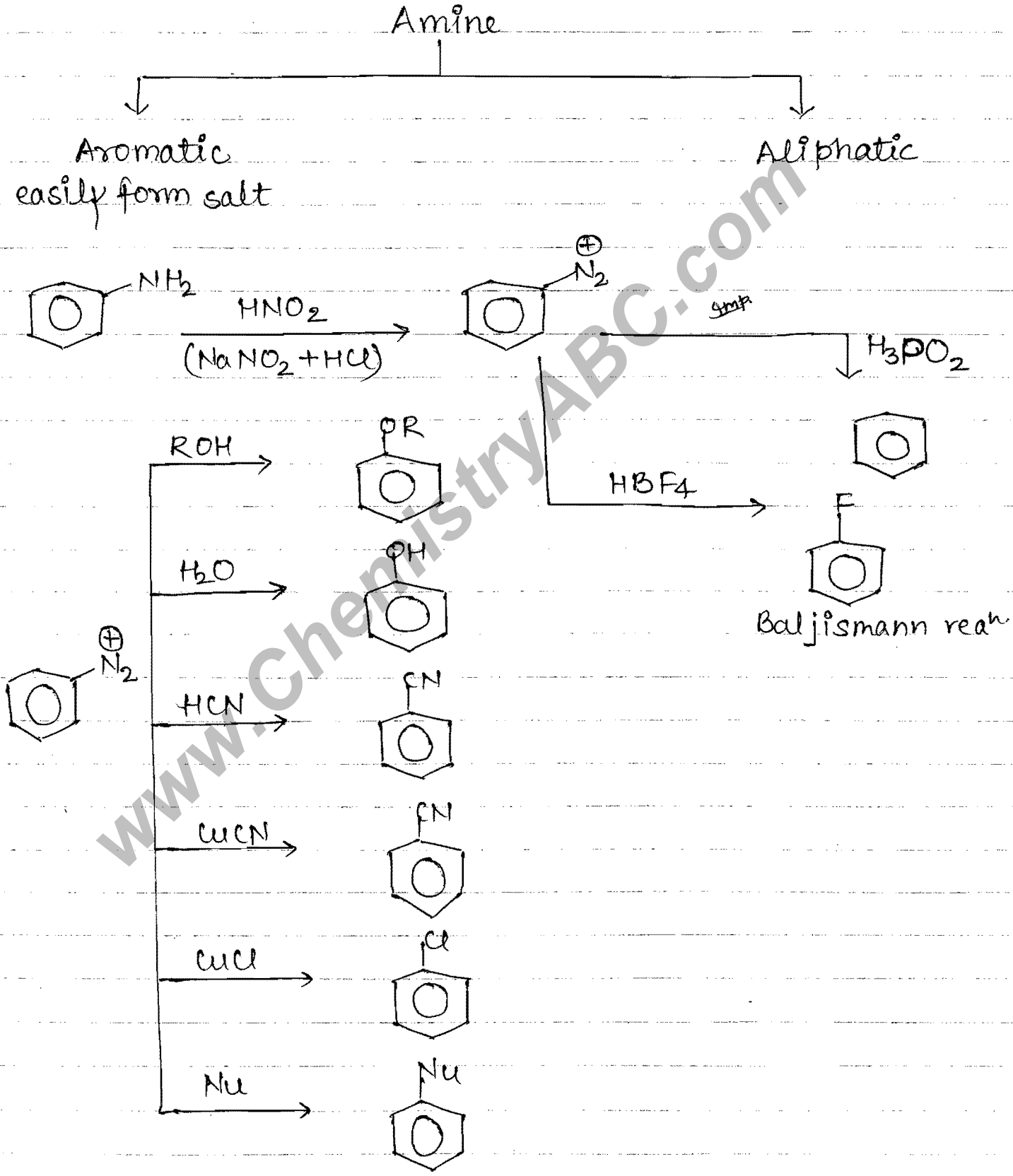
Formation of Alkyl Halide by Nitrogen containing comp.

$R-NH_2 \xrightarrow{NOCl\ (Tilden\ Reagent)} R-Cl$

LUCAS Reagent ($ZnCl_2$ + con. HCl)

Lucas reagent used to differentiate 1°, 2° & 3° alco. Lucas reagent gives turbidity with 3° Alco at ones and doesn't give " with 1° alco.

Formation of Diazonium Salt:-



Chemistry of Cyanide Compound:-

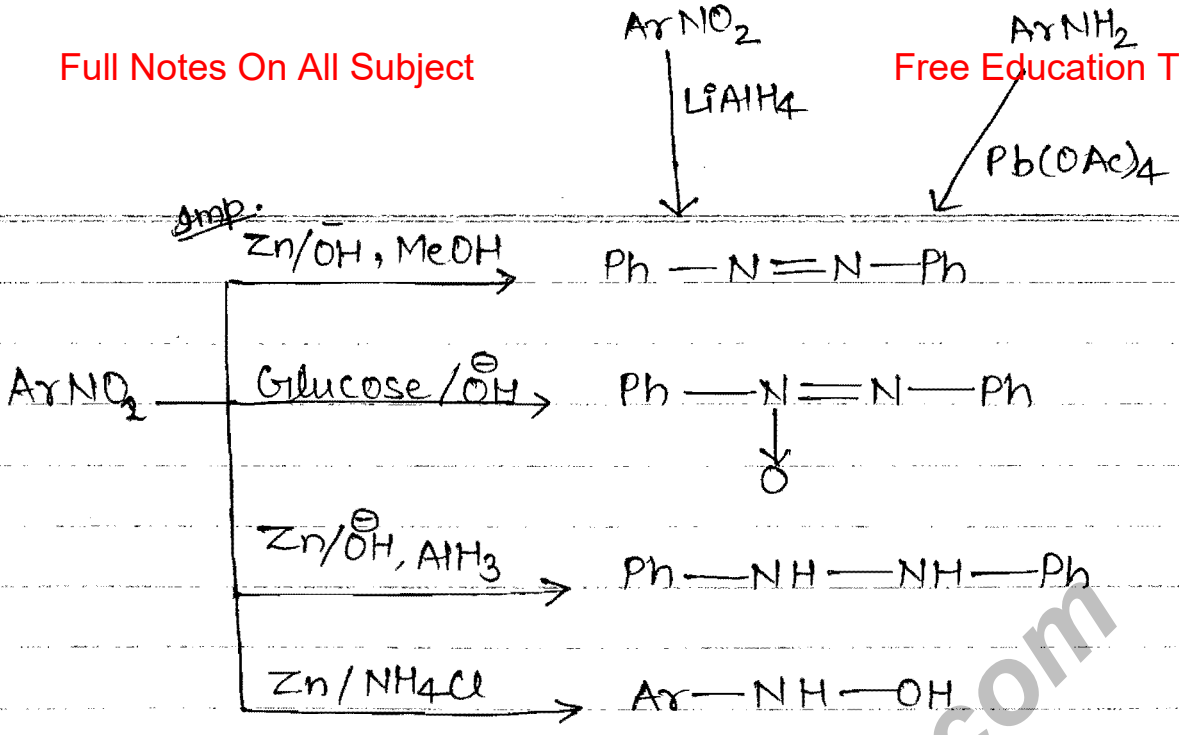
$R-C\equiv N$

- $H_2O/H^{\oplus}$, acidic Hydrolysis → $R-COOH$
- $H_2O/\overset{\ominus}{O}H$, Basic Hydrolysis → $RCOOH \xrightarrow[-H_2O]{\overset{\ominus}{O}H} R-COO^{\ominus}$
- Reduction, $Pd/C/H_2$ or $LiAlH_4$ → $R-CH_2-NH_2$
- Partially Reduction, Hydrolysis → $RCHO$ (Stephen Rxn.)
- $Na/EtOH$ → $R-CH_2-NH_2$ Mandius Rxn.

Chemistry of Nitro Compound:-

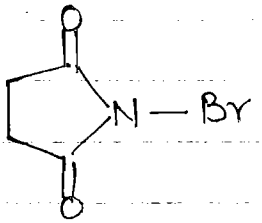
$R-NO_2$

- $Pd/C/H_2$ → $R-NH_2$
- $LiAlH_4$, R = Aliphatic → $R-NH_2$
- $LiAlH_4$, R = Aromatic → $Ph-N=N-Ph$
- Zn/NH_4Cl → $R-NH-OH$ V. Imp.
- conc. H_2SO_4, 1° Nitro comp. → $R-COOH$ (Neph rxn.)
- conc. H_2SO_4, 2° Nitro comp. → $R-\overset{O}{\overset{\|}{C}}-R$



V. Imp.

N-BROMO SUCCINAMIDE [NBS]



1) NBS is the source of bromine.
2) Yellow solid comp.
3) Moisture sensitive
4) CCl_4 use as a solvent in NBS Rxn.

Applications :-

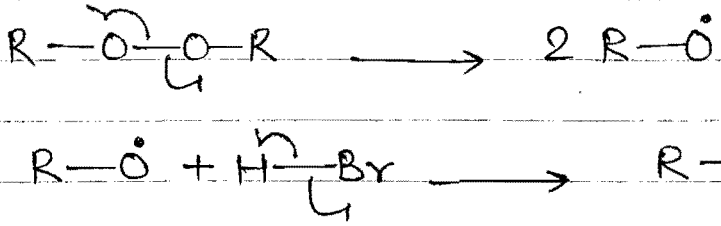
NBS

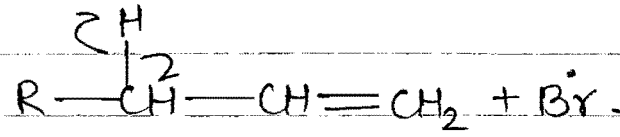
- V. Imp. → Bromination at allylic, benzylic, propargylic position.
- Imp. → Bromination at α-position w.r.t. keto group.
- Oxidation of Alcohol.
- M. Imp. → Addⁿ. of Bromine on Alkene in the ₹nce of $Nu^{\ominus}$
  * Addⁿ. Acc. to Marconicoff.
  * Anti product form.

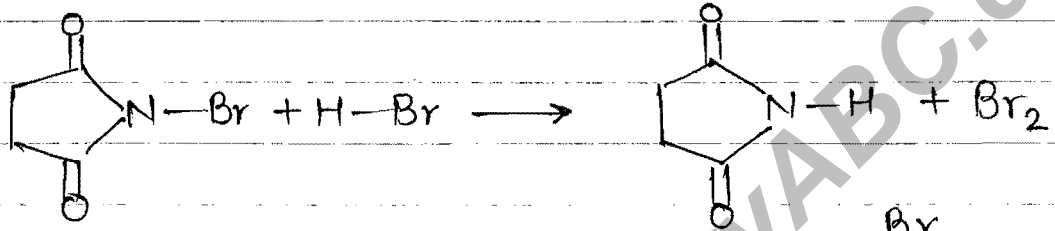
Bromination at Allylic, benzylic & propargylic Position :-

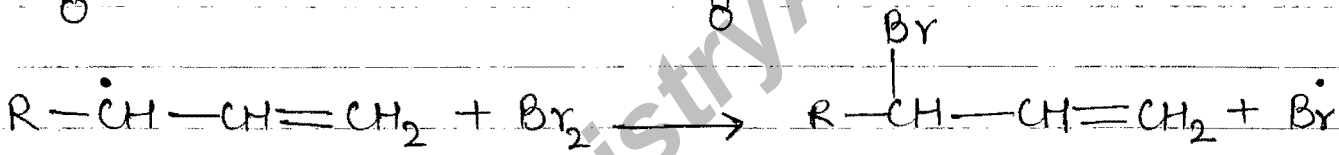
$$R-CH_2-CH=CH_2 \xrightarrow[R-O-O-R/HBr \text{ (or) } AIBN \text{ (or) } h\nu]{NBS} R-\underset{Br}{CH}-CH=CH_2$$

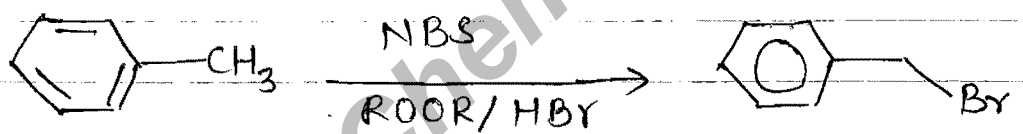
Mechanism :- Free Radically

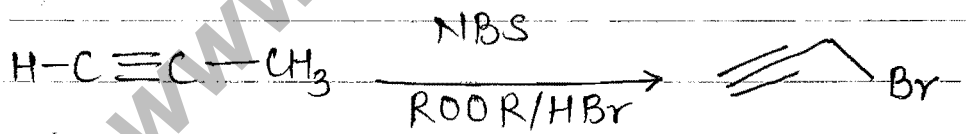






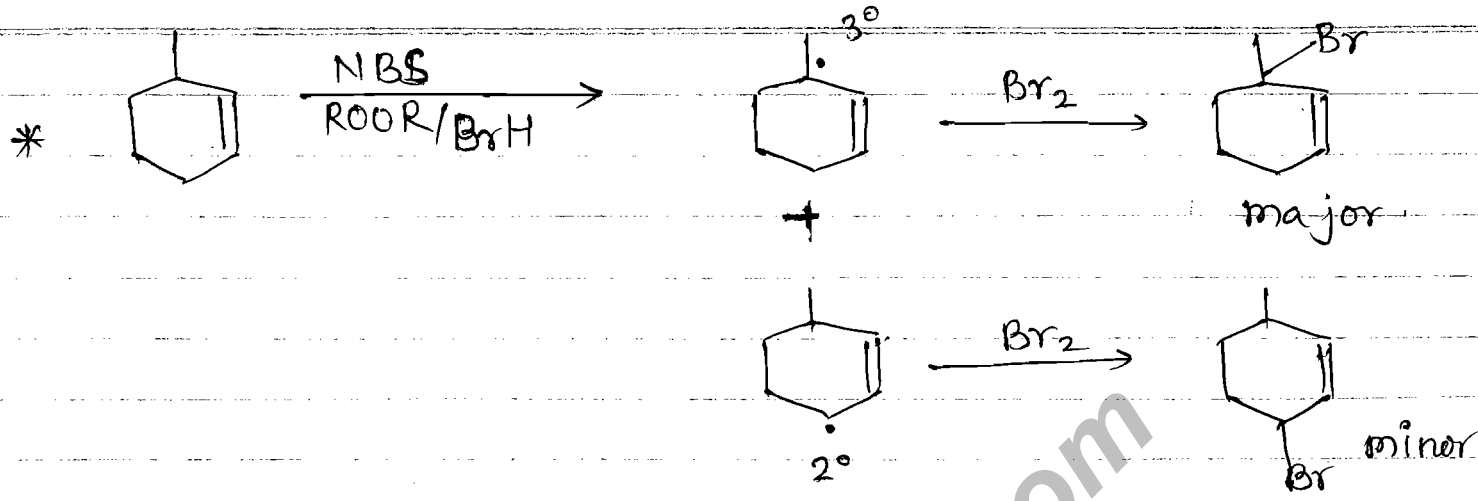


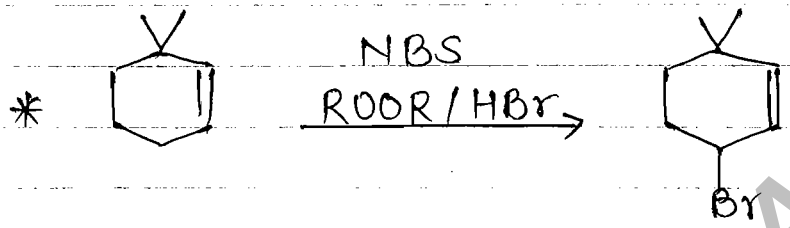
Q 

Q 

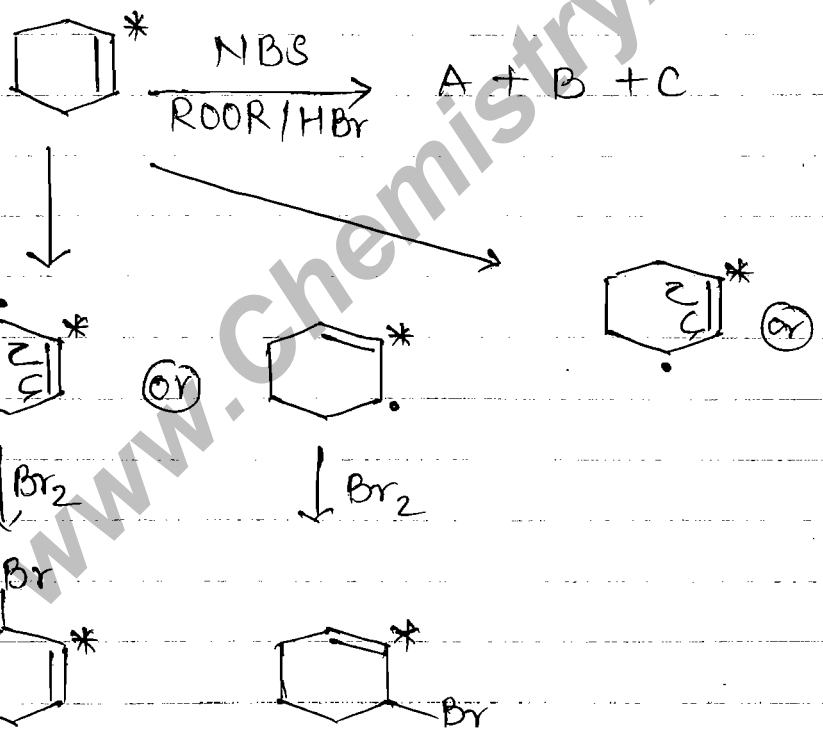
If in a comp. allylic and propargylic both group ↑nt then majorly Bromination takes place at propargylic position.

If in a comp. more than one allylic position ↑nt the majorly Bromination take place at more reactive site.

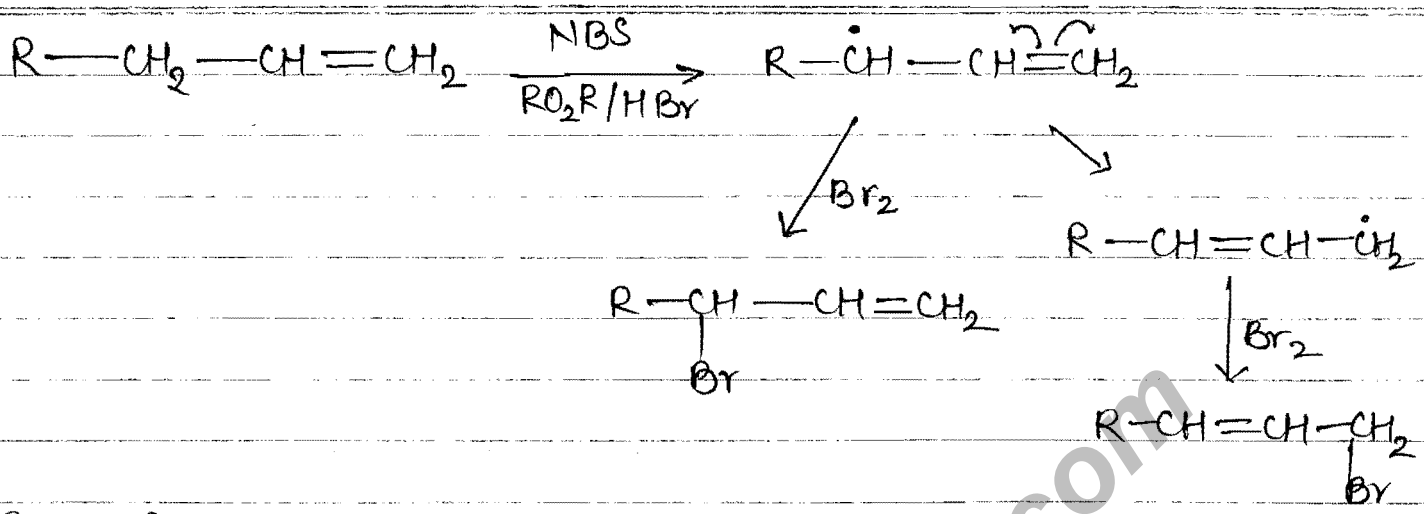




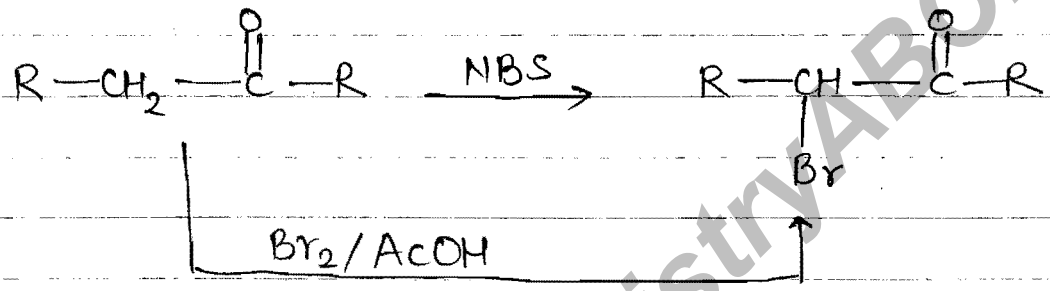
Prob

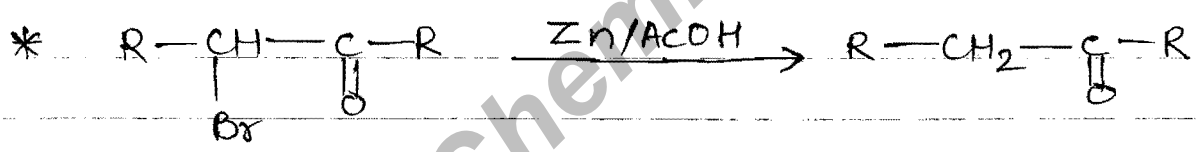


- Some times when allylic position are unsymmetrical then allylic rearrangement takes place & form mixture of possible products.



Bromination @ α-position w.r.t Keto Group:-





Oxidation of Alcohol:-

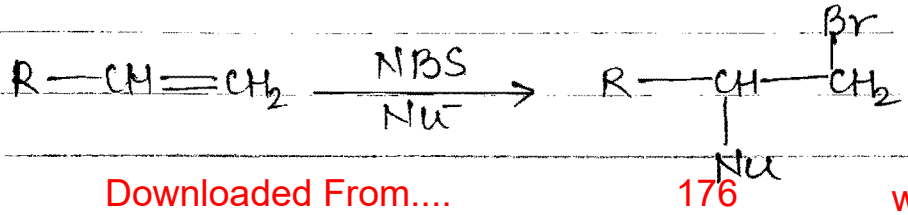
NBS oxidise 1° & 2° alcohol into carbonyl.

V.V.Imp.

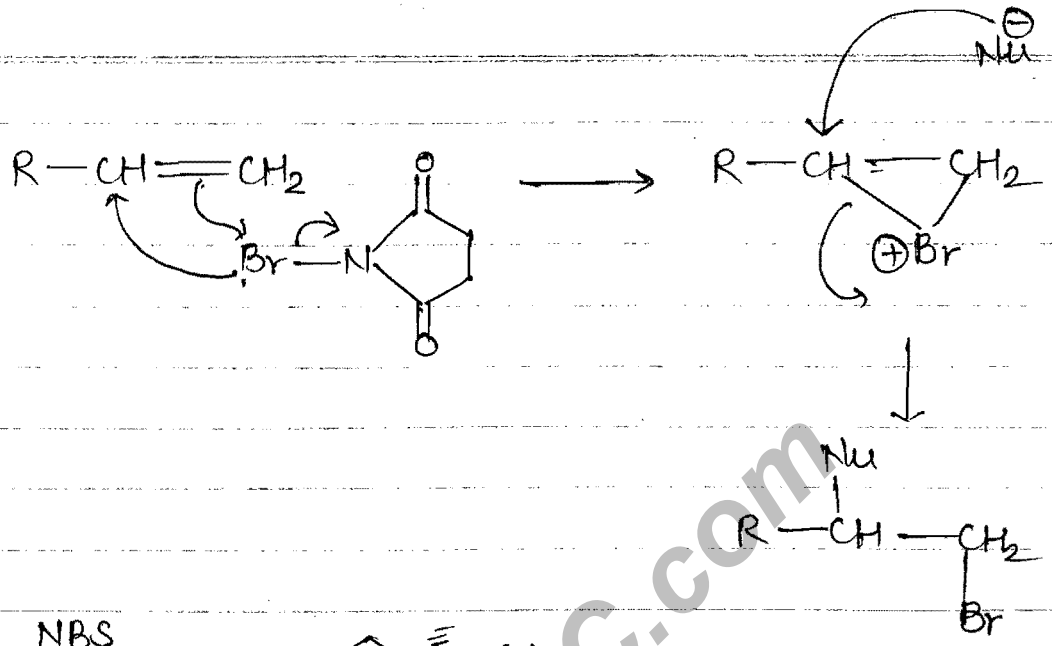
Addition of Bromine on Alkene in +nce of Nucleophile:-

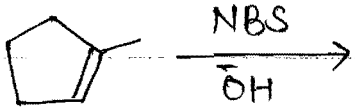
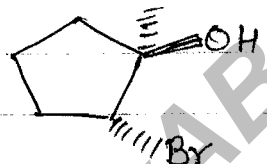
Add^{n} of Br takes place in +nce of $Nu^{\ominus}$ acc. to marconikoff pdt. and prod. is anti

NBS form bromonium ion with alkene.

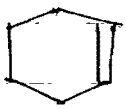


Mechanism:-

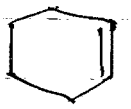
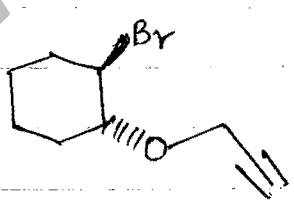


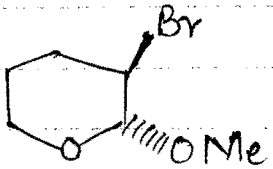
Q.  NBS, ⁻OH → 

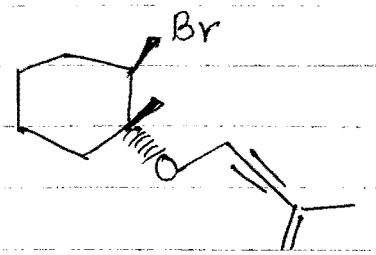
TRANS PRODUCT

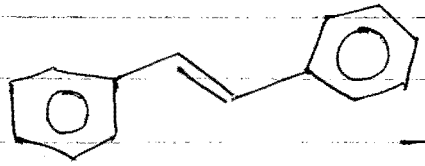
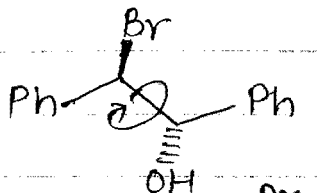
Q.  NBS, HF → 

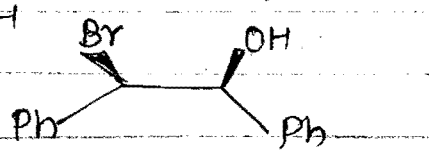
Generally Nu⊖ is alcohol.

Q.  HO, NBS → 

Q.  Br_2, MeOH → 

Q.  HO, NBS → 

Q.  NBS, H_2O → 

Rotation → 

M.Gmp:

Reagent addition:

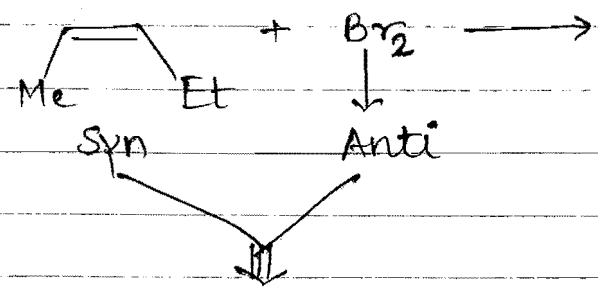
- Syn addn:
  - OsO_4
  - $KMnO_4$
  - Woodword.
- Anti addn:
  - Br_2
  - NBS & $Nu^{\ominus}$
  - Prevost

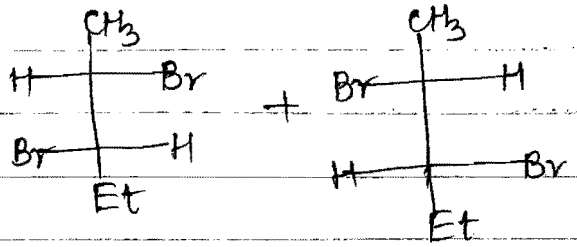
Alkene

- cis or Syn
- Trans or anti

M.Gmp Table

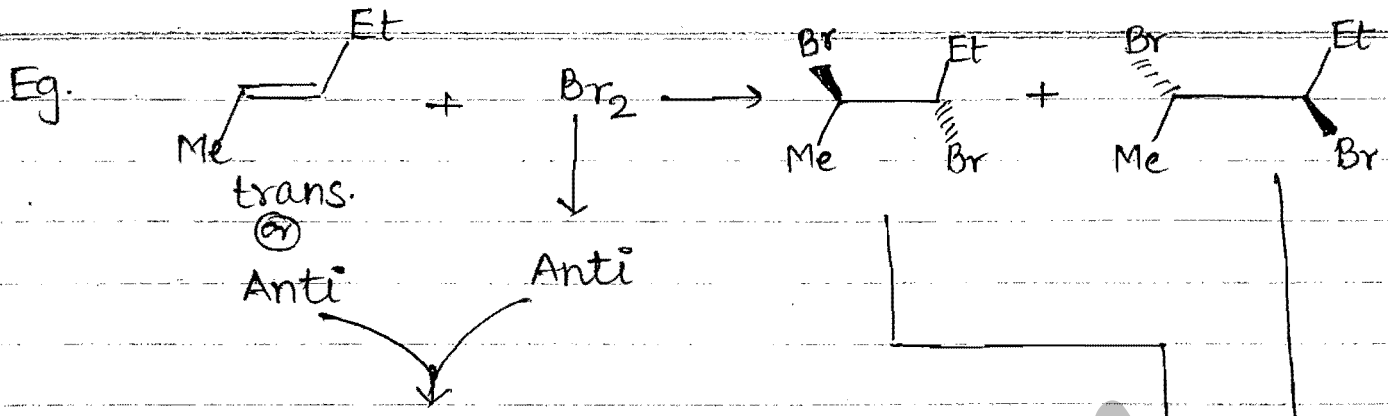
Substrate	Reagent	Product
Syn	Syn	Erythro → Meso / Pair of Enantiomer
Anti	Anti	Erythro → Meso / Pair of enantiomer
Anti	Syn	Threo → Pair of enantiomers
Syn	Anti	Threo → Pair of Enantiomers

Eg. 

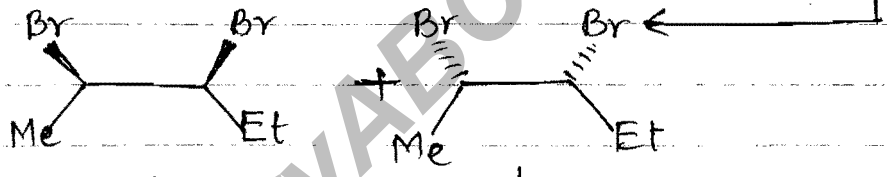


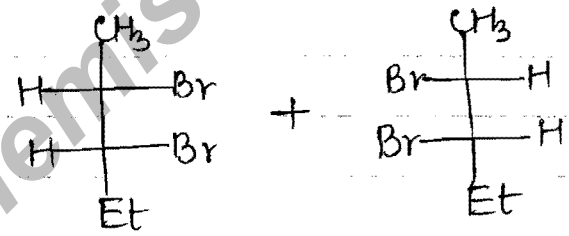
Pair of Enantiomers

Threo ⇒ Pair of Enantiomers.

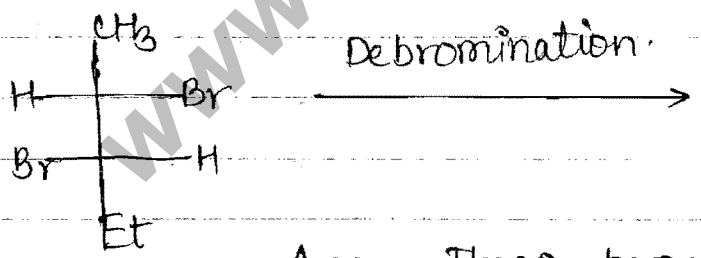
Eg. 

Erythro ⇒ Pair of Enantiomers.



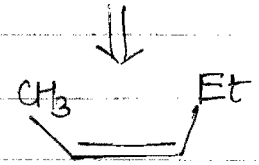
Pair of Enantiomers. 

Short Tricks



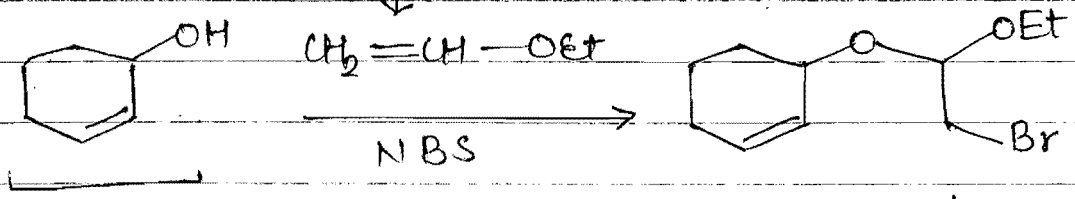
Debromination. → Which alkene form? Syn (cis) Alkene.

Ans: Threo prod. i.e. formed by Br_2 which gives anti addⁿ. ⇒ so Br_2 (Anti) + Alkene (cis) ⇒ Threo product.

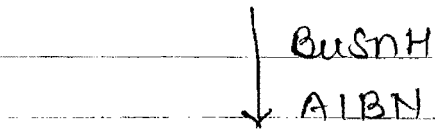


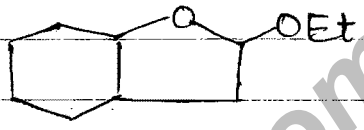
Addⁿ on Alkene

Q

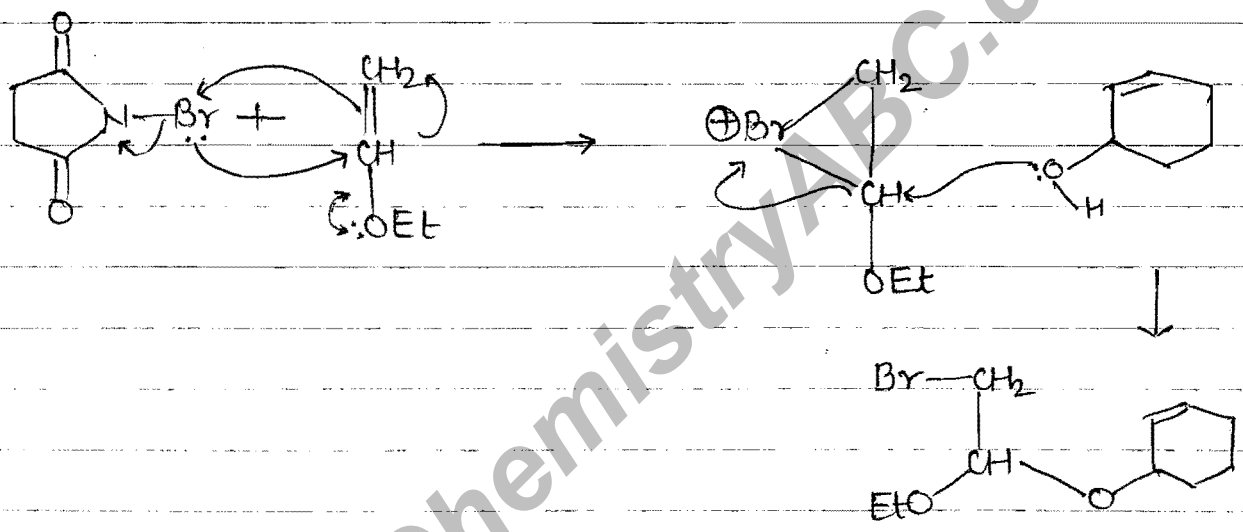


Nucleophile

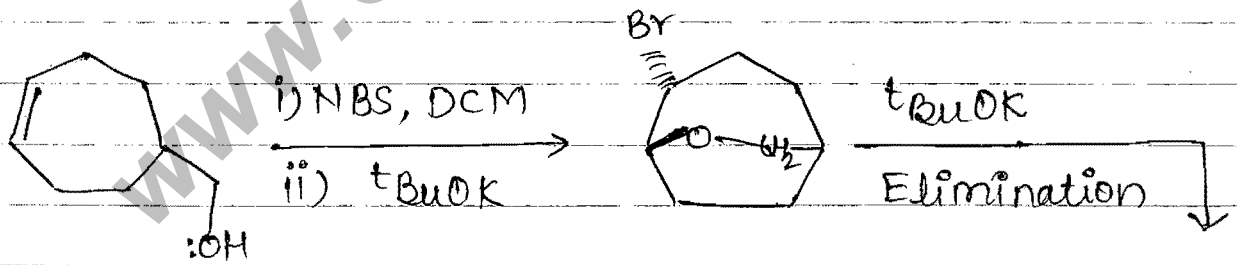




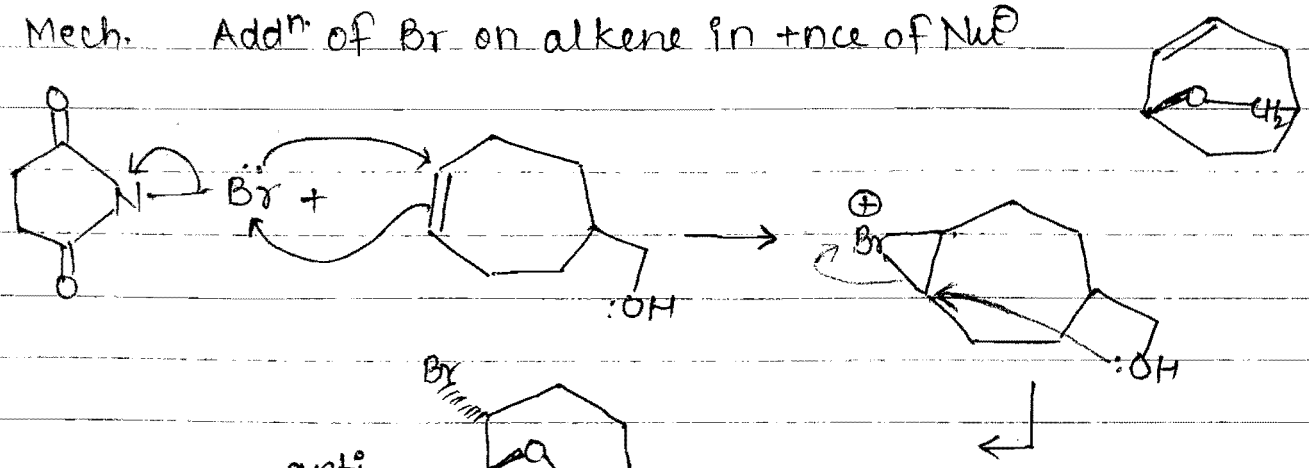
Mech.



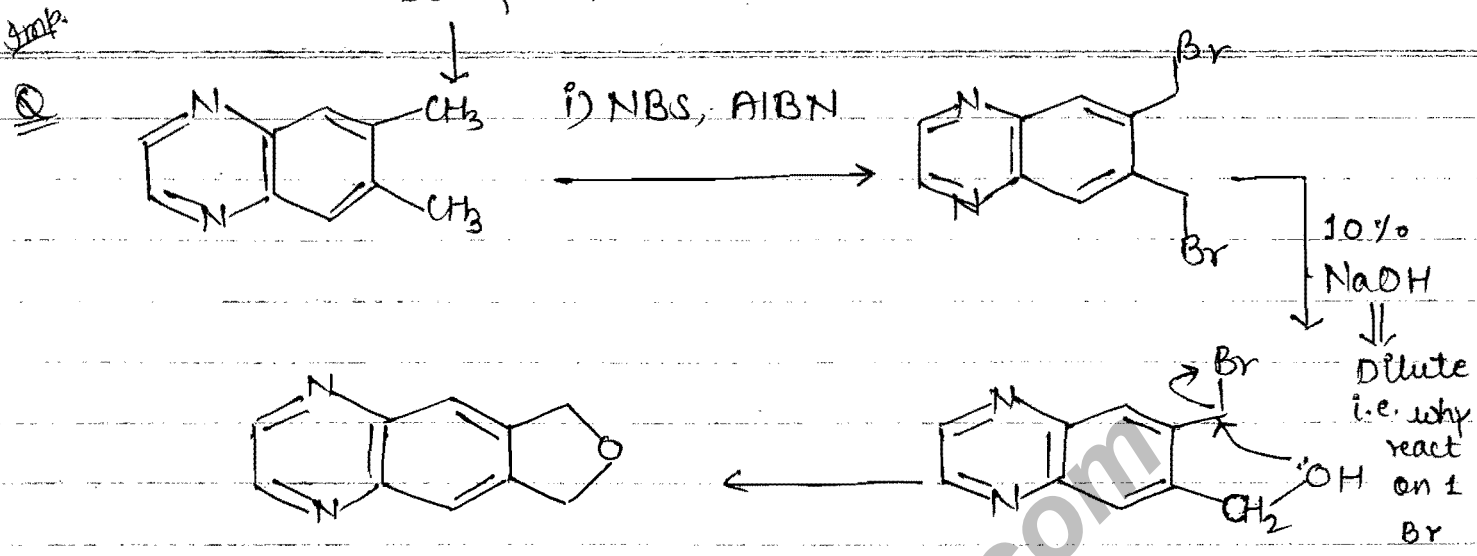
Q

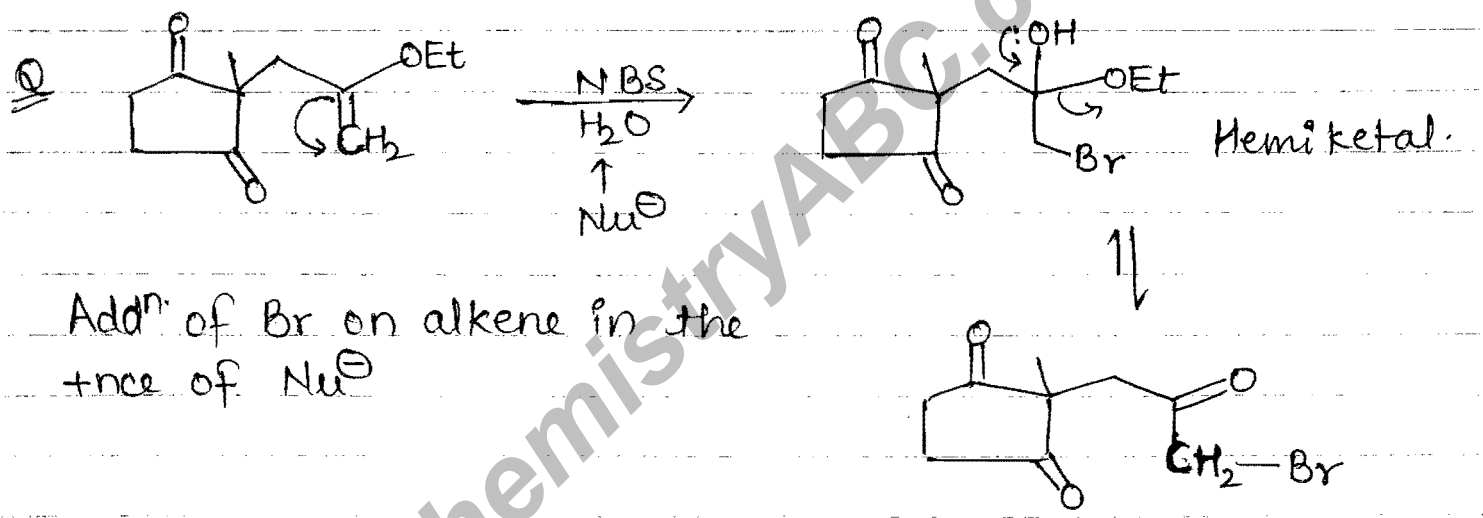


Mech. Addⁿ of Br on alkene in ᵗⁿᶜᵉ of Nuᶿ



Benzylic position





Addⁿ. of Br on alkene in the ⁺nce of $Nu^{\ominus}$

RANEY Ni (Ni—H)

Preparation:-

$$NiAl + NaOH\ (ice\ cold) + H_2O \longrightarrow NaAlO_2 + H_2 + Ni{-}H$$

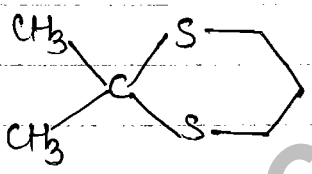
Application

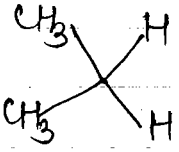
Ni—H

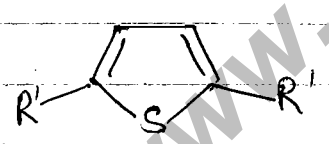
V.V.Imp.

