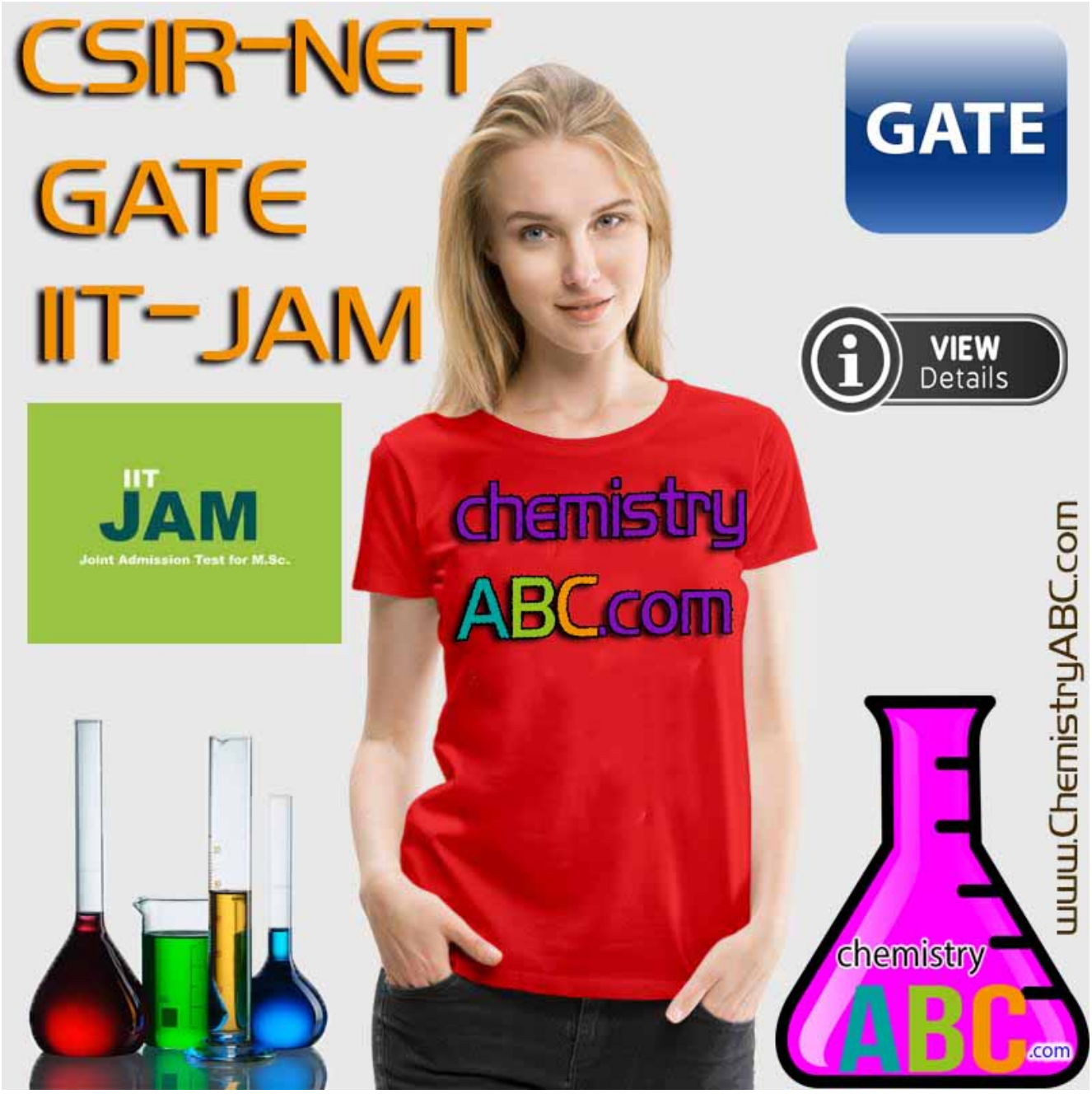
# Aromaticity

## +PERICYCLIC

## +PHOTOCHEMISTRY

### Handwritten Notes for CSIR NET GATE etc.

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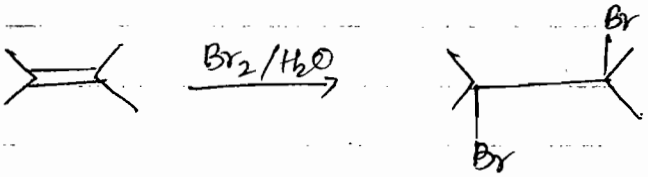
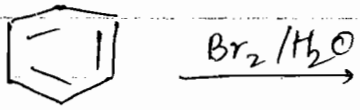
# AROMATICITY

Aromaticity is the chemical property of comp. Aromatic comp follows following points-

* Aromatic comp. are highly stable
* Aromatic comp shows electrophilic substitution rxn. rather than addition rxn.




Addition Rxn.




No addition Rxn.

It means aromatic comp. doesn't decolourised to Bromine water i.e. Brownish

* Aromatic comp. follow Hucket Rule $(4n+2)\pi$ delocalized $e^-$, $n = 0, 1, 2, 3, 4, \ldots$
* Presence of diamag. ring current.
* Each carbon is $sp^2$ hyb. or sp hyb.
* System must be cyclic, conjugated & planar.

## High degree of Stability:-

$$\text{Stability} \propto \text{Resonance Energy} \propto \frac{1}{\text{Pot. Energy}}$$

R.E. ⇒ किसी syst. से निकली हुई Energy.

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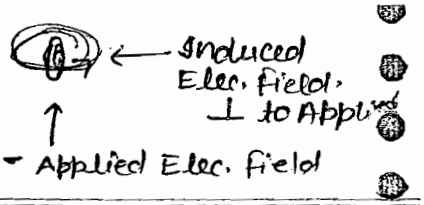
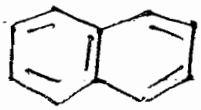
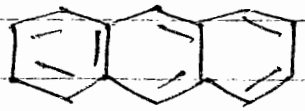


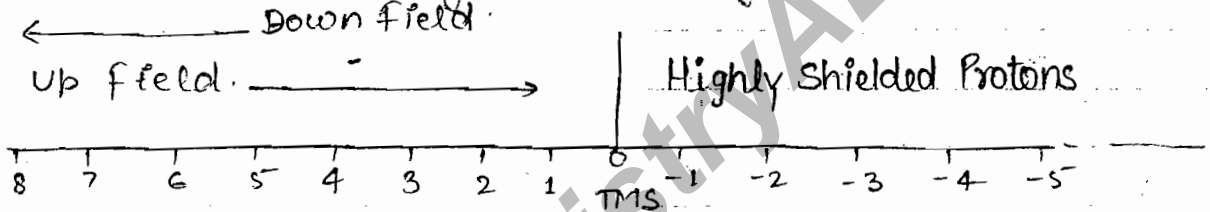

Ques Most aromatic comp. ?

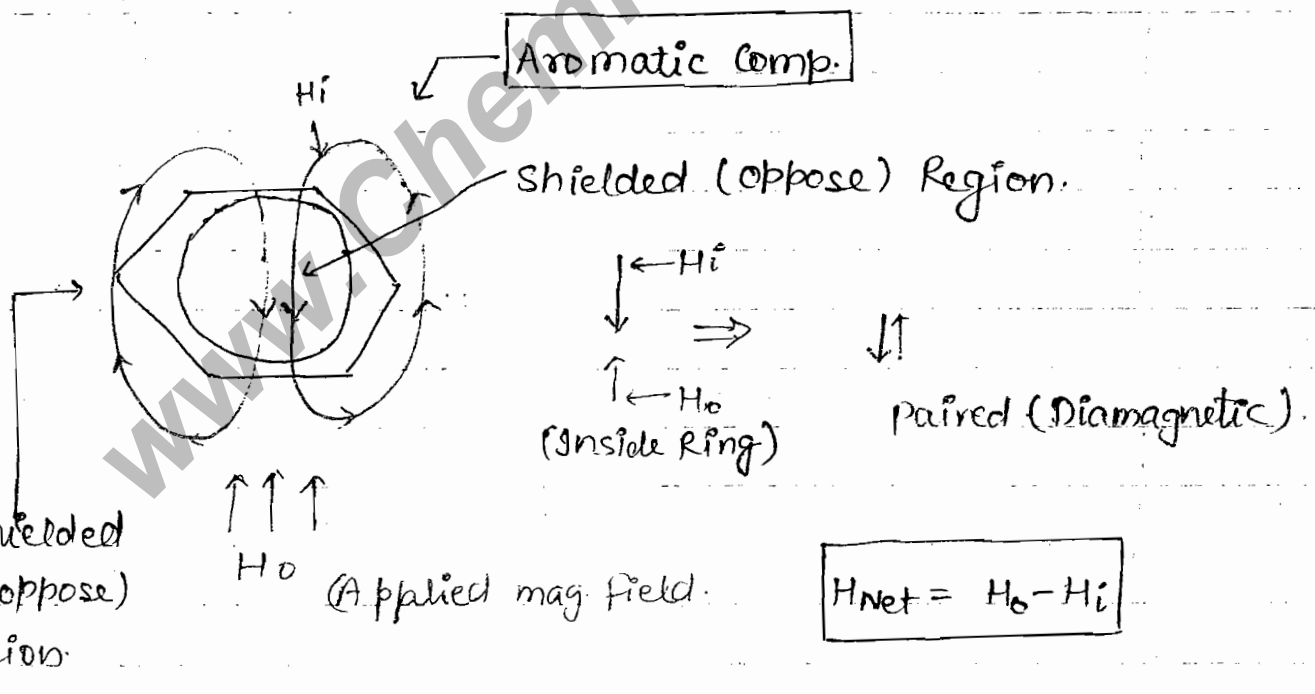
i) ii)  iii) 

| 36 K Cal/mole | 59 K Cal/mole | 71 K Cal/mole |
|---|---|---|
| per ring | per two ring | per three rings. |

⇒ Aromaticity is seen by per benzene ring

Presence of Diamagnetic Ring Current:-




Note ⇒ In aromatic comp. Applied mag. field & Induced mag. field (inside ring) opposite to each other i.e. why Ring current is Diamagnetic.