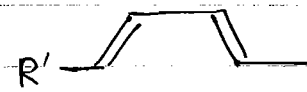
- Desulphurination
- Reduction of C—C multiple Bond.
- Redⁿ of Nitro Group
- Redⁿ of Cyanide

Desulphurination.

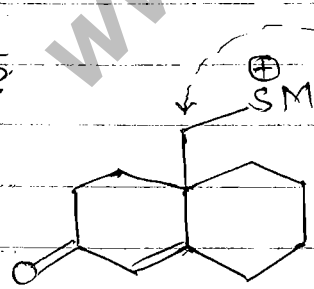
Q 

Raney Ni → 

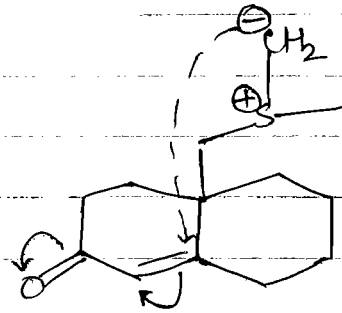
Q 

Ni—H → R'  R' Ni—H → R'—$(CH_2)_4$—R'

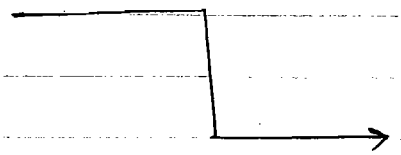
GATE M.Imp Q.

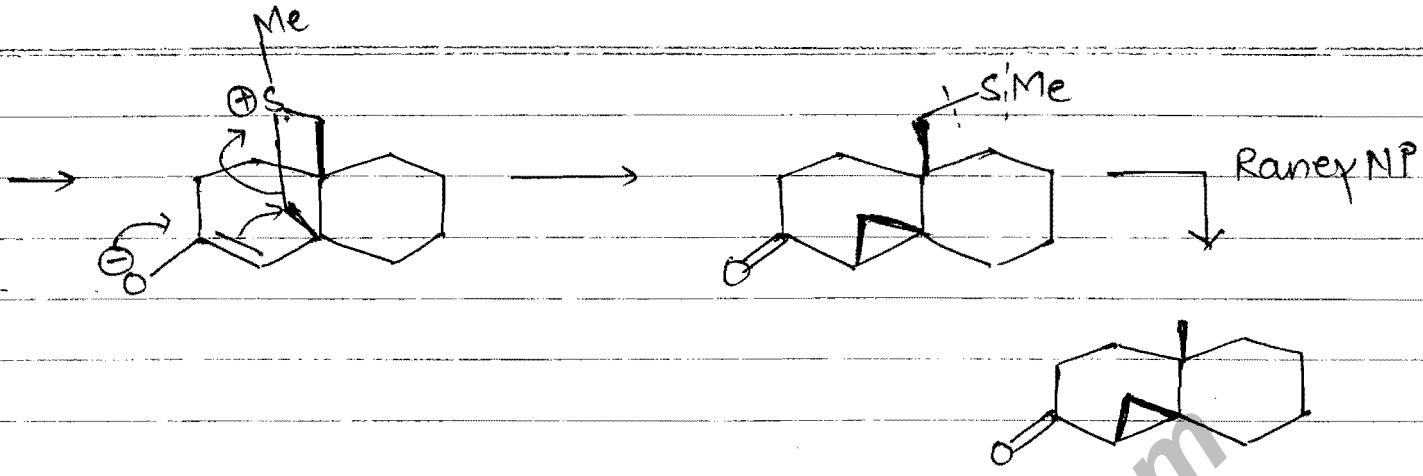


tBuOK →

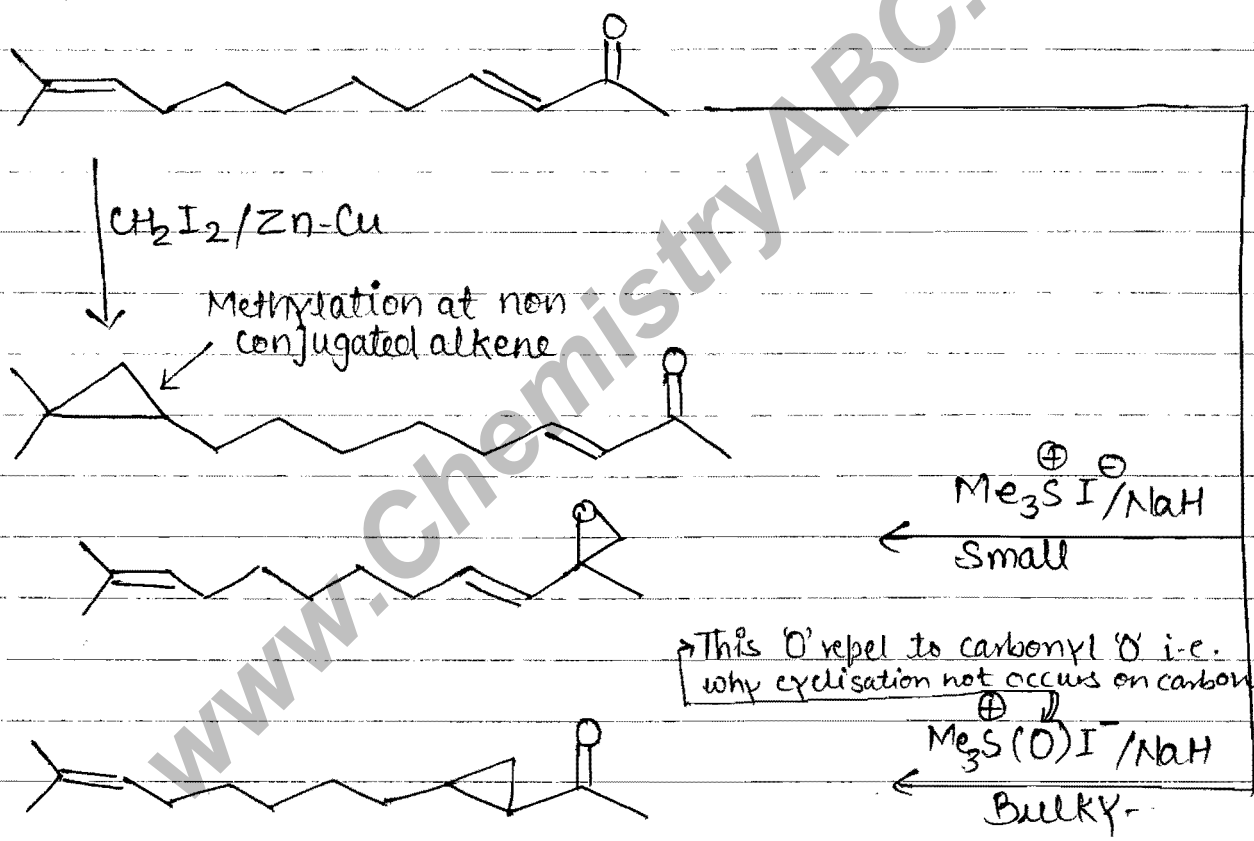


More stable conj base.





M. Imp.



* $Me\ddot{S}Me + MeI \longrightarrow Me_3S^{\oplus}I^{\ominus} \xrightarrow{NaH} {}^{\ominus}CH_2-S^{\oplus}Me_2$

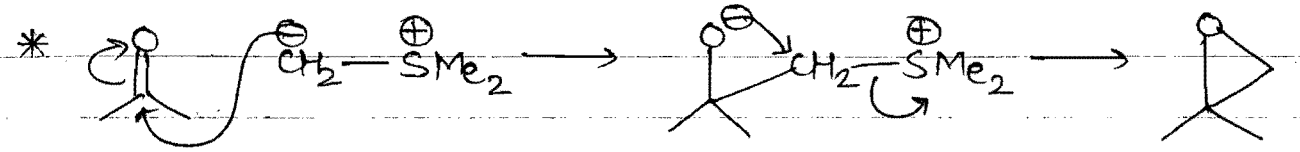
Small ylide

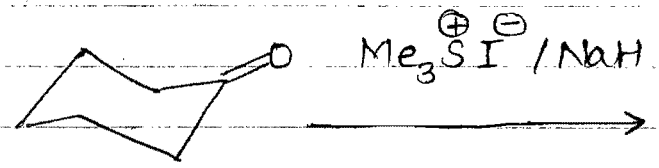
* $Me-\overset{\overset{O}{\|}}{S}(:)-Me + MeI \longrightarrow Me_3S^{\oplus}(O)I^{\ominus} \xrightarrow{NaH} {}^{\ominus}CH_2-\overset{\overset{O}{\|}}{S}^{\oplus}Me_2$

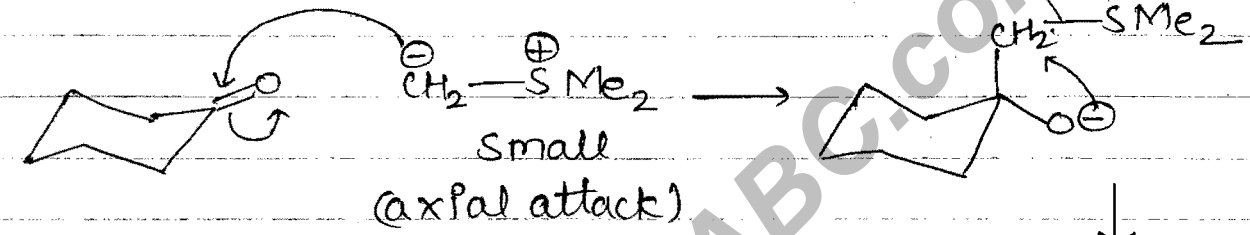
DMSO

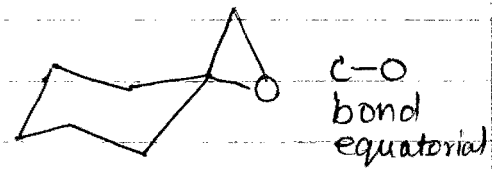
attack at α-β unsaturated $\leftarrow$ Bulky ylide

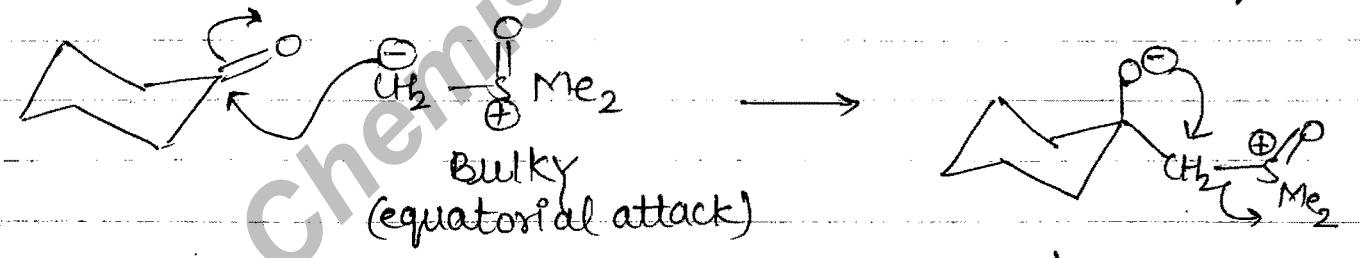
C=C bond.

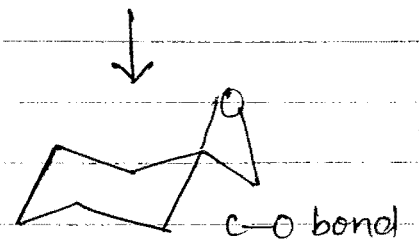


Q 

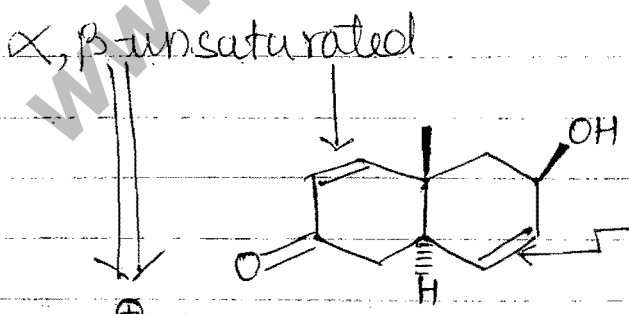


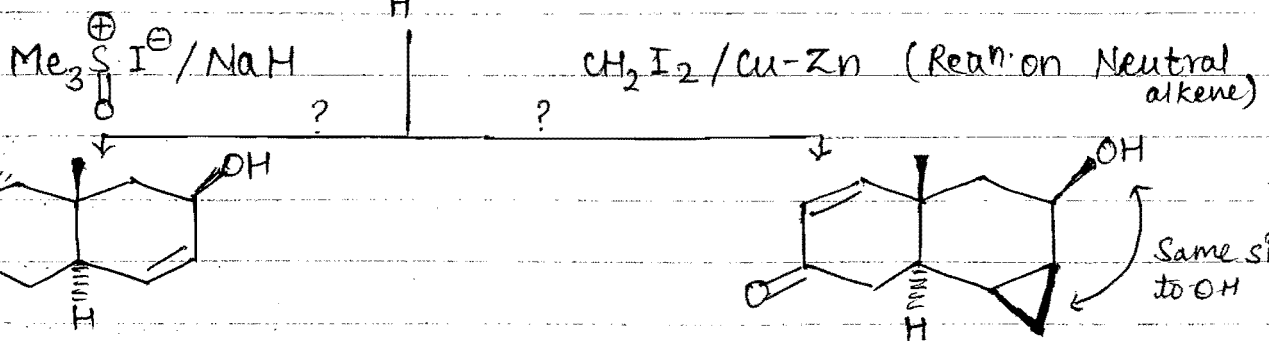


Q 



Q Imp.



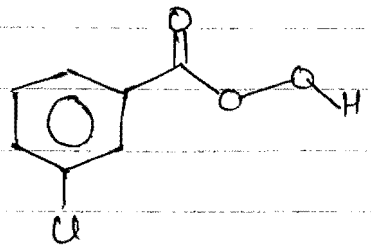


OXIDATION

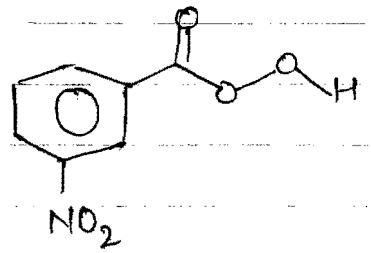
PERACIDS (or) PEROXY ACIDS

Some per acids:-

$F_3C-\overset{O}{\overset{\|}{C}}-OOH$ (Peroxy trifluoroacetic acid)



meta-Chloro perbenzoic acid.
m-CPBA



meta Nitroperbenzoic acid.
m-NPBA

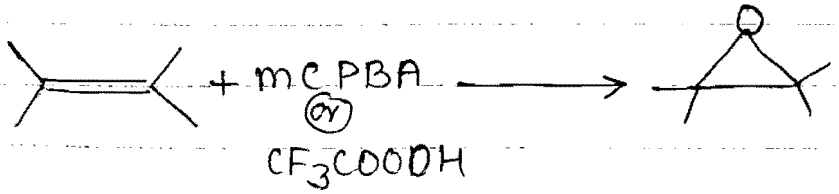
m-CPBA is widly used because-

* More stable
* Non toxic
* Good reagent for epoxidation

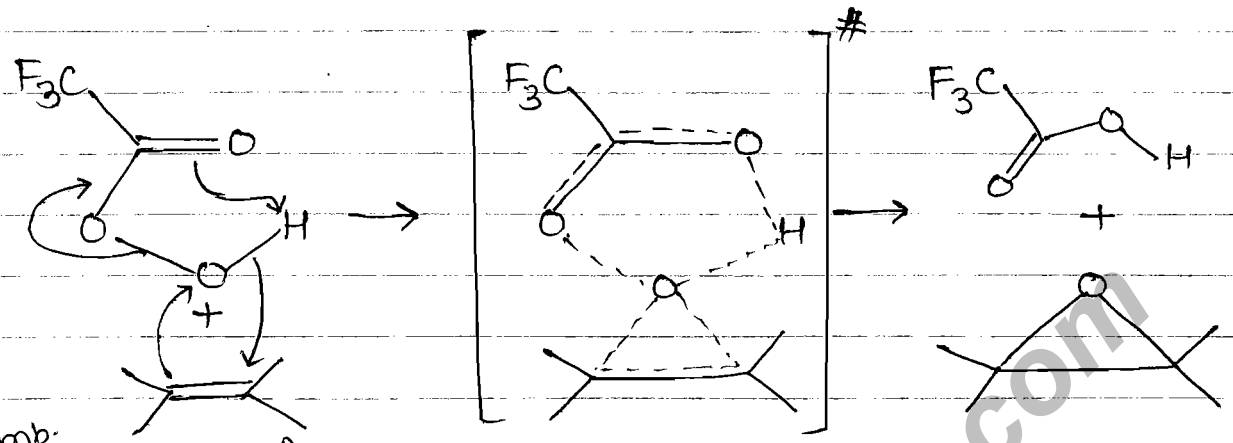
Applications of per acids:-

- Epoxidation
- Bayer Villigar Oxidn. (B.V.O.)

Epoxidation:-

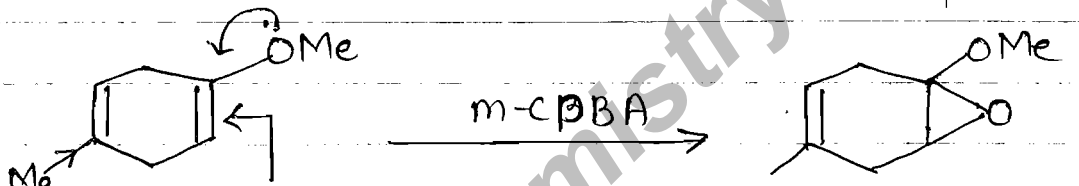


Mechanism:-

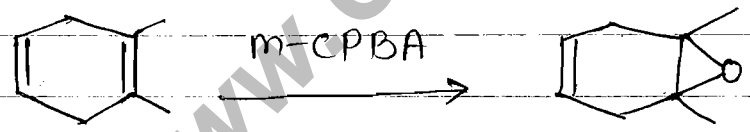


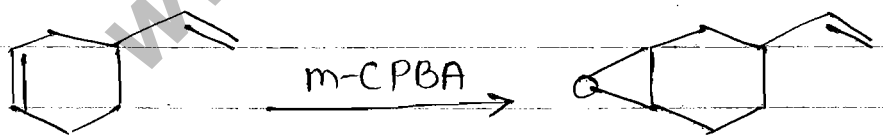
M. imp.

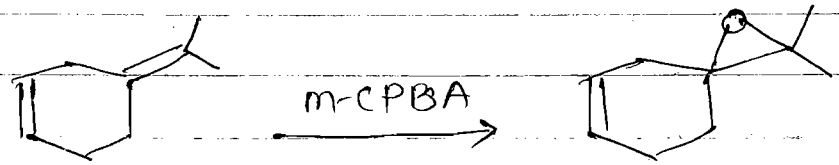
Per acids $\xrightarrow{m\text{-}CPBA}$ are electrophilic in nature so if in a comp. two double bond +nt then epoxidation takes place at more electronically rich alkene.

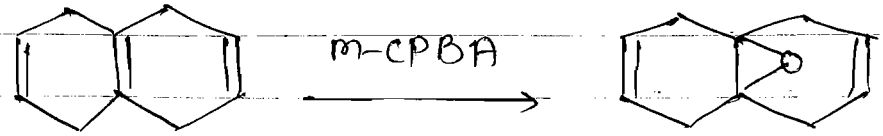
Q 

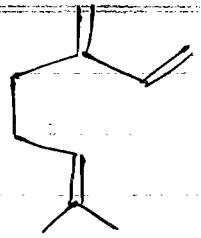
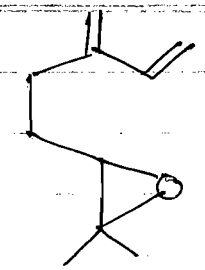
More e⁻ rich (+R effect)

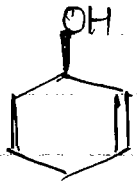
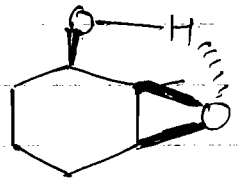
Q 

Q 

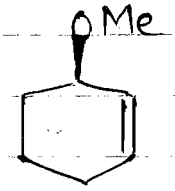
Q 

Q 

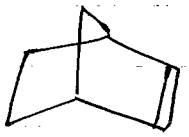
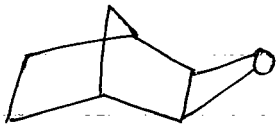
Q  m-CPBA 

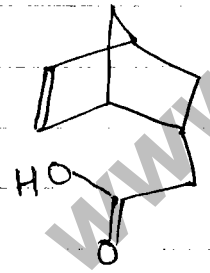
M. Imp. Q  m-CPBA 

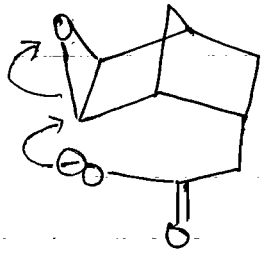
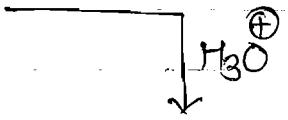
Don't confuse in stereo chemistry.

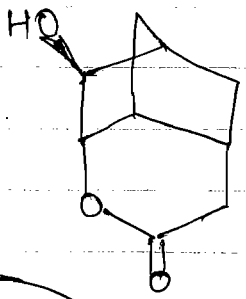
Q  " 

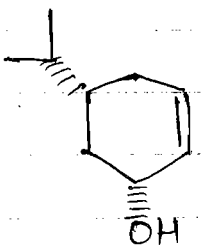
No H.B i.e why. below the plane. (Less steric Hind!)

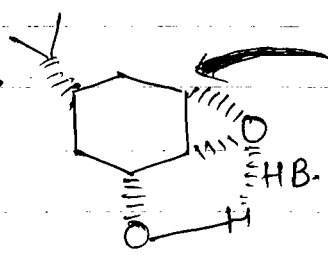
Q  "  exo.

Q 

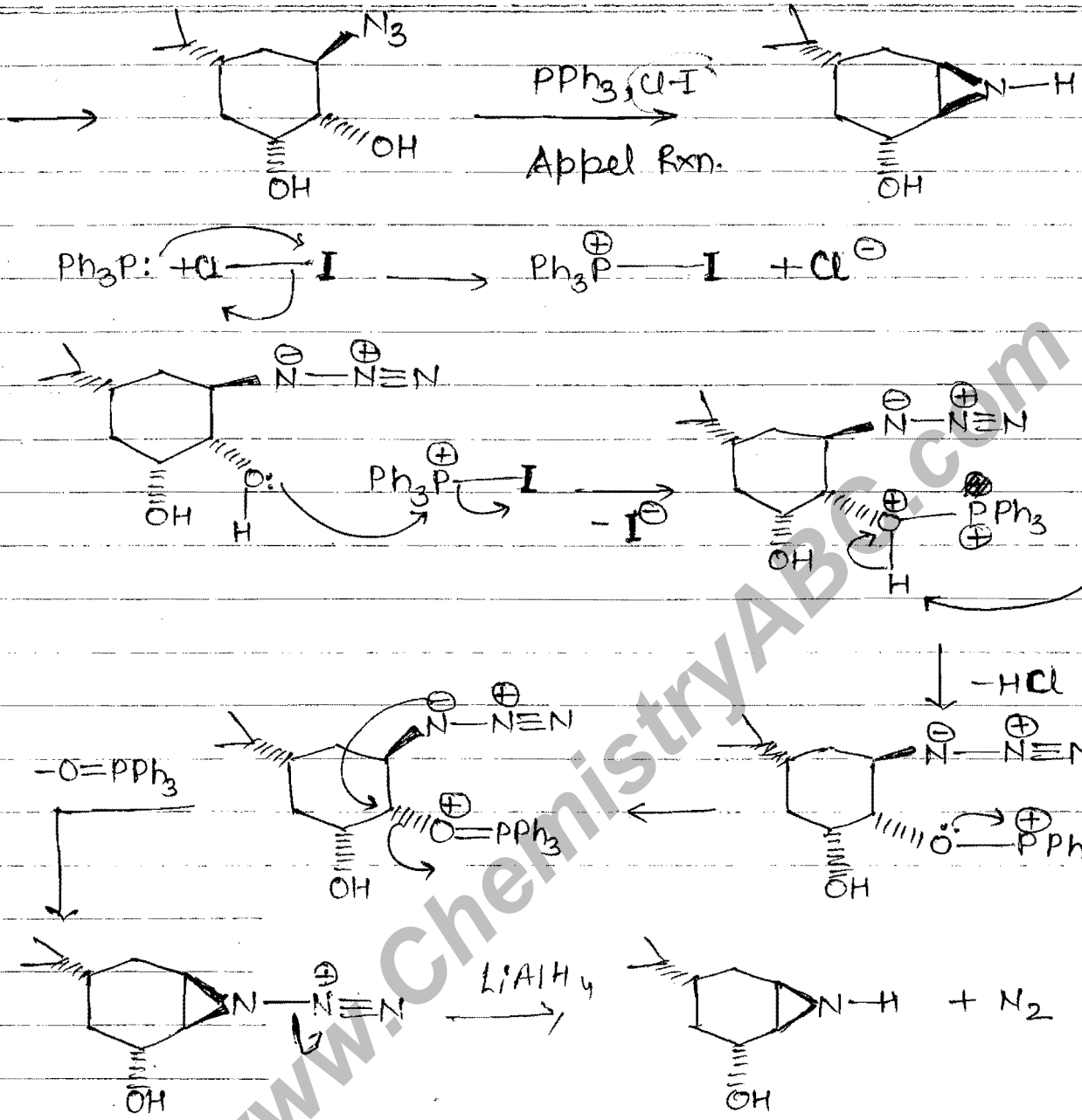
m-CPBA
$NaHCO_3$
(Base)



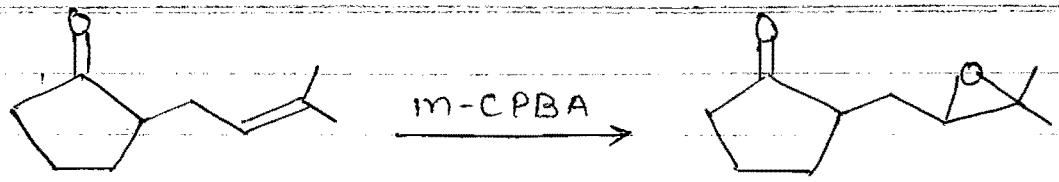


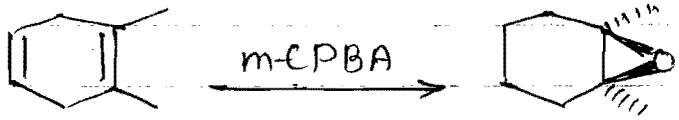
V. V. Imp Q 

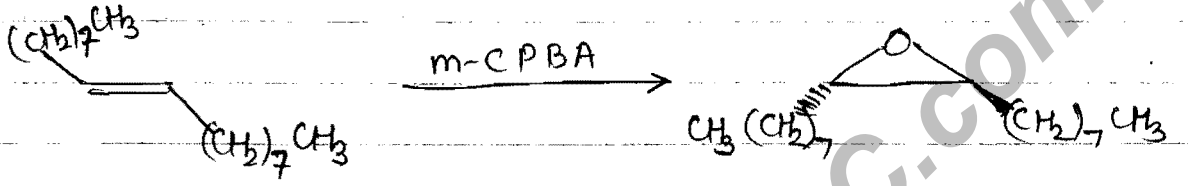
m-CPBA


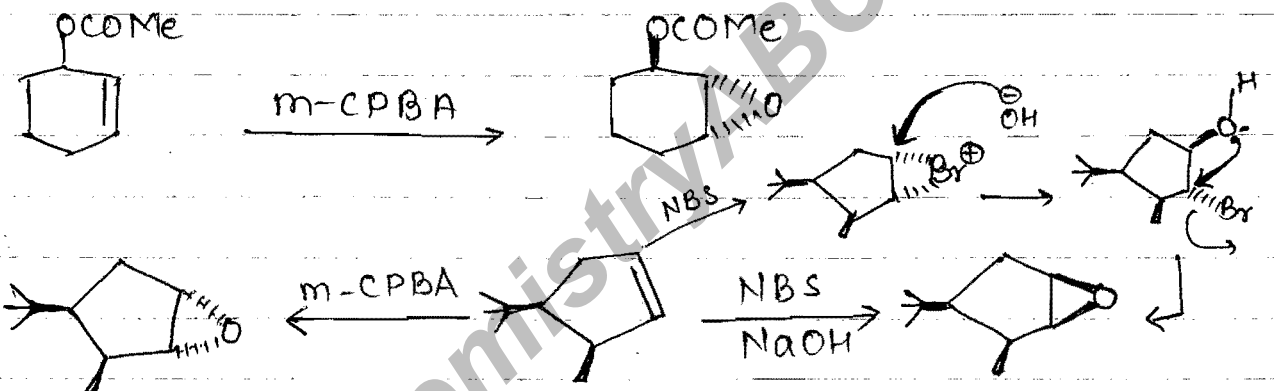
NaN_3

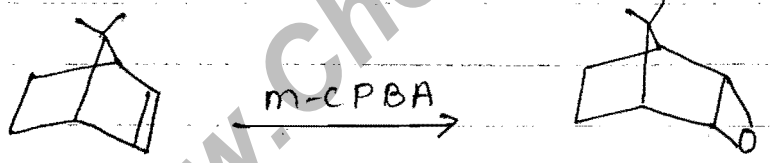


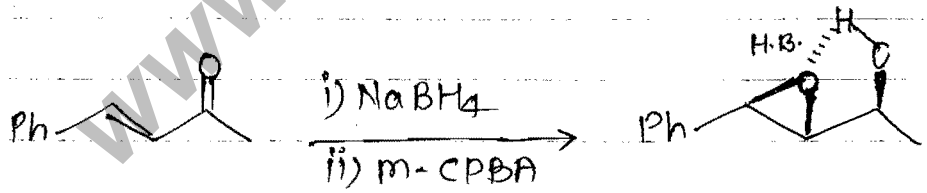
Q 

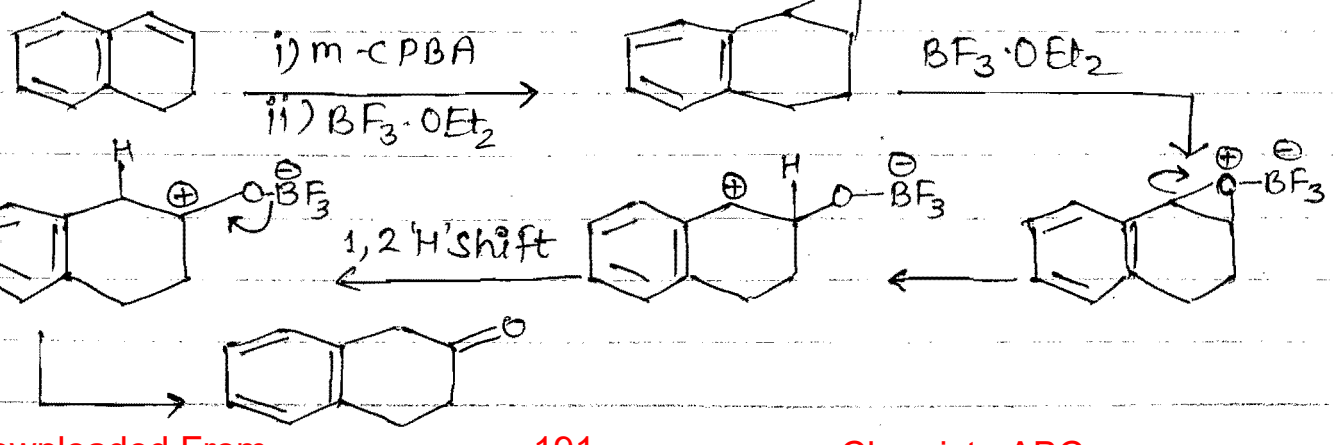
Q 

Q 

Q 

Q 

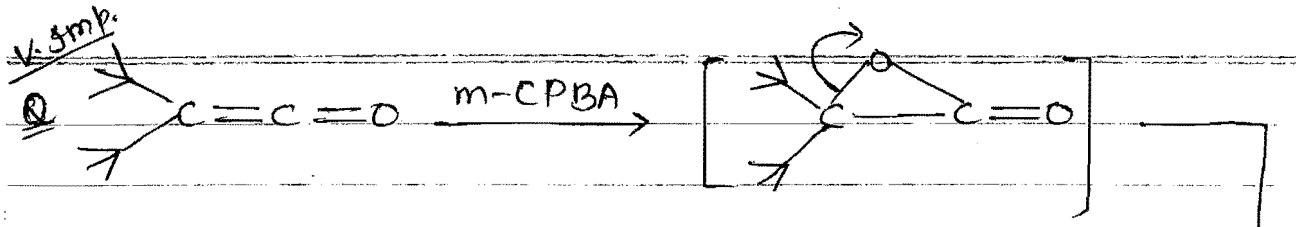
Q 

V. Imp. Q 

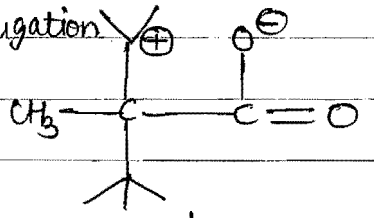
Whenever you found -OH group on adjacent carbon of carbon having silicon ⇒ think about Piterson Elimination.

V. Imp.

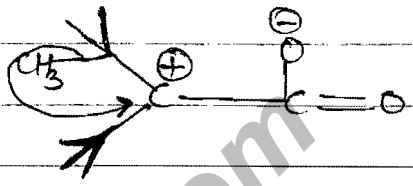
Q



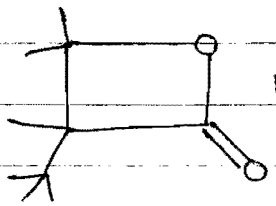
cation is stabilized by +I as well as Hyperconjugation



1,2 methyl shift



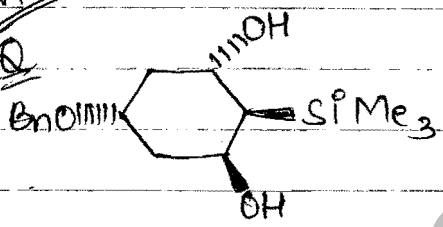
Cation is stabilised by +I effect only.



Unexpected product.

M. Imp.

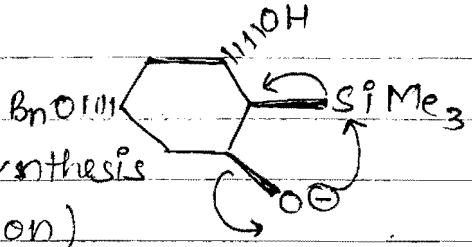
Q



(Basic medium)

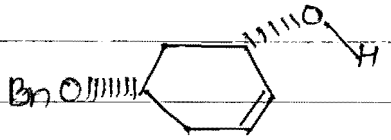
i) KH

Piterson olefin synthesis (SYN Elimination)

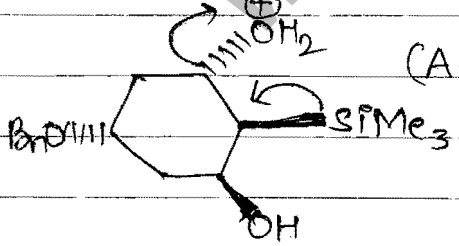


H⊕ acidic Medium

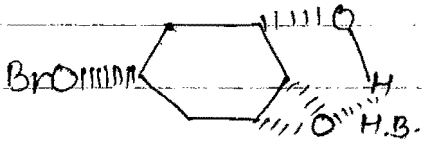
Piterson

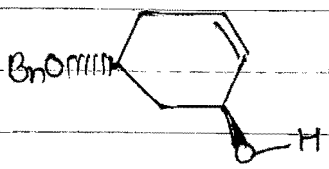


(Anti elimination)

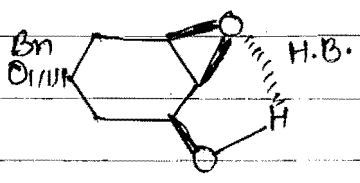


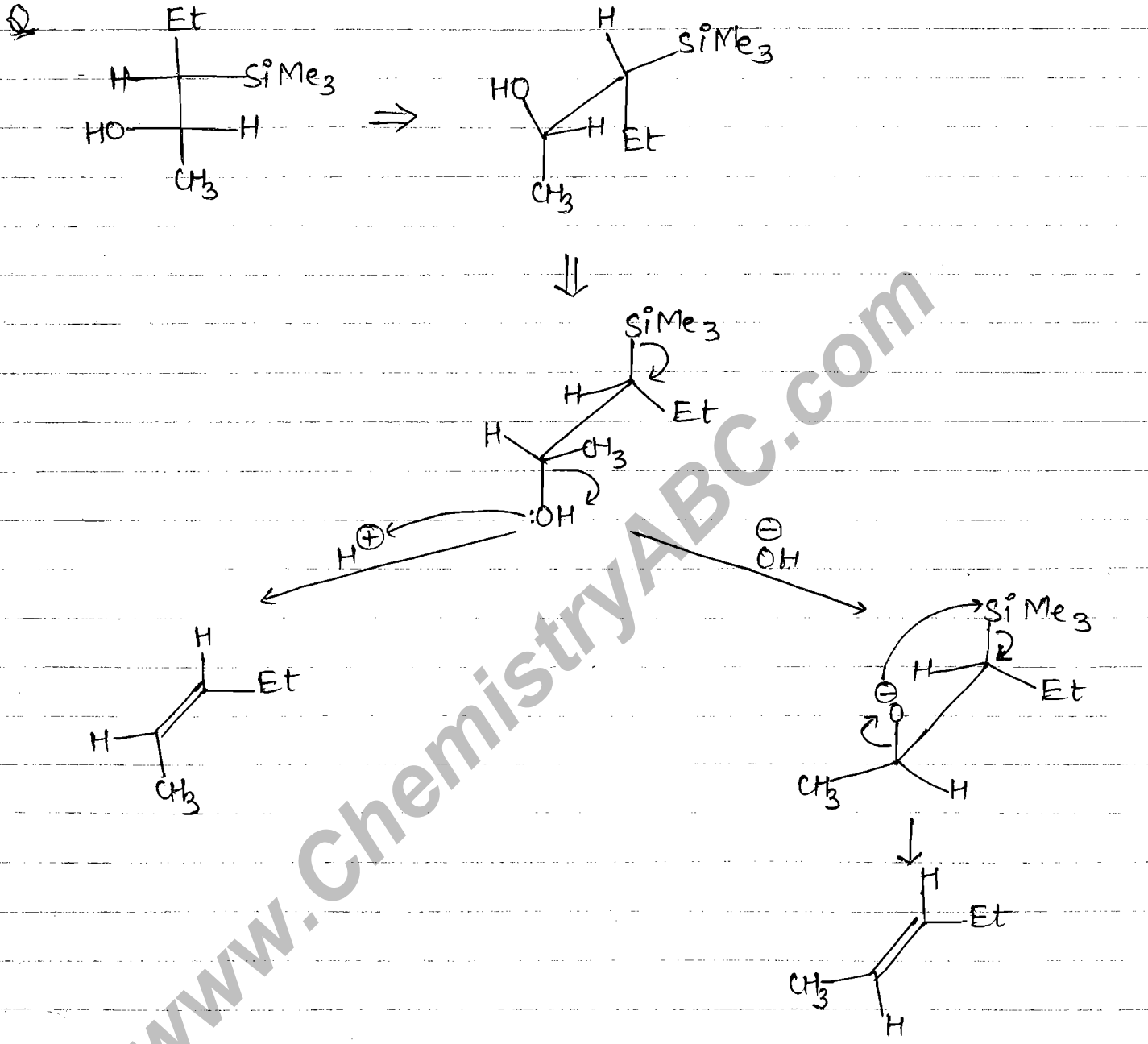
m-CPBA





m-CPBA

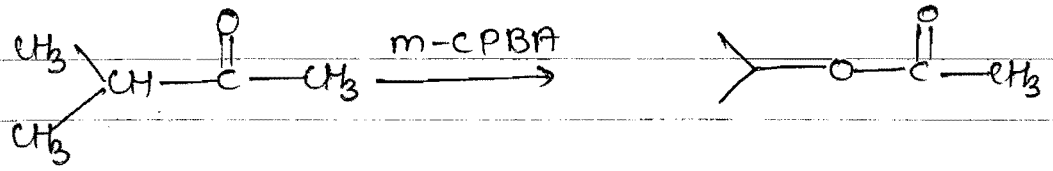




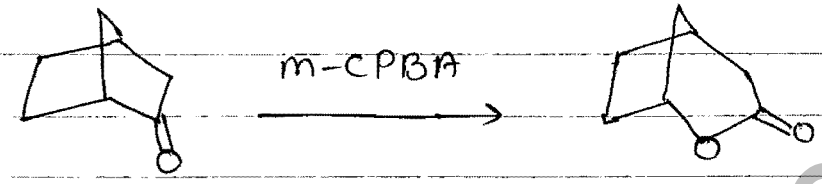
BAYER VILLIGER Oxidⁿ :-

B. V. O. is the method for formation of ester by ketone (or aldehyde) in the presence of peracids.

B.V.O. is the oxy insertion reaction. Insertion of Oxygen is depend on the migrating aptitude of alkyl groups.

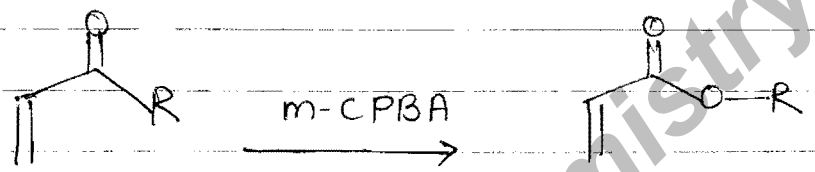
Ex. 

Migratory aptitude $3^\circ > 2^\circ > 1^\circ$

Ex. 

M.imp.

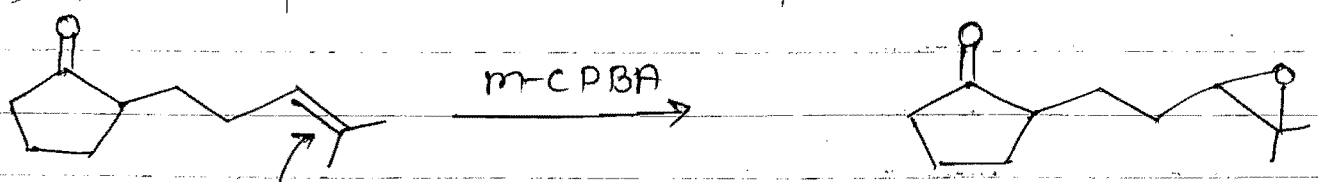
α-β unsaturated carbonyl comp. gives B.V.O. because C=C double bond is electron defficient.



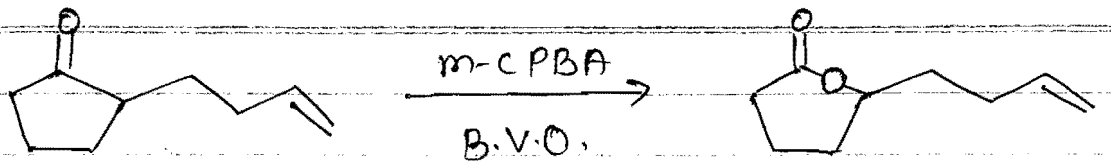
If in a comp. isolated double bond and carbonyl both are +nt then epoxidation & B.V.O. depends on — How much alkene is e⁻ rich or Nucleophilic and How much ketone is e⁻ defficient or Electrophilic.

i) If alkene is more Nucleophilic ⇒ Epoxidation.

ii) If Carbonyl is more Electrophilic ⇒ B.V.O.



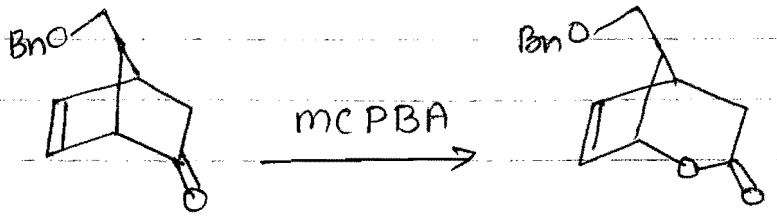
Note:: If alkene has more than 2 (+I) gps then ⇒ Epoxidation.



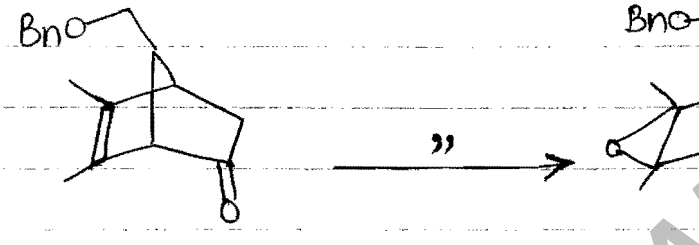
Ester

V. gmp.

Q

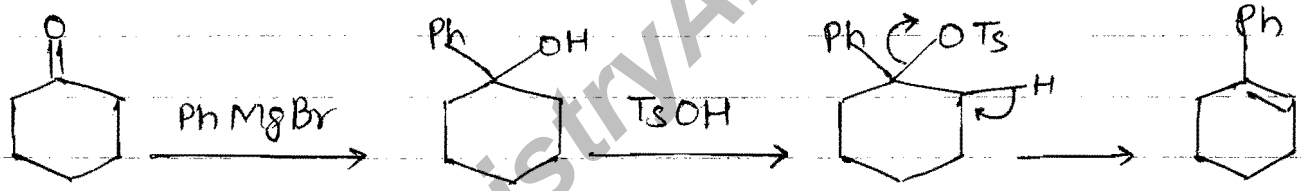


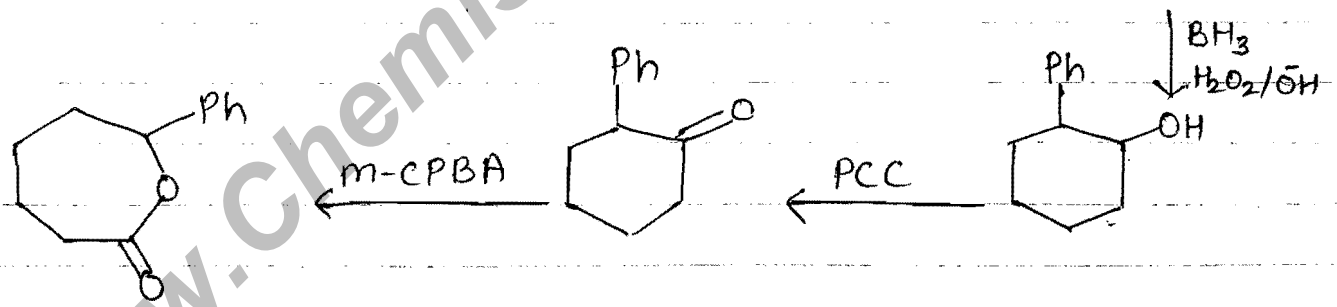
Q



M. gmp.

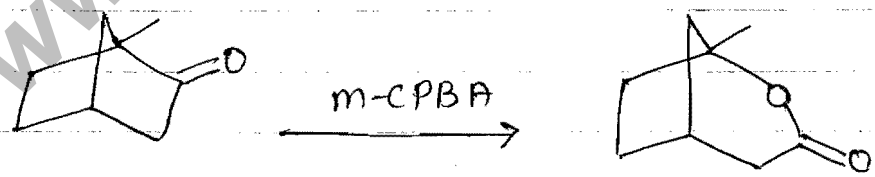
Q





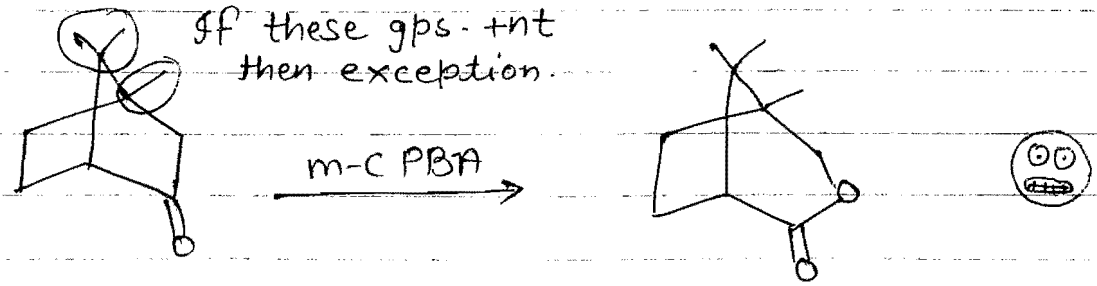
V. V. gmp.

Q

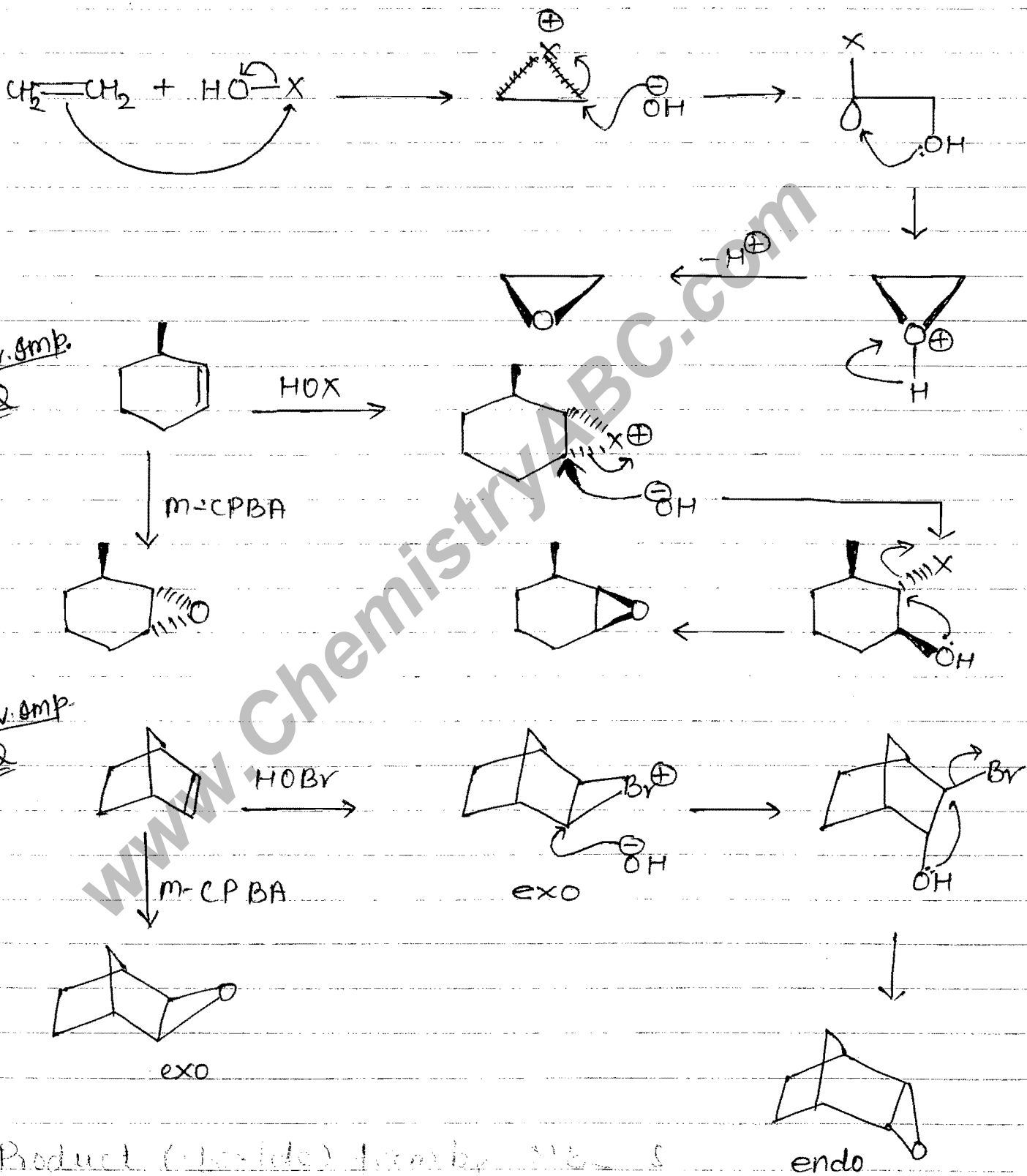


V. V. gmp

Q



HYPOHALOUS ACIDS [HO—X]



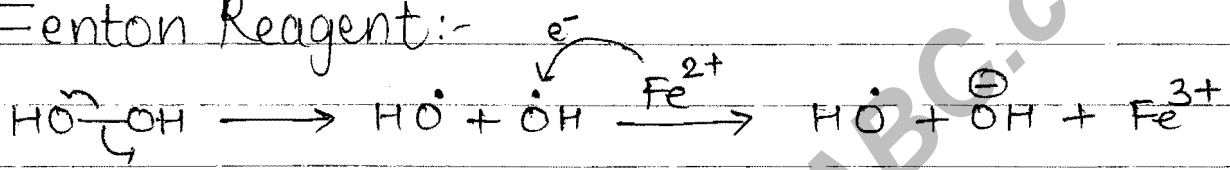
Product (Halohydrin) formed by HO—X is Hypohalous Acids are same ⇒ Double inversion

HYDROGEN PEROXIDE H_2O_2

H_2O_2

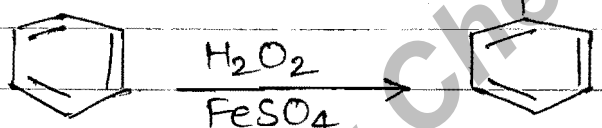
- H_2O_2 / Fe^{2+} — Fenton Reagent
- H_2O_2
- $H_2O_2 / \overset{\ominus}{O}H$
- $H_2O_2 / H^{\oplus}$

1) Fenton Reagent:-

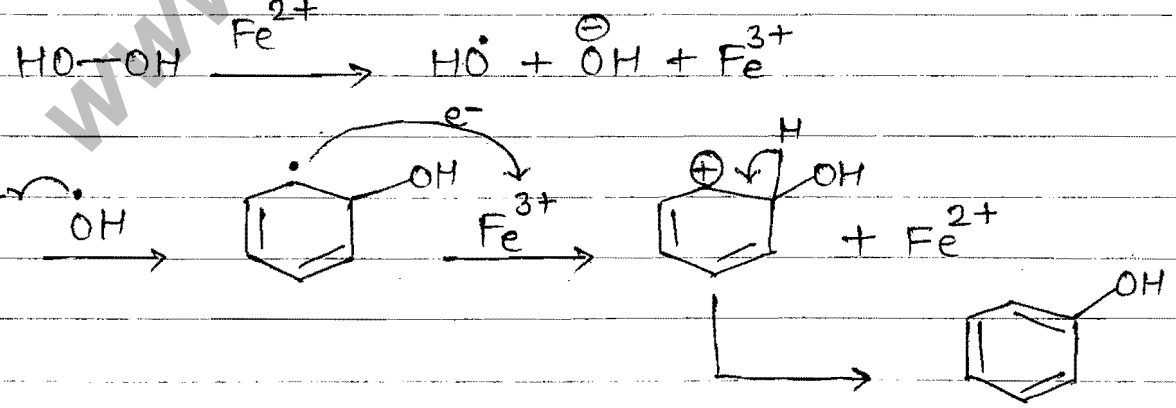


Application of Fenton Reagent:-

* Formation of phenol by benzene.
* Oxidation of α-hydroxy carboxylic acid.

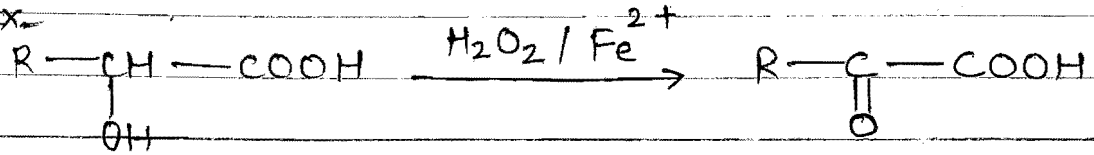


Mech:



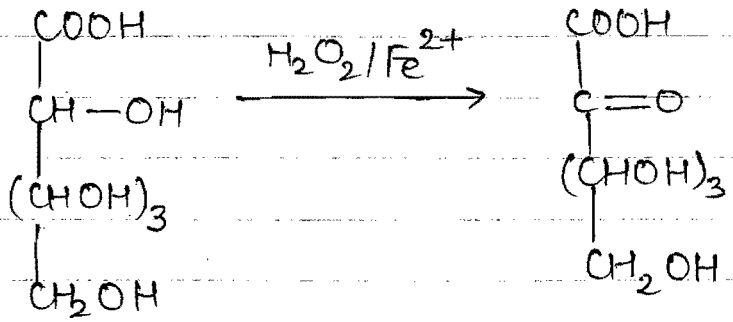
α-Hydroxy acid oxidised into α-keto acid.

Ex.



Imp.

Ex.

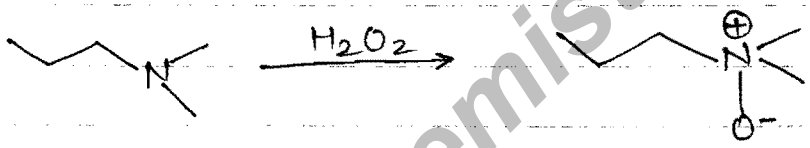


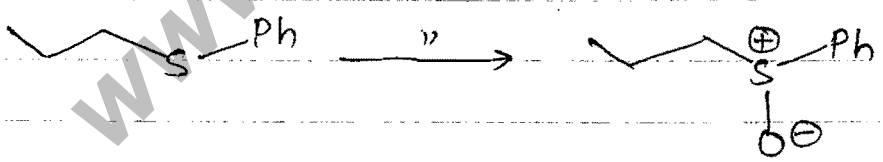
2) Neutral H_2O_2 :- H_2O_2 is the oxidising agent

i) Peracid formation :-

$$R-COOH \xrightarrow{H_2O_2} R-COOOH$$

ii) Formation of $\overset{\oplus}{N}$—Oxide, $\overset{\oplus}{Se}$—Oxide, $\overset{\oplus}{S}$—oxide

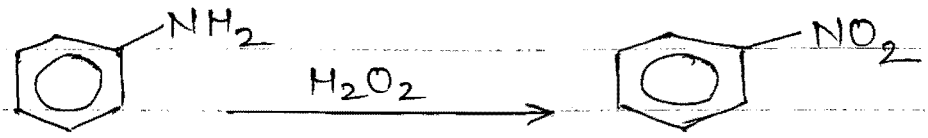




iii) Oxidation of amine into nitro :-

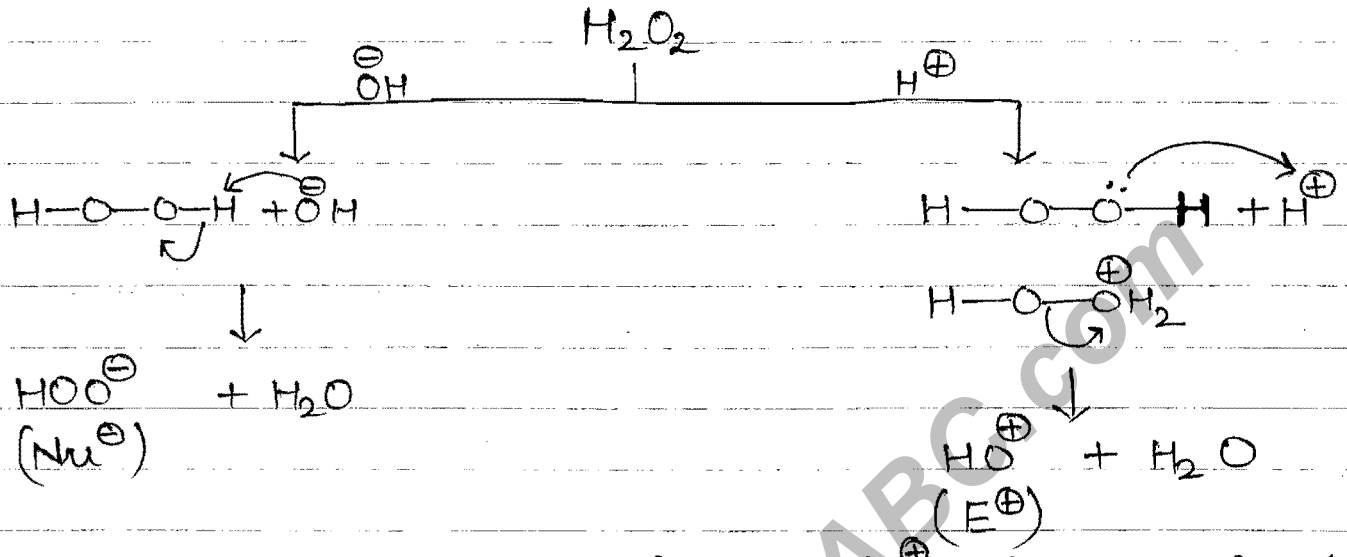
Ex. $CH_3-CH_2-CH_2-NH_2 \xrightarrow{H_2O_2} CH_3-CH_2-CH_2-NO_2$

Ex.



Imp.

3) H_2O_2 in acidic and basic Medium:-



Existance of $^{\oplus}OH$ is very difficult & it is highly reactive & it form Oxonium ion with alkene.

Imp.

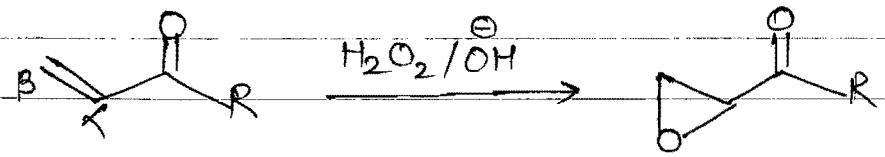
Applications of $H_2O_2/^{\ominus}OH$:-

1) Hydroboration
2) Epoxidation of α,β-unsaturated carbonyl.
3) Use in Dakin Rxn.

M. Imp.

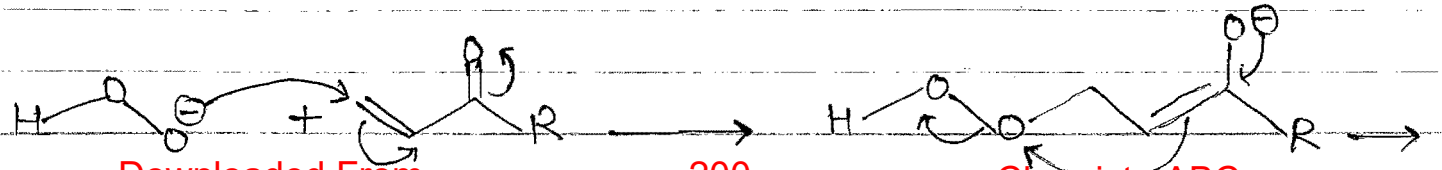
* Epoxidation of α,β-unsaturated Carbonyl comp.

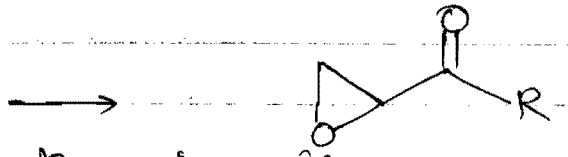
Ex.



Mechanism:-

$H_2O_2 + {}^{\ominus}OH \longrightarrow {}^{\ominus}O-O-H + H_2O$





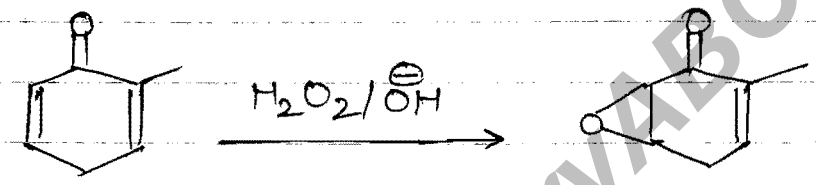
imp. in presence of Base

* H_2O_2 is the best reagent for epoxidation of α-β unsaturated carbonyl comp.

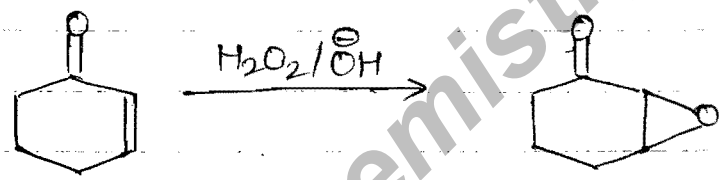
imp. Carbonyl

⇒ If in a comp. two α-β bond not then epoxidation takes place at e⁻ efficient α, β-unsaturated C=C bond.

Ex.



Q



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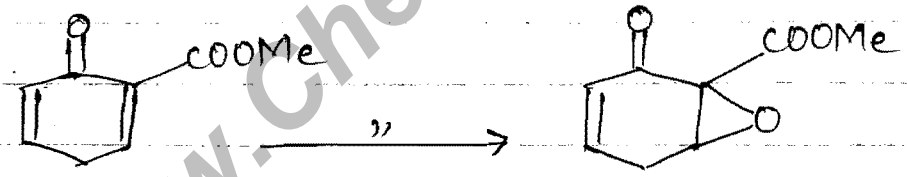

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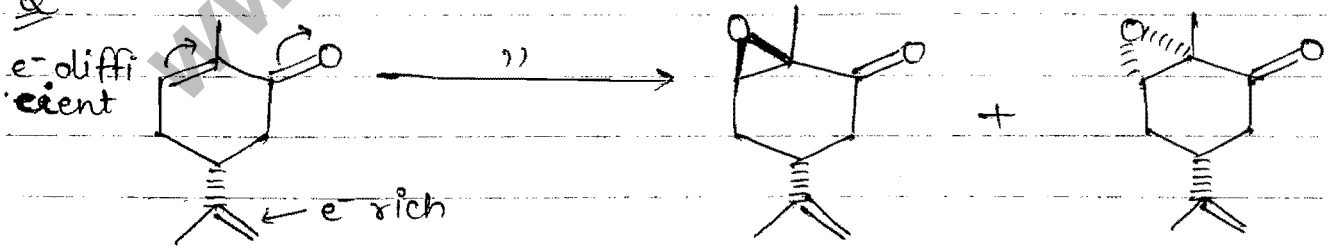
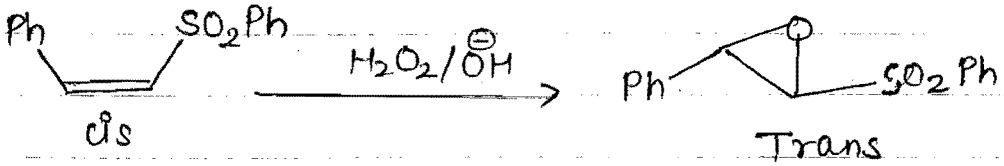


major minor

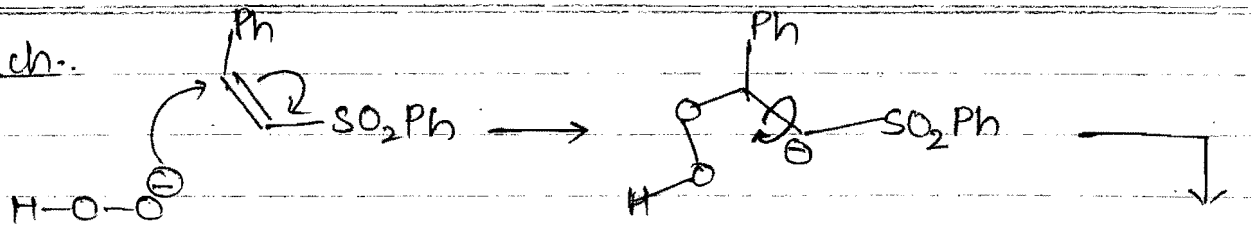
V.V. imp.

Q

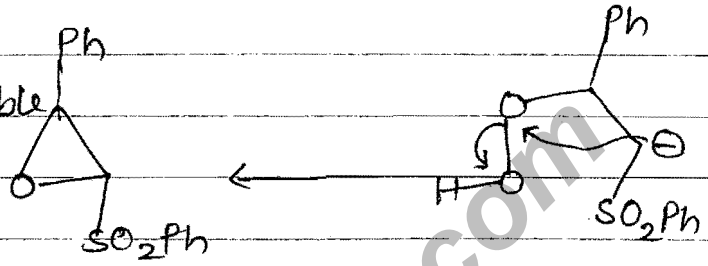


cis Trans

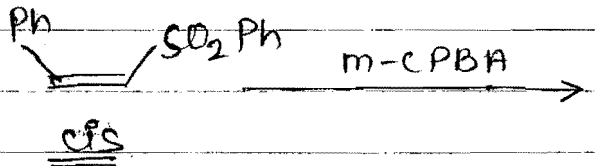
Mech.-

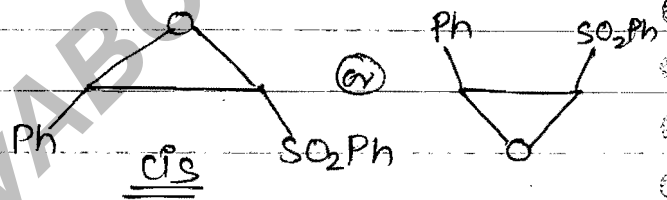


Trans form is more stable due to steric fav. pdt.



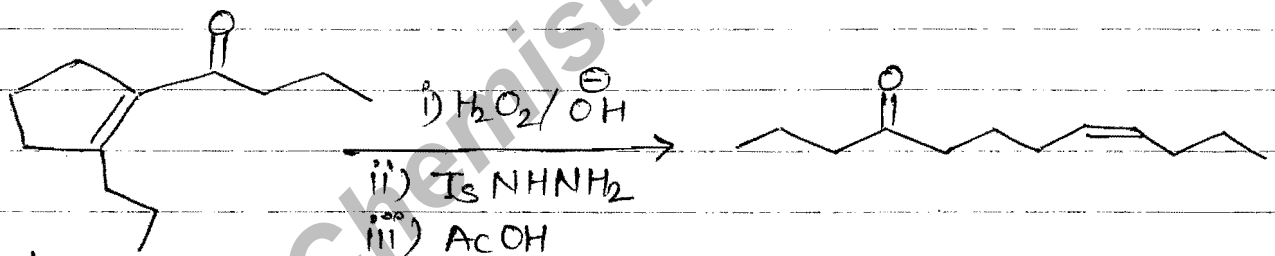
Q

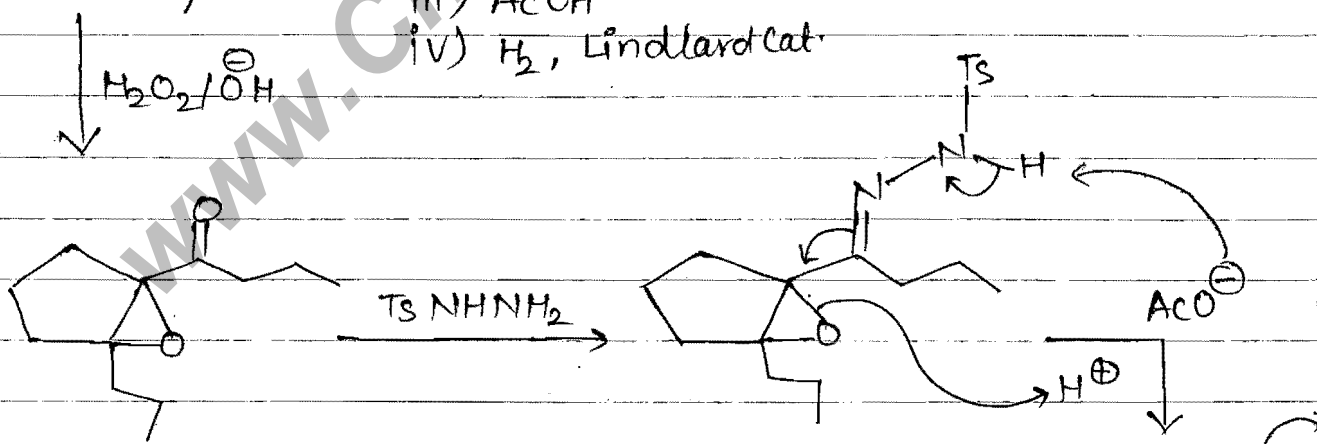


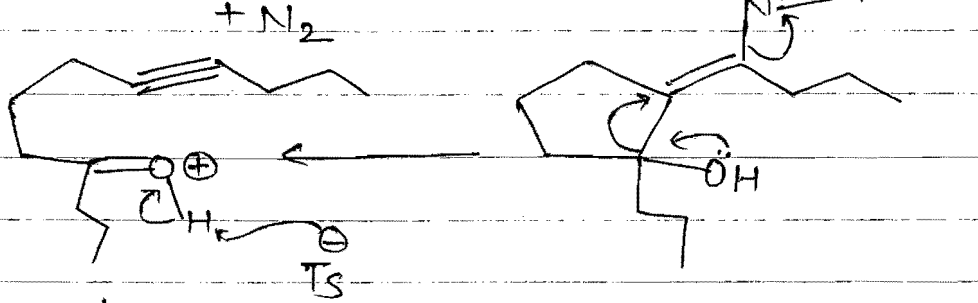


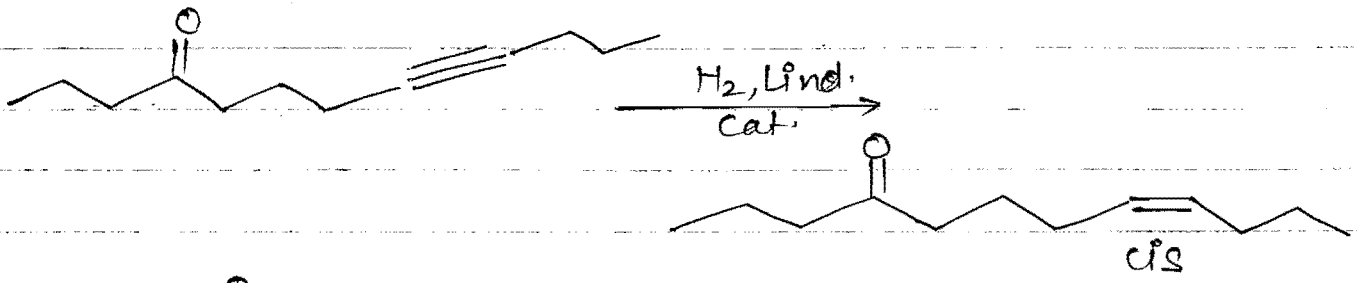
V. Imp.

Q

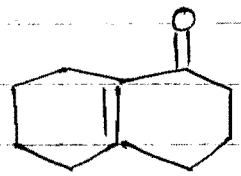




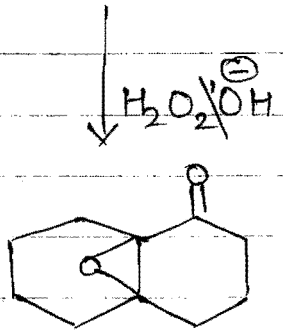




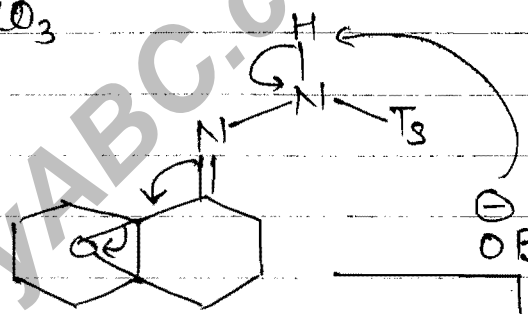
V. Imp. Q

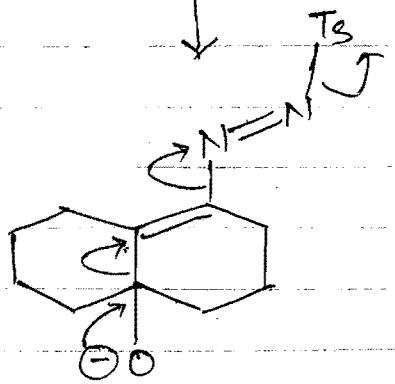


i) $H_2O_2/\overset{\ominus}{O}H$
ii) $TsNHNH_2 \longrightarrow$?
iii) $KOBu^t$
iv) $H_2/Pd/CaCO_3$

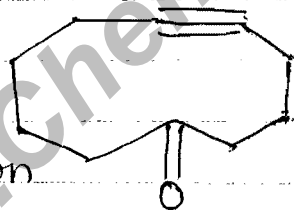


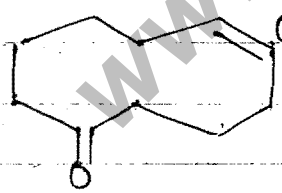
$TsNHNH_2$





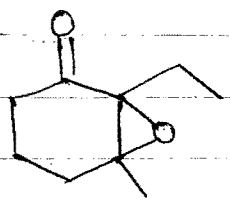
$H_2/Pd/CaCO_3$
↓ cis Reduction



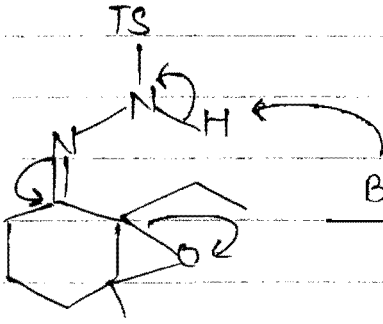


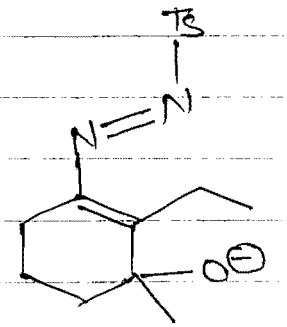
cis double Bond.

Q

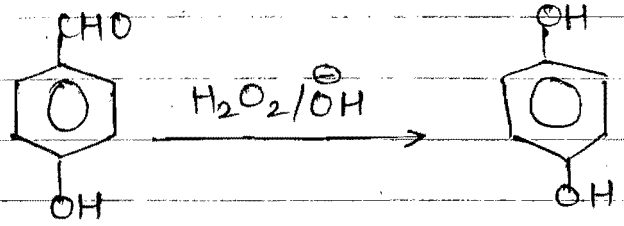


i) $TsNHNH_2$

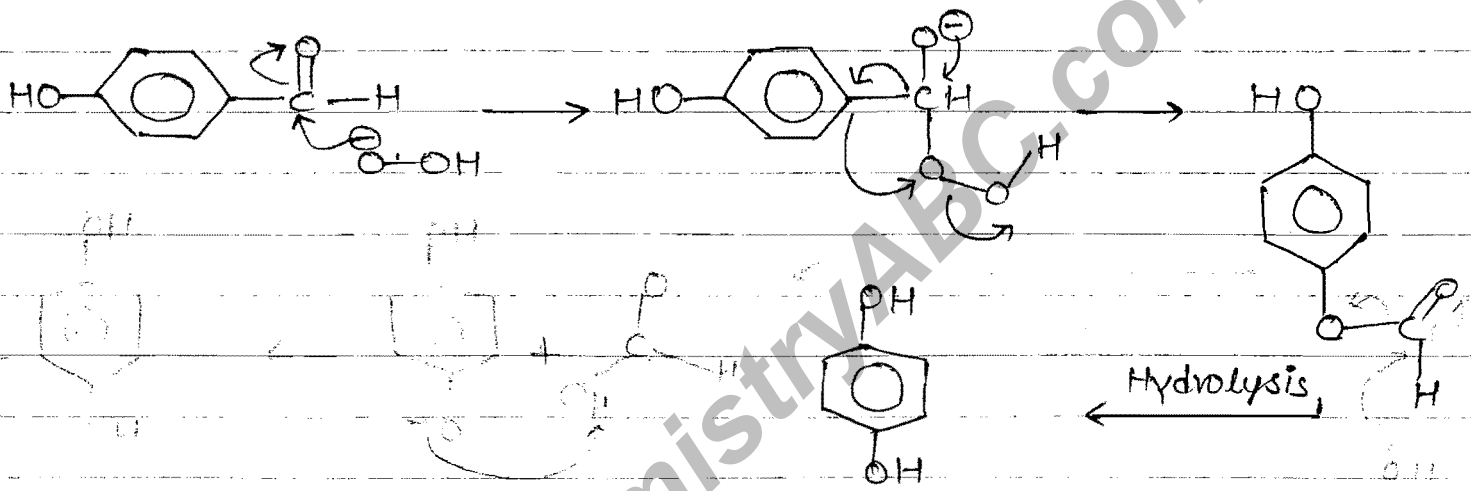


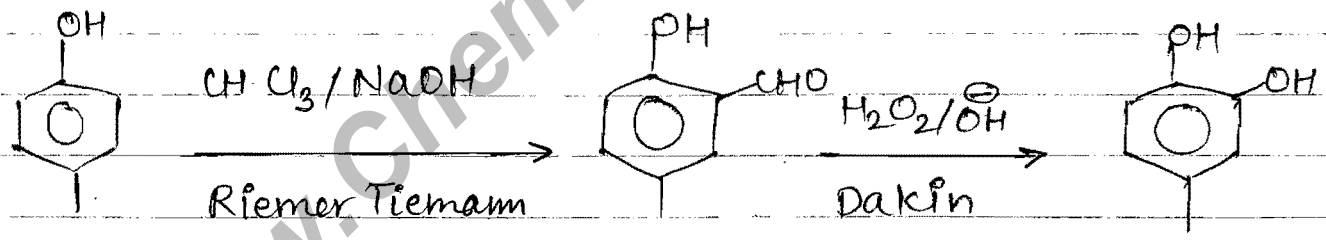


DAKIN Rxn.