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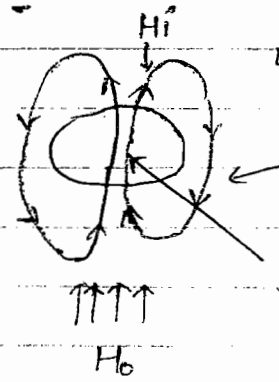
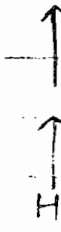



Antiaromaticcomp.

Shielded Region.

Deshilded Region




⇒ ↑↑ unpaired (Paramag.)

Inside the ring. Hi & Ho does not opposing oneanother i.e. paramagnetic ↑↑

$$H_{Net} = H_o + H_i$$

* Inner protons of Porphyrin ring highly shielded δ value negative

## Huckel Rule:-

The planar monocyclic conjugate syst. having $(4n+2)\ \pi$ delocalised $e^-$.

Huckel Rule apply only for conjugated monocyclic System (or) Polycyclic Benzanoid Syst. But in the case of polycyclic non benzanoid syst. Crag's Rule apply.

The comp. which shows aromaticity are aromatic (or) Diatropic compound.

The comp. which shows antiaromaticity are antiaromtic (or) Paratropic in nature.

## Classification of Urganic Compounds:

i) Aromatic ii) Antiaromatic, iii) Non aromatic.

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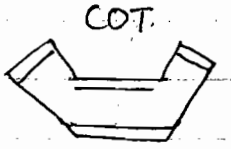
Aromatic comp. ← Planar & conjugation +nt → Antiaromatic compounds → Nonaromatic Compounds.

Aromatic comp.
- Huckle Rule $(4n+2)\pi e^-$
  - → Monocyclic
  - → Polycyclic Benzanoid Syst.
- Crag's Rule Polycyclic nonBenzanoid System.

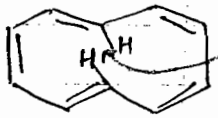
Antiaromatic compounds
$(4n)\pi$ delocalisede$^-$
$n = 1, 2, 3, 4, \ldots$
$4\pi e, 8\pi e, 12\pi e, 16\pi e \ldots$
In antiaromatic comp. $\pi e^-$ are divisible by 4

Nonaromatic Compounds.
Restriction of delocalisation of $\pi$-$e^-$
- $sp^3$ Carbon.
- Non planar.

COT.



Non planar.




planarity lost.

* Aromaticity is the property of the periphery of the $\pi$ $e^-$.
* Diamag. ring current is generated by periphery of the ring

## Crag's Rule:

Crag's Rule applied for polycyclic non benzanoid system to find out aromaticity. Comp. which show Crag's Rule, may be aromatic or non aromatic, not possibility of antiaromatic.

Comp. having $C_2$-axis follow Crag's Rule, comp. which doesn't have $C_2$-axis, not follow Crag's Rule.

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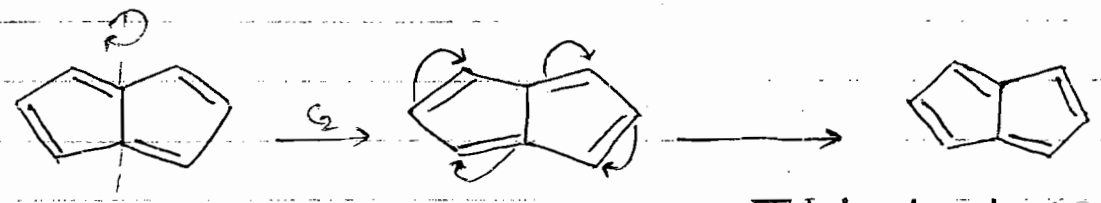
For Crag's rule, System must ~~have~~ be polycyclic non benzanoid & $C_2$ axis should be present.

Ex.



Polycyclic non Benzanoid. (Pentalene)

Total π bond = 4

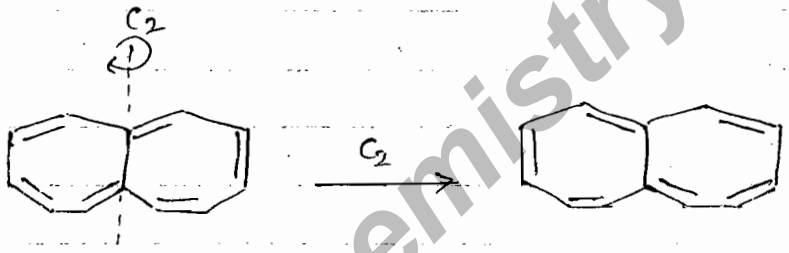
(4 - 1) ⇒ 3 (odd)

Non aromatic.

(Total No. of π bonds − 1) → If even ⇒ Aromatic

→ If odd ⇒ Non aromatic

Ex.



Heptalene

(Total π bond − 1)

(6 − 1) = 5 (odd).

Non aromatic

Explain the aromaticity of Azulene:-

Azulene is aromatic in nature according to Crag's Rule.

(Total π bond − 1)

(5 − 1) = 4 (even)

Aromatic

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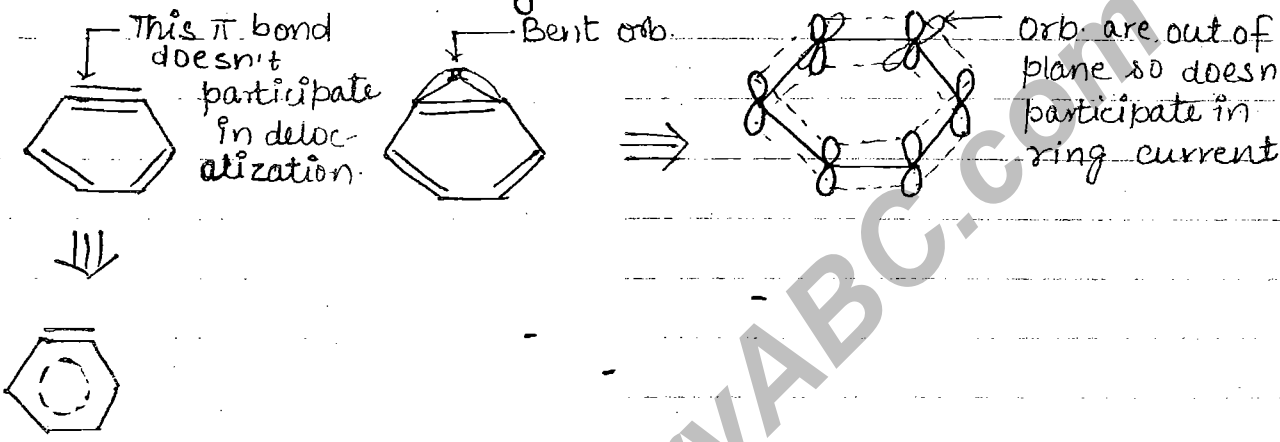
28/May/2014

Q. Benzyne having $8\pi e^-$, even it is aromatic why?

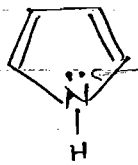
Ans. In Benzyne there are $8\pi e^-$ but only $6 e^-$ produces ring current which are in a plane, so system is aromatic, remaining $2\pi e^-$ are out of plane so don't take part in ring current.



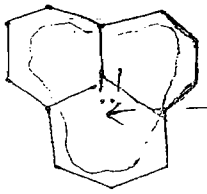

Calculation of $\pi e^-$ in Aromaticity:-

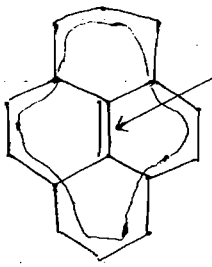
→ $2\pi e^-$ (for one double bond)

→ $2\pi e^-$ (for one tripple bond)

→ lone pair count  l.p. in conj

→ lone pair doesn't count l.p. is not in conj (means not contributing in ring current)

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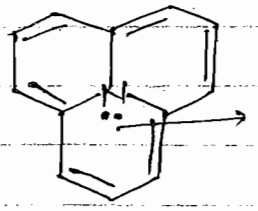
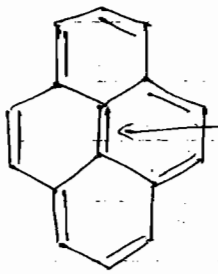
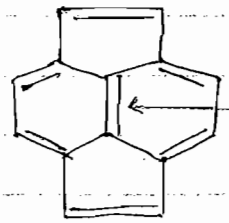


Non Huckle lone pair because Aromaticity is the property of peripherey ring and here l.p. is not present on peripherey.

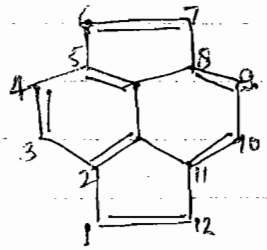
परिधि (घेरा)



Double Bond not on peripherey i.e. Non Huckle π bond (doesn't participate in aromaticity)



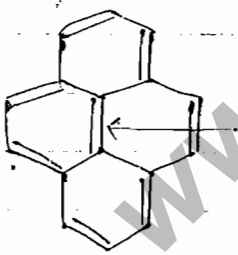
non Huckle π-bond.
Antiaromatic (12 π e⁻)



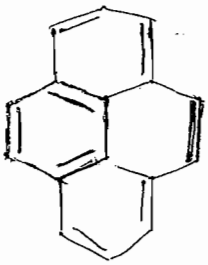

12 peripherey C = 12 e⁻ ⇒ Antiaromatic

**No. of Periphery Carbon = No. of π e⁻**

Note:- Valid for Neutral Molecules.



Non Huckle π bond
Aromatic (14 e⁻)



14 Perripherey C = 14 e⁻ ⇒ Aromatic

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Election Withdrawing and Election Releasing both stabilize to Radical spp.c.

Homoaromatic >

Aromatic > Non Aromatic > Antiaromatic

← Stability or R.E.

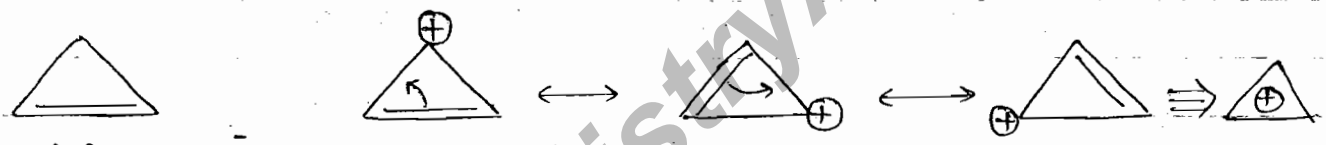
## Aromaticity of Carbocation (or) Carbanion :-

Carbocation ⇒ $sp^2$

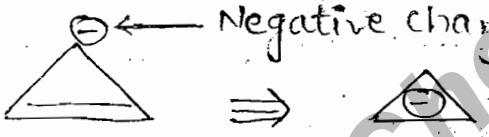
When carbanion is not in conj ↓

Carbanion ⇒ $sp^2$ , $sp^3$

↑ When Carbanion is in conj with = (or) ≡ bond

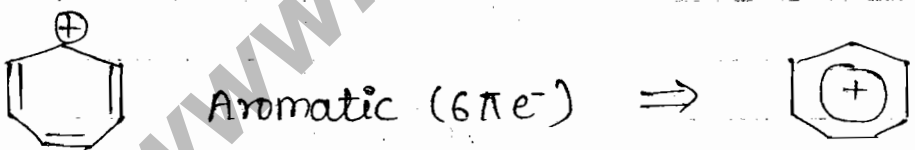


N.A. Aromatic ($2\pi e^-$)

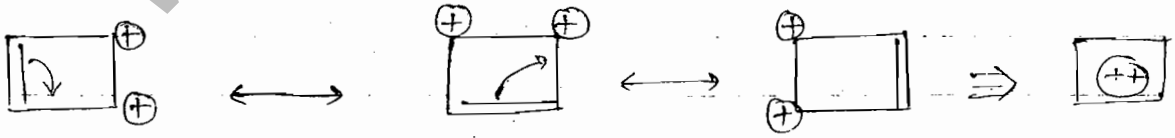


Negative charge on periphery, Count.

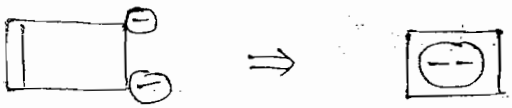
Antiaromatic ($4\pi e^-$)



Aromatic ($6\pi e^-$)



Aromatic ($2\pi e^-$)



Aromatic ($6\pi e^-$)

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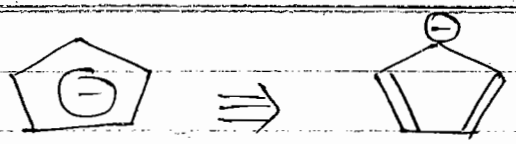
Radical (odd e⁻s pp)

Neither Aromatic nor antiaromatic


Aromatic ($6\pi e^-$)

Antiaromatic ($4\pi e^-$)

## Energy levels of Aromatic & Antiaromatic Comp. :-

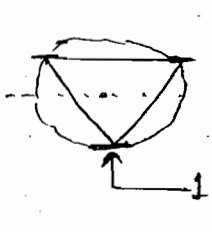
To find out energy levels of aromatic & antiaromatic comp. we use frost diagram or circle.

## FROST DIAGRAM :-

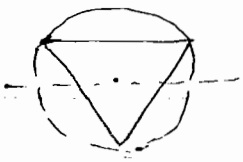
* One angle should be below. (Bottom side)
* Draw circle touching all angles.
* Below the half line ⇒ BMO.
* On the half line ⇒ Non Bonding.
* Above the " " ⇒ ABMO.

Ex:

A.



A.A.



1 1 ABMO

1L BMO.

Note:- Frost diagram doesn't applicable for Non aromatic

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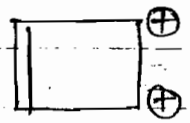
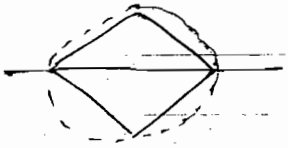
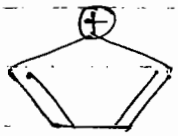


A.

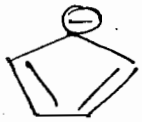


— ABMO
— — Non bonding
↑↓ BMO

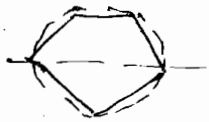


A. A.

— — ABMO
↑ ↑ N.B.
↑↓ B.MO



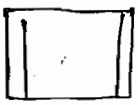
A.



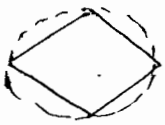
— — AB.MO
↑↓ ↑↓ N. B.
↑↓ BMO.

A.

— ] ABMO.
— — ]
↑↓ ↑↓ ] BMO.
↑↓



A. A.



— ABMO
↑ ↑ N.B.
↑↓ BMO.

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Aromatic comp. ⇒ All paired e⁻ (See above frost Diagrams).

Antiaromatic comp. ⇒ 2 ⇆ unpaired e⁻ (See Above)

⇓

Paramagnetic.

* Due to 2 unpaired e⁻ antiaromatic comp. behaves as biradical comp. (Highly unstable).

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# Type of AROMATIC Compound:-

## Two π Electronic System:-

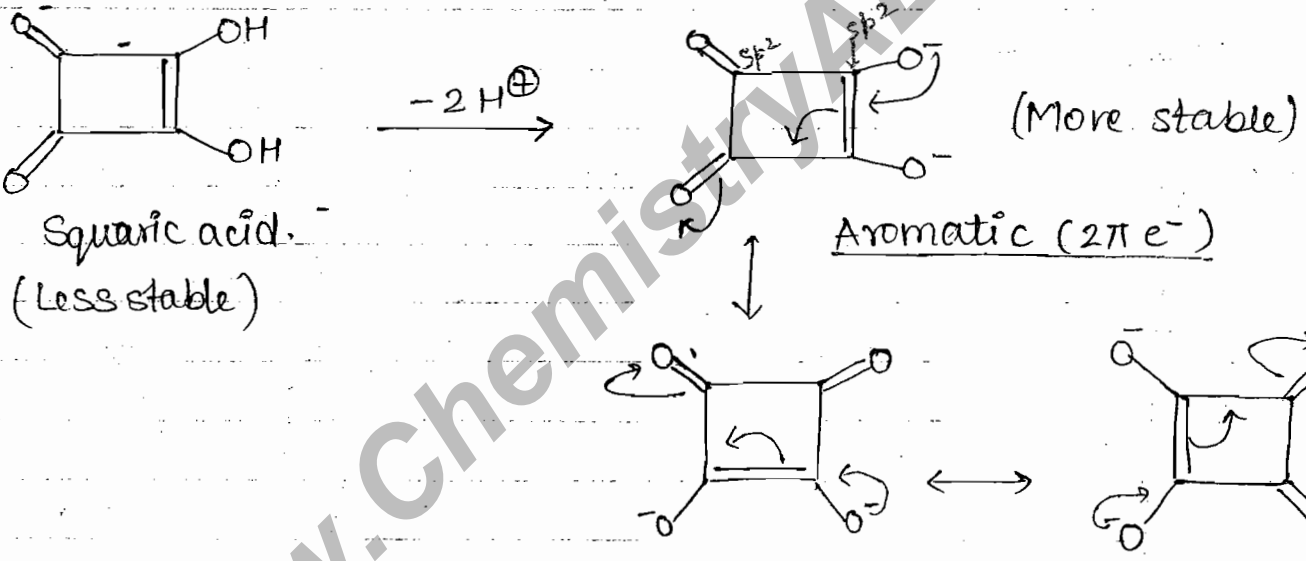
⇒ Follow $(4n+2)$ π $e^-$ Rule.

⇒ If $e^-$ delocalise then aromatic

⇒ If $e^-$ do not delocalise then non aromatic never be antiaromatic.

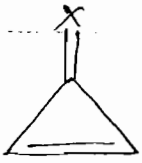
Ex.

Q Squaric acid is acidic like $H_2SO_4$ why?




complete delocalisation of π - bond.

## Aromaticity of comp. which contain Exocyclic double bond :-




'X' may be C, or Heteroatom.

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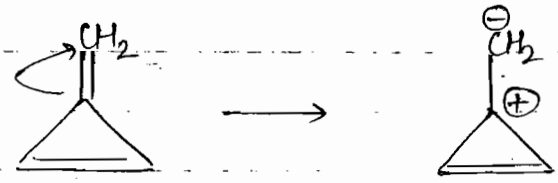
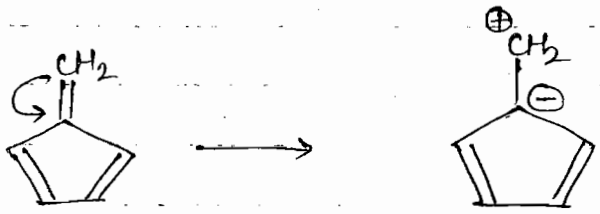
CSIR Choose most correct option if more than two options seems to be right

Ex. 

aromatic ($2\pi e^-$)

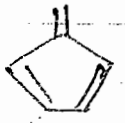
Ex. 