Q 

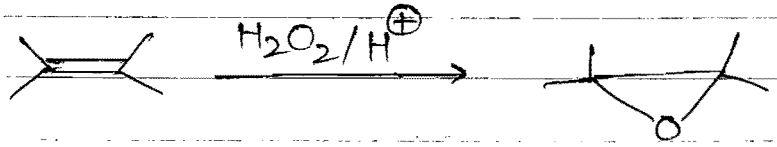
Mechanism:-

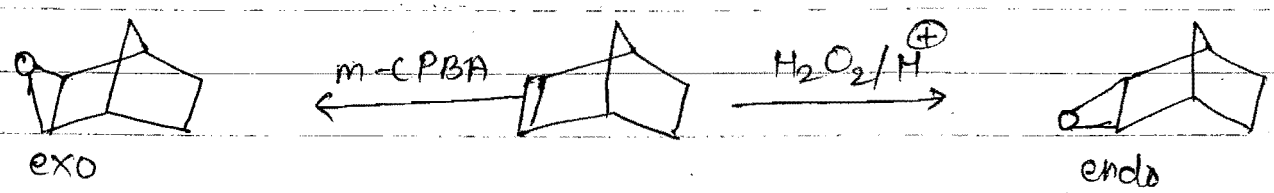


Q 

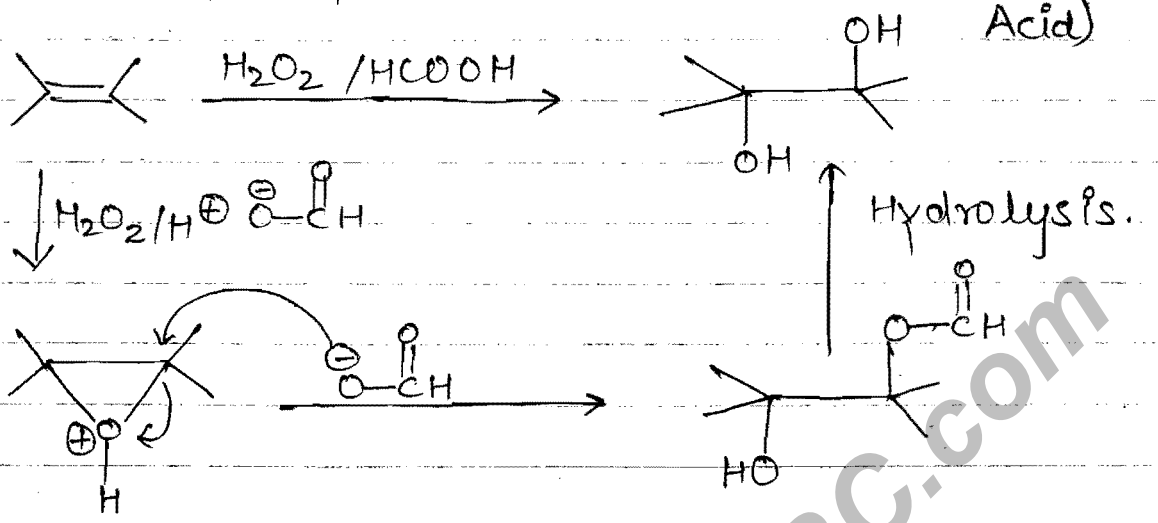
*Application of $H_2O_2/\overset{\oplus}{H}$:-

Used for epoxidation

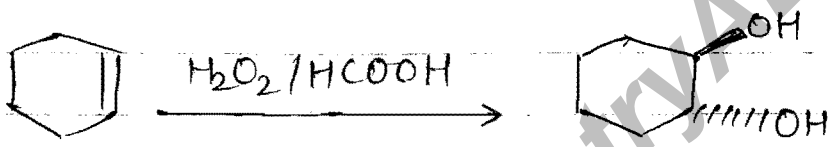


Q 

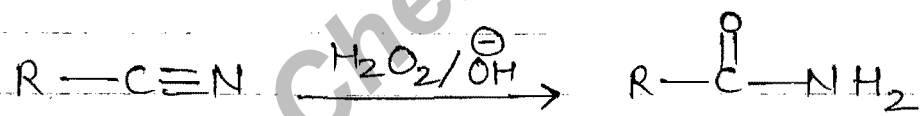
Trans Hydroxylation of alkene:- (If HCOOH not as an Acid)

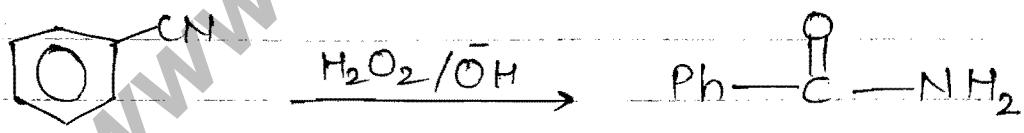


Ex



⇒ Oxidn of Cyanide into Amide:-



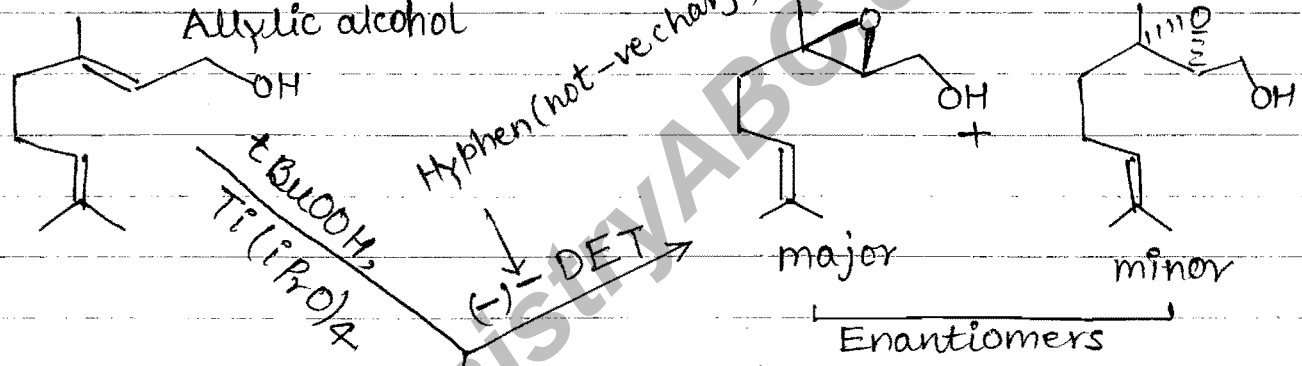


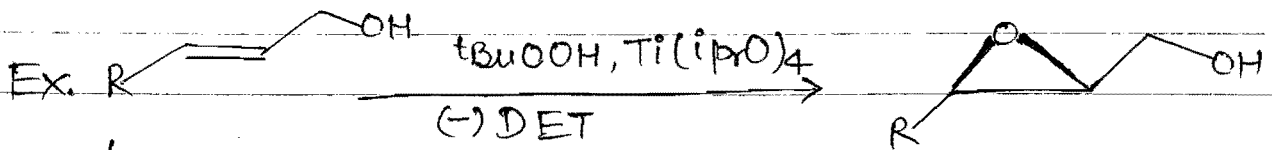
M.Sharp

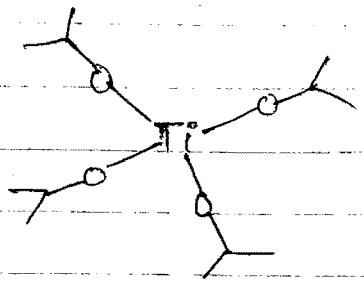
SHARPLESS ASYMMETRIC EPOXIDATION

In involve the epoxidation of allylic alcohol. When Allyl alco is treated with ^tBuOOH, Ti-tetra isopropoxide [$Ti(iPrO)_4$] and diethyl tartrate (± DET), yield asymmetric epoxide. Sharpless Asymmetric Epoxidation is enantio selective Rxn.

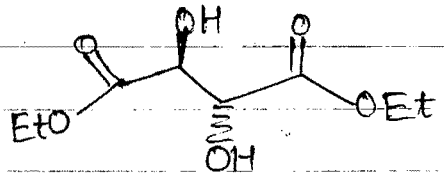
Ex.



Ex. 

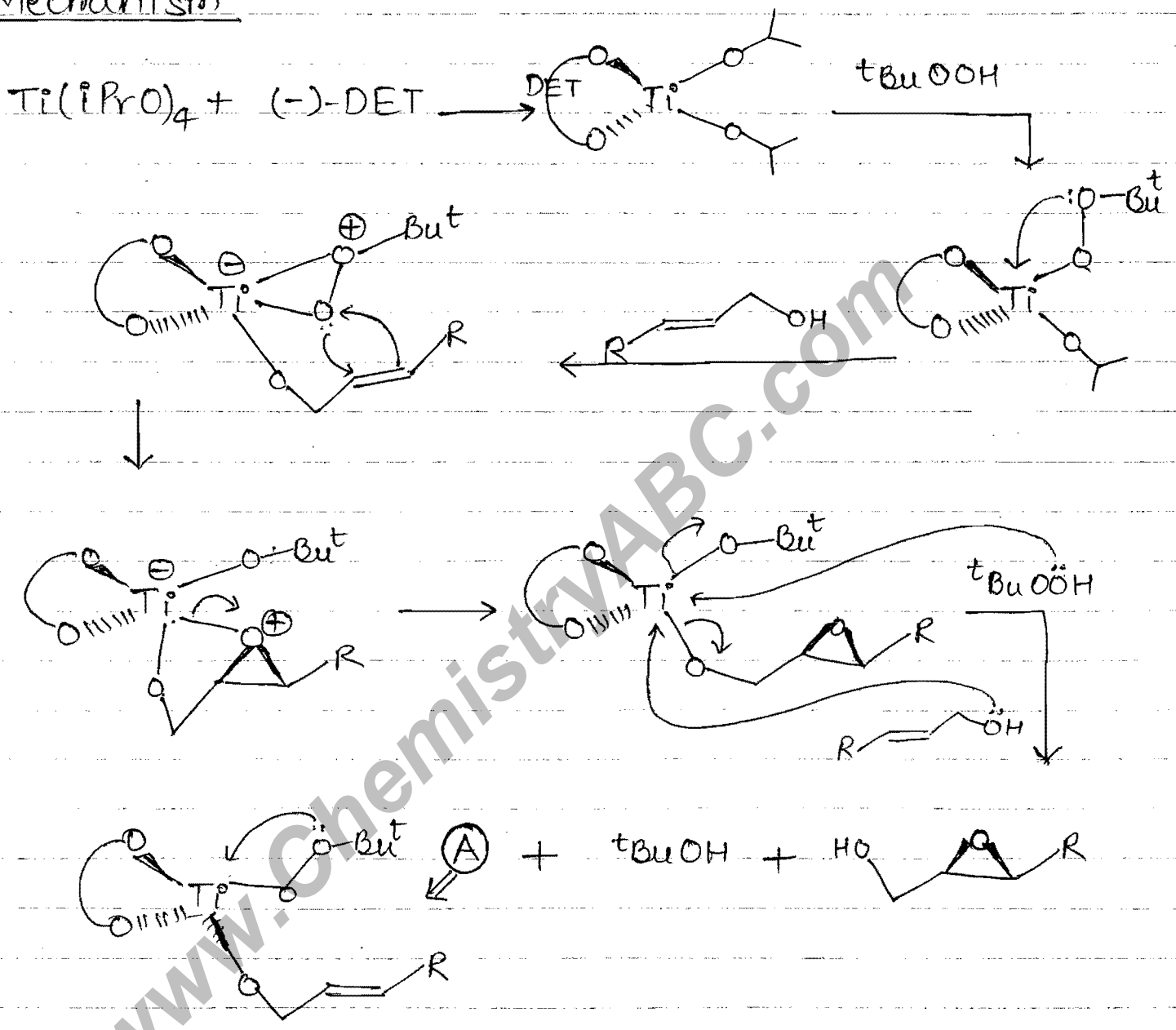


$Ti(iPrO)_4$



(±) DET

Mechanism



KEY POINT :-

1) Show the double bond in vertical diagonal.
2) CH_2OH group must be +nt down side
3) If CH_2OH group is in right hand side then -
   (-)- DET ⟹ Epoxidation Towards the viewer
   (+)- DET ⟹ " Away from the "
   ↑ Hyphen

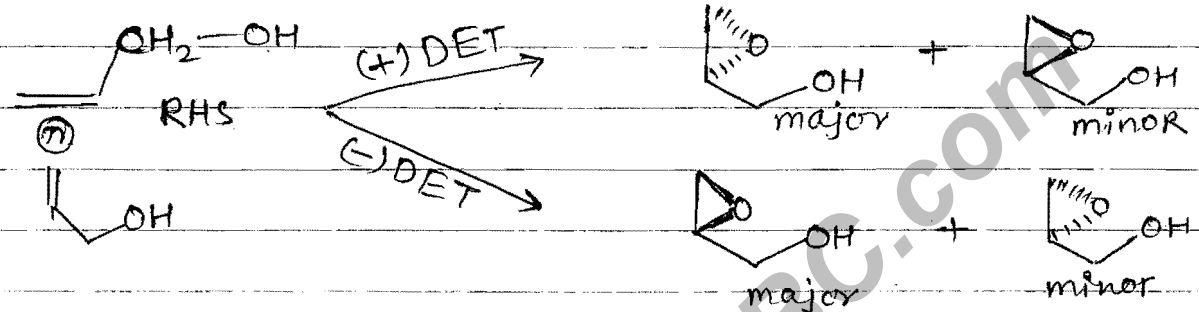
M. grp

4) If CH_2OH group is in LHS then -

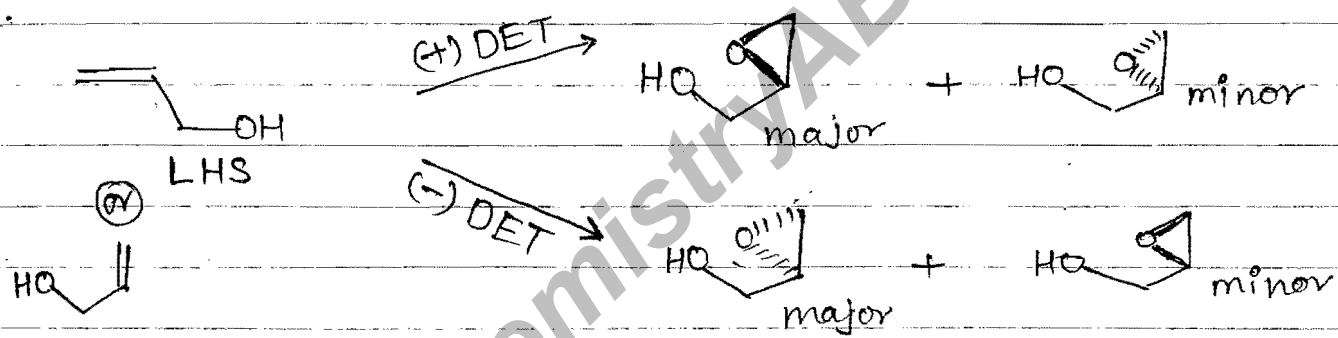
(+)DET ⇒ Epoxidation towards the viewer

(−)-DET ⇒ " Away from " "

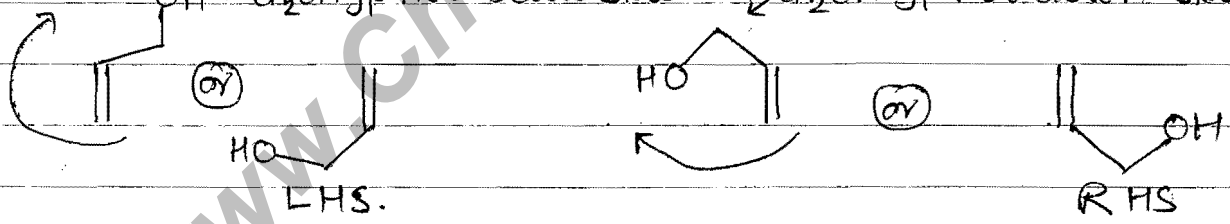
Ex.



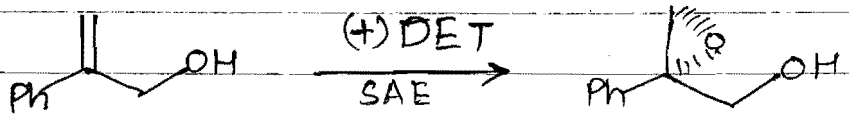
Ex.



⇒ OH ← CH_2OH gp not below side ↙ CH_2OH gp not down side



Q



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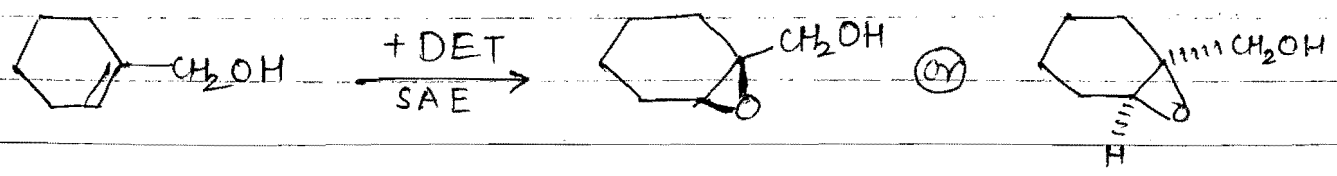

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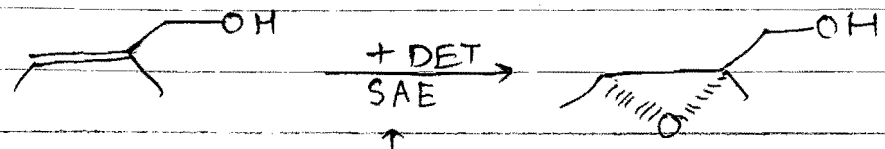
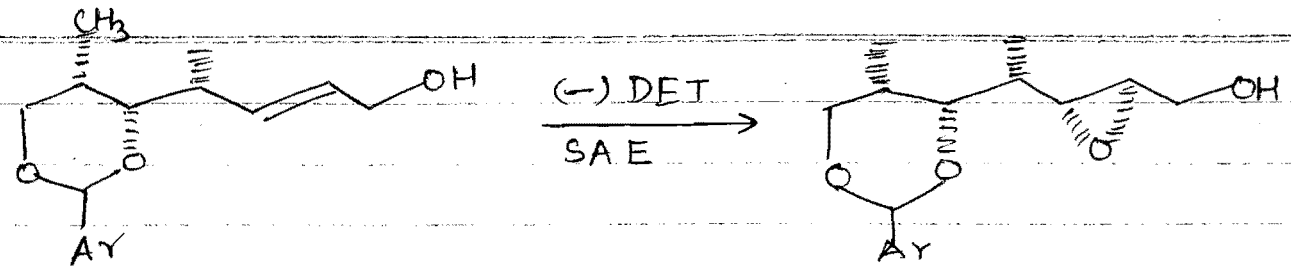
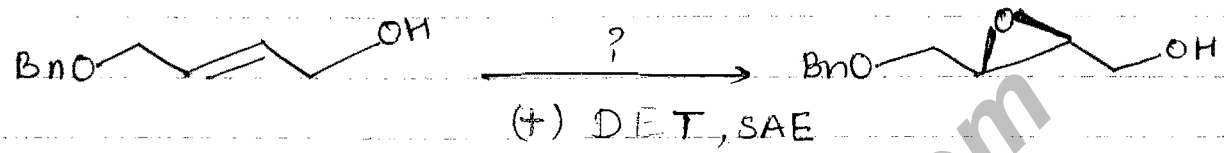
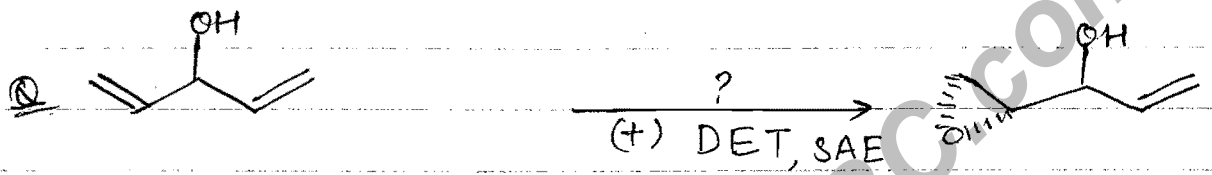
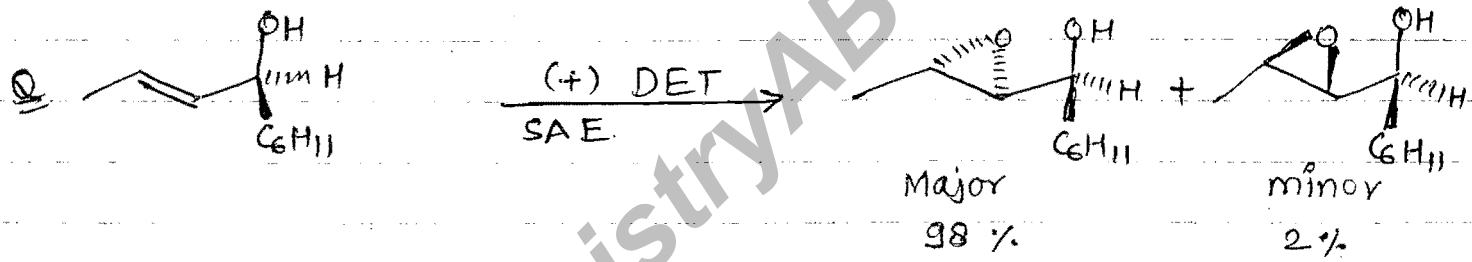


↑ Sharpless Asym. Epoxidation

Q 

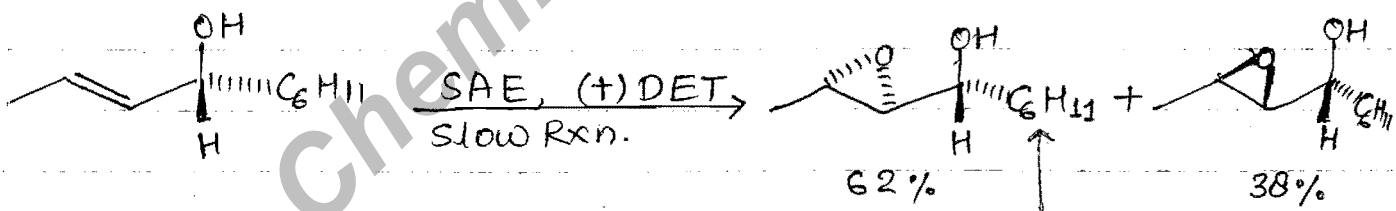
Q 

Q 

Q 

Major
98 %

minor
2 %

Q 

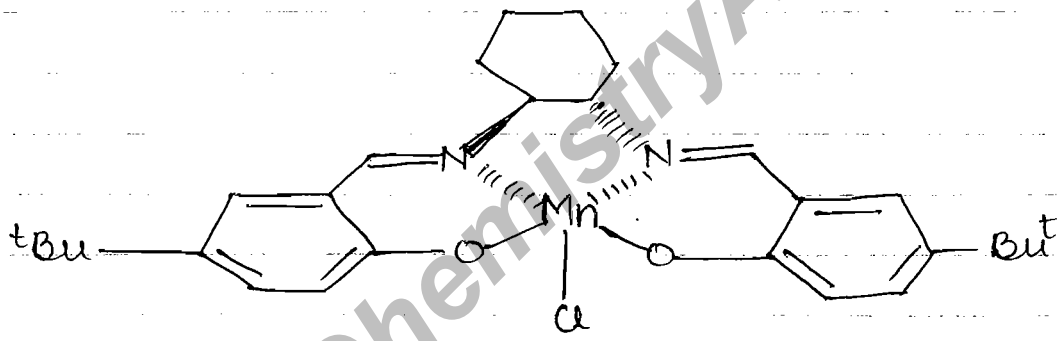
62 %

38 %

Due to this bulky gp ratio of product affected.

JACOBSEN EPOXIDATION

For the enantiomerically pure epoxidation of an unfunctionalized alkene can be carried out by the help of Jacobsen epoxidation. Jacobsen epoxidation suitable for cis alkene. In Jacobsen epoxidation S,S Salen (or) R,R Salen used as a catalyst. Salen is a Magnese (Mn) containing catalyst. Rxn. carried out in the +nce of NaOCl (or) m-CPBA. Jacobsen Epoxidation Mechanism is not well developed.

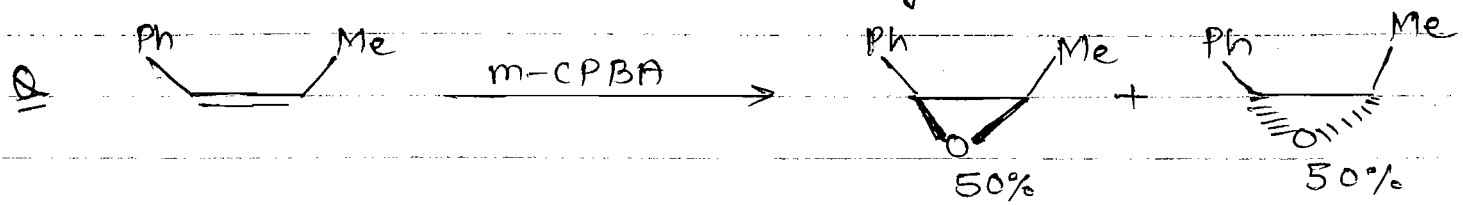


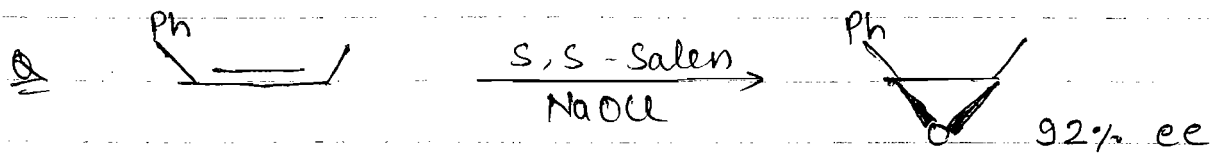
S,S Salen (Cat. For Jacobsen Epoxidation)

⇓

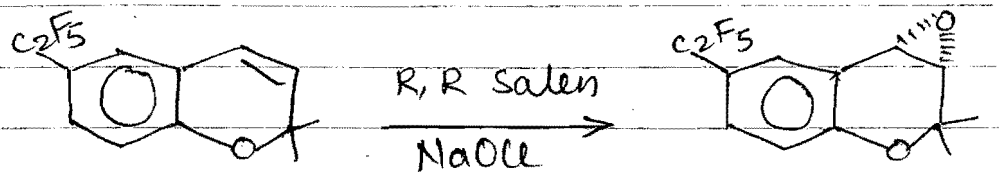
Oxygen supply from top side

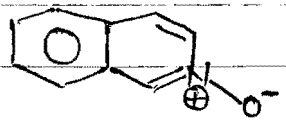
R,R-Salen :- Oxygen supply from bottom side



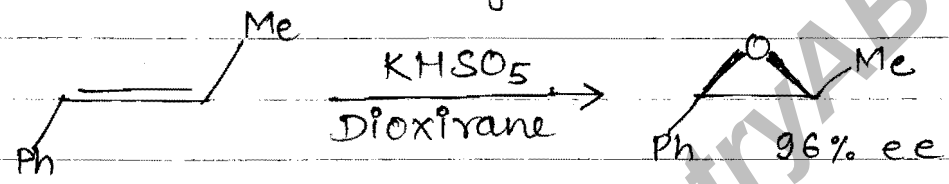


Jacoben epoxidation also k/a Jacobsen-Katsuki epoxidation

Q 

Rate of Rxn increases ⟹ 

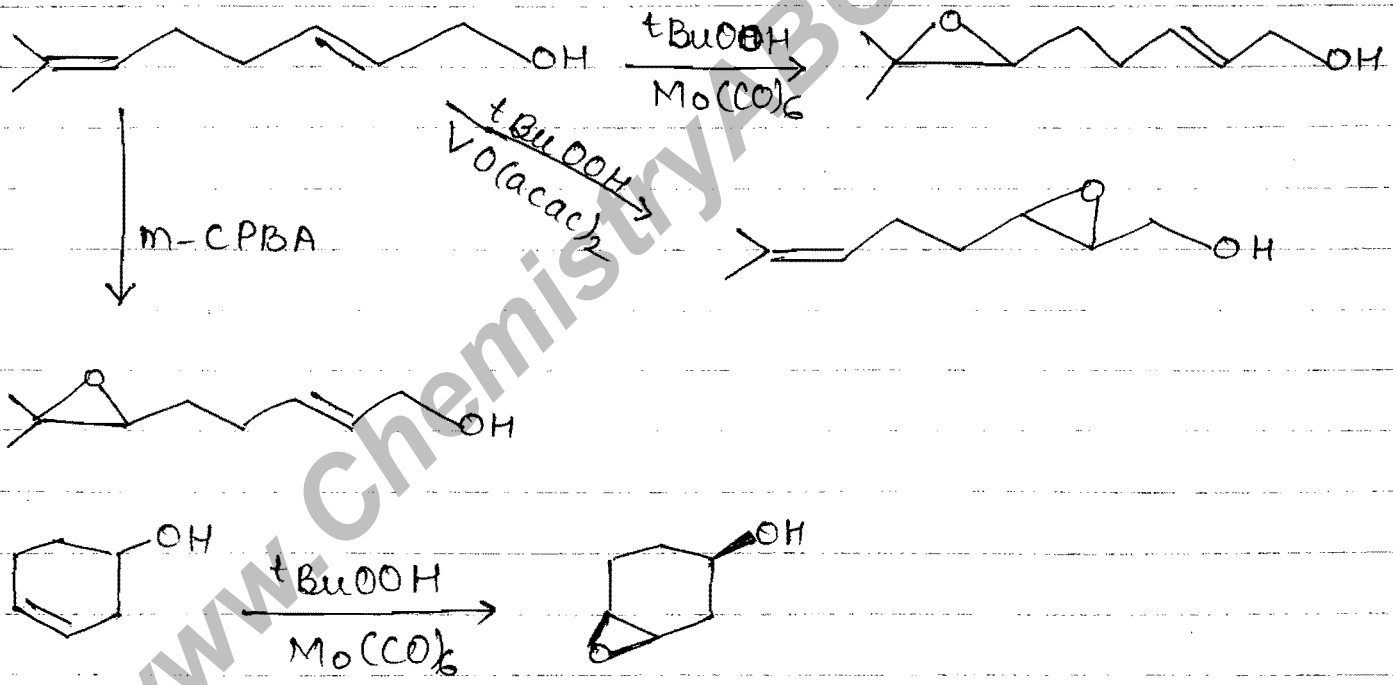
The asymmetric synthesis of trans (or) tri substituted epoxide can be achieved by $KHSO_5$



The rate of Jacobsen epoxidation can be enhance in the +nce of pyridine N-oxide (or) related Aromatic N-oxide.

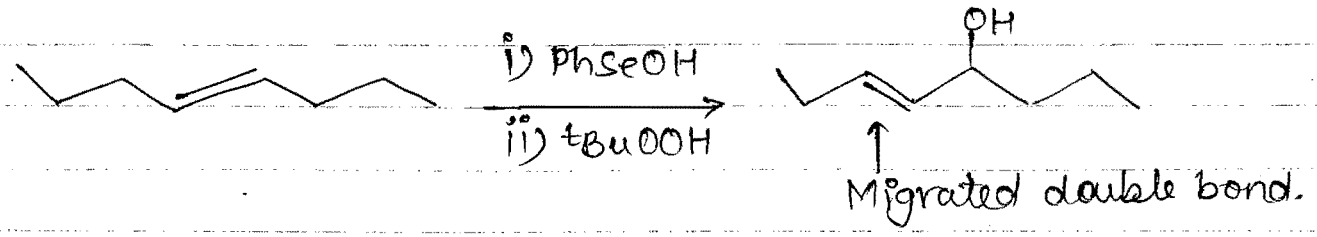
TERTIARY BUTYL HYDROGEN PEROXIDE

^{t}BuOOH is a oxidising agent this reagent used as an epoxidation of alkene. Rxn. ~~with~~ of Alkene with ^{t}BuOOH in the ₹nce of transition metal catalyst. For ex. V(V), Mo (VI) (or) Ti (IV) + complex provide an excelent method for the preparation of epoxide. Mo(VI) is most effective for isolated double bond. Ti(IV) (or) V(V) most effective for allylic alcohol.



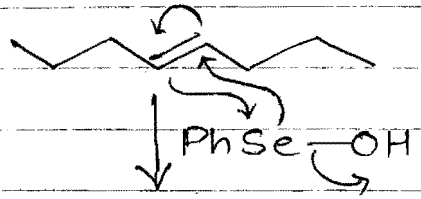
Allylic alco. with migration of double bond in alkene can be achieved by ^{t}BuOOH and PhSeOH

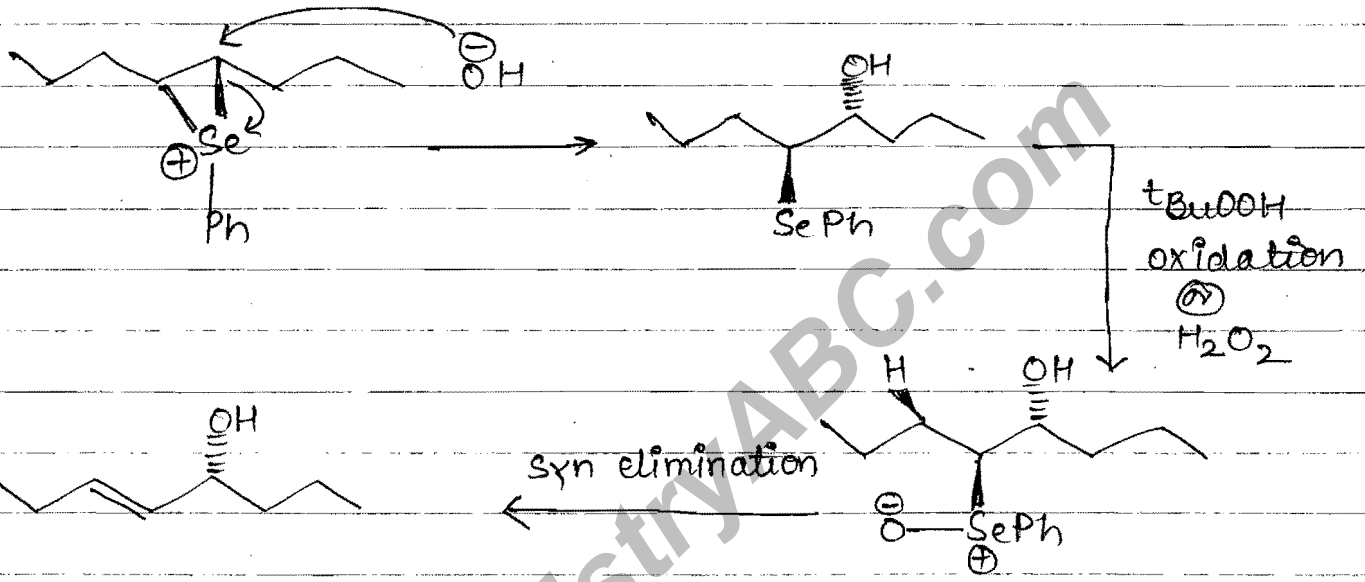
Imp.
Ex.

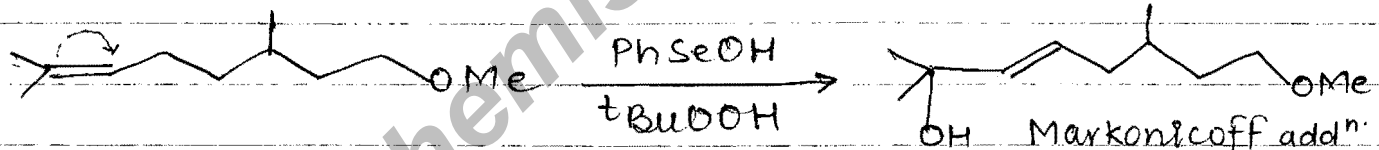


Ph–Se–O–H ⇒ Peroxide ⇒ epoxidation
⇓
just like 'O'

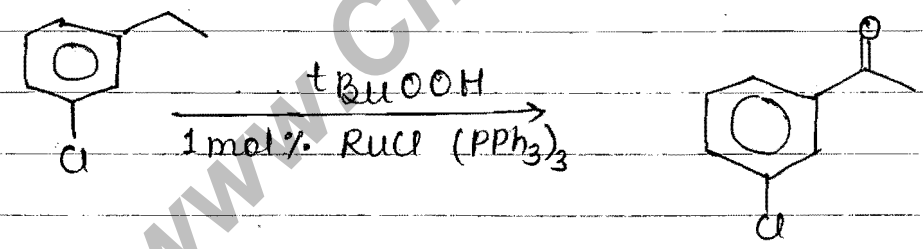
Mech.

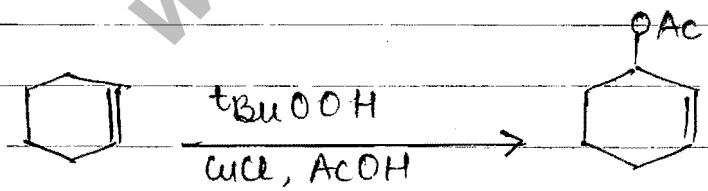




Q 

Markonicoff addⁿ of $\bar{O}H$

Q 

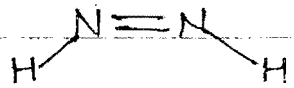
Q 

Kharash Sosnovsky Rxn.

⇓

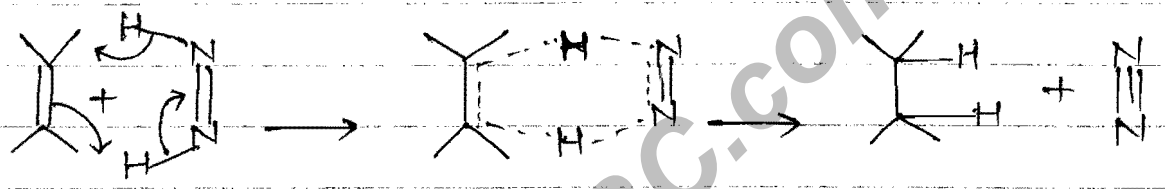
Cu(I)

DI IMIDE



Diimide is a reducing agent, Diimide is suitable for the reduction of C=C multiple bond (or) N=N bond, but it doesn't reduce C=N, C≡N, N=O, C=O, S=O.

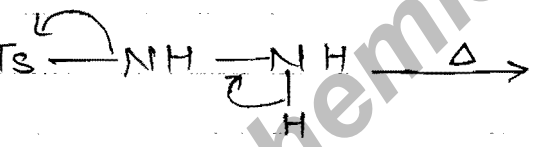
Ex.



Preparation of diimide:-

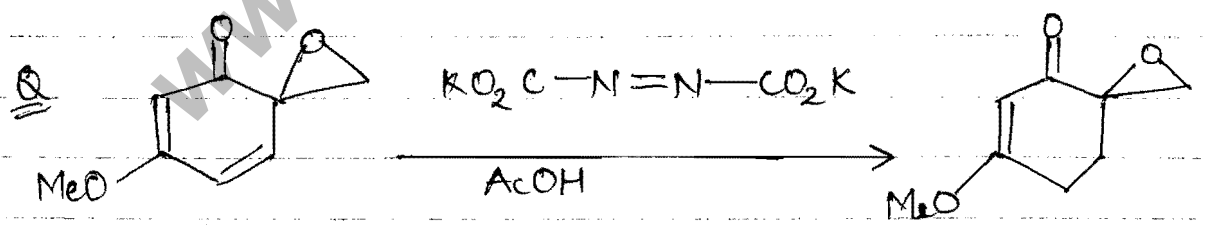
i) $H_2NNH_2 \xrightarrow{O_2 \text{ (or) } H_2O_2} HN=NH$

ii)



V.Imp $K.O_2C-N=N-CO_2K \xrightarrow{AcOH} HN=NH$

Q



* Diimide doesn't reduce α, β unsaturated C=C d.b.

DIOL FORMATION By ALKENE

Alkene

Cis diol

1) Imp. OsO_4

(or)

2) Alkaline $KMnO_4$

(or)

V. Imp. 3) Woodword Reagent (I_2, AgOAc/H_2O)

Trans diol

Imp. 1) Prevost reagent (I_2, AgOAc, Anhydrous condition)

(or)

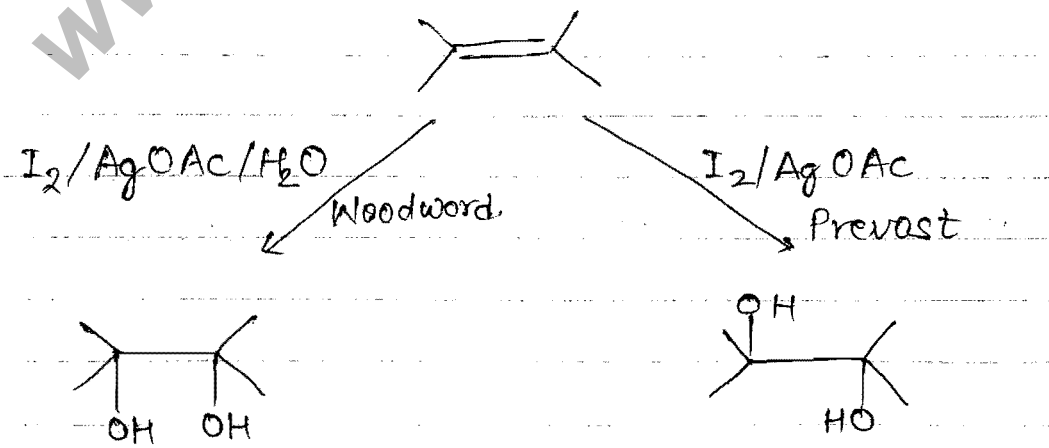
2) H_2O_2 / HCOOH

(or)

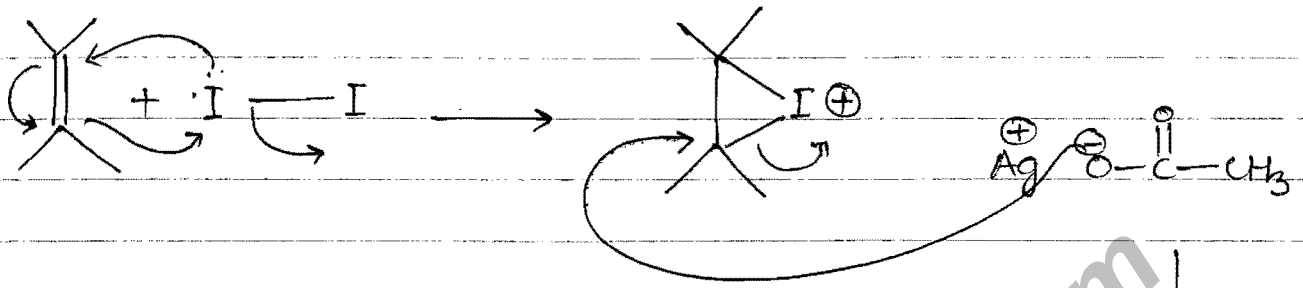
3) Epoxidation ring opening by $\ominus OH$

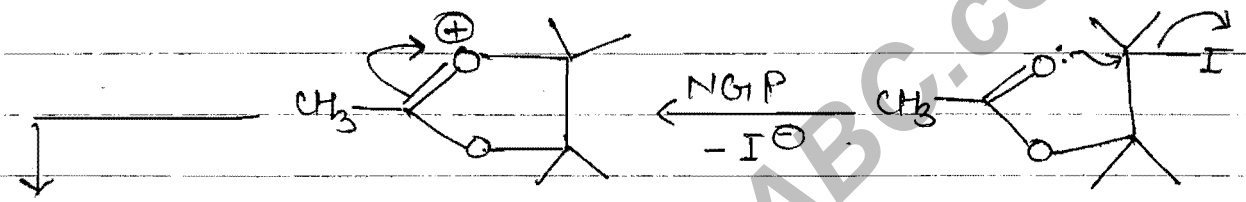
Formation of diol from alkene is k/a Hydro oxylation.

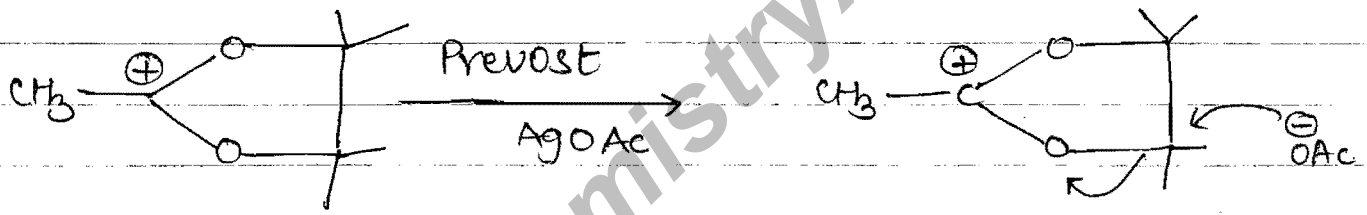
V. Imp. ## WOODWORD & PREVOST Rxn.



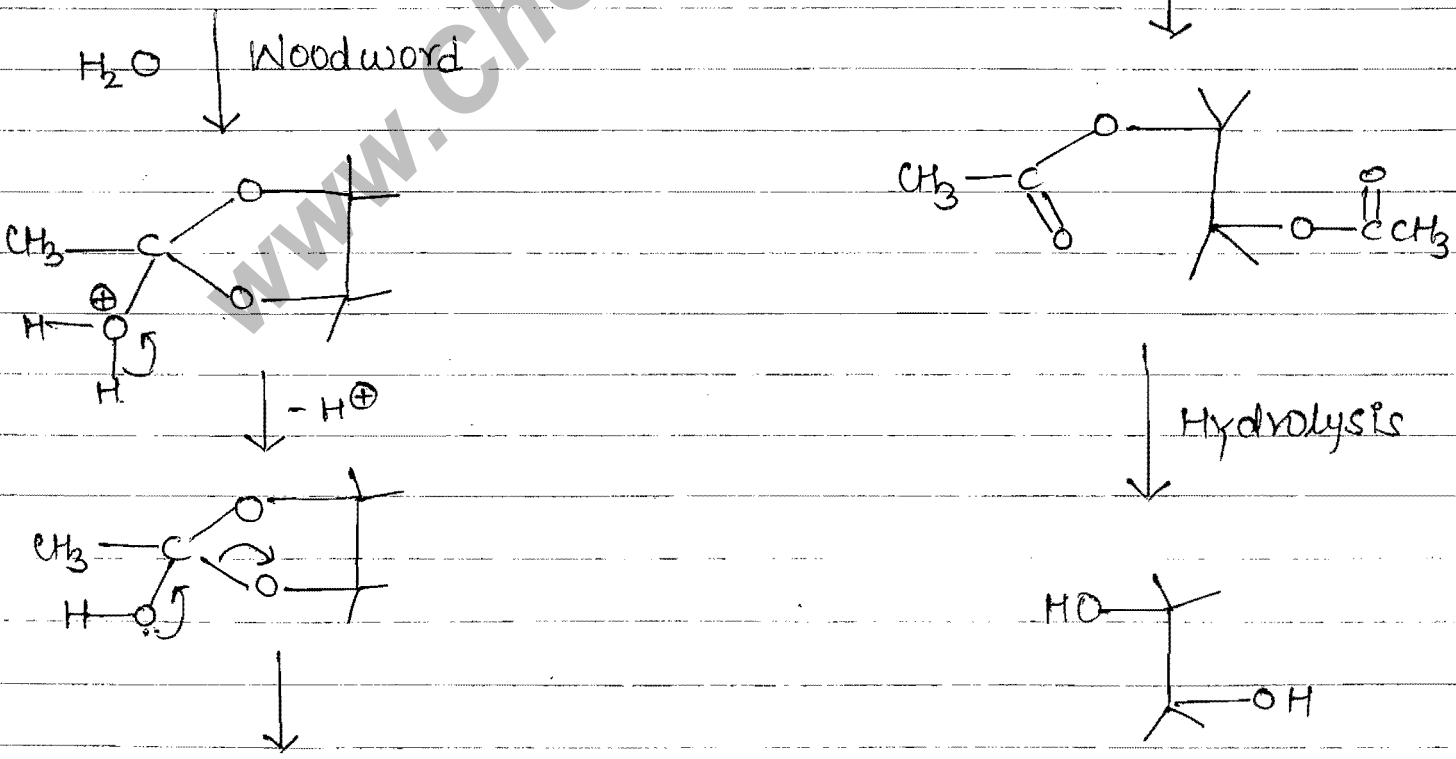
Mechanism :-



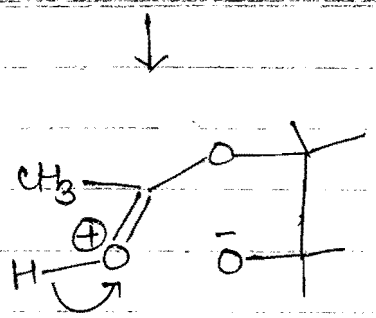


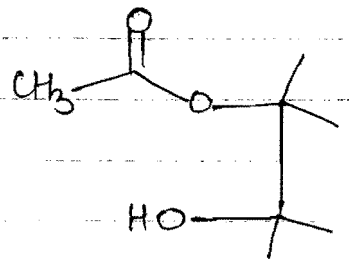


Cyclic Acetoxonium

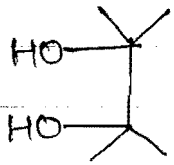


trans diol.



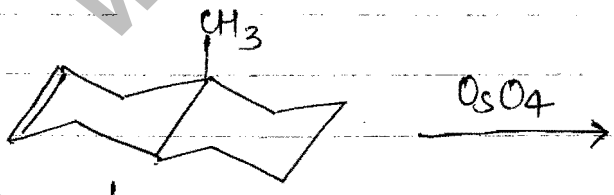


Hydrolysis



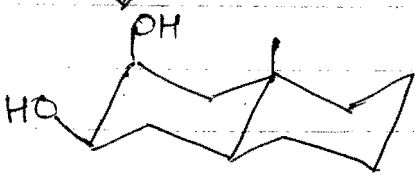
cis diol.

gmp. Woodword form less stable diol than OsO_4.



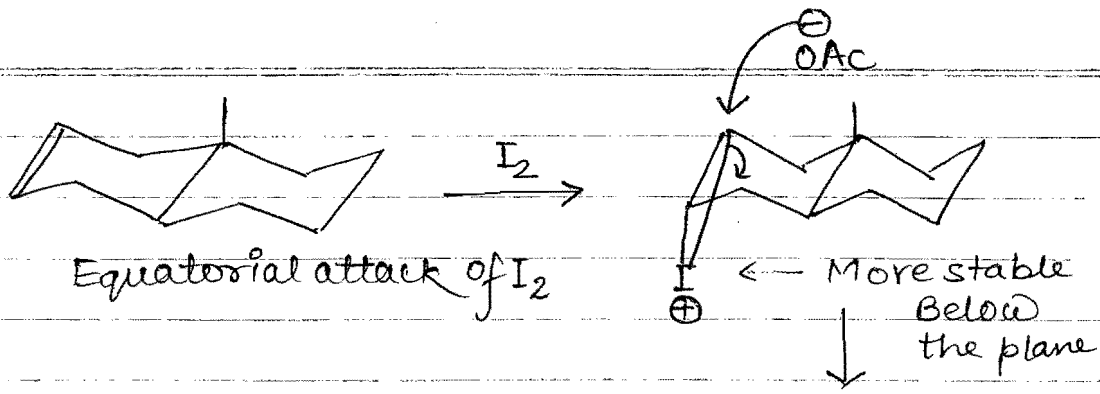
$I_2/AgOAc/H_2O$

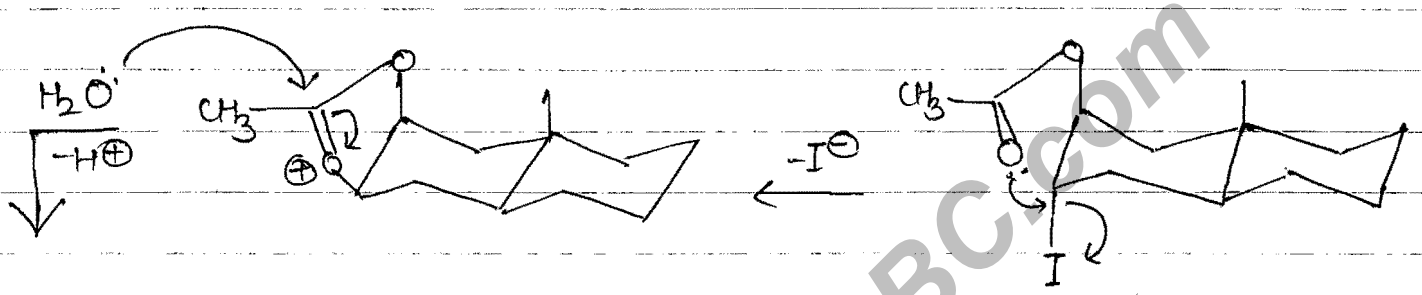
more stable cis diol.

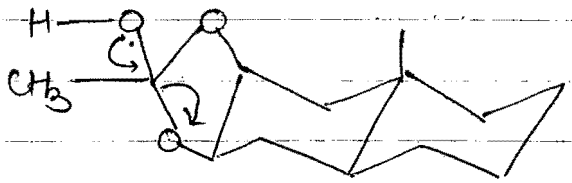


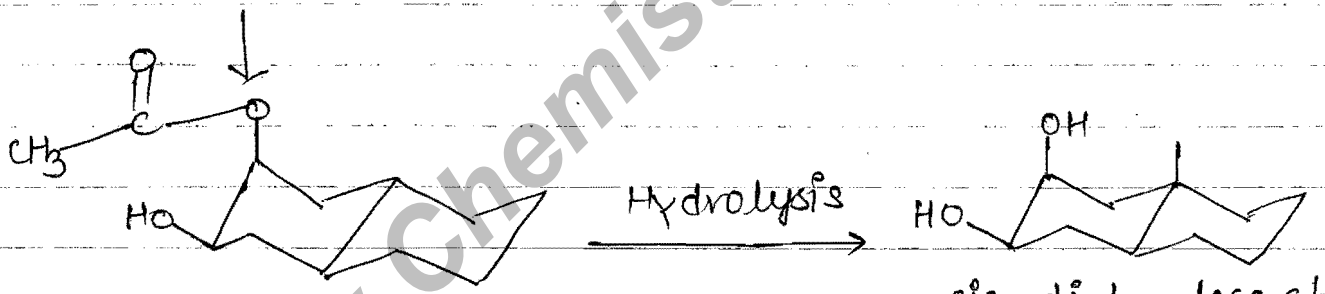
Less stable.

Mechanism:-

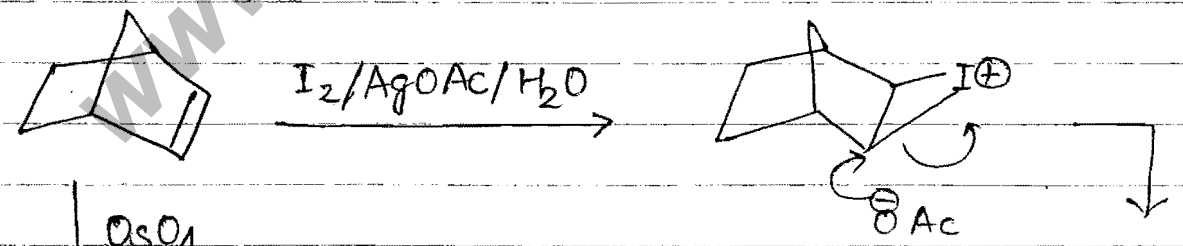


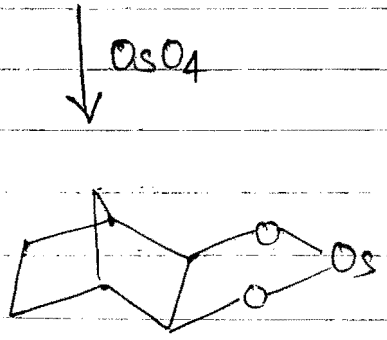


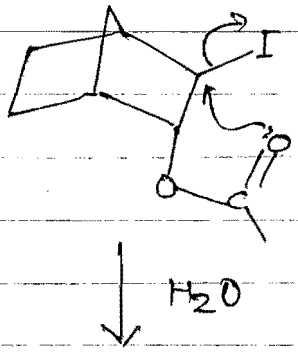


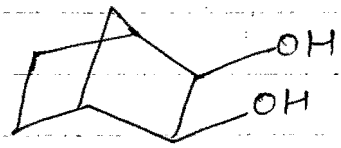


V. V. Imp.
Q

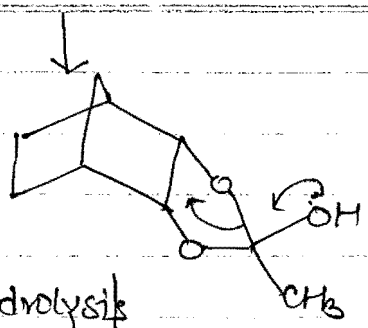




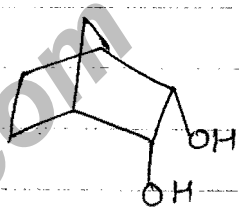




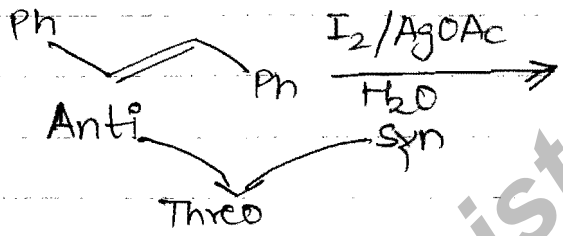
exo diol

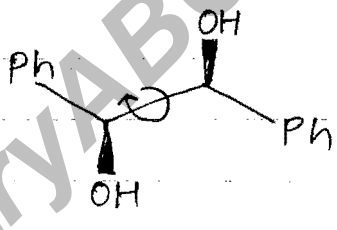


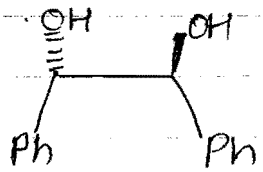
Hydrolysis

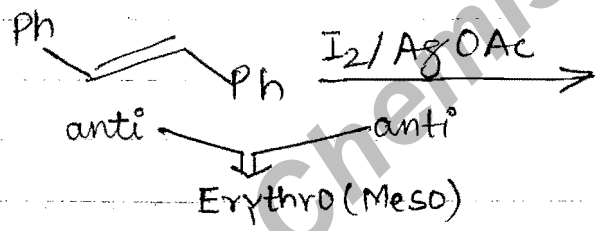


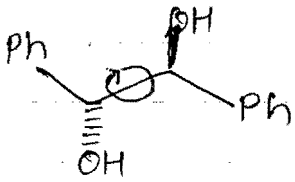
endo diol

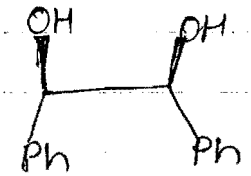
Q 



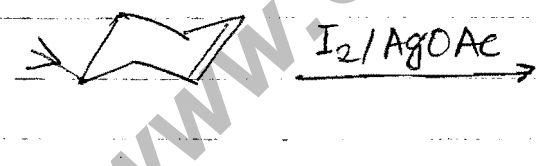
(or) 

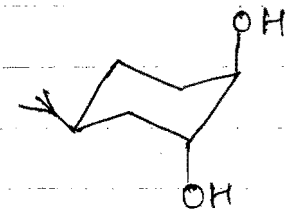
Q 



(or) 

Meso

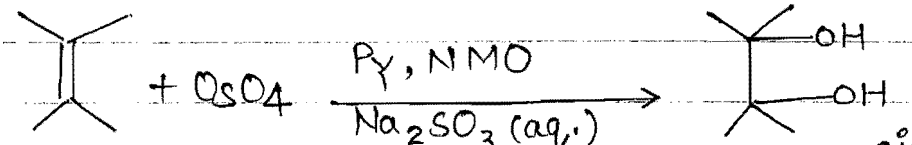
Q 



OsO_4 ⇒ e^- defficient (+8 oxidⁿ state) so prefer to attack on e^- rich alkene.

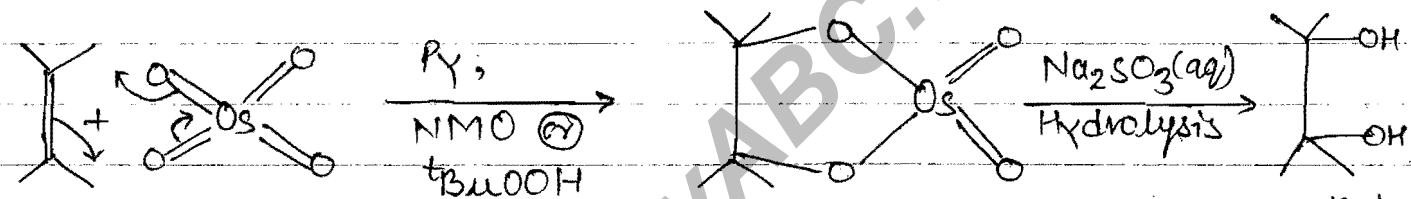
OSMIUM TETRA OXIDE OsO_4 (+8)

OsO_4 is an oxidising agent, it gives cis diol with alkene.

Ex. 

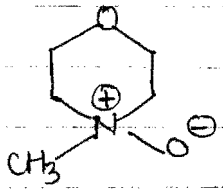
cis diol.

Mechanism:-



Cyclic osmate Ester

cis diol

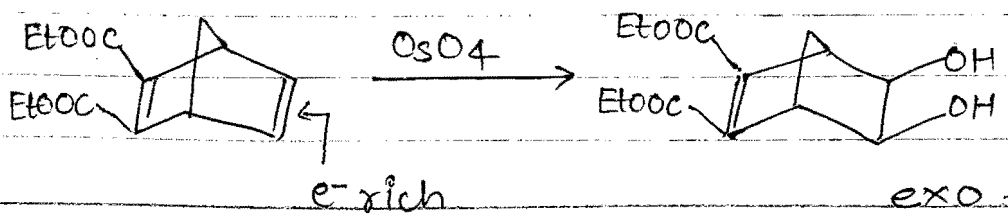


⇒ NMO ⇒ N-methyl morpholine N-oxide.

It is the case of 3+2 cycloaddⁿ. (w.r.t. atom) Rxn. Os is a toxic and explosive in nature, so rxn. carried out in the +nce of oxidising agent like tBuOOH or NMO

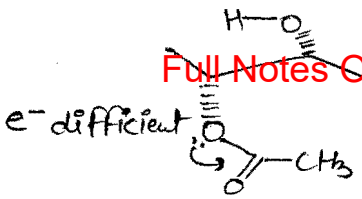
Characteristics of OsO_4 Rxn.

1) Gives cis diol
2) If in a comp. two double bond +nt then diol formation will take place on more e^- rich double bond.



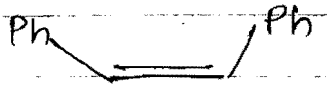
e^- rich

exo-diol.



⇒ No Hydrogen bonding.

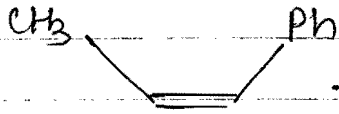
3) OsO_4 gives pair of enantiomers (or) meso meso comp.



+ OsO_4

cis — syn addⁿ.

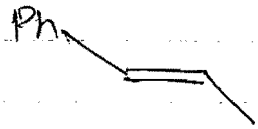
Erythro ⇒ Meso



+ OsO_4

cis — syn addⁿ.

Erythro ⇒ Enantiomers



+ OsO_4

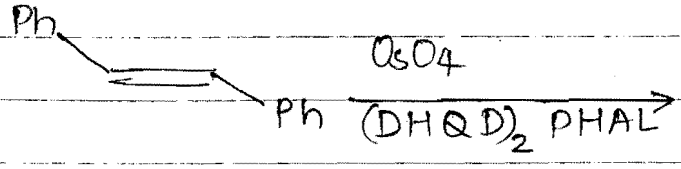
Syn addⁿ.

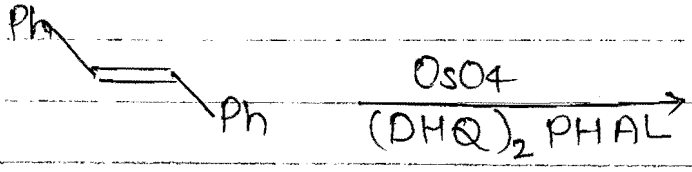
Threo ⇒ Enantiomers.

4) Enantioselectivity can be carried out by the two alkaloids.

$(DHQD)_2$ PHAL ⇒ Supply Oxygen from top side.

$(DHQ)_2$ PHAL ⇒ " " " Bottom side.



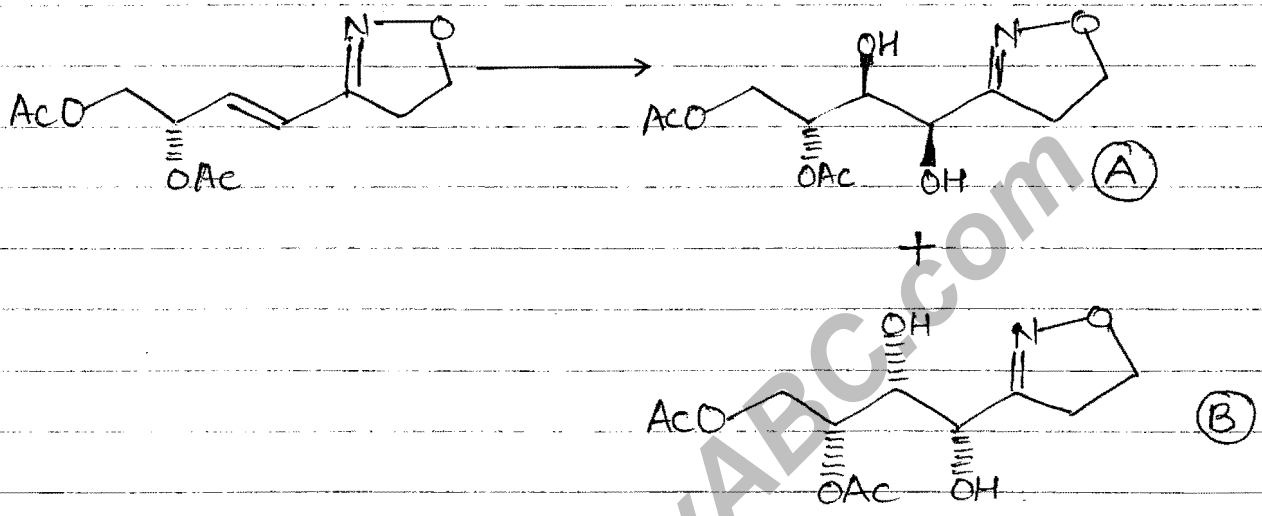


छोटा → नीचे बड़ा → ऊपर

DHQ = Dihydroquinine (or) AD mix – α

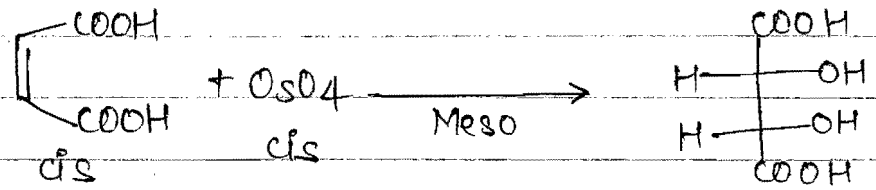
DHQD = Dihydro quinidine (or) ADmix – β

Q

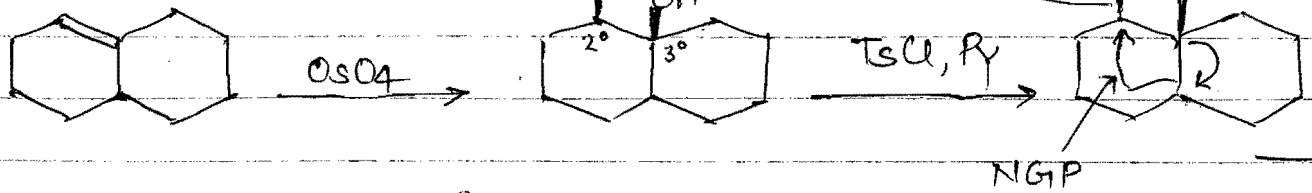


Reagent	Major	Minor
OsO_4, NMO, Na_2SO_3	A	B
OsO_4, NMO, Na_2SO_3 $(DHQD)_2$ PHAL	A	B
OsO_4, NMO, Na_2SO_3 $(DHQ)_2$ PHAL	B	A

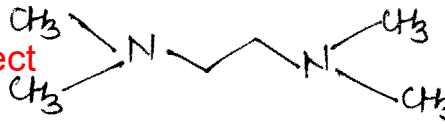
Q

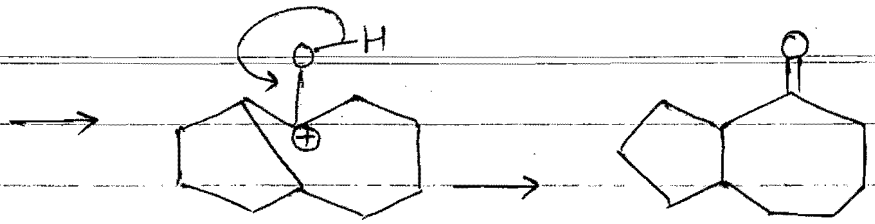


Q

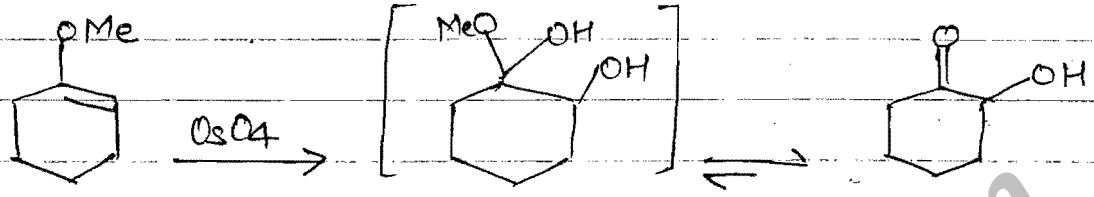


gmp Note :- Tosylation of 2° alco. faster than 3° alco. in Basic(Py) medium.





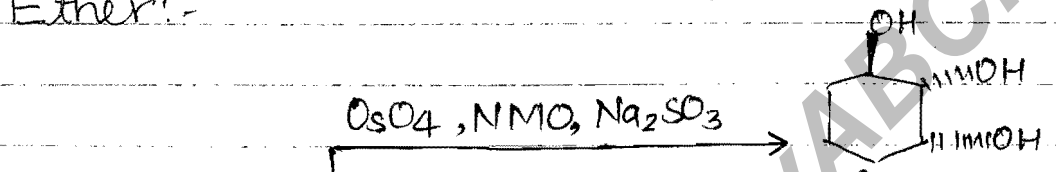
V.V.Imp.
Q

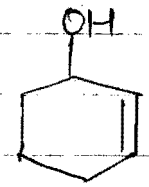


2014
M. Imp

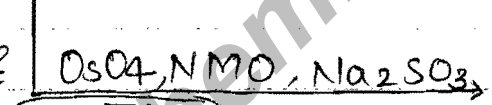
Hemi Ketal

Rxn. of OsO_4 with Allylic alcohol and Allylic Ether:-

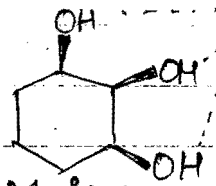




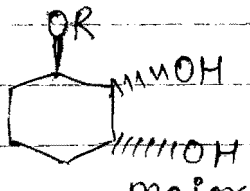
2014 M. Imp

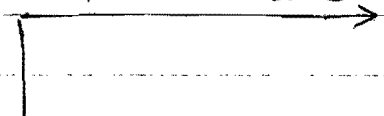


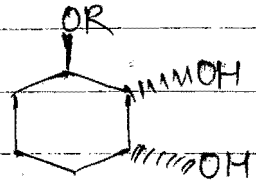
TMEDA
$K_3[Fe(CN)_6]$



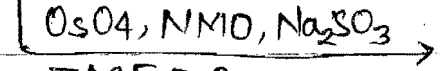
TMEDA take part in Hydrogen bonding with all -OH gps.







No H.B. with TMEDA.

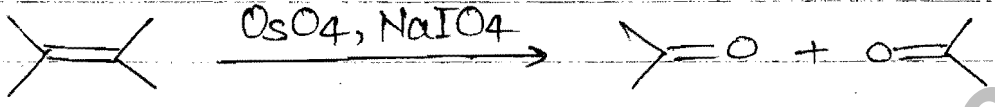


TMEDA
$K_3[Fe(CN)_6]$

Imp.

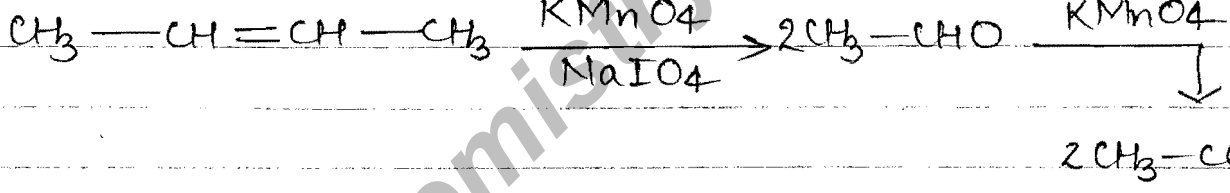
LEMIEUX JOHNSON Reagent

Combination of OsO_4 & $NaIO_4$ is K/a Lemieux Johnson reagent. L.J. reagent is used for the formation of carbonyl by alkene.



Combination of $KMnO_4$ & $NaIO_4$ is also K/a L.J. reagent but this reagent is not good reagent because further oxidation may be take place due to $KMnO_4$.

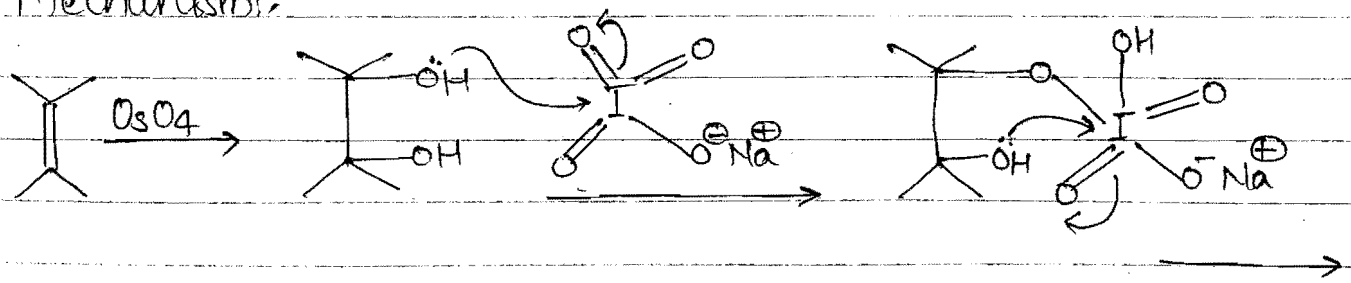
Ex.



L.J. Reagent is an alternate method of ozonolysis.

$NaIO_4$ or HIO_4 is used for the glycolic bond cleavage or diol bond cleavage. & this oxidation is K/a Malaparade Oxidation.

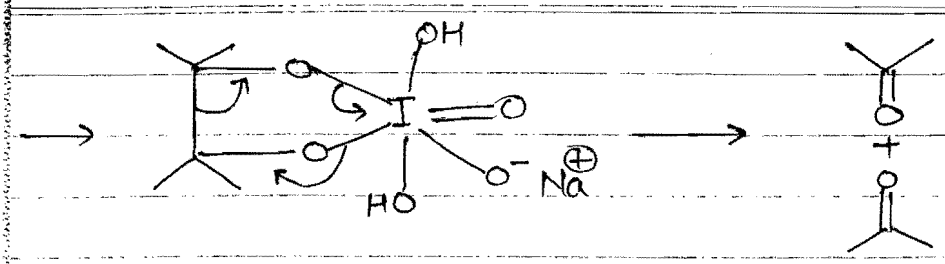
Mechanism:-



R–OH alcohol $\xrightarrow{HIO_4}$ Carbonyl (Ald or Ket) } V. V. Imp.

Carbonyl Acid $\xrightarrow{HIO_4}$ Acid

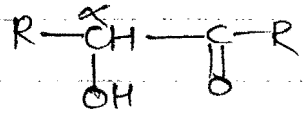
Acid $\xrightarrow{\quad''\quad}$ CO_2



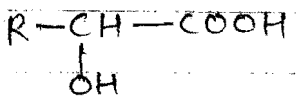
Substrate $\xrightarrow{\text{Reagent}}$ Product

i) Alkene $\xrightarrow{OsO_4 + NaIO_4}$ carbonyl

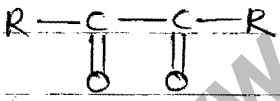
ii) α-Hydroxy carbonyl $\xrightarrow{HIO_4 \text{ (or) } NaIO_4}$ carbonyl + Acid



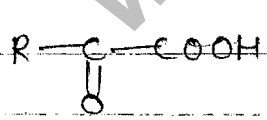
iii) α-Hydroxy acid $\xrightarrow{HIO_4}$ Carbonyl + CO_2

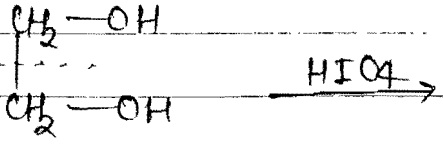


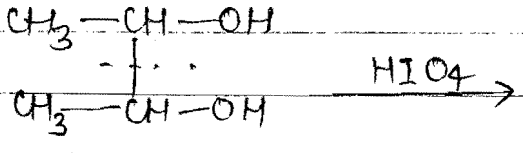
iv) 1,2-diketone $\xrightarrow{HIO_4}$ 2 Acids

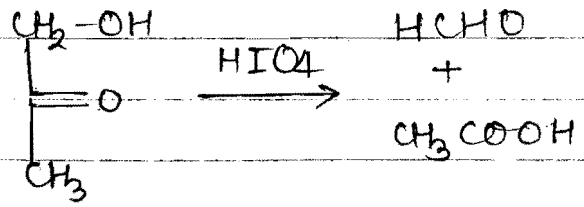


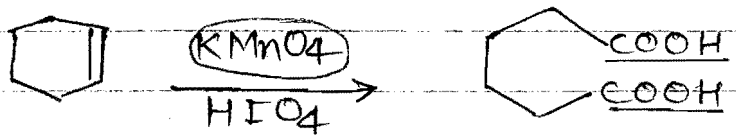
v) α-Keto acid $\xrightarrow{HIO_4}$ Acid + CO_2



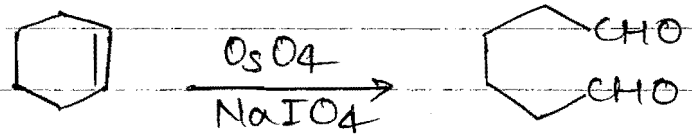
Q 

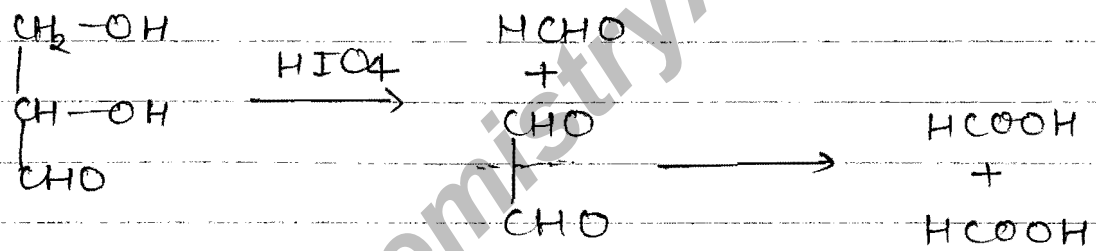
Q 

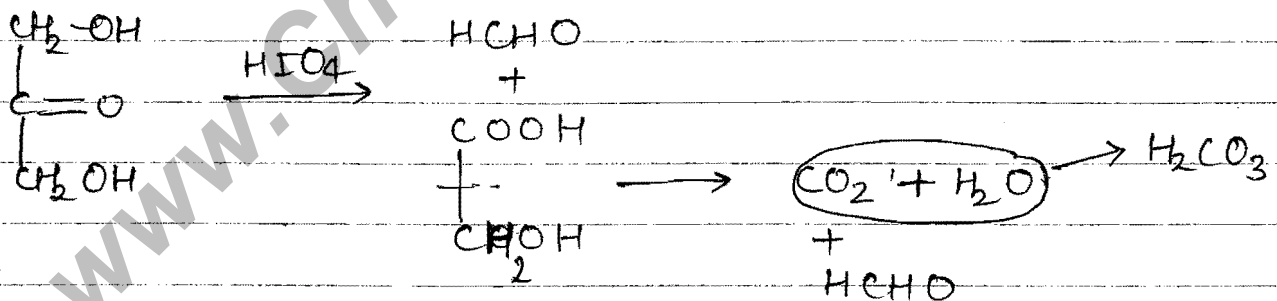
Q 

Q 

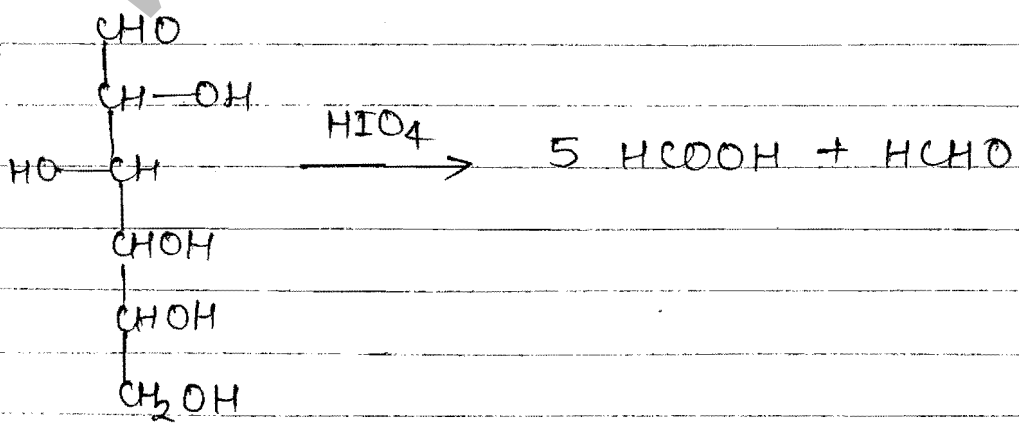
Over oxidation due to $KMnO_4$

Q 

Q 

Q 

V. Imp.

Q 

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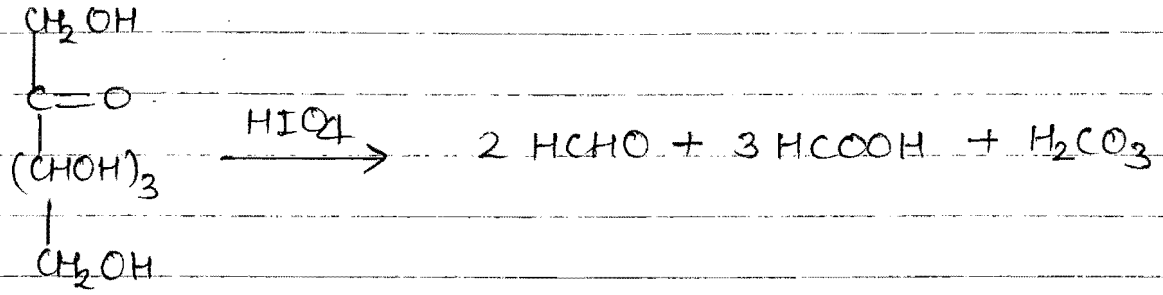

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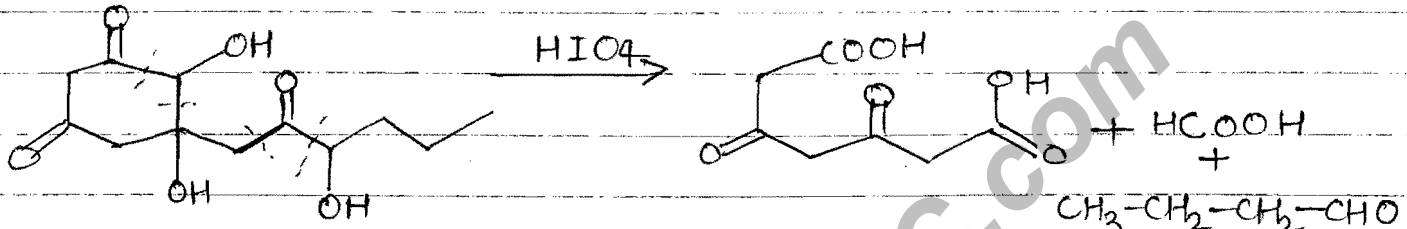

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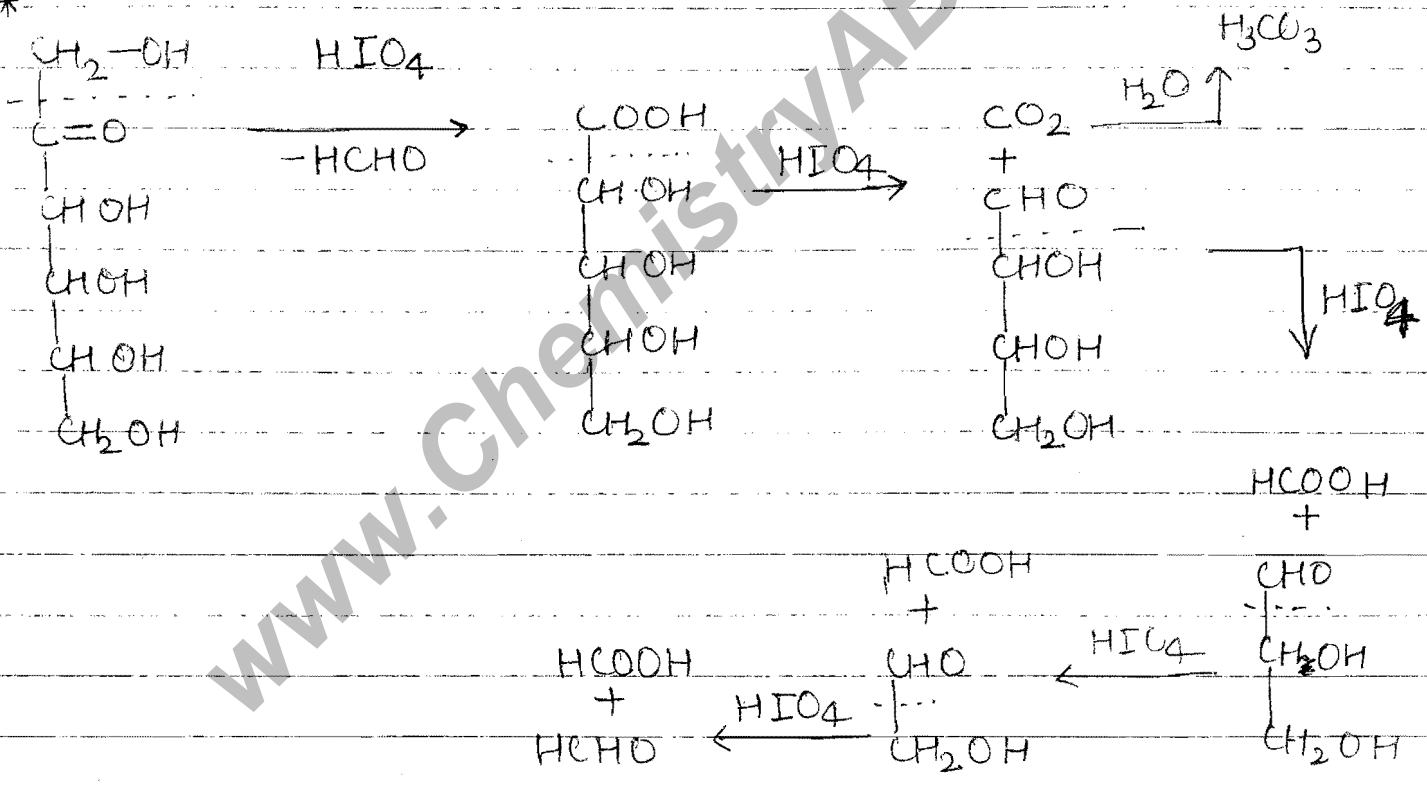
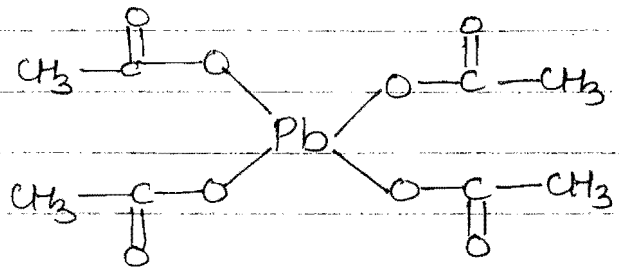


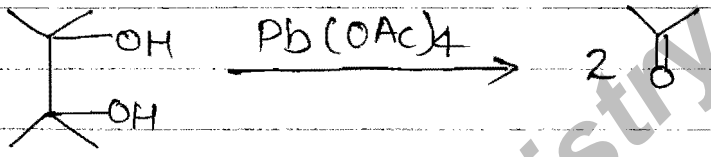
LEAD TETRA ACETATE [LTA]

$Pb(OAc)_4$

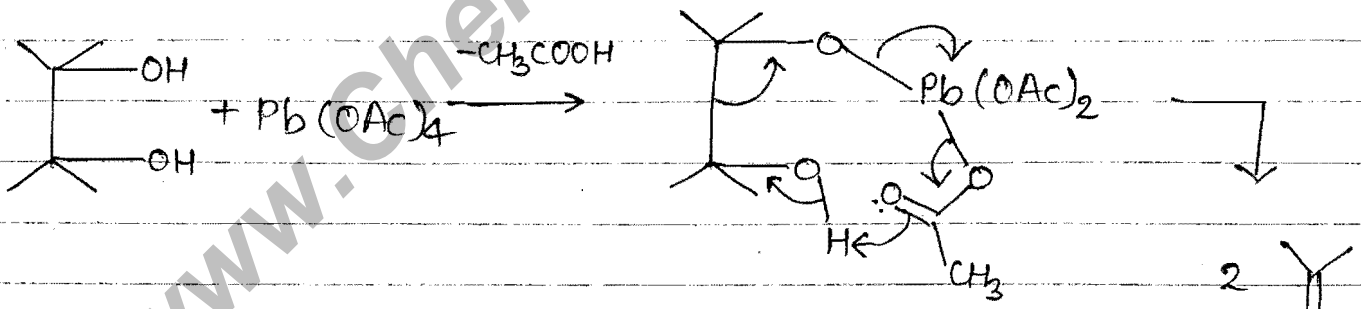


Functions of $Pb(OAc)_4$

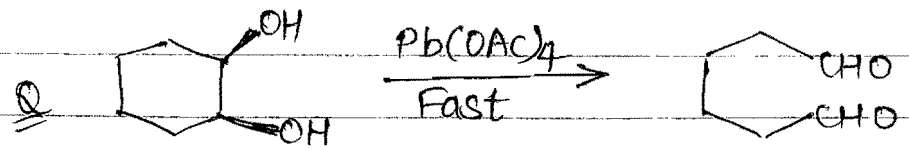
1) Cleavage of 1,2-diol bond into carbonyl

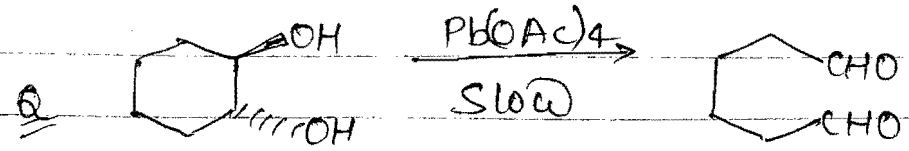


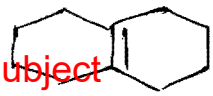
Mechanism:-



$CH_3COOH + Pb(OAc)_2$



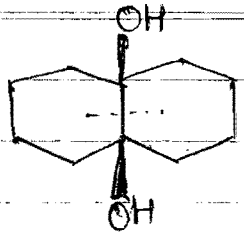




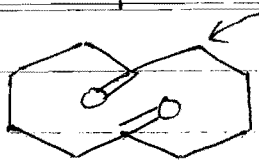
$TiCl_3, LiAlH_4 \xrightarrow{\Delta}$ Ti(0)

Memerry Rxn.