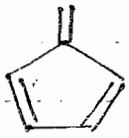
Aromatic ($6\pi e^-$)

Q1 Which of the following comp. aromatic in nature ?

i) ii) iii) iv)

Q2 Which of the following comp. is aromatic in nature?

i) ii) iii) iv) 

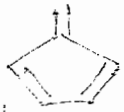
Q.3  comp. is ?

i) Non Aromatic ii) Aromatic iii) Antiaromatic iv) None

Q.4 $\xrightarrow{\text{Reagent}}$ P

Product is –

i) Aromatic ii) Non aromatic iii) Antiaromatic iv) None.

Such type of comp.  ; non aromatic but in the pres of reagent they convert into aromatic.

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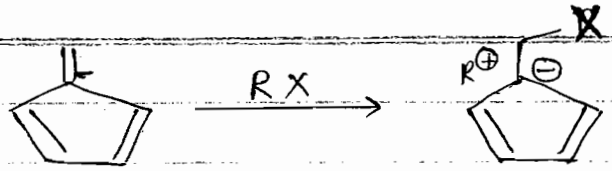
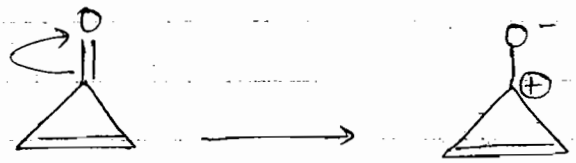
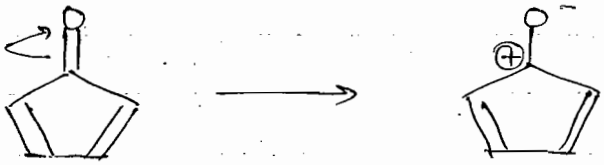



aromatic ($6\pi e^-$)

Quasi aromatic compound



Aromatic ($2\pi e^-$)



Antiaromatic ($4\pi e^-$)

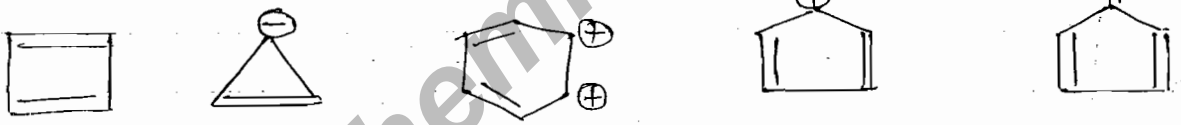
## $4\pi$ $e^-$ System:

⇒ Belong $(4n)\pi$ $e^-$ Rule.

⇒ If $e^-$ delocalised then antiaromatic

⇒ If $e^-$ not " then Non aromatic, Never be aromatic.

Ex.



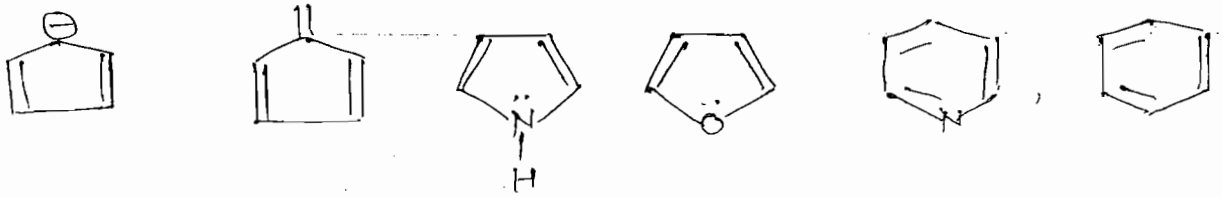
## 6 $\pi$ electronic System:

⇒ Follows $(4n+2)\pi$ $e^-$ Rule

⇒ If $e^-$ delocalised then aromatic

⇒ If $e^-$ not " then Non aromatic, Never be antiaromatic.

Ex.



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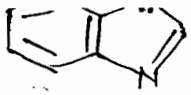
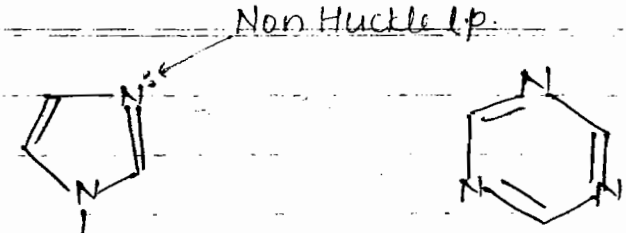
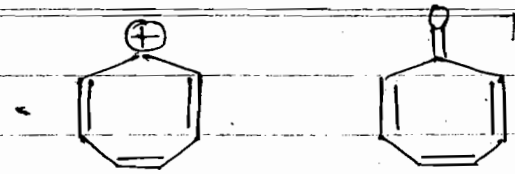


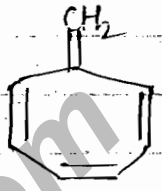
Benzimidazole



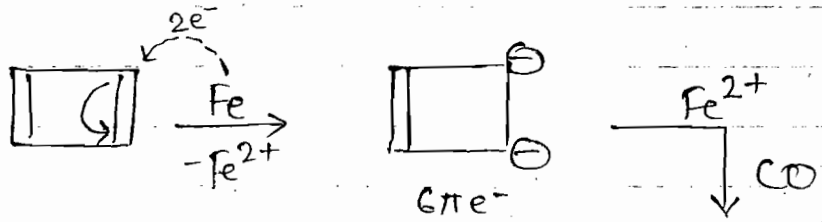

Imidazole



Tropone

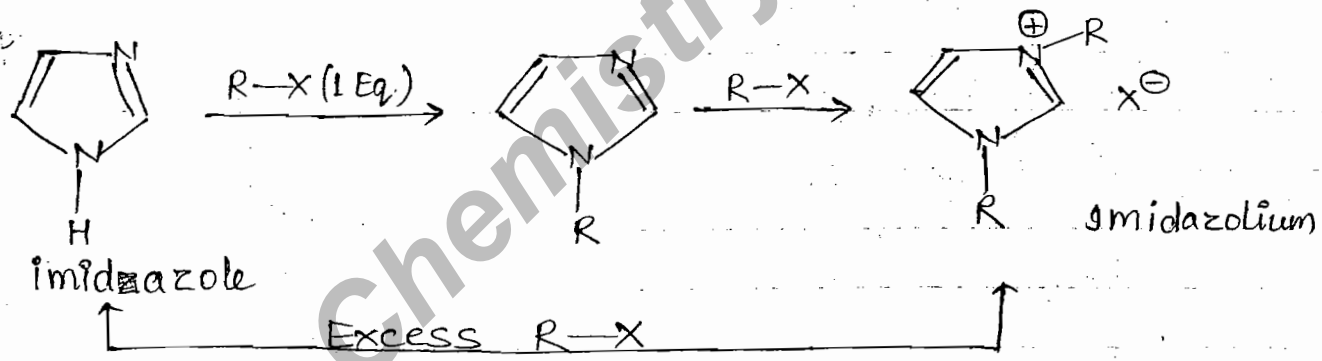



Imp. *



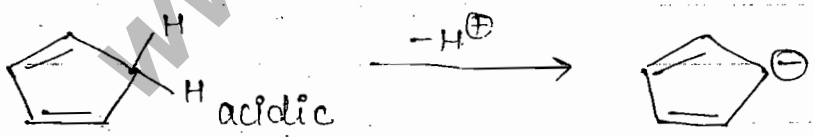

Aromatic ⇒

V. Imp. *




imidazole

Q. Cyclopentadiene is acidic in nature ; Why ?



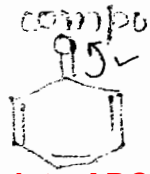

Less stable (Non aromatic)

Conjugate Base more stable (Aromatic)

Q. Which of the following compound react with RX.

a)

b)

c) 

d) b & c both

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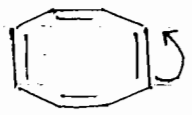
## 8 π electronic System :-

* follow (4n)1 π e⁻ Rule.
* If e⁻ delocalised then antiaromatic
* If e⁻ not delocalised then non aromatic, never be aromatic

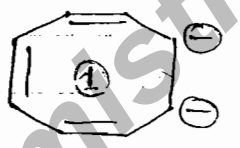
Ex


Non planar.
no delocalisation of π e⁻
Non Aromatic

Note
* When 8π monocyclic Syst. react with, Na, K or Li metal then it becomes aromatic comp. becoz. system obtain planarity.


COT

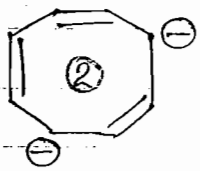
$\xrightarrow[-2K^{\oplus}]{2K}$



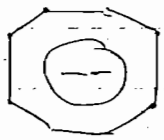
Planar

Aromatic (10π e⁻)

① < ②
Stability



More stable
Resonating str. due to opposite charge seperation.