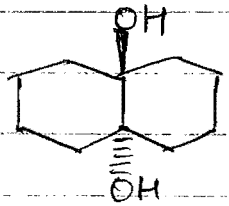
Q



$Pb(OAc)_4$ (Fast)

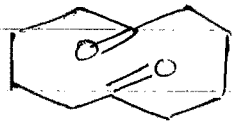


Q

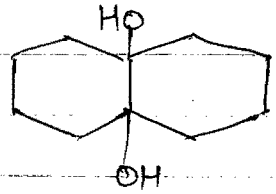


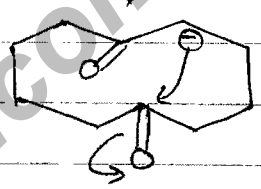
$Pb(OAc)_4$ → Inert.

*

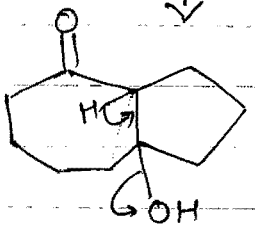


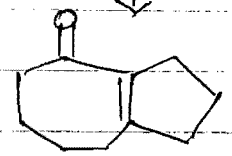
$TiCl_3, LiAlH_4$
Low temp.



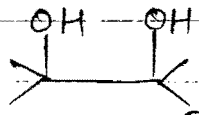


H_2O

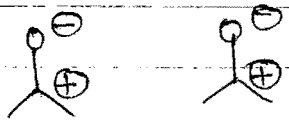




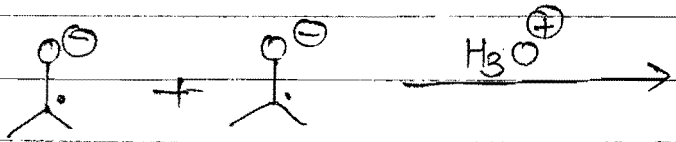
Mg



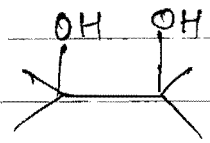
Pinacole.



Mg

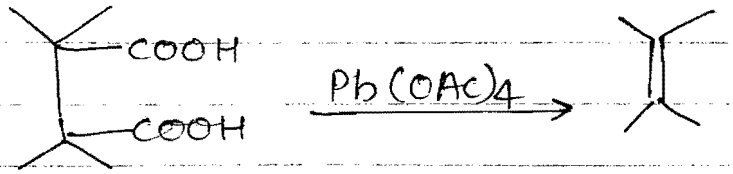


$H_3O^{\oplus}$

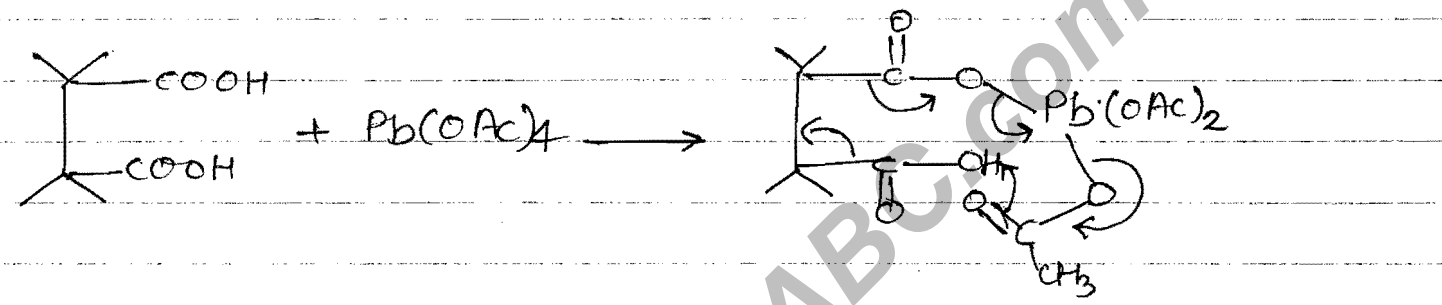


V. Imp.

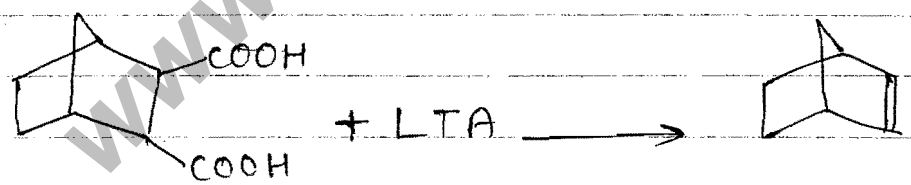
Bis decarboxylation :-



Mechanism



Q 

Q 

* Cleavage of α-amino alco. into carbonyl.
* Cleavage of 1,2-diamino into carbonyl.
* Cleavage of α-Hydroxy carbonyl compound into carbonyl and acid.
* Cleavage of 1,2-diketones into carboxylic acid.
* Cleavage of α-keto carboxylic acid into carboxylic acid and CO_2.

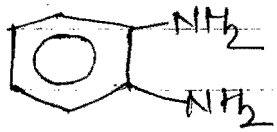
* Oxidation of Simple alco into carbonyl.
* Acetoxylation or methylation at active position.

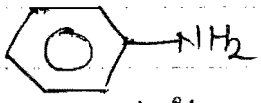
Q $R-CH(NH_2)-CH(OH)-R \xrightarrow{LTA} R-CH=NH + R-CHO$

$R-CH=NH \xrightarrow{H_2O} RCHO$

Q $R-CH(NH_2)-CH(NH_2)-R \xrightarrow{LTA} 2\,R-CH=NH \xrightarrow{H_2O} RCHO$

Note but aromatic diamine gives following product.

Q  $\xrightarrow{Pb(OAc)_4}$ 

Q  Anilene $\xrightarrow{LTA} Ph-N=N-Ph$

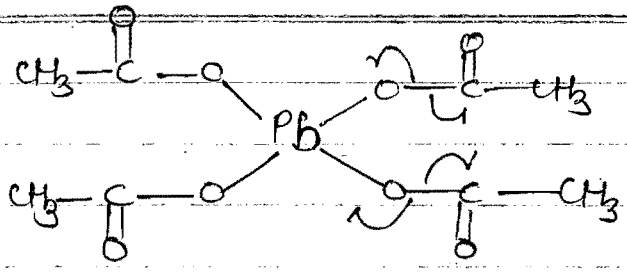
Q $R-CH(OH)-C(=O)-R \xrightarrow{LTA} RCHO + R-COOH$

Q $R-C(=O)-C(=O)-R \xrightarrow{LTA} 2\,RCOOH$

Q $R-CH_2-OH \xrightarrow{LTA} R-CHO$

Acetoxylation of methylation at active site

$R-H \xrightarrow{LTA} R-O-C(=O)-CH_3 + R-CH_3$



$\longrightarrow Pb(OAc)_2 + 2\ CH_3-\overset{O}{\overset{\|}{C}}-O^{\bullet}$

$\downarrow R-H$

$R^{\bullet} + CH_3-\overset{O}{\overset{\|}{C}}-OH$

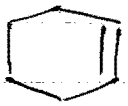
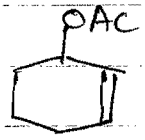
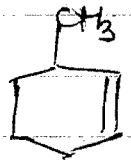
* $R^{\bullet} + CH_3-\overset{O}{\overset{\|}{C}}-O^{\bullet} \longrightarrow R-O-\overset{O}{\overset{\|}{C}}-CH_3$

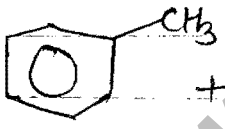
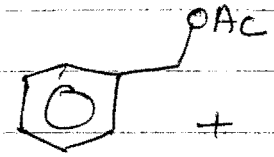
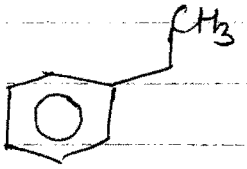
Acetoxylation

* $CH_3-\overset{O}{\overset{\|}{C}}-O^{\bullet} \longrightarrow CO_2 + \dot{C}H_3$

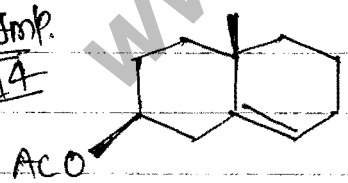
At high temp. Methylation only.

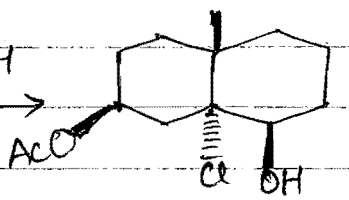
$\Rightarrow R^{\bullet} + \dot{C}H_3 \longrightarrow R-CH_3$ Methylation.

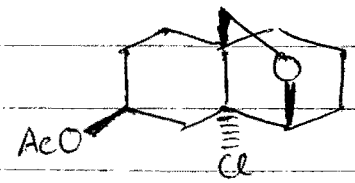
Q  + LTA $\longrightarrow$  + 

Q  + LTA $\longrightarrow$  + 

M.Imp. 2014



$\xrightarrow{NaOCl, NaOH}$ 

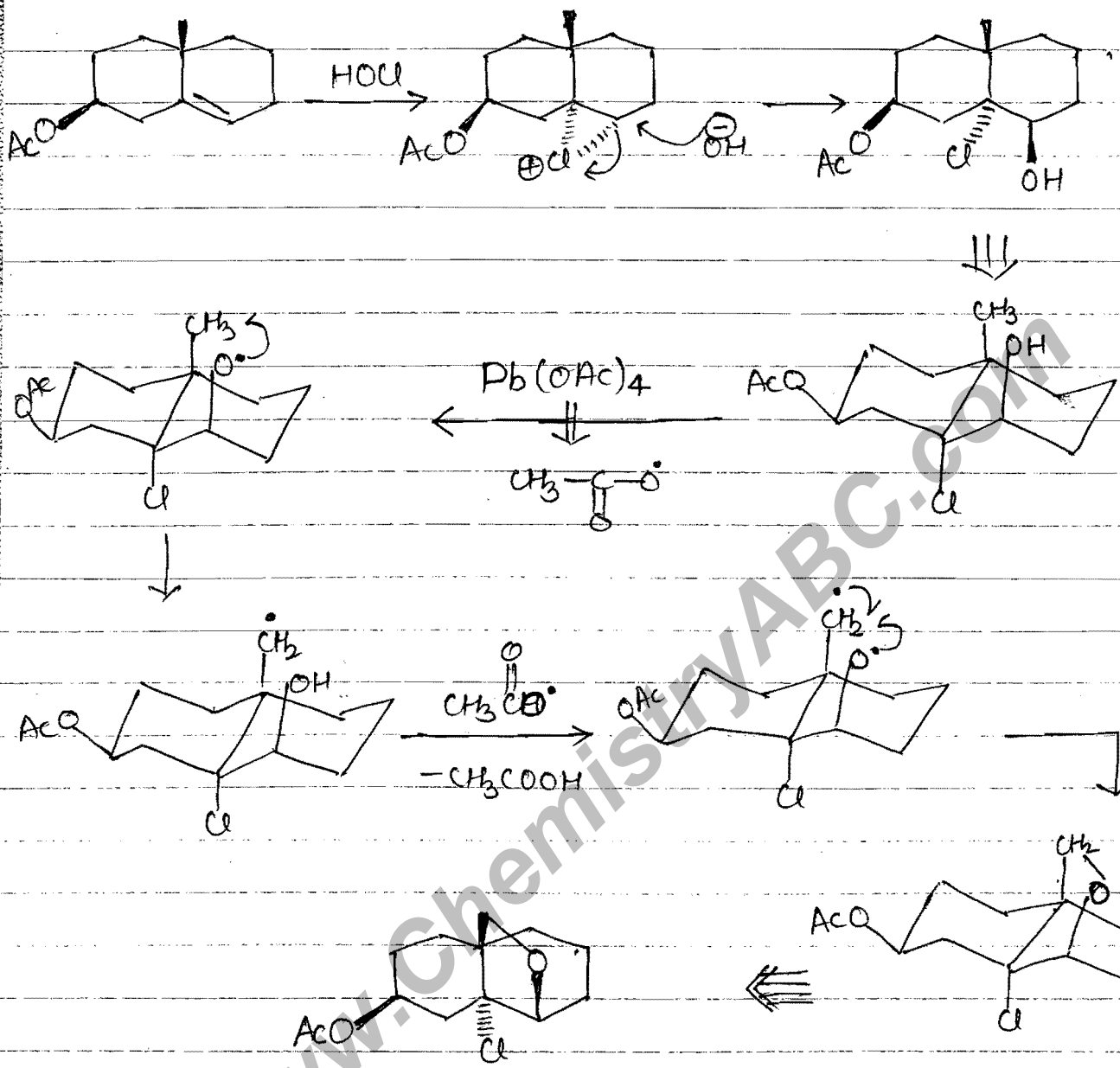
$\xrightarrow{LTA}$ 

Mechanism,

$NaOCl + AcOH \longrightarrow HOCl$

Tebbe's Reagent ⇒ Most Imp.

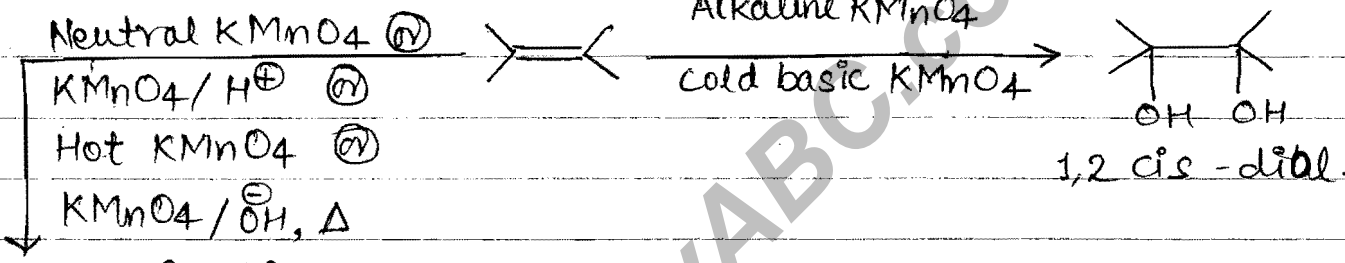
Just like Wittig



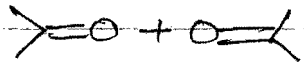
$KMnO_4$

Neutral $KMnO_4$ $KMnO_4/H^{\oplus}$ $KMnO_4/\overset{\ominus}{O}H$

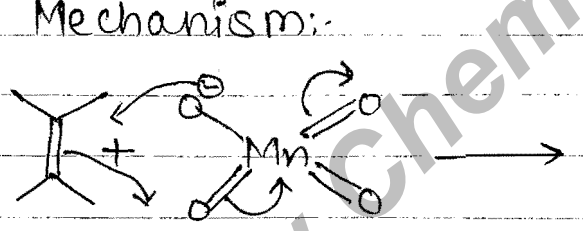
$KMnO_4$ Reactions depends upon conc. of $KMnO_4$ (low or high) and state (hot or cold @ normal) of $KMnO_4$.

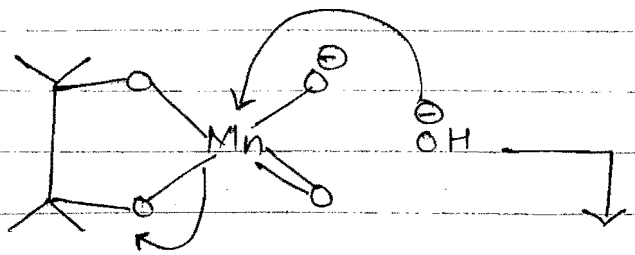


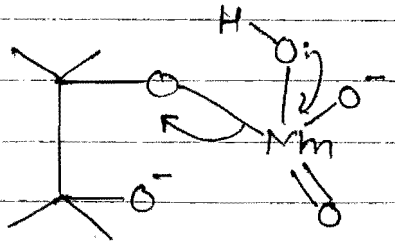
Over oxidation

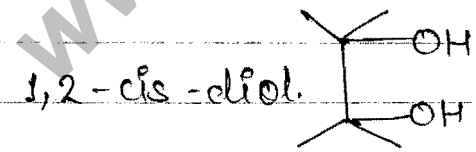


Mechanism:-



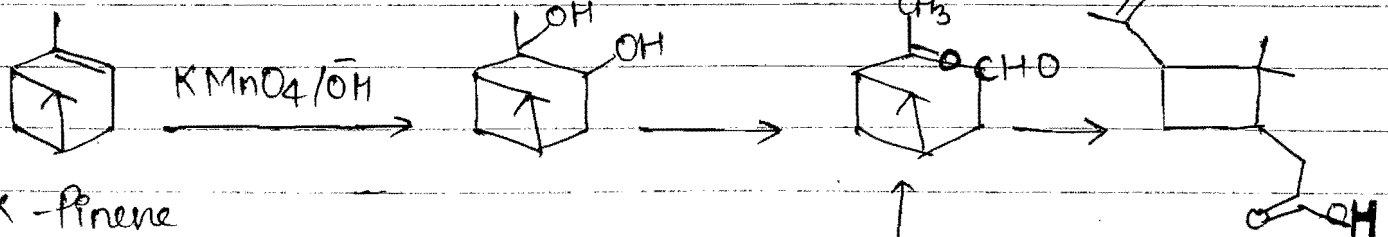






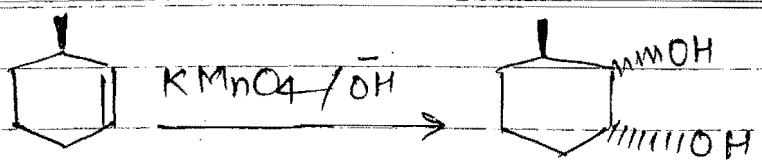
$H^{\oplus}$ workup

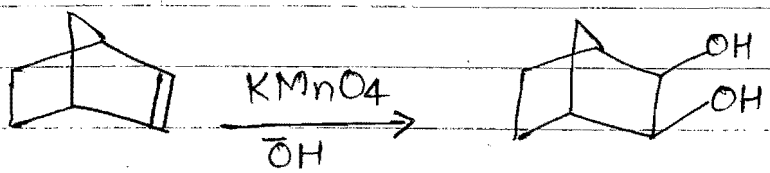
Q

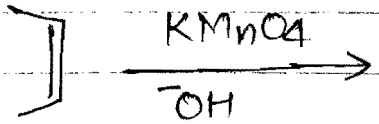


α-Pinene

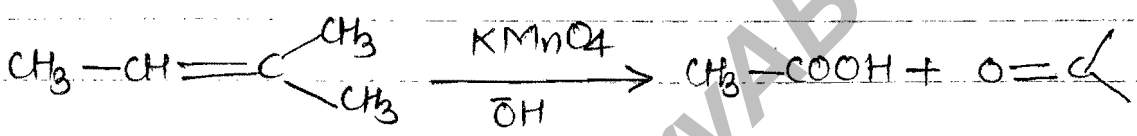
It gives Haloform test

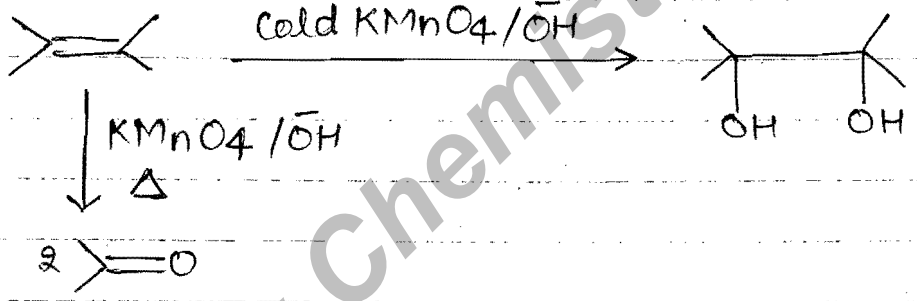
Q 

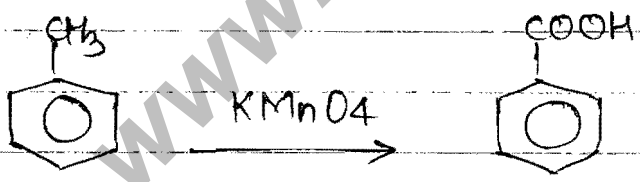
Q 

Q 

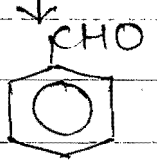
Meso

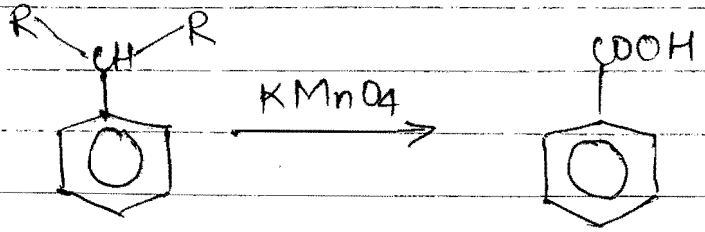
Q 

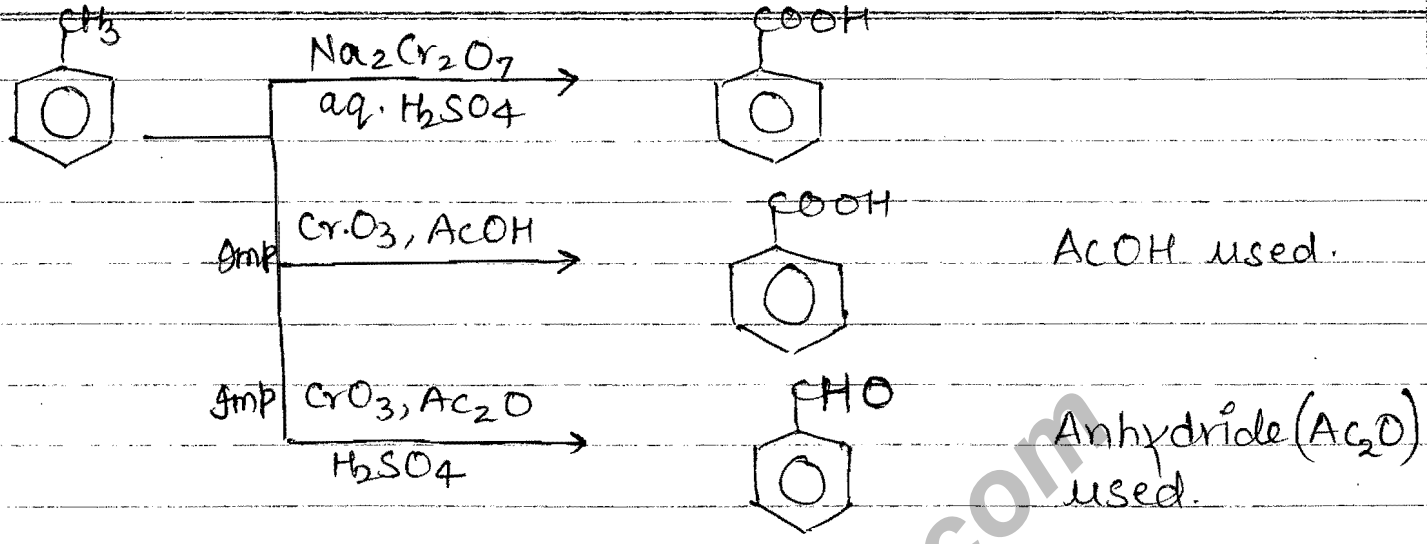
Q 

Q 

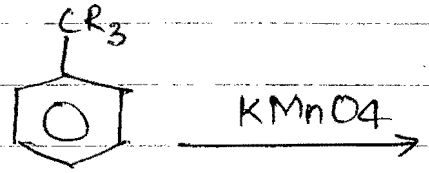
Etard Rxn. CrO_2Cl_2 ← Chromyl chloride



Q 

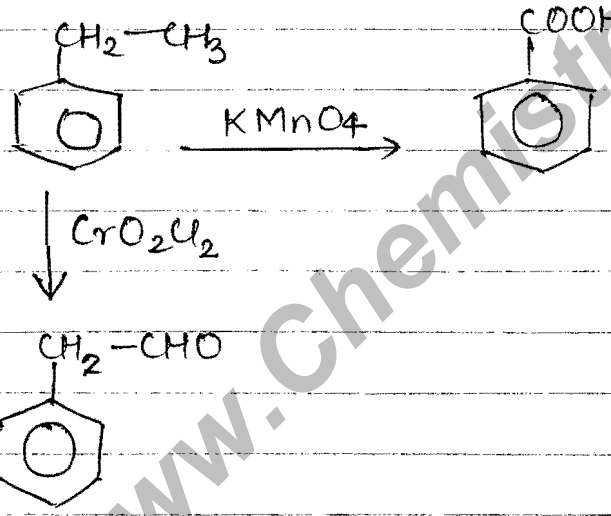


Q

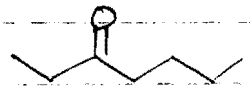


No Rxn.

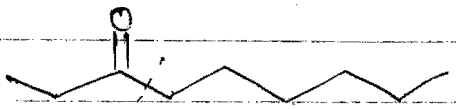
Q



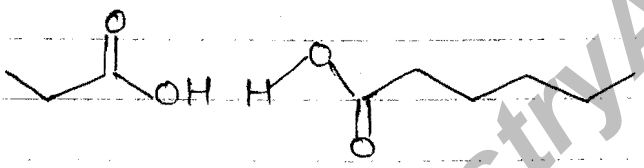
POPOFF RULE

For asymmetric ketone () if oxidation takes place in the ~~+nce~~ presence of strong oxidising agent ($K_2Cr_2O_7$, $KMnO_4$, HNO_3) then the carbonyl group is attached the group that have less no. of carbon.

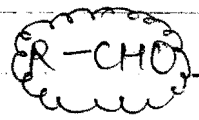
Ex.



$\downarrow$ [O]



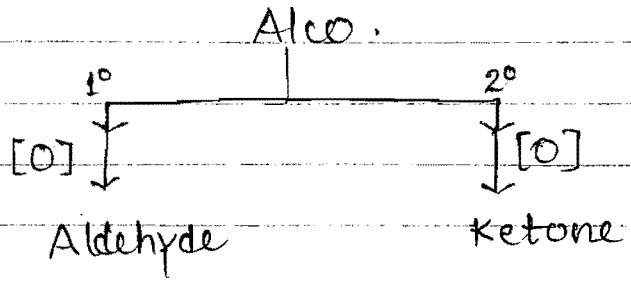
V. V. Imp



H_2O_2 @ CrO_3 @ Ag_2O @ $KMnO_4$ @ John's Reagent

* Most Imp. *

OXIDATION OF ALCOHOL



REAGENTS

1) Collins Reagent
2) John's Reagent
3) PCC (or) PDC

* Order of Oxidn.
benzylic alco. > 1° > 2°
(or)
Allylic Alco.

Ag_2CO_3

Order of Oxidn.
Allylic (or) benzylic > 2° > 1°

SWERN Oxidn.
&
Moffat Oxidn.

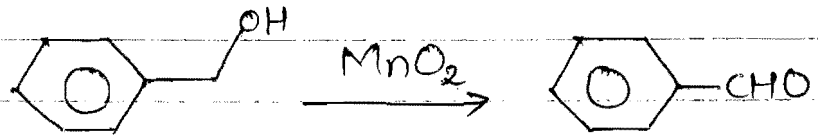
Allylic (or) benzylic > 1° > 2°

MnO_2

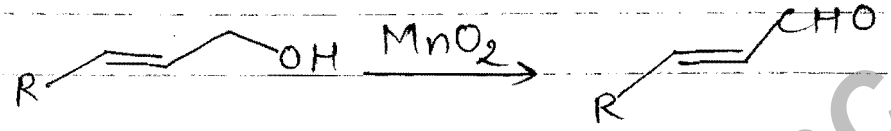
Oxidise only Allylic (or) benzylic Alco.

MnO_2 :- It is very selective reagent. It is best reagent for the oxidation of allylic (or) benzylic alcohol.

Ex.



Ex.



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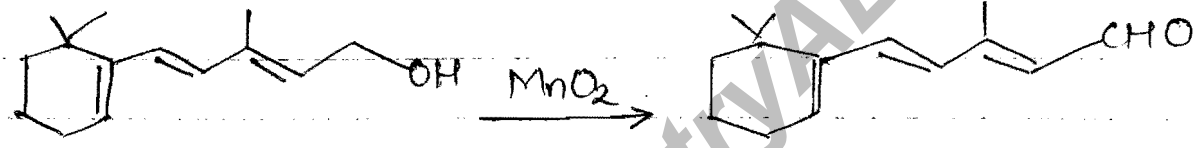

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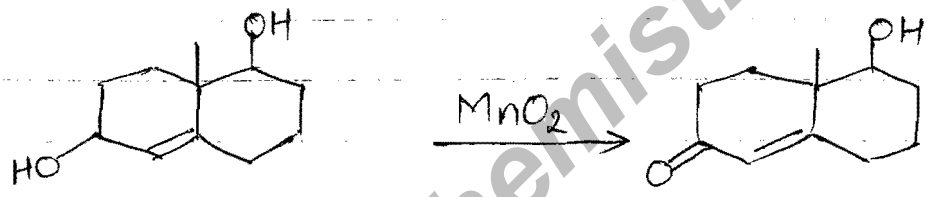

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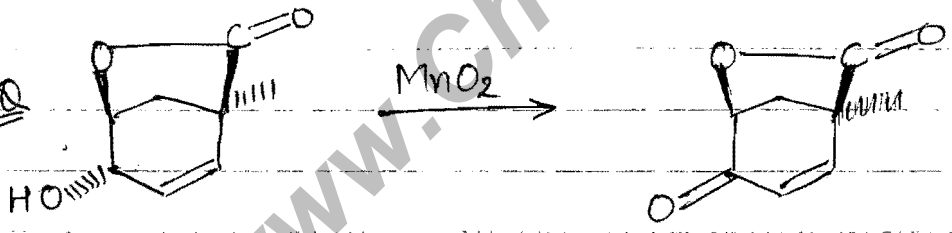

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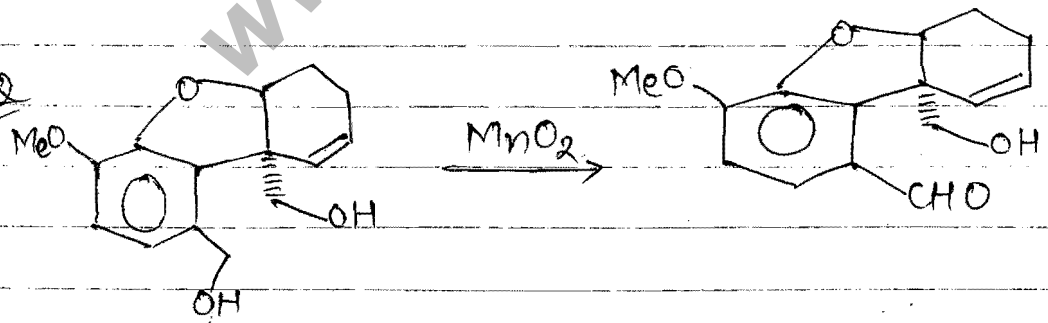
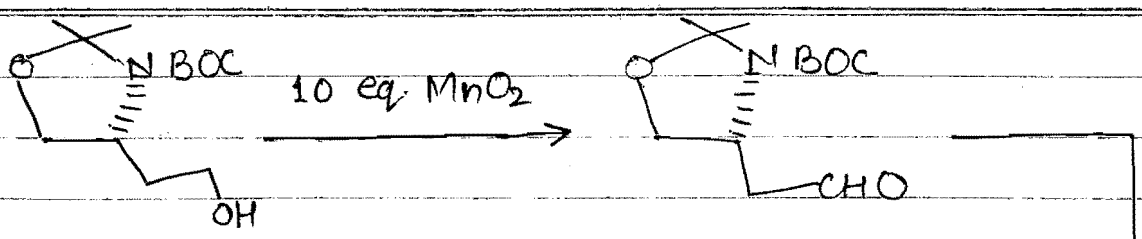
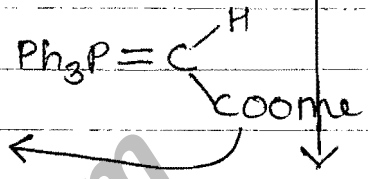


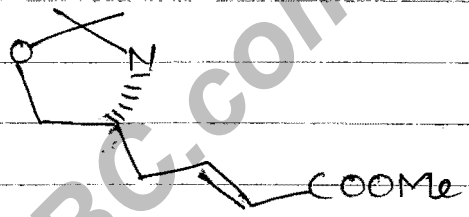
* MnO_2 doesn't oxidise 1° (or) 2° alco. but exess amount of MnO_2 (approximate 10 to 15 eq.) may be oxidise 1° alcohol.

Q =



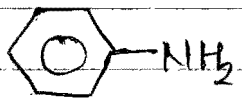


If EWG + nt then
Trans alkene



Trans.

Wittig

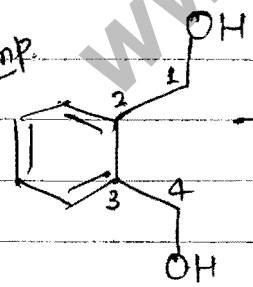
Q =  $\xrightarrow[\text{LTA}]{MnO_2}$ Ph—N=N—Ph

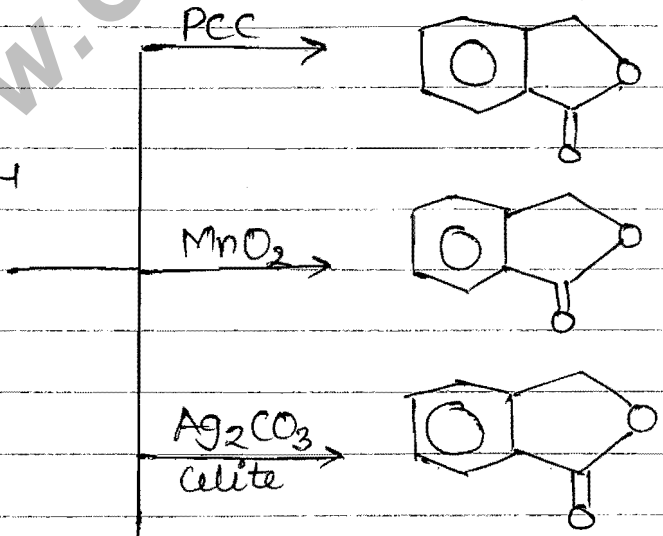
M.Imp.

Rxn. of MnO_2 with 1,4 diol.

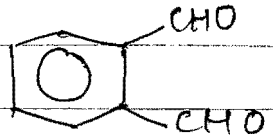
MnO_2 when react with 1,4 diol, then lactone forms.

M.Imp.



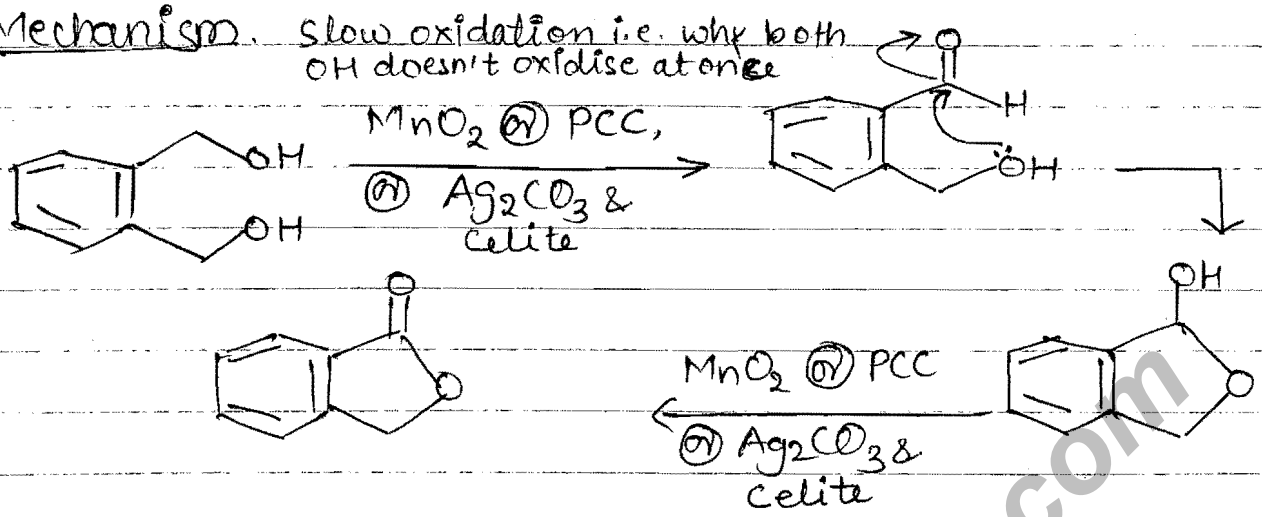


SWERN Oxidn.
DMSO, $COCl_2$
Et_3N

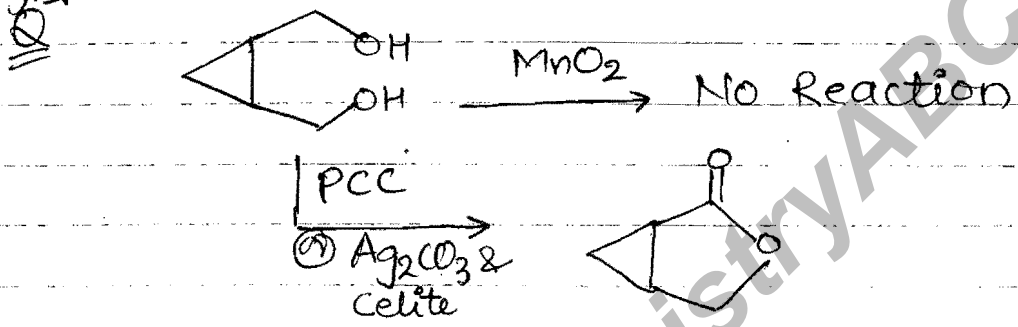


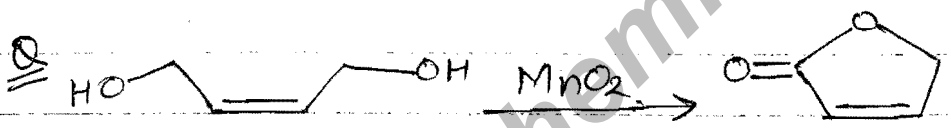
Very fast Oxidn.

Mechanism. Slow oxidation i.e. why both OH doesn't oxidise at once



Imp.

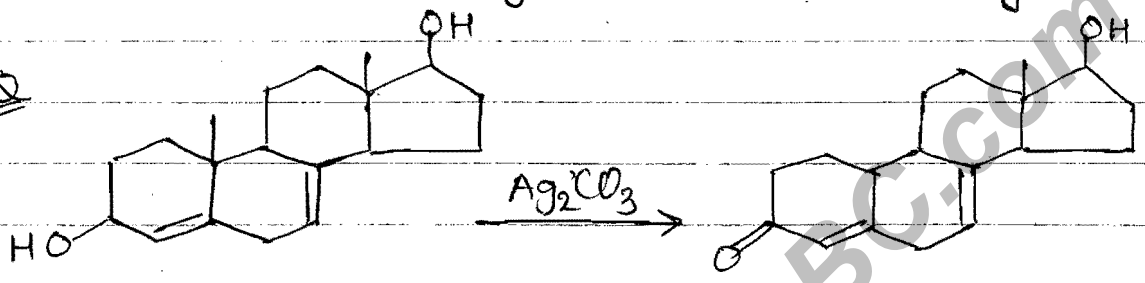




SILVER CARBONATE [Ag_2CO_3]

* Order of oxidⁿ ⇒ Allylic @ benzylic > 2° > 1°
* For the Oxidation of 2° alco. Ag_2CO_3 is the best reagent.
* Unhindered -OH group is selectively oxidised.

Q



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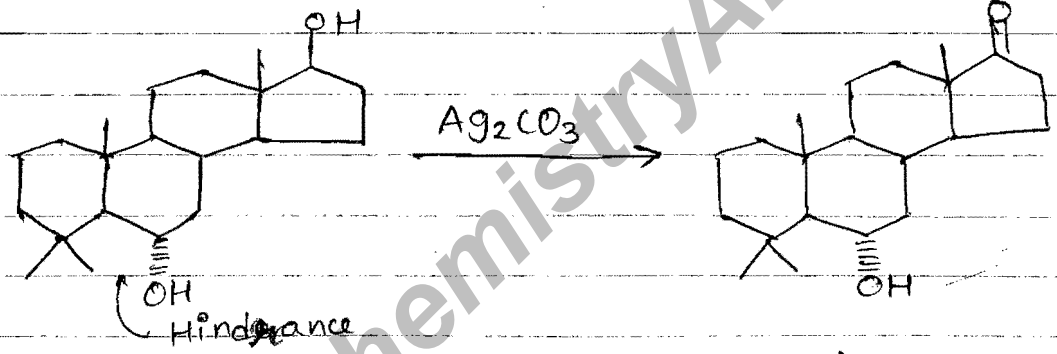
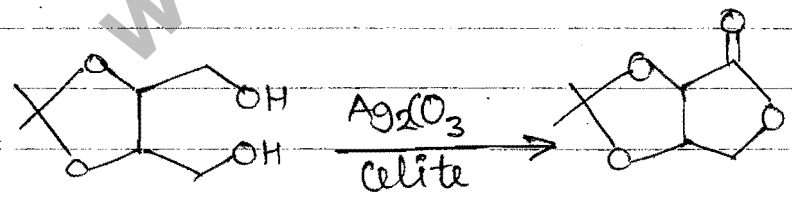


Fetizons reagent (Ag_2CO_3 + Celite)
⇓
Sand

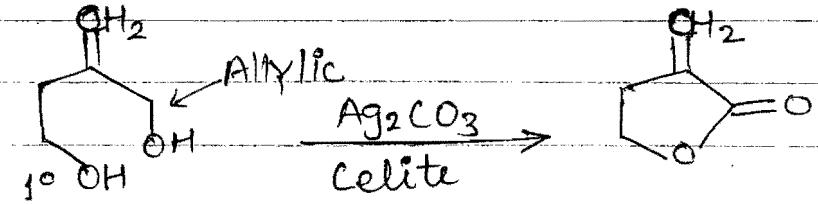
grp. Fetizons reagent oxidsed 1,4 & 1,5 alcohol into ester

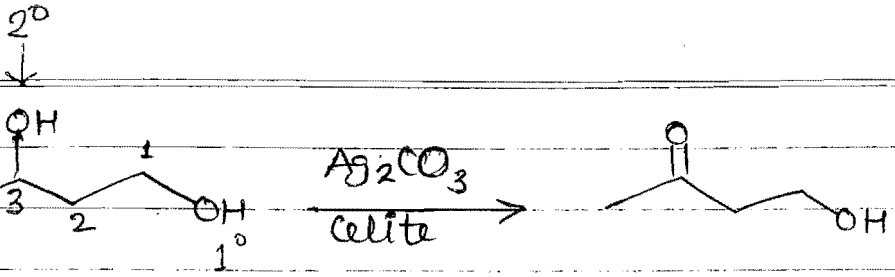
Q

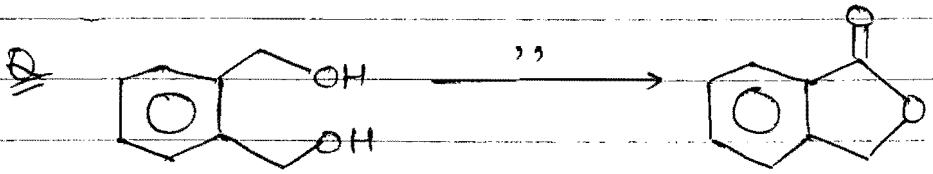


grp.

Q

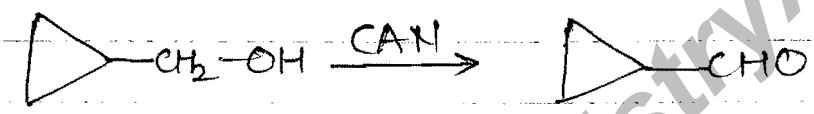






* CAN ⇒ Ceric Ammonium Nitrate ⇒ $(NH_4)_2[Ce(NO_3)_6]$
Oxidⁿ of alcohol into carbonyl.

Order Allylic @ Benzylic > 2° > 1°



Ag_2CO_3 ⇒ 2° Alco. oxidise first then 1° Alco.

OXIDATION BY DMSO

SWERN Oxidⁿ.

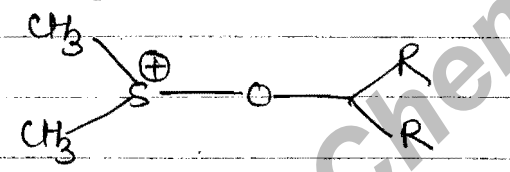
DMSO + $(COCl)_2$

Et_3N

MOFFAT Oxidⁿ.

DMSO + DCC

* Alco oxidise into carbonyl.
* Rxn. takes place at low temp.
* If NEt_3 used then carbonyl form
* If NEt_3 doesn't use then alkyl halide form.
* In Swern oxidⁿ. so many intermediates form but major intermediate is alkoxy sulphonium salt.



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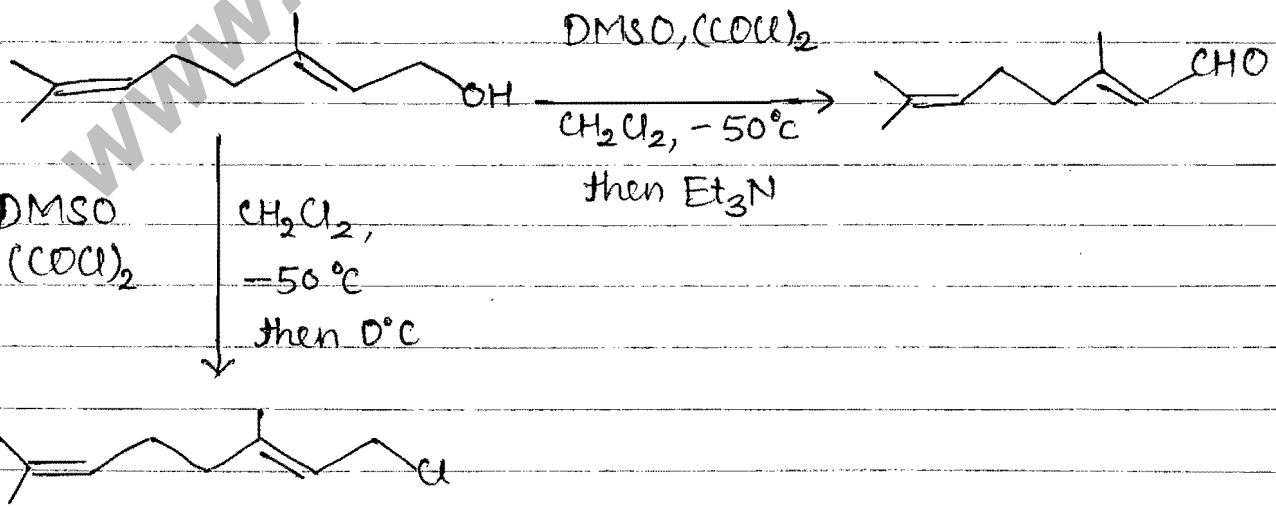

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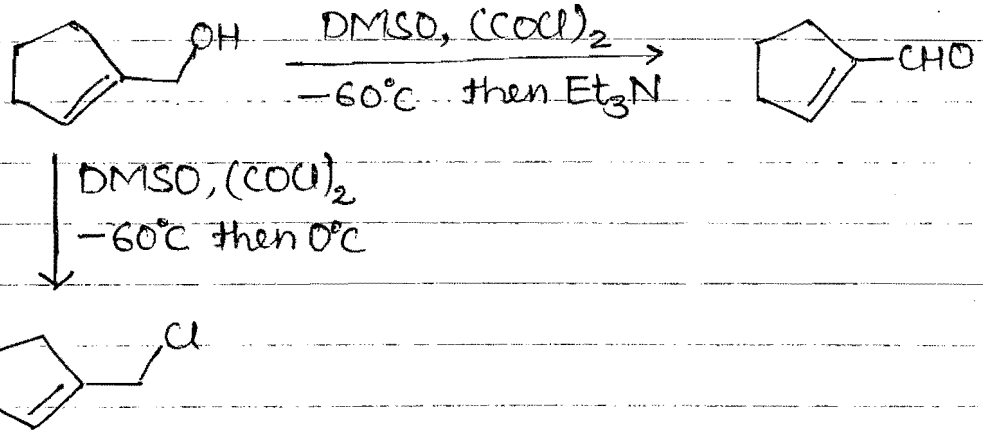
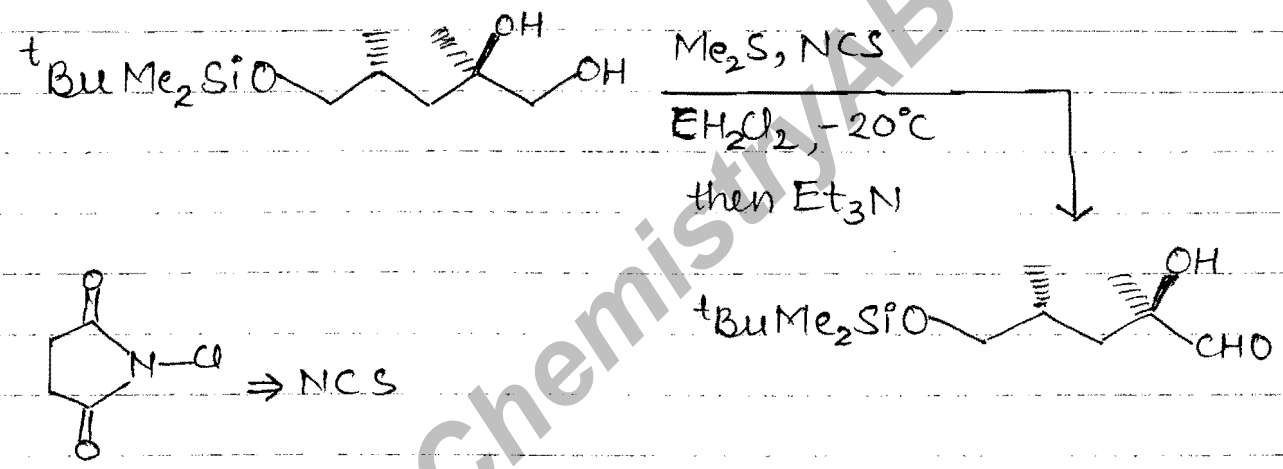
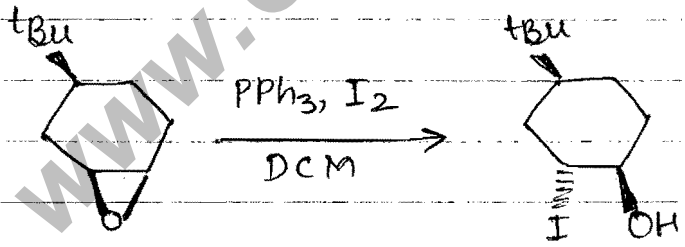


KOREY KIM OXIDATION



V. imp.

Q



V.V. Amp

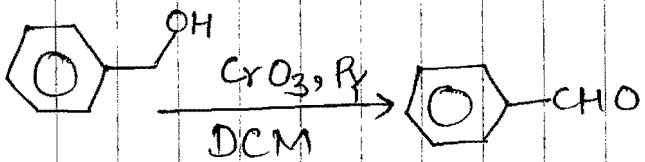
COLLINS Reagent

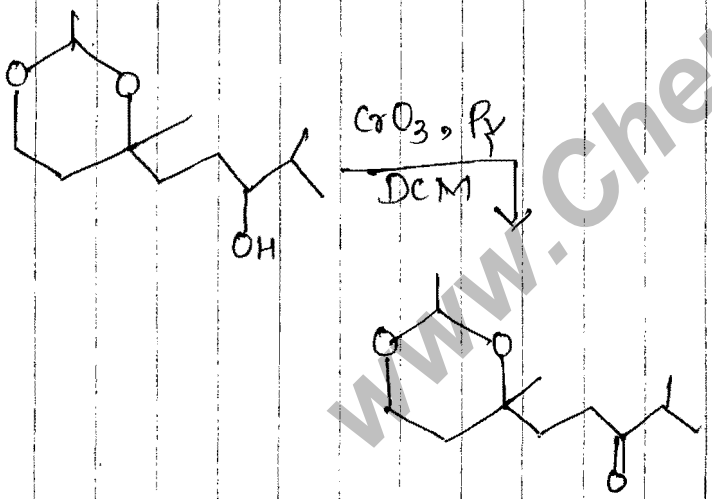
CrO_3 + Pyridine + DCM (CH_2Cl_2)

Oxidation Order

Benzylic @ Allylic > 1° > 2°

No further Oxidation





JOHN'S Reagent

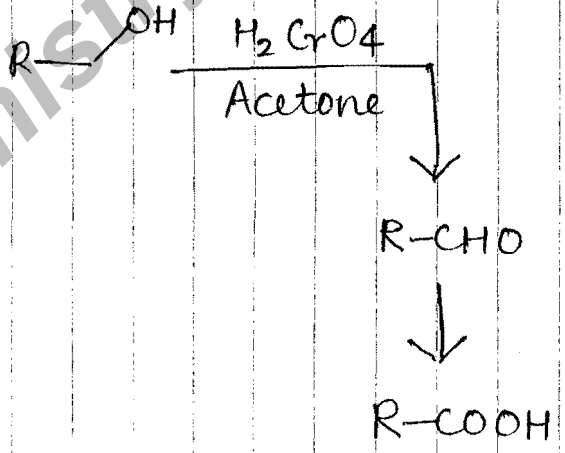
CrO_3 + Acetone + aq H_2SO_4

@ H_2CrO_4 + Acetone

Oxidation Order

Benzylic @ Allylic > 1° > 2°

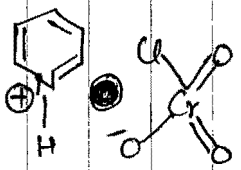
but further Oxidn. takes place, ald. into carboxylic acid.



PCC

Pyridium Chloro Chromate

$Py + CrO_3 + HCl$



@

$Py\overset{\oplus}{H} \cdot CrO_3Cl^{\ominus}$

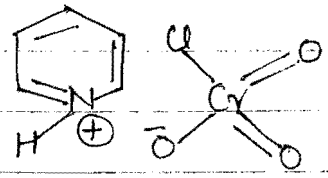
PDC

Pyridium dichromate @ Conforth Reagent

$Py + CrO_3 + Water$

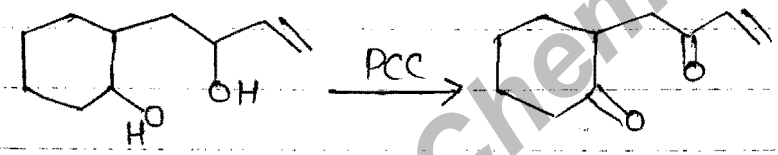
PCC

PYRIDIUM CHLORO CHROMATE

Py + CrO_3 + HCl ⟹ 

Function of PCC

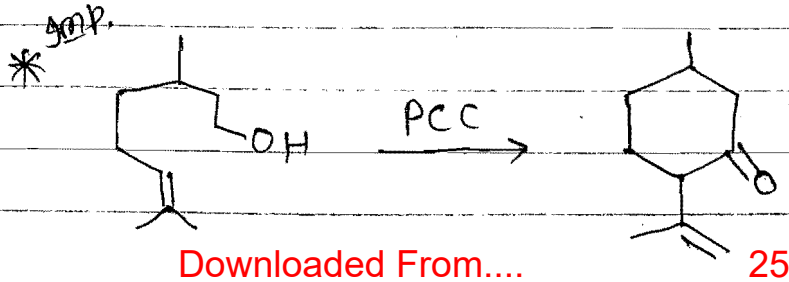
- Only oxidⁿ of Alco.
  - Benzylic > 1° > 2°
  - @ Allylic
- v.imp. Side Rxn. of PCC
- V. imp. Oxidation of 3° allylic alcohol.



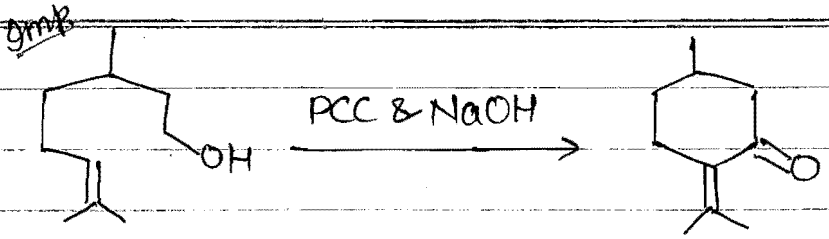
V.V. imp. Side Rxns of PCC [Abnormal Behaviour of PCC]

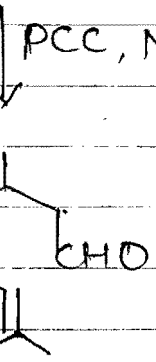
PCC oxidise alco. into carbonyl, Since the medium is acidic so some side rxn may be takes place, the comp. which have double bond (C=C) as well -OH gp. To prevent the side rxn. buffer soln (Sod. acetate) used.

imp.

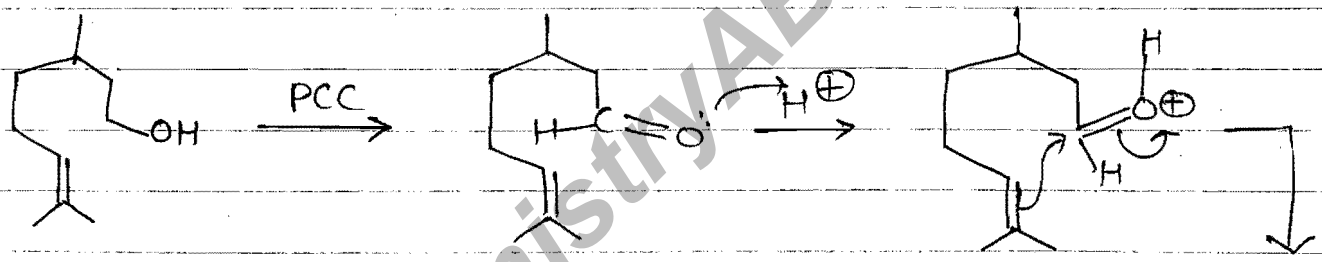


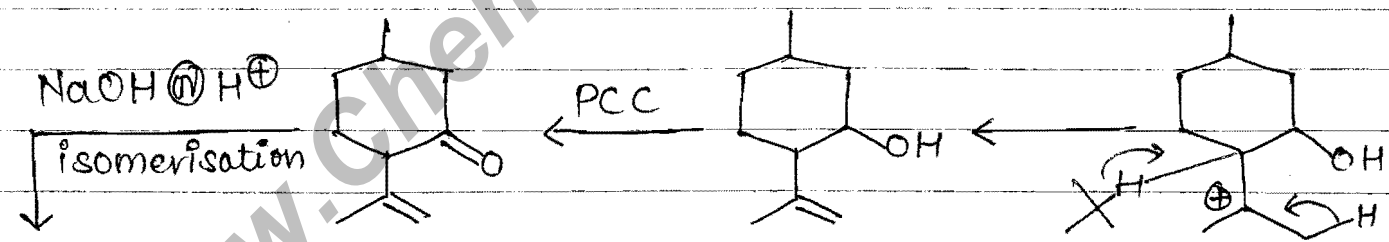
gmb



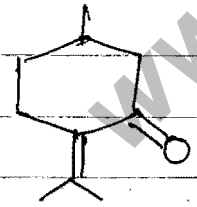


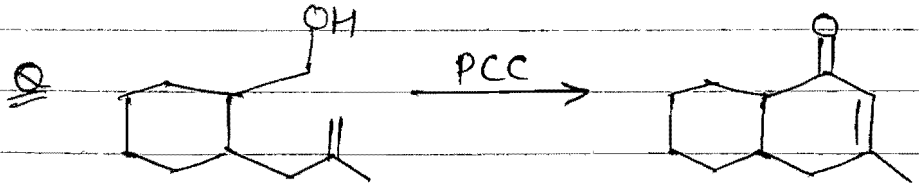
Mechanism

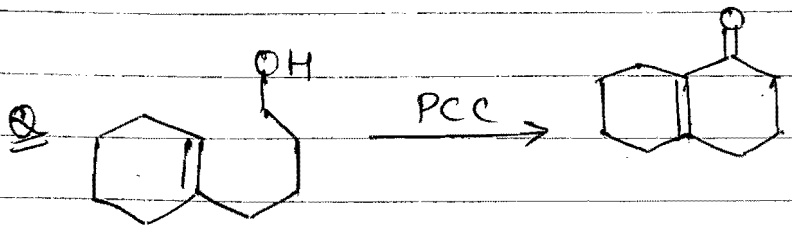




Less substituted Alkene form





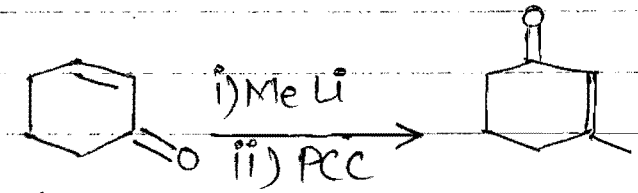


Singlet :CH_2 ⟹ Stereo specific

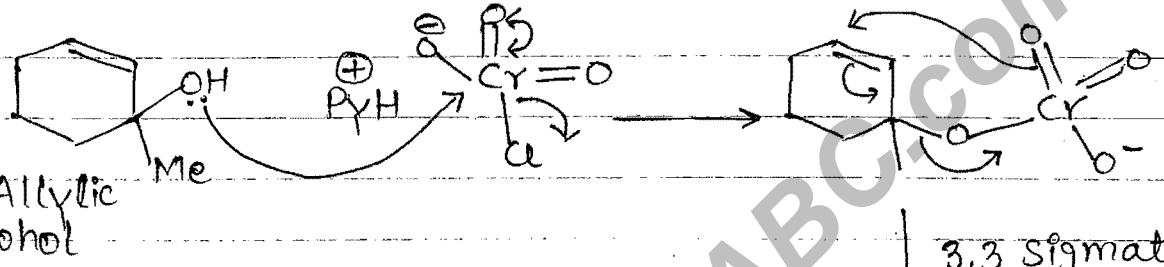
Triplet :CH_2 ⟹ stereo selective.

Rxn. of PCC with 3° Allylic Alcohol :-

2014 V.V.Imp

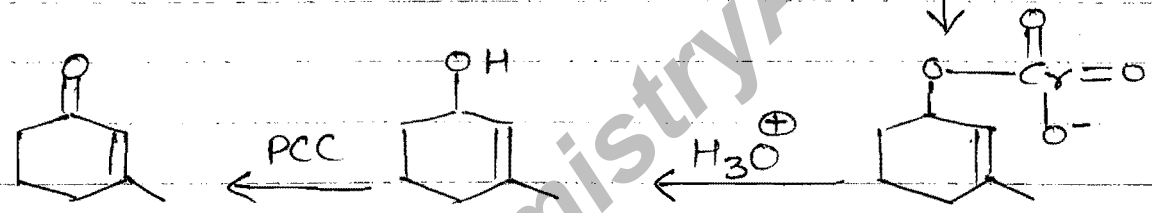
Q 

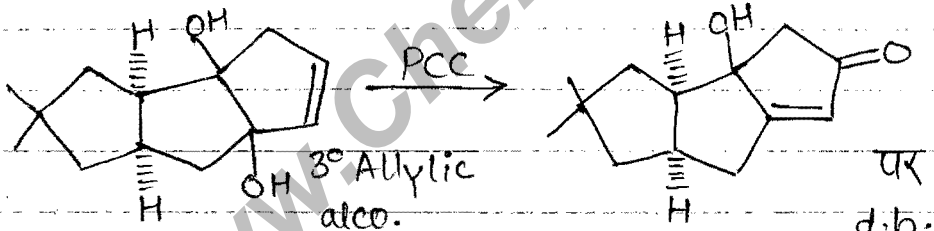
Direct ↓ Me Li addn.



3° Allylic alcohol

3,3 Sigmatropic ↓

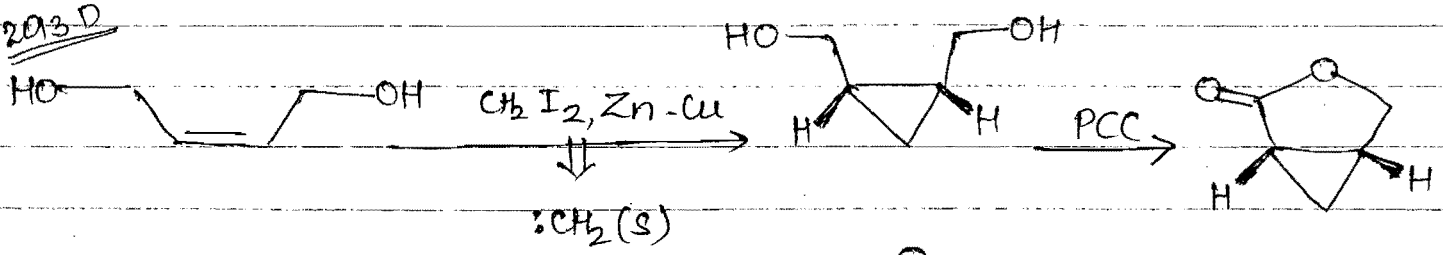


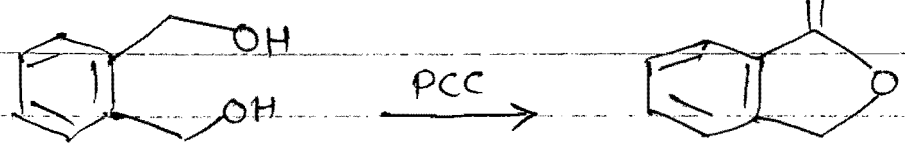
Q 

Allylic d.b. के End पर Carbonyl लगाओ & d.b. alco. की तरफ shift कराओ।

Rxn. with 1,4 diol.

2013 D

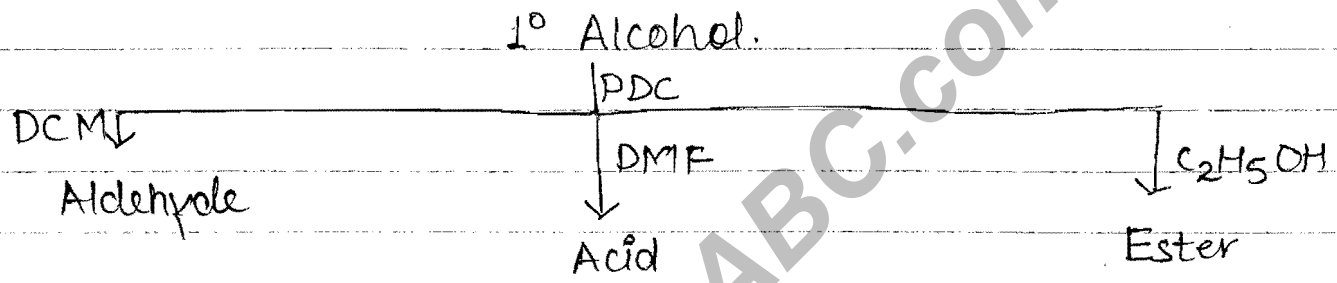


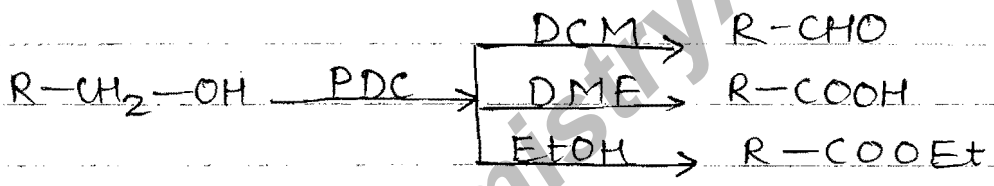
Q 

PYRIDIUM DICHROMATE [PDC]

$PyH^{\oplus}\ CrO_7^{2-}$

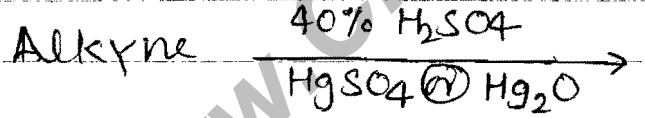
* Oxidation of alcohol.
* Formation of product depends upon nature of solvent.

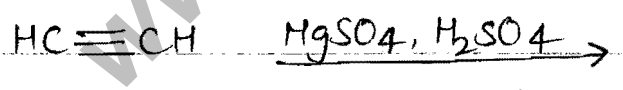


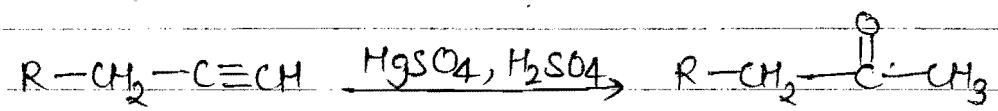


V.V.Imp.

Kucherov Rxn:

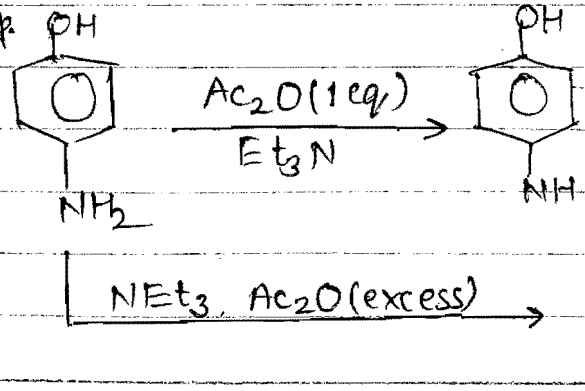






V.V.Imp.

Q.



V.V gmp.

$R-C\equiv CH \xrightarrow{NaNH_2} R-C\equiv C^{\ominus}\,Na^{\oplus}$

NSR NAR

$R-C\equiv C^{\ominus}\,Na^{\oplus} \xrightarrow{HCHO/BrH} R-C\equiv C-CH_2-Br$

$\xrightarrow[S_N1]{HCHO} R-C\equiv C-CH_2OH$

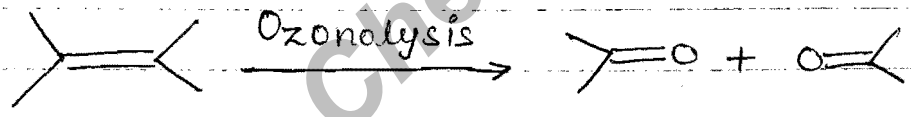
$R-C\equiv C-CH_2-\ddot{O}H \xrightarrow{HBr} R-C\equiv C-CH_2-\overset{\oplus}{O}H_2$

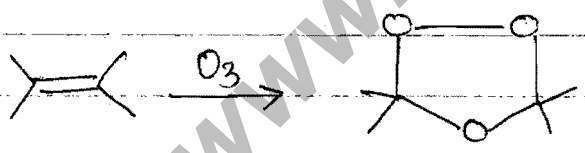
$\downarrow$

$R-C\equiv C-CH_2-Br \xleftarrow[Br^{\ominus}]{S_N1} R-C\equiv C-\overset{\oplus}{C}H_2$

Stable Intimate

OZONOLYSIS





Ozonide

V. gmp. gmp. gmp.

Me_2S H_2O_2 $LiAlH_4$ (or) $NaBH_4$ Zn H_2O (or) Zn/CH_3COOH

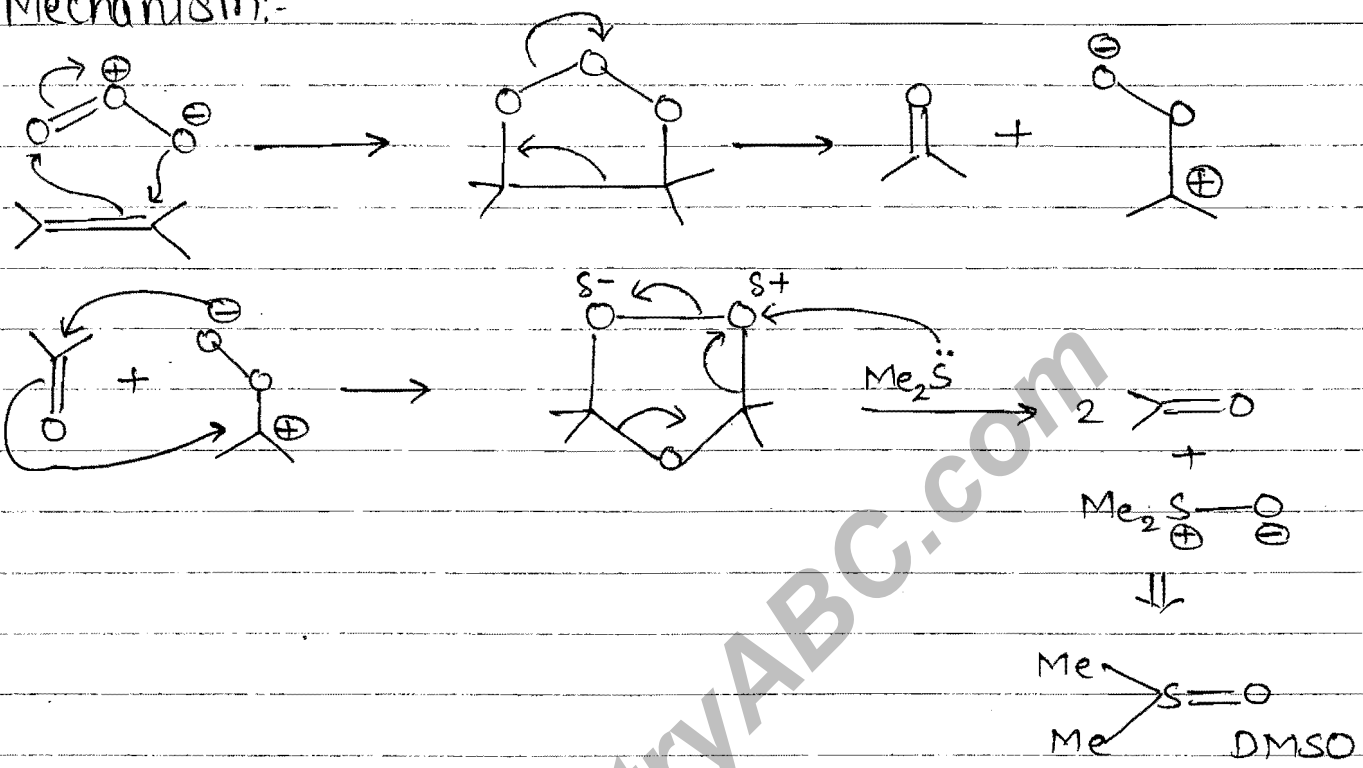
Carbonyl

Carbonyl but further oxidⁿ. may take place due to H_2O_2

Alcohol

Carbonyl.

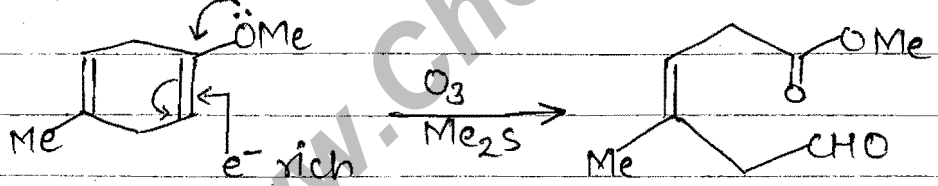
Mechanism:-



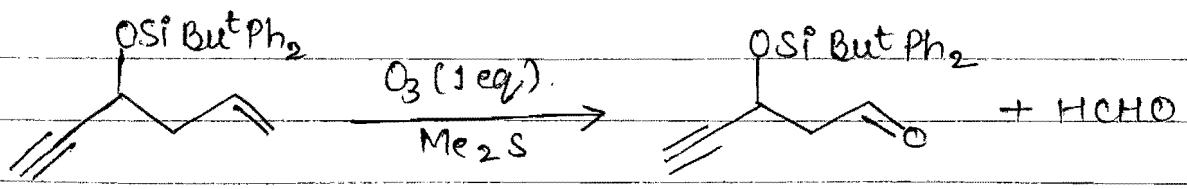
M.imp:

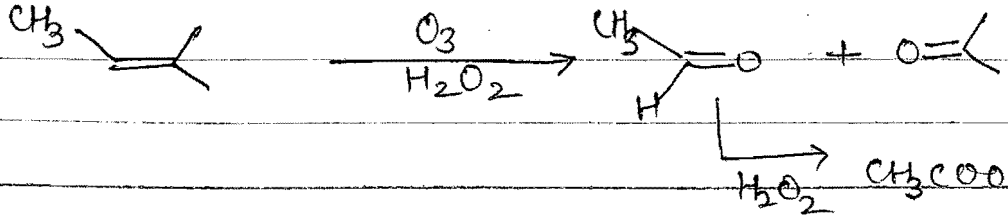
If in a compound two double bond +nt then ozonolysis takes place at more e⁻ rich double bond (c=c).

Ex.



If in a comp. both double & tripple bond are +nt then ozonolysis takes place at c=c double bond.

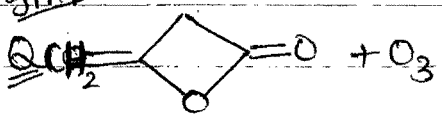
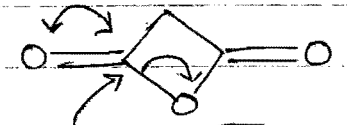




Ozonolysis of alkyne:-

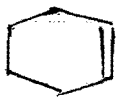
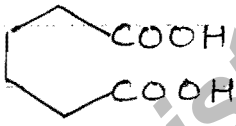
Q $R-C\equiv C-R + O_3 \longrightarrow R-COOH + R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R$ (Major)

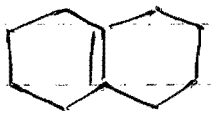
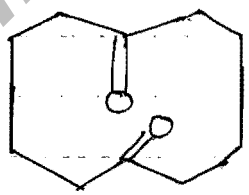
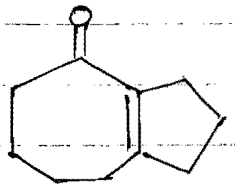
Imp.

Q  $\xrightarrow{-HCHO}$  Anhydride

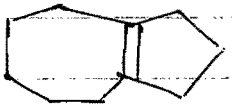
$PhNH_2$

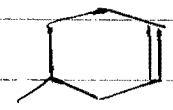
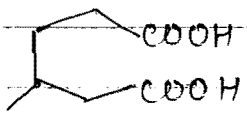
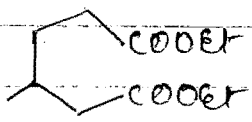
$\downarrow$ NSR

Q  $\xrightarrow[H_2O_2]{O_3}$ 

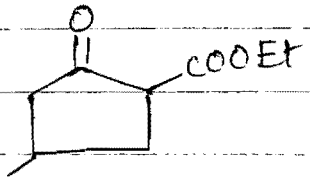
Q  $\xrightarrow{i)\ O_3, Me_2S}$  $\xrightarrow[Base]{ii)\ NaOEt}$ 

Aldol

 $\xleftarrow{Wolf\ N_2H_4/\bar{O}H}$

Q  $\xrightarrow[H_2O_2]{O_3}$  $\xrightarrow[Esterification]{EtOH/H^{\oplus}}$ 

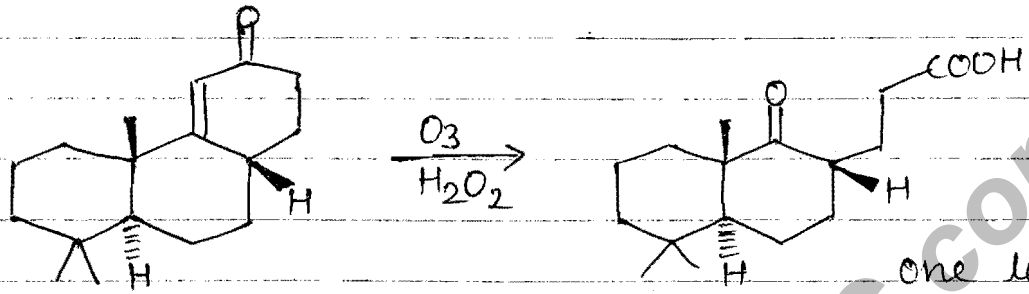
$\xrightarrow{\ominus OH}$ Dickmann



α-keto ester

V.V. imp

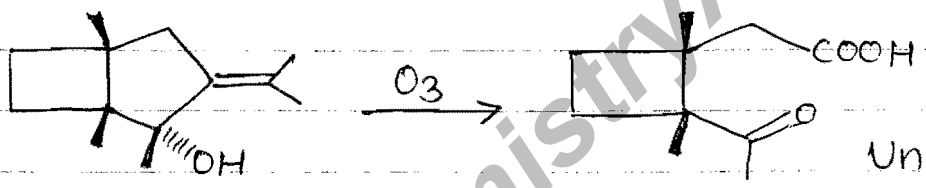
Ozonolysis of α,β-unsaturated carbonyl compound gives a product containing one less carbon atom than in starting materiál.



one less carbon atom.

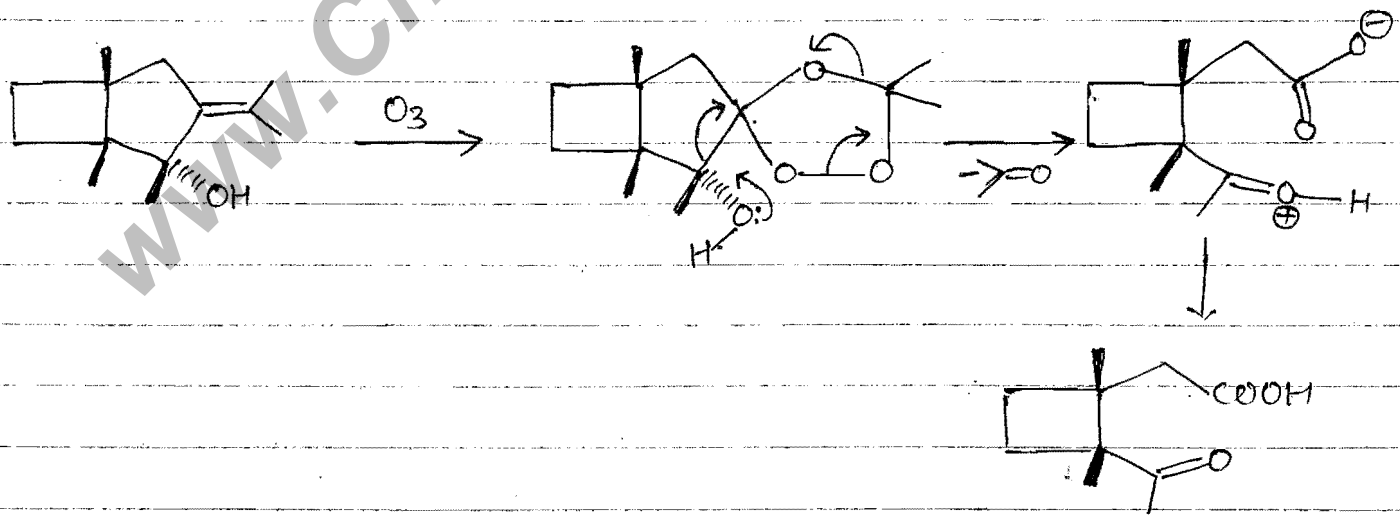
2014
V.V. imp

Ozonolysis of allylic alcohol C=C.