Q. Which comp. gives $H_2$ gas when it react with metal.

i)

ii)

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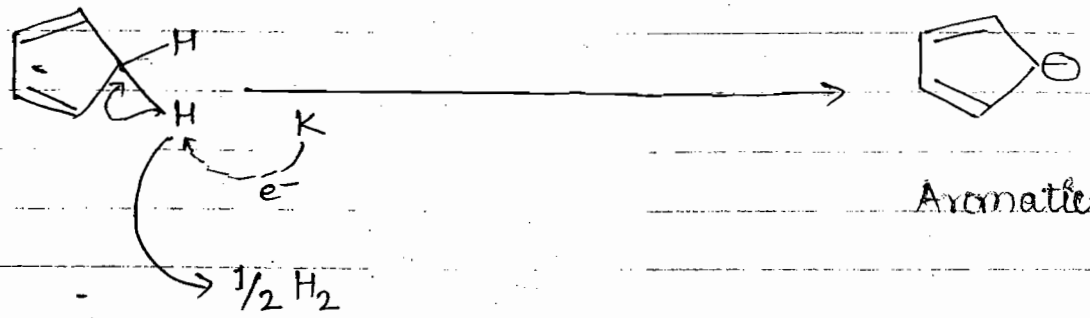


* $H^{\oplus} + K \longrightarrow \frac{1}{2} H_2 + K^{\oplus}$

Q. Which of the comp. is most anti aromatic in nature ?

i) चुहिया

ii) चूहा ⇐ More flexible ⇒ More tendency to become Non planar i.e. Non aromatic

Q. Which of the following comp. is more stable.

i)

ii) ⇐ More flexible (Nonplanar) (Non aromatic)

* Antiaromatic tries to become non planar for stabilisation. so big ring (antiaromatic) more stable than small ring (antiaromatic)

* Almost non aromatic becoz it undergo boat form (Non planar)

* Antiaromatic comp. have tendency to adopt non planarity to increase its stability.

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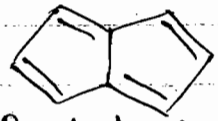
Annulene ⇒ Monocyclic, conjugated ring

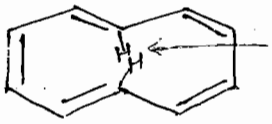


Pentalene

## Non Aromatic Acc. to Crag's Rule

10 π Electronic System:-

* follows $(4n+2)\pi$ e⁻ rule
* If e⁻ delocalise then aromatic
* If e⁻ not " " Non " Never be antiarom—

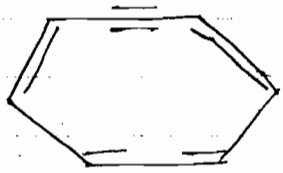


Repulsion ⇒ Non planar ⇒ Non Aromatic

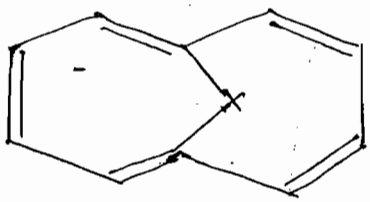
Dehydration.

Bridging

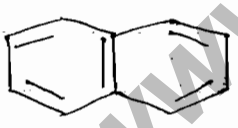
X = Heteroatoms or C



aromatic (10πe⁻)
Planar

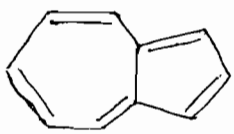


Planar (Aromatic)
10π e⁻

* 

10πe⁻ + Planar ⇒ Aromatic

Aromaticity of Azulene:

*  Aromatic

Azzulene (Isomer of Naphthalene)

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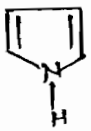
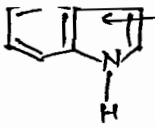
6πe⁻ distributed among 6C (less e⁻ density per carbon atom)

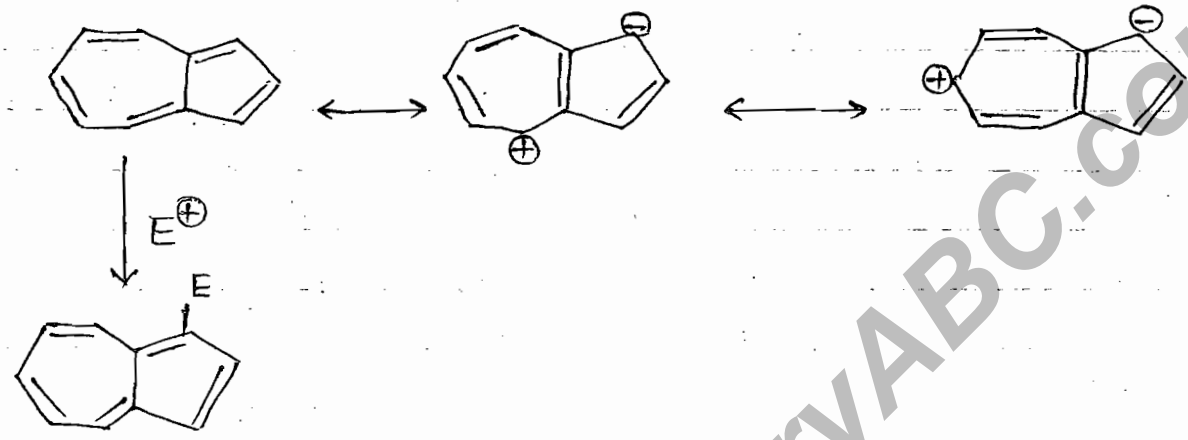


6πe⁻ distributed among 5 atoms. (More e⁻ density per atom)

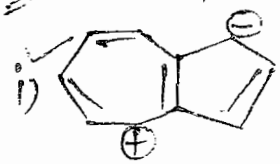


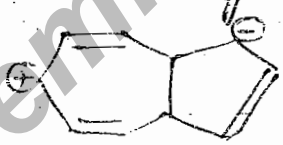
More e⁻ rich
More Electrophilic Rxn favouring by this ring.

* Azzulene is less stable than Naphthalene.
* Azzulene is a deep blue coloured comp.
* Azzulene have permanent dipole moment 0.8 D
* 5-memb ring gives Electrophilic Substitution Rxn. because it is e⁻ rich.

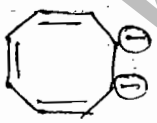


Q Which of the following Resonating str. is more stable?

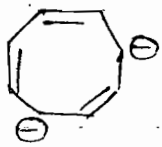
i) 

ii) 

* Opposite charges present at min. distance, then resonating str. more stable.
* If same charges present at max. distance, then more stable reso. str.

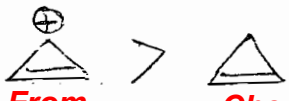


Less stable



More stable

Note:- Generally Neutral spp. is more stable than charged spp. but, any charged spp. get aromaticity then that will be more stable than Neutral spp. Ex.



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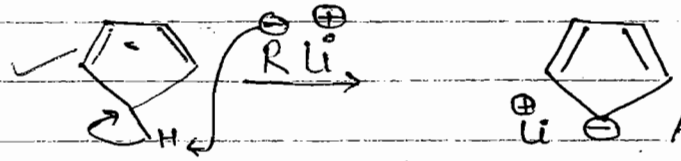
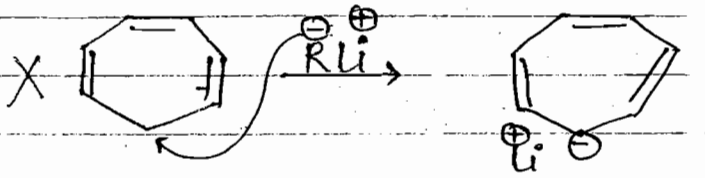
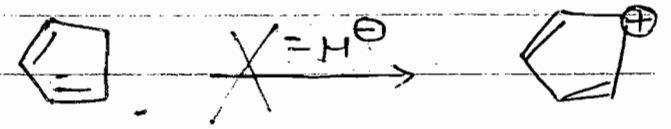
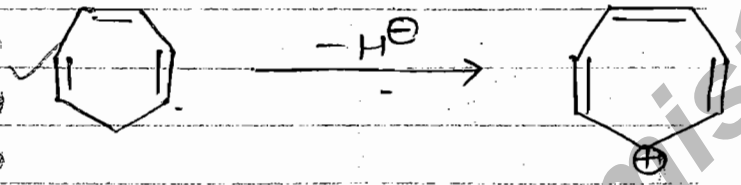
Q Which of the following comp react with RLi ?



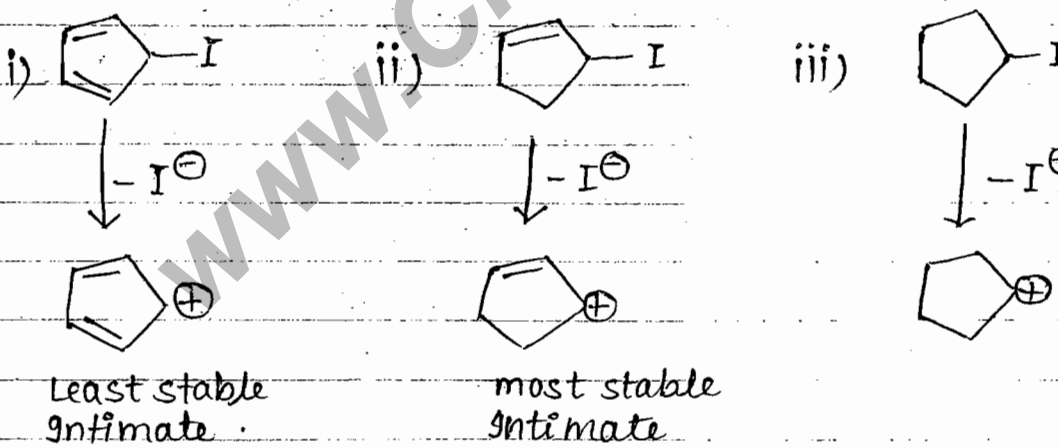




Q Which of the following comp is best Hydride donor?




Q. Write the correct order of reactivity towards $S_N1$ Rxn




Order will be ii > iii > i

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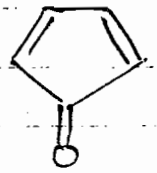
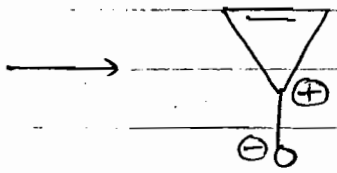
Q. Which of the following comp. have more dipole moment ?

i) 

ii)

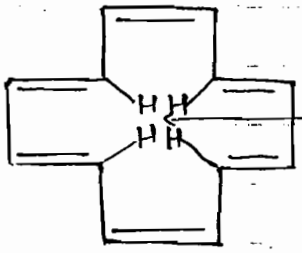


Aromatic

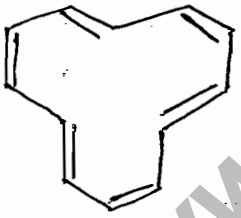
More charge seperation.
(More dipole moment)

## 12-π Electronic System:-

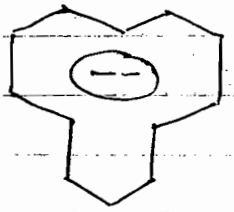
* Follow (4n) π e⁻ Rule.
* If e⁻ delocalise then anti aromatic
* If e⁻ not " " non aromatic, Never be aromatic



Repulsion ⇒ Non planar ⇒ Non Aromatic



Li/Na/K →

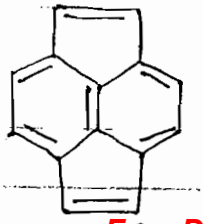


Aromatic (14π e⁻)

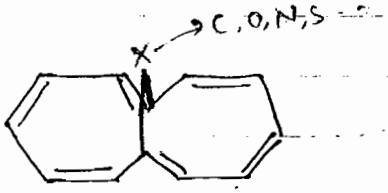
Non planar
Non aromatic

12π e⁻

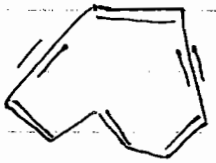
Cyclization — Bridging — dehydroderivative



A.A. (12π e⁻)




A.A. (12π e⁻)



A.A. (12π e⁻)

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8πe⁻, 10πe⁻, 12πe⁻

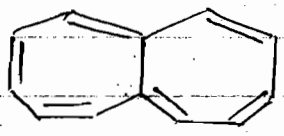
⇓

Monocyclic System
(If only double bond +nt)

⇓

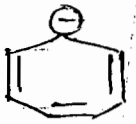
Non Aromatic

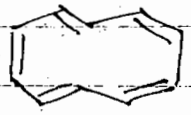
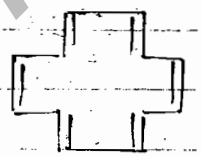
8πe⁻ or 12πe⁻ System —Rxn with Metal (K, Li.)→ AROMATIC
(Double anionic system)

* 

12πe⁻ ⇒ N.A (Acc. to Crag's Rule)
Heptalene

Imp

COT, Heptalene, Pentalene, Cycloheptatrienyl anion 

 and  are NON AROMATIC

⇒ 14π e⁻ System
* follow (4n+2) π e⁻ Rule.
* If e⁻ delocalise then aromatic.
* If e⁻ d not " " Non aromatic, never be anti aromatic.

Note:- Check Non planarity in monocyclic rings upto 12πe⁻ system, After 12πe⁻ system, System (Ring) become big in size so possibility of non planarity is very less.

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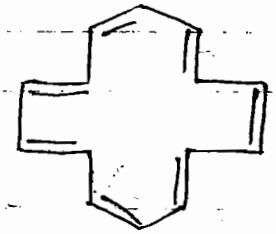
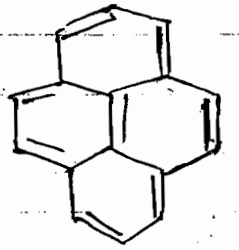
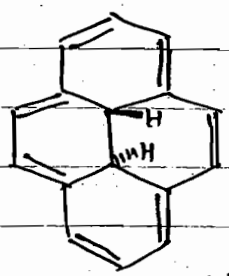


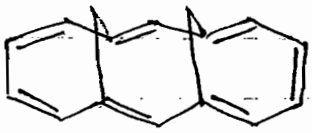
aromatic



aromatic

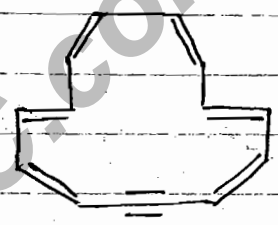


aromatic



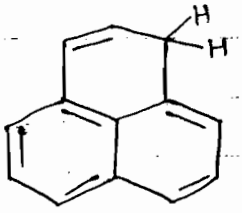
aromatic

Non planar
Non aromatic



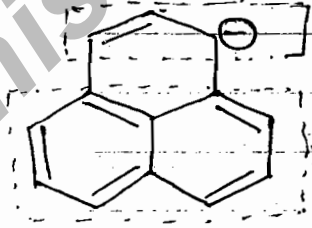
aromatic

Q Pheneline is acidic in nature, why ?



Pheneline
Non Aromatic

$-H^{\oplus}$



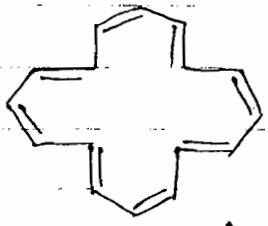
$4\pi e^-$

Naphthalene fragment = $10e^-$

Total $\pi e^-$ = 14 (Aromatic)

16-$\pi$ electronic System;

* Follows $(4n)\pi e^-$ Rule.
* If $e^-$ delocalise then Antiaromatic.
* If $e^-$ not " " Non aromatic, never be aromatic.



A.A. ($16\pi e^-$)

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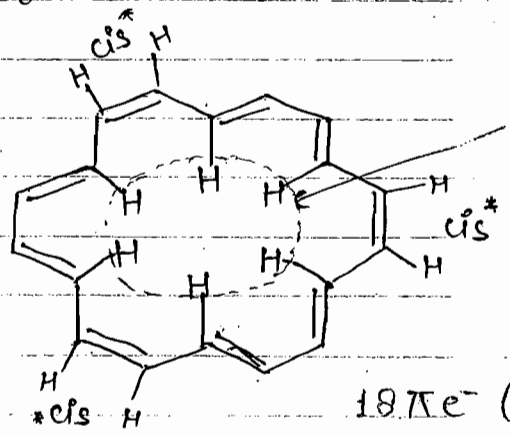
## 18 π-e⁻ System:-

* follows $(4n+2)\pi$ e⁻ Rule
* If e⁻ delocalise then, aromatic
* If e⁻ not " then non " but never be antiaromatic.

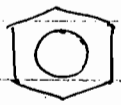


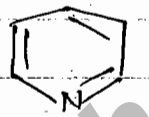

δ Highly shielded Proton
Low δ value (Negative)

18 π e⁻ (Aromatic)
also called [18] Annulene

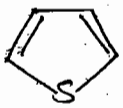
⇒ Three cis double bond
⇒ Six Trans double bond.

## Resonance Energy of some Organic Compound

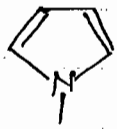

36 K Cal/mole



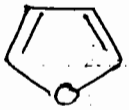
32 K.Cal/mole



29 K.Cal/mole



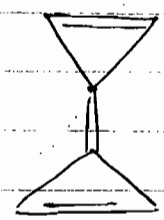
12 K.Cal/mole

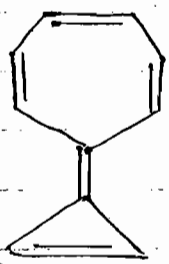


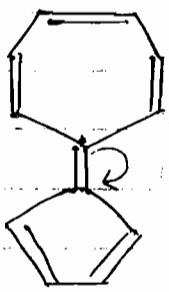
16 K Cal/mole

## Aromaticity of some organic Compounds:-

Aromatic


Non Aromatic




Aromatic

Such type of compounds may be aromatic or non aromatic, never antiaromatic. After the delocalisation of common double bond, if both rings are aromatic

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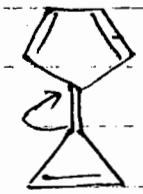
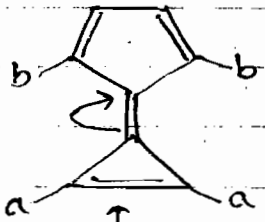
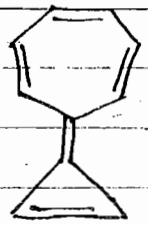
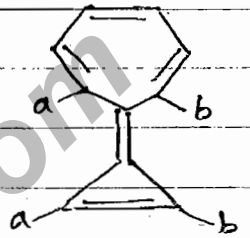
then whole system is aromatic, otherwise system is non aromatic.

Q Which of the following comp. show geometrical isomerism

a) 

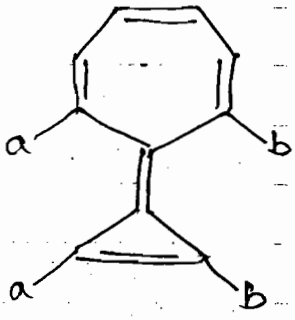
b) 


c) 

d) 


In these cases single bond rotation possible ⇒ No geometrical isomerism.

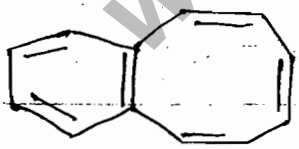
Double bond permanently present so no single bond Rotation but same gps on both ends of double bond.



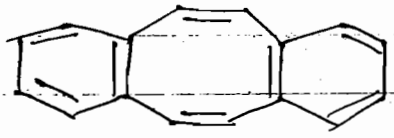

single bond rotation imposible Both ends of double bond have diff. groups ⇒ Geometrical isomerism possible.

* Exceptions:

?



8π e⁻ A.A.



8π e⁻ A.A.

12 16

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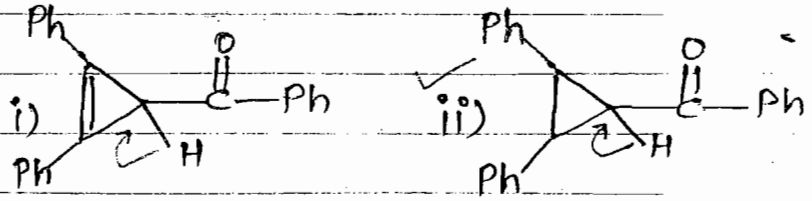
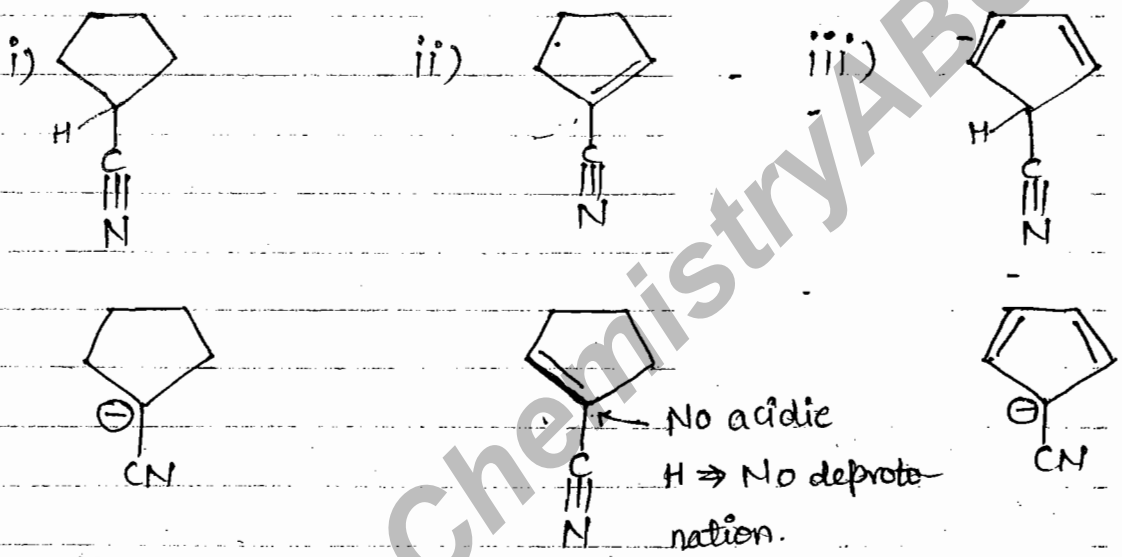
Q Which of the following compound loss proton easily?




After $H^{\oplus}$ loss
Antiaromatic
Highly unstable.

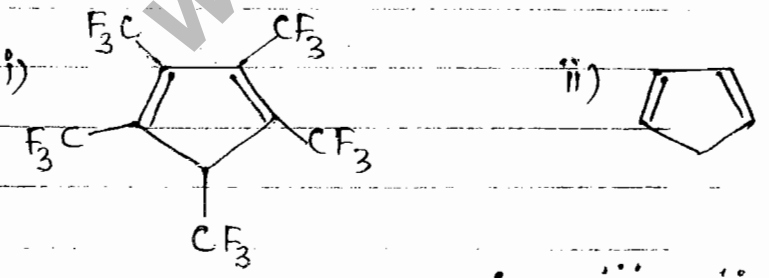
After $H^{\oplus}$ loss.
Non aromatic

Q Write the order of deprotonation.




iii > i > ii

Q. Write the acidity order of following compound.




iii) $HNO_3$

i > iii > ii

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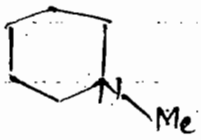
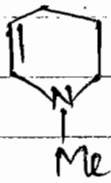
Acidity $\propto$ E.W.G. $\propto \frac{1}{E.R.G.} \propto -R \propto -H \propto -I \propto \frac{1}{+R} \propto \frac{1}{+H} \propto \frac{1}{+I} \propto K_a \propto \frac{1}{pK_a}$

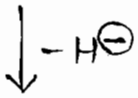
Q. Best Hydride donor ?

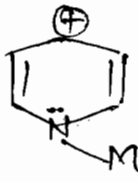
i) 

ii)

iii) 

iv)

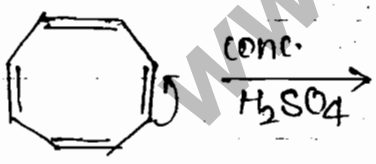


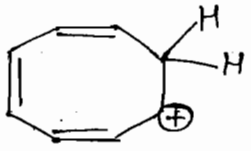
$6\pi e^-$ System  Aromatic

## Aromatic Acids

$HCOOH > Ph-COOH > RCOOH > Ph-OH > MeOH > H_2O > EtOH > HC\equiv CH > NH_3$.

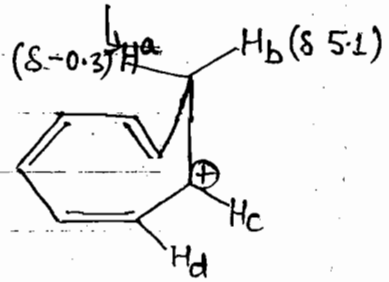
## HOMOAROMATICITY :-



Homotropylium

Most shielded




$\delta$ value $H_d > H_c > H_b > H_a$

comp. ~~that contain~~ which contains one $sp^3$ hyb. 'C' in a conjugated system but $sp^3$ hyb. carbon atom are force to lie almost vertically above the plane of the aromatic atoms K/a Homoaromatic comp.

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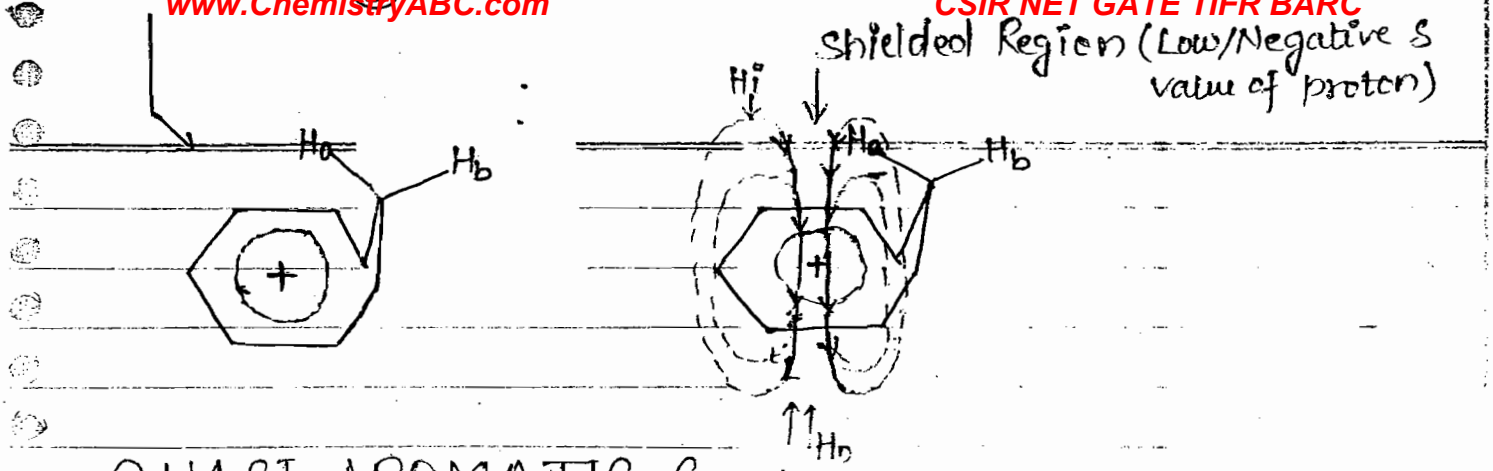
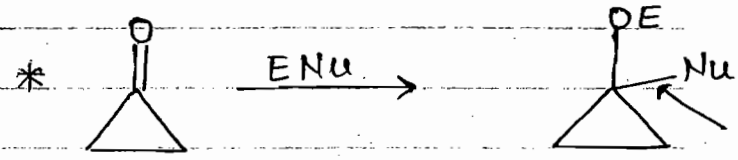
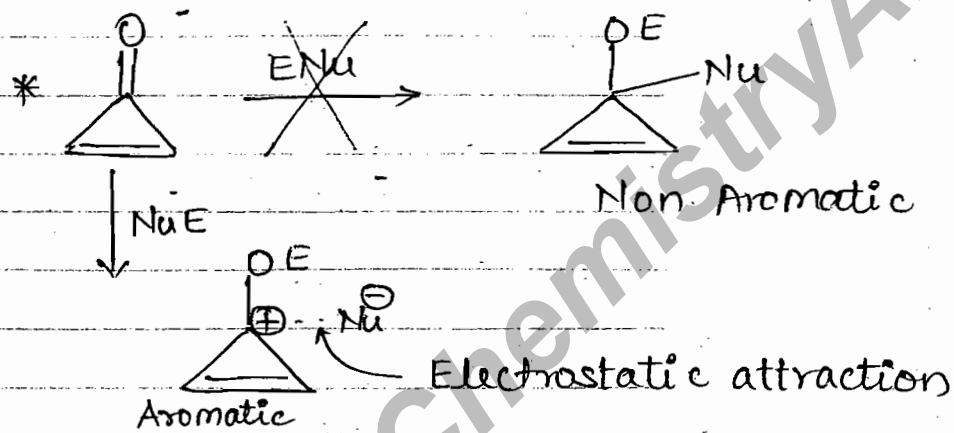


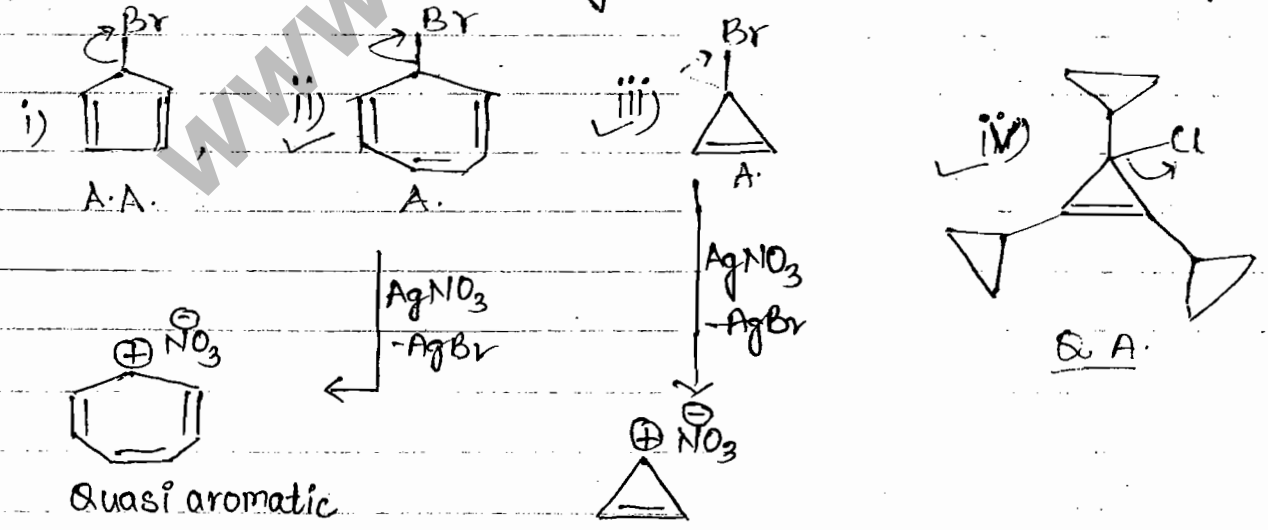

# QUASI AROMATIC Comp:

Quasi Aromatic comp. are ionic aromatic compound.




Q. Which of the following comp. gives ppt with $AgNO_3$?

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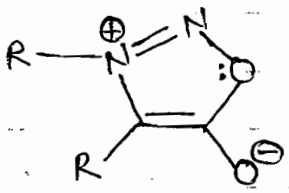
Aromatic

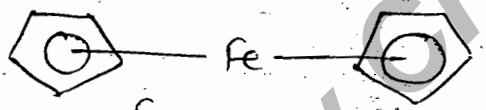
## MESOIONIC AROMATIC COMPOUND :-

These comp. are aromatic in nature, show diamagnetic ring current show electrophilic substitution Rxn. Sydon is first mesomeric aromatic comp. These comp. are also K/a internal salt.

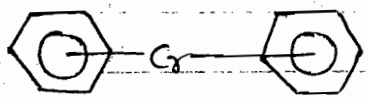


Sydon

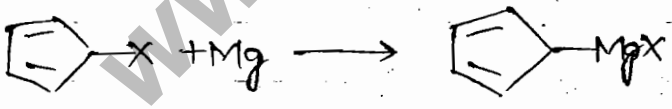
## ORGANOMETALLIC AROMATIC COMPOUND :-




Ferrocene. $6\pi e^-$




Cromocine

* 

Ferrocene.

* Aromaticity of Allotropes of Carbon :-

- Diamond — Non aromatic
- Graphite — Aromatic
- Fullerene — Aromatic

imp. Graphite & fullerene gives electrophilic Addition Rxn.

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* Fullerene ⇒ 20 Hexagons + 12 Pentagons.

Diamond (N.A.) ⟶ Graphite (Aromatic) ΔH = -ve

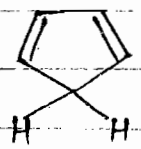
Graphite (Aromatic) ⟶ Diamond (N.A.) ΔH = +ve

System is going to N.A. from aromatic, so more Energy require.

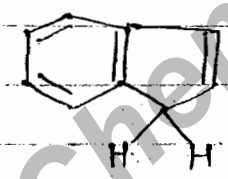
## Annelation Effect:

Each ring in fused system give the part of aromaticity to the adjacent ring, this effect is k/a Annelation effect.

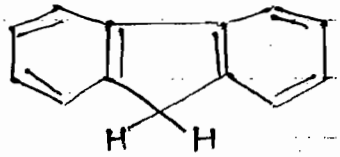
Q Write the correct order of acidity of following comp.?

i) 

pKa = 16

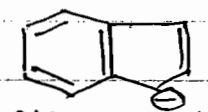
ii) 

pKa = 20

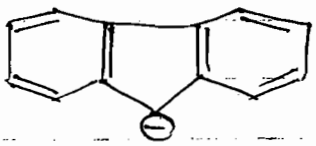
iii) 

pka = 23

Order ⇒ i > ii > iii



only one ring giving it's π bond (Aromaticity) to cp ring, This effect is k/a Annelation. Due to Annelation aromaticity of only one ring decreases.



Both benzene rings giving some part of Aromaticity (by participation of common double bond), This effect is called Annelation. Due to Annelation Aromaticity of both rings decreases

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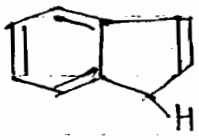
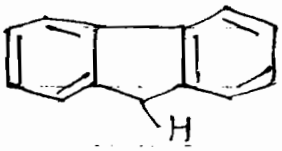
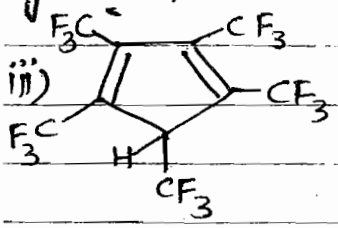
Q Explain the acidity of following compounds.

i) 

ii) 

iii) 

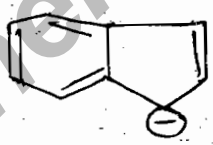
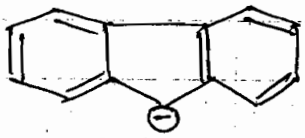
iv)

Order of acidity iii > iv > i > ii

1,2,3,4,5 Pentakes (Trifluoromethyl) cyclopentadiene is most acidic because of five -I groups. It is more acidic than $HNO_3$.

Now remaining three (i, ii, iv) can be explain on the basis of Annelation Effect.

More the disturbance in aromaticity of benzene ring, less will be acidicty of cpyrrole ring. or less will be aromaticity of cpyrrole ring.

>  > 

No any benzene ring aromaticity effected by cp ring.

One benzene ring aromaticity affected by cp ring

Aromaticity of two benzene rings are affected by cp ring.

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# PERICYCLIC REACTIONS

Pericyclic Rxn are the simple GAME of p-orbitals or π-electrons. Pericyclic means at the periphery of the ring.

Characteristics of Pericyclic Reactions:-

* Pericyclic reactions takes place via concerted mechanism (Bond forming & bond breaking takes place simultaneously).

* Pericyclic reactions takes place under thermal or photochemical conditions.
* In pericyclic reactions a cyclic transition state form.
* They don't involve ~~in~~ the formation of ionic or free radical intermediate.
* They don't involve electrophilic or nucleophilic reaction
* These reactions don't affected by solvent or catalyst.
* Generally pericyclic Reactions are stereospecific reaction.

Stereo Reactions

- Stereoselective
- Stereospecific

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Stereoselective

Enantioselective | Diastereoselective

Regioselective | Chemoselective

Structural isomers

One Major | One Minor.

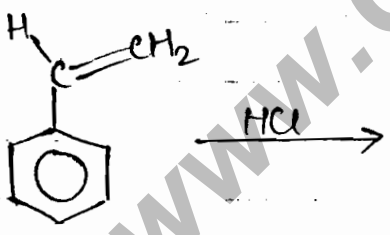
Stereospecific

Regiospecific | Enantiospecific | Chemospecific

* $R-\underset{H}{\underset{|}{C}}=CH_2 \xrightarrow{HCl} R-\underset{H}{\underset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_3 + R-CH_2-\underset{Cl}{\underset{|}{CH_2}}$

major | minor

Regioselective Rxn.

* 

100%

Regiospecific Rxn.

⇒ See always the stability of carbocation.

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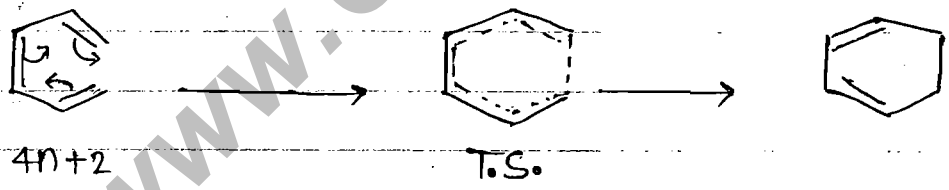
# TYPEs OF PERICYCLIC REACTIONs.

There are three types of pericyclic reactions.

1) Electrocyclic Rxn.
2) Cycloaddition Rxn.
3) Sigmatropic Rxn.
* Ene Rxn.
* Group transfer Rxn. ] Not type of pericyclic Rxn.

## ELECTROCYCLIC Rxn.

It involve the intramolecular cyclization of polyene (conjugated) under thermal condition or photochemical condition.




The electrons which participate in the pericyclic reaction are count only in 4n or 4n+2 system.

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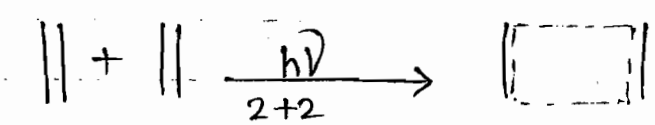
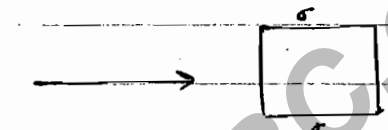