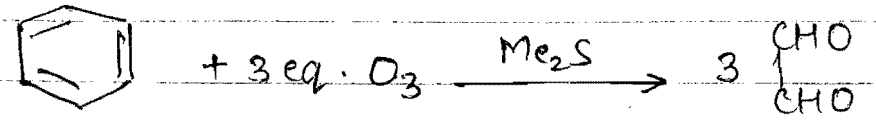


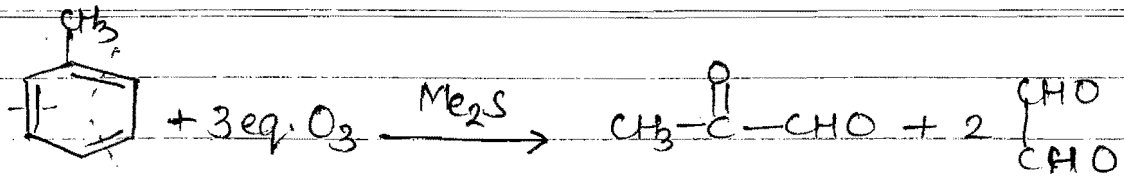
Unexpected product

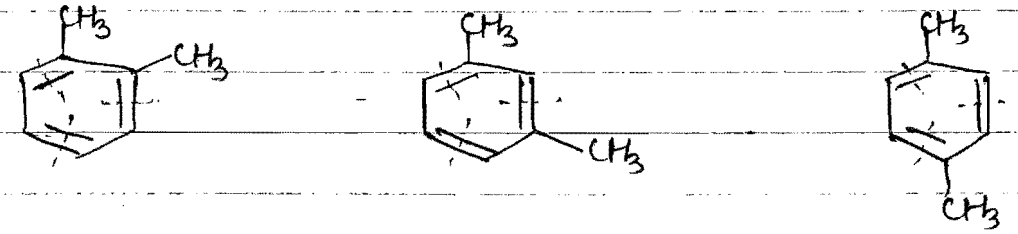
Mechanism:-



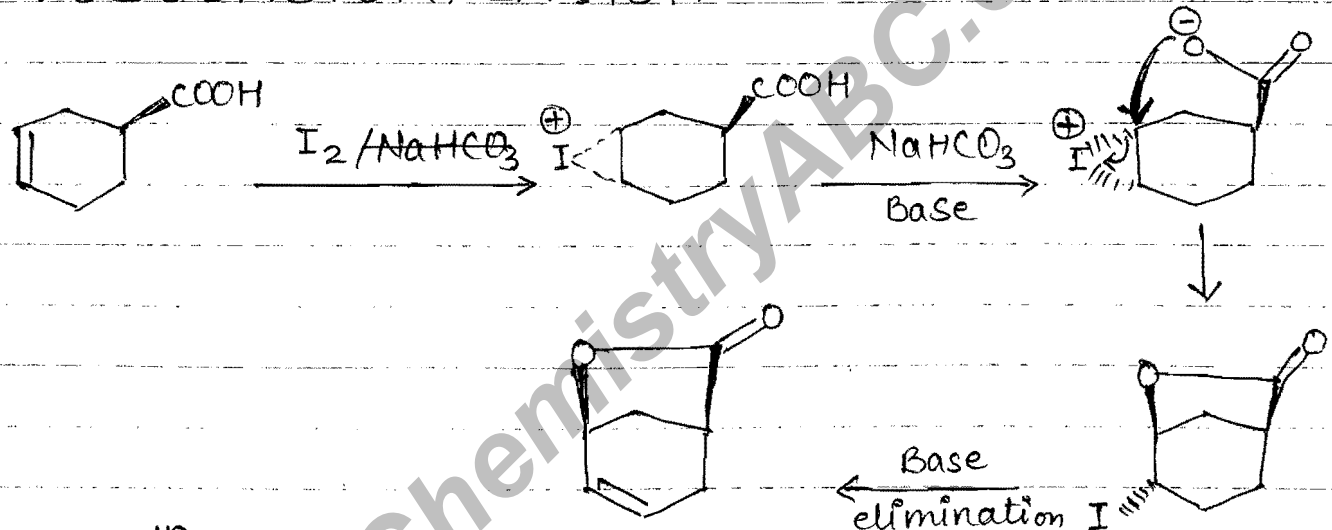
Ozonolysis of Benzene

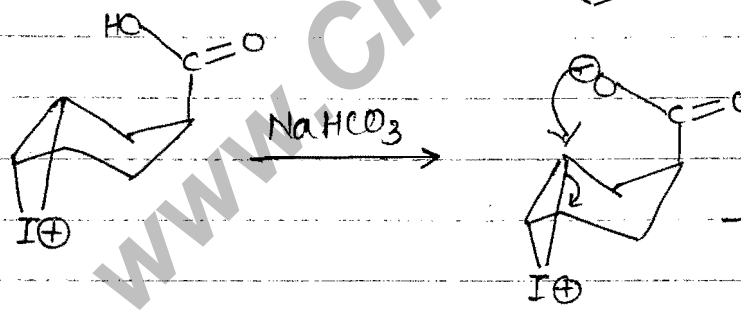


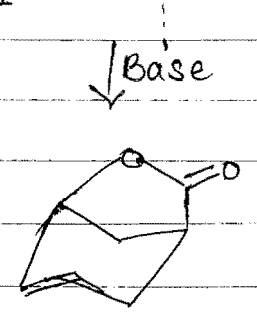
Q) 

* 

IODOLACTONIZATION

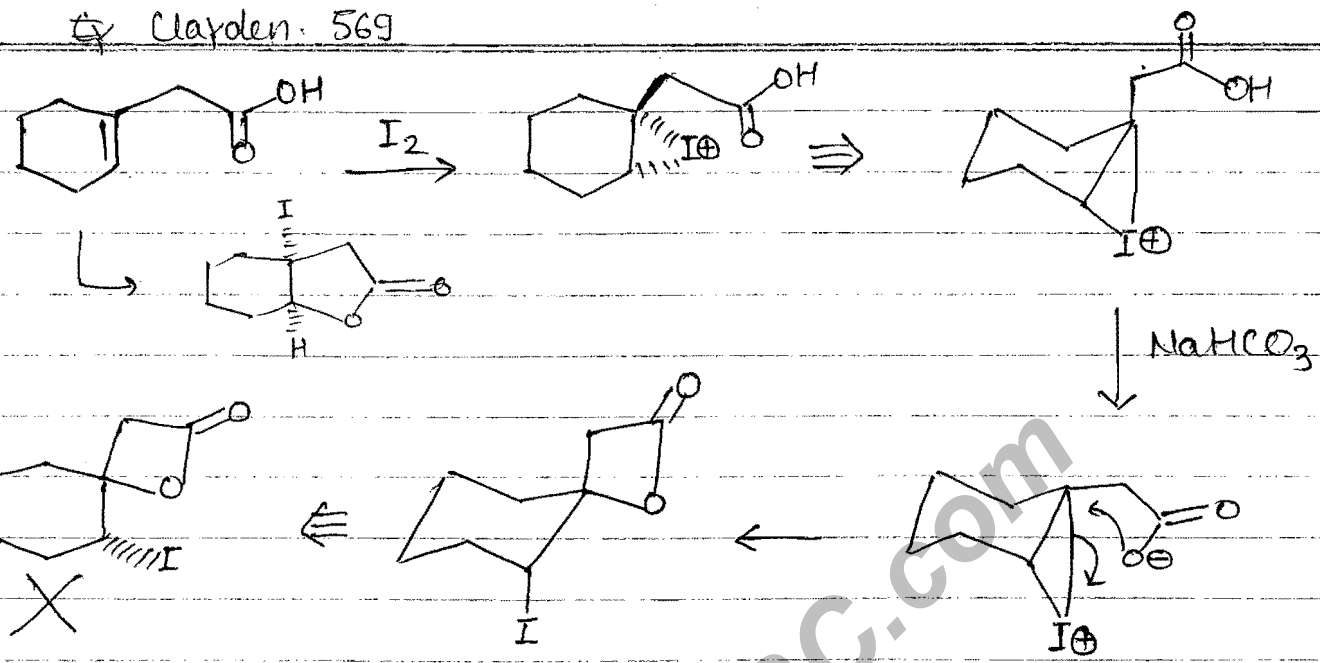


a) 



Imp. Ex Clayden. 569

Q



V.V.V.Imp.

SELENIUM DIOXIDE SeO_2

* Oxidation at allylic & Benzylic position

Reaction with H_2O.

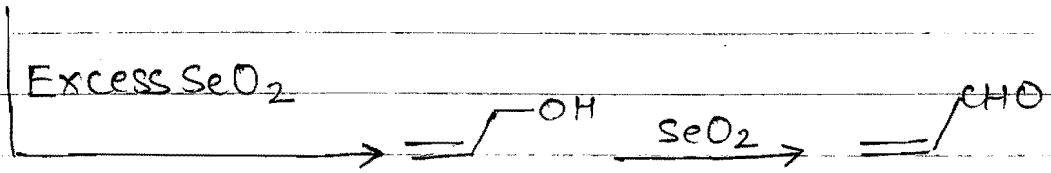
$$SeO_2 + H_2O \longrightarrow H_2SeO_3$$

Function of SeO_2

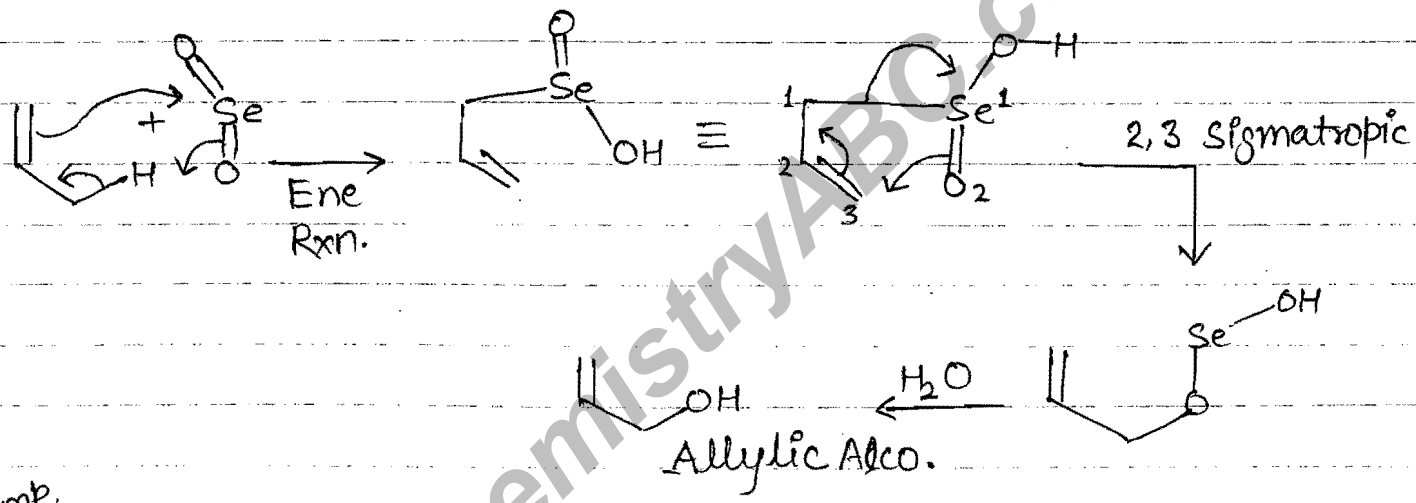
- Formation of allylic alco. by alkene
- Formation of 1,2 di carbonyl by carbonyl comp.
- Oxidation at α methyl group w.r.t. Nitrogen

Dehydration in 1,4 diketone & 1,2 diaryl comp. at high temp.

1) Generation of -OH gp at allylic position :-



Mechanism :-



V. Imp.

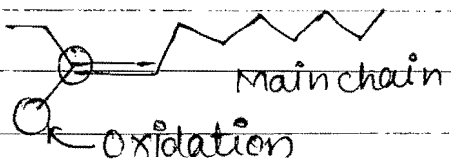
Key Points

i) Select more substituted end of the double bond

Ex.

ii) Oxidation takes place at trans to the main chain

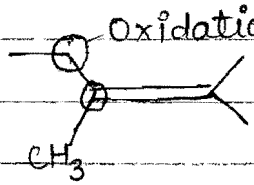
Ex.



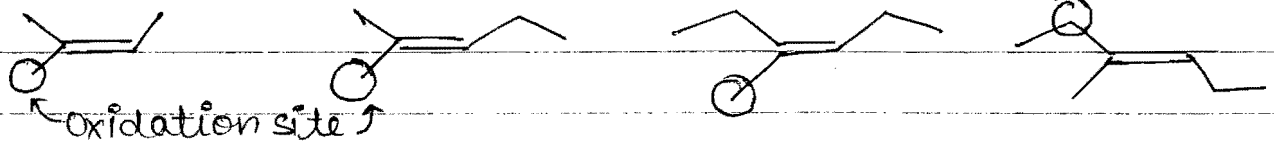
iii) If in main chain gp's are same then order of oxid^{n} is -

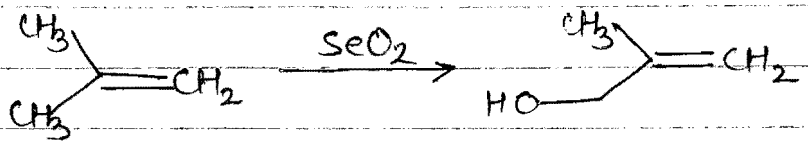
$-CH_2- > -CH_3$

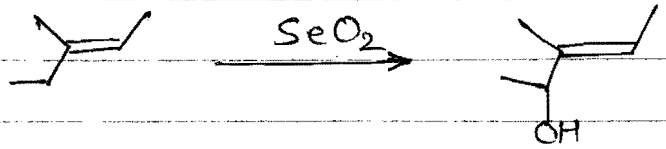
Ex.

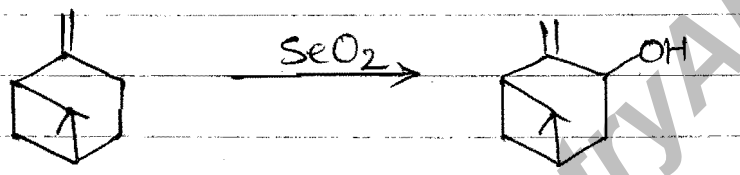


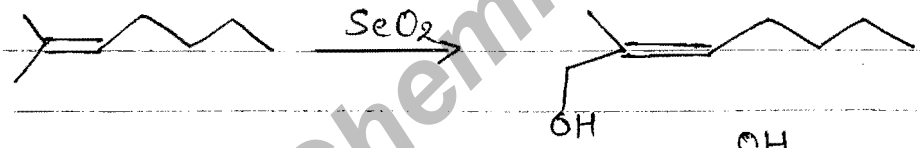
Ex.

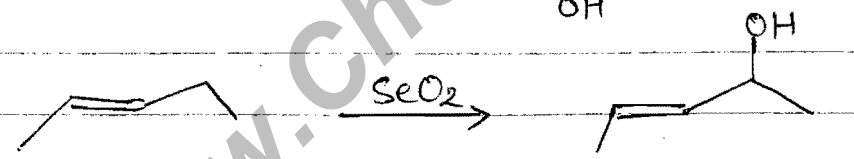


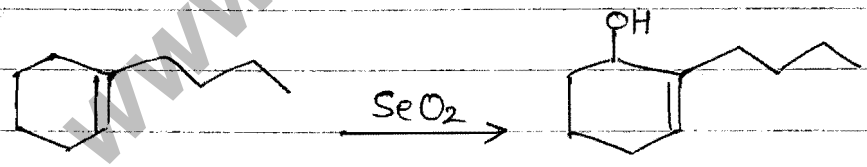
Q 

Q 

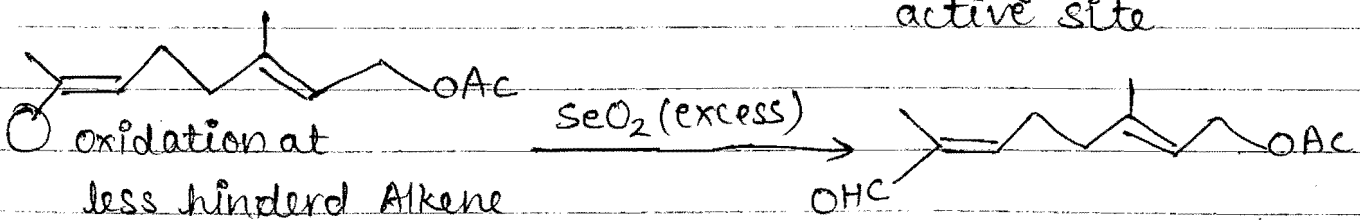
Q 

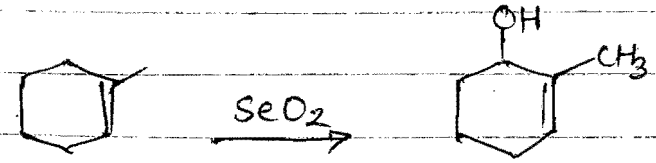
Q 

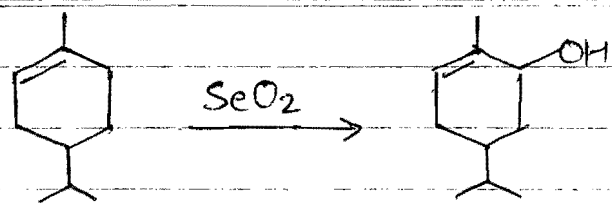
Q 

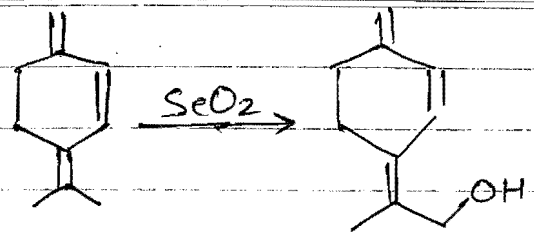
Q 

Firstly oxidⁿ take place at ring becoz of more active site

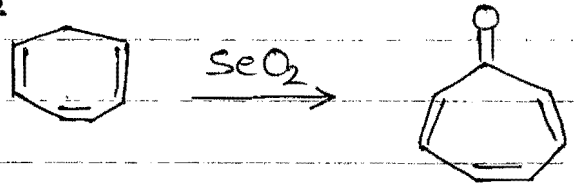
Q 

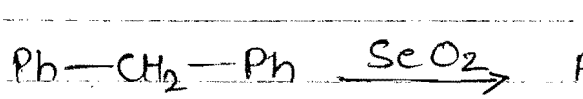
Q 

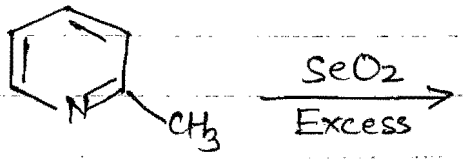
Q 

Q 

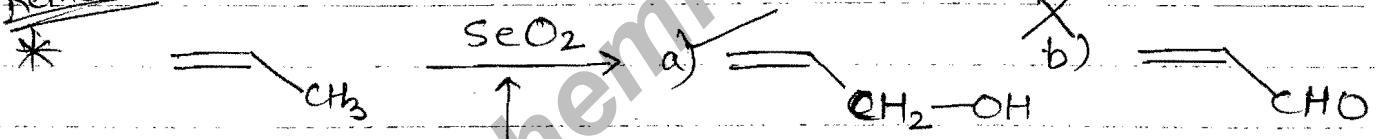
Some times SeO_2 produce carbonyl comp.

Imp. 

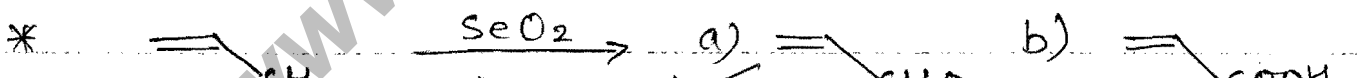


Q 

Remember



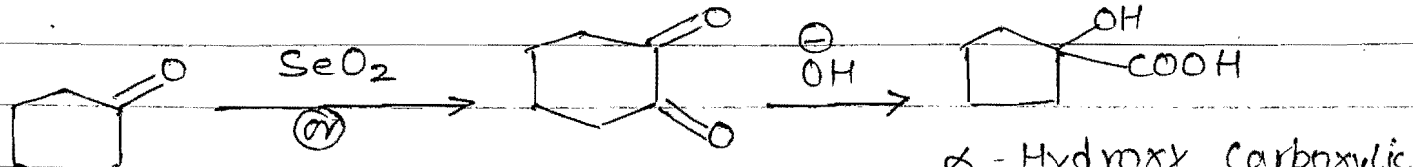
If excess then -CHO



Here -OH not in option so choose -CHO

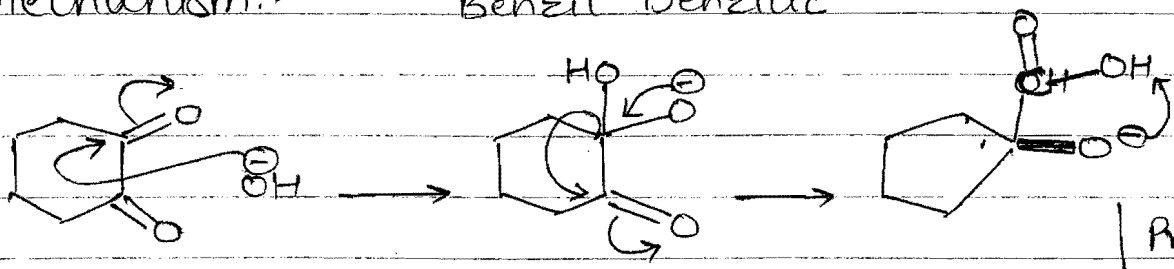
2014 V.V. Imp

2) Formation of 1,2 dicarbonyl from Carbonyl Comp. :-

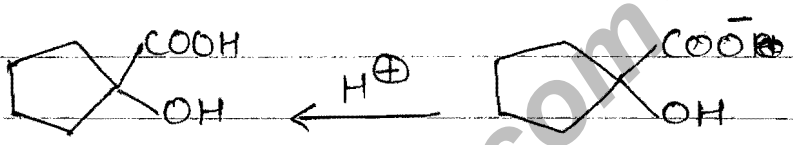


α - Hydroxy Carboxylic Acid.

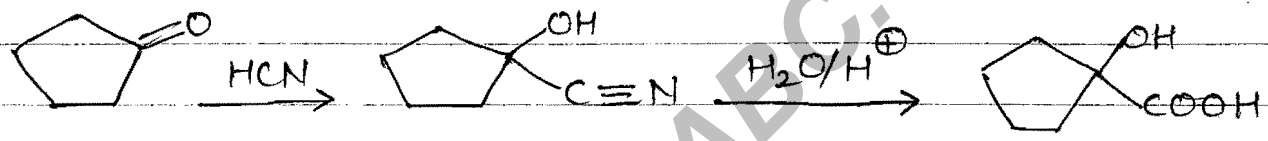
Mechanism:- Benzil Benzilic

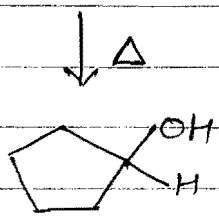


Proton Abstraction



Q





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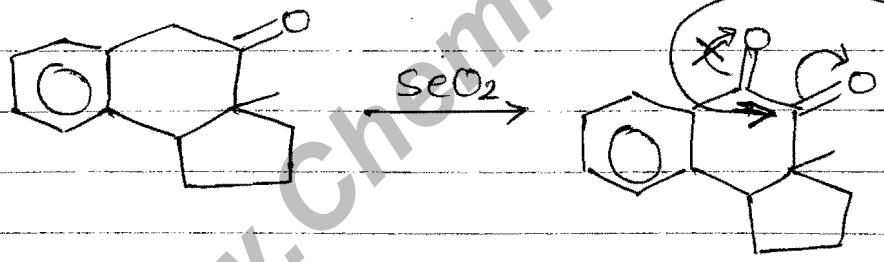

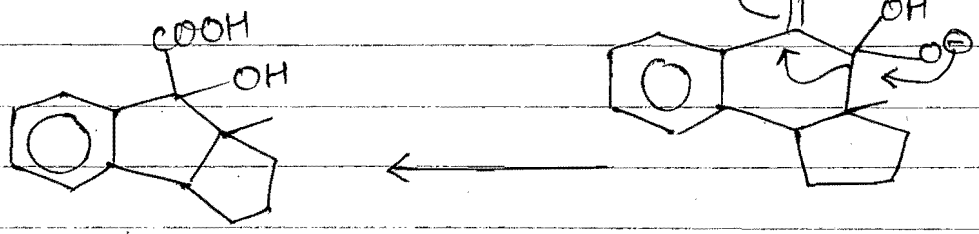

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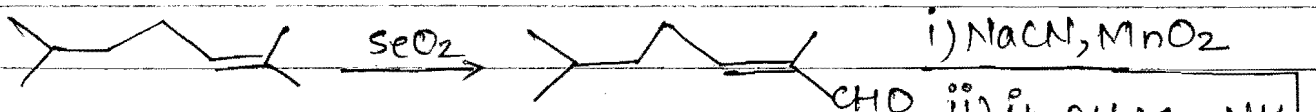
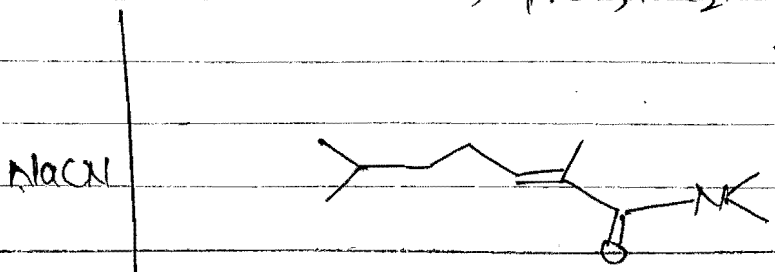
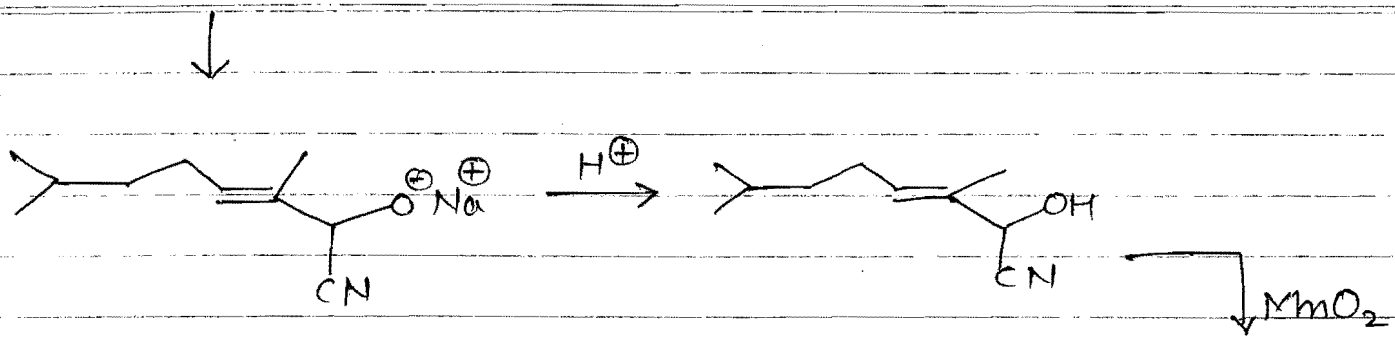
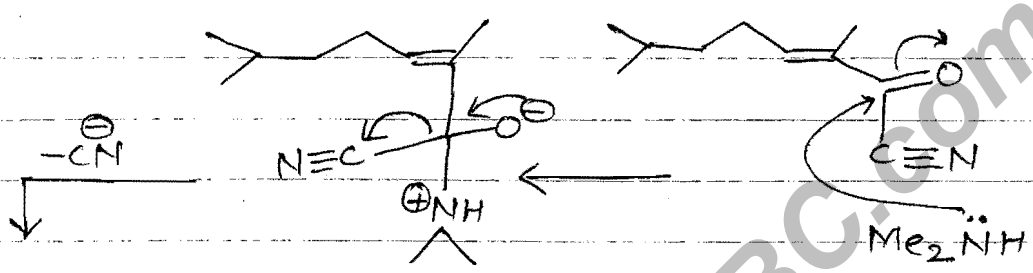
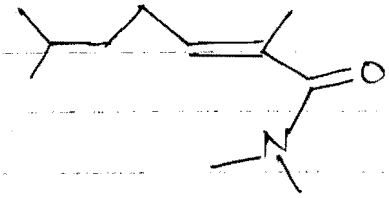
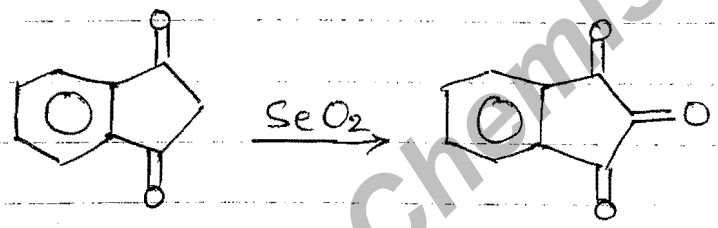


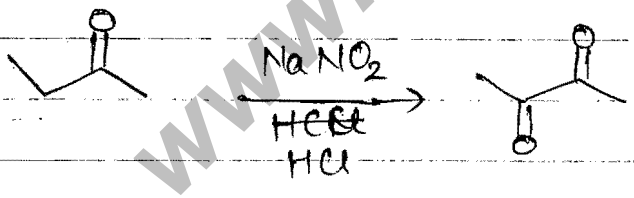


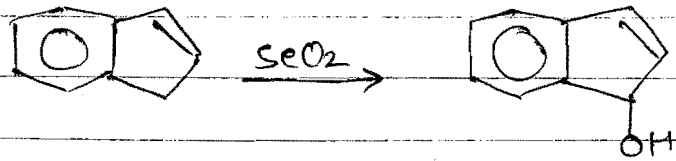


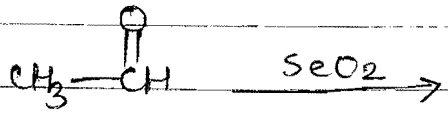


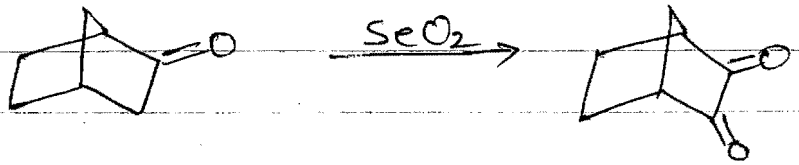


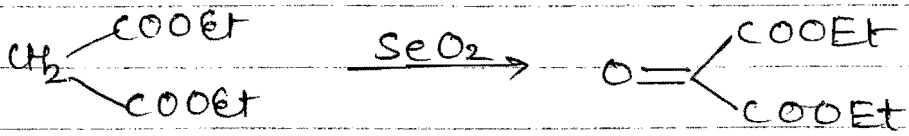
Q 

Q 

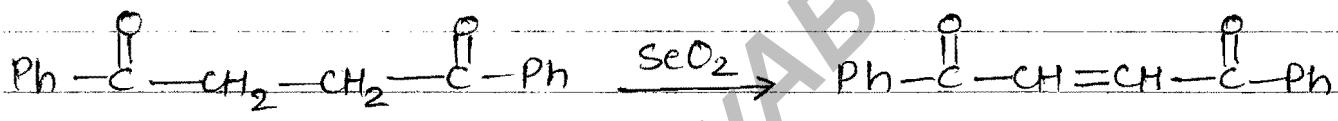
Q 

Q 

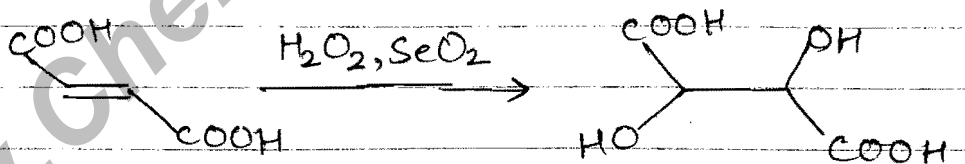
Q 

Q 

3) SeO_2 also posses dehydrogenation in 1,4 diketone & 1,2 diaryl ethane:-

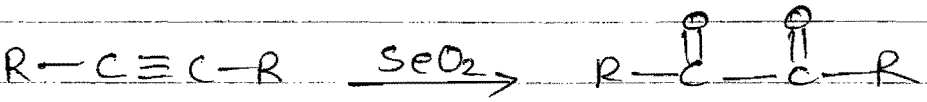


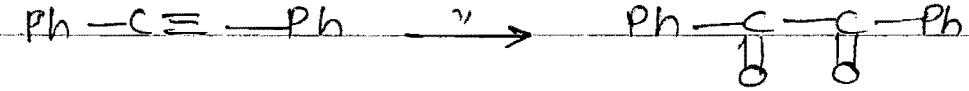
Trans Hydroxylation also takes place in the +nce of H_2O_2



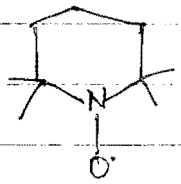
trans diol

Rxn with Alkyne

* 

* 

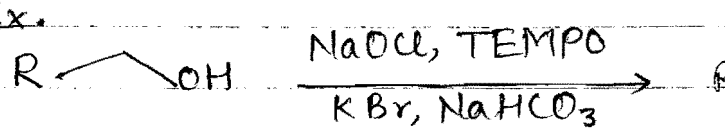
TEMPO OXIDATION

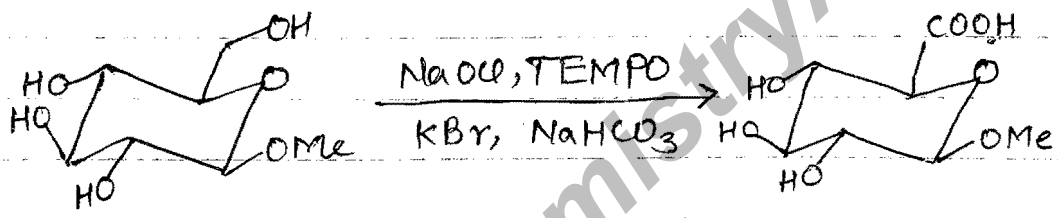


TEMPO (Stable Radical)
2,2,6,6 tetramethyl piperidine - 1 - oxyl.

* TEMPO is a camarcially available free radical.
  ↳ Teta methyl penta hydro pyridine oxide
* Oxidation of 1° alcohol.

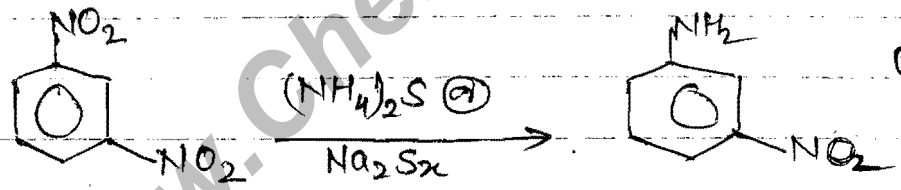
Ex.





V. V. imp.

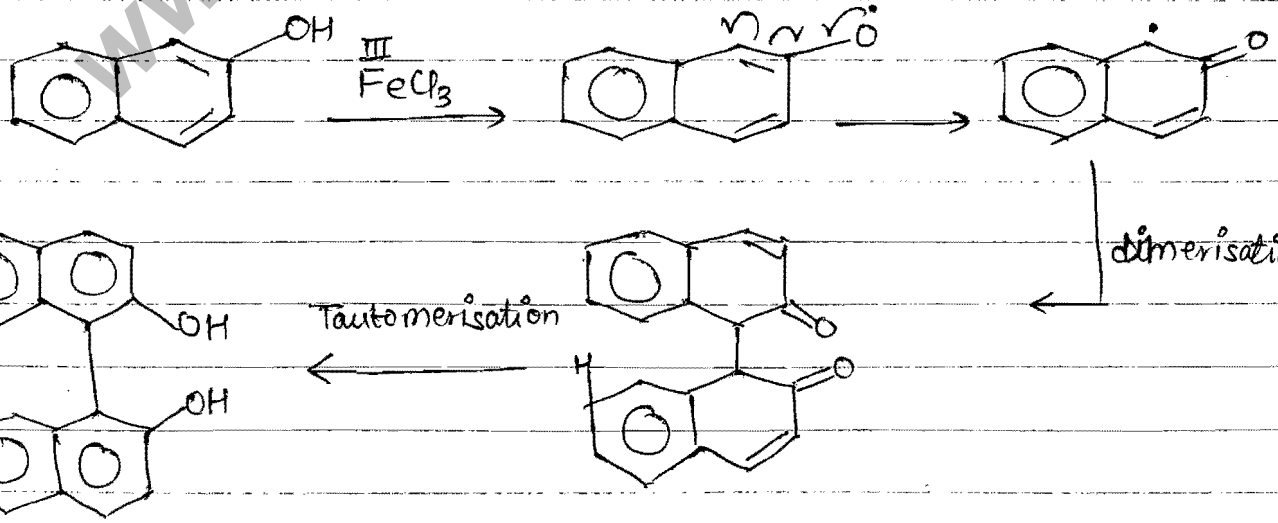
Q



Selectively Only one $-NO_2$ reduced

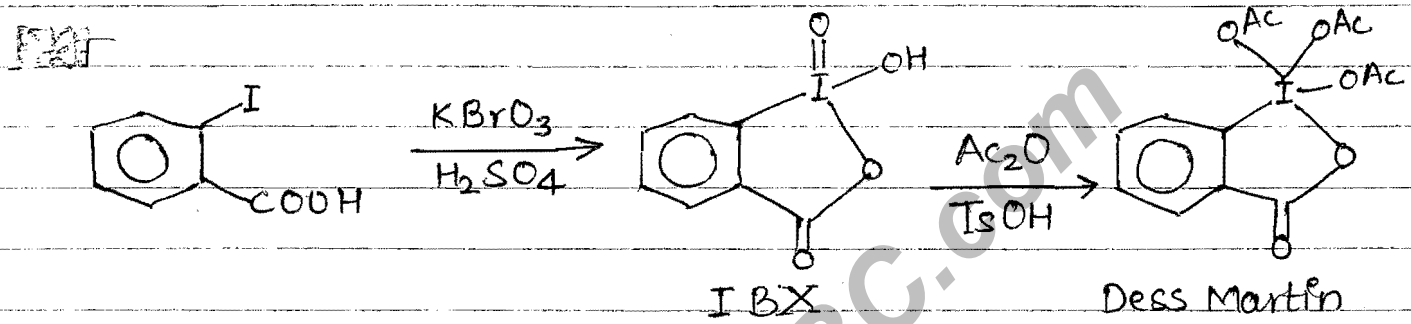
↳ Sod. poly sulphide

Q



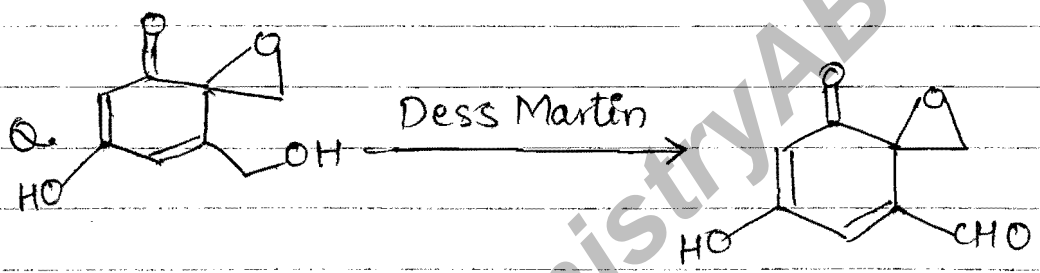
IBX & Dess Martin Reagent

IBX & Dess Martin Reagent is a oxidising reagent mainly. It oxidised alco. into carbonyl.



IBX

Dess Martin Reagent



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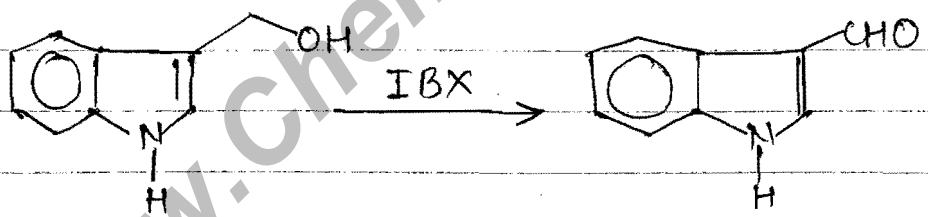
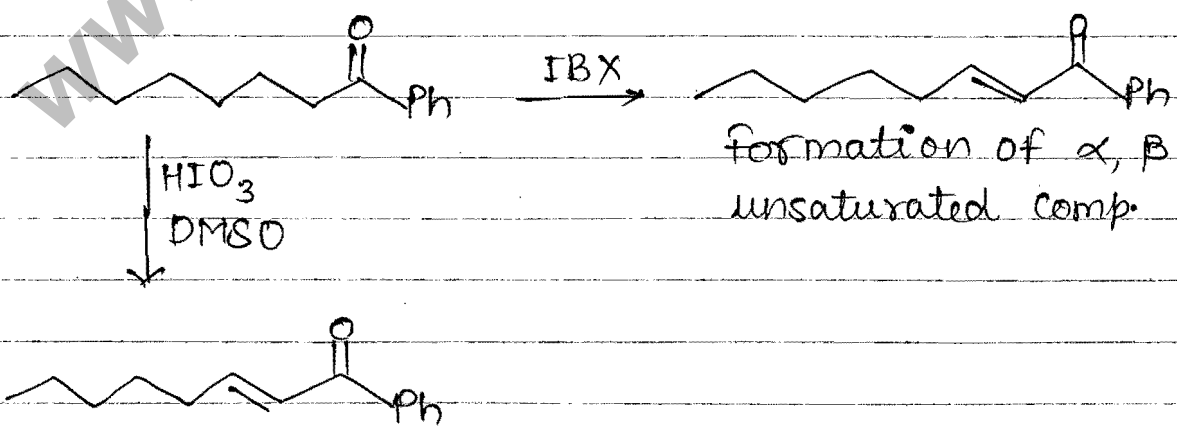
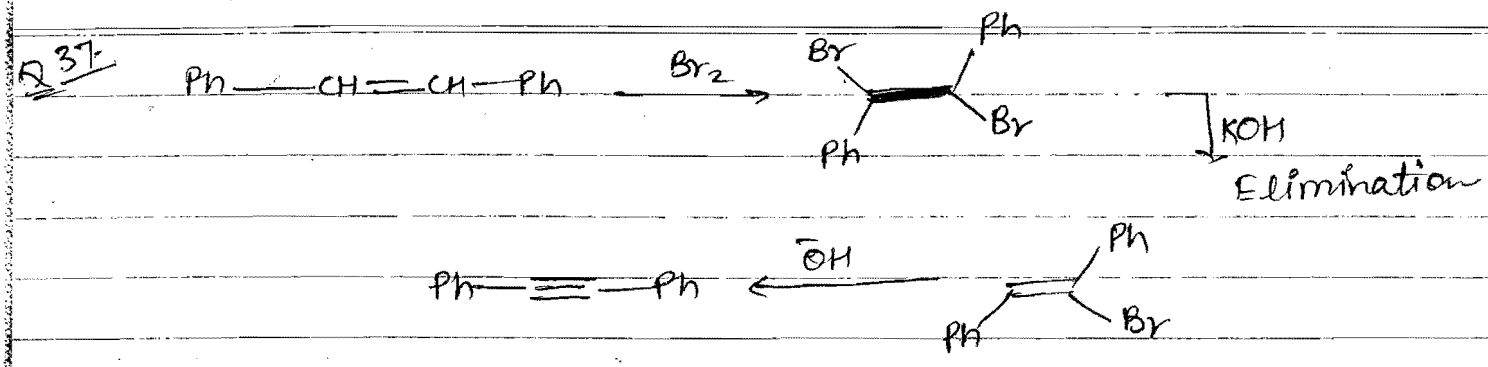


V. imp. Q



formation of α, β unsaturated comp.

Q 37.



(39)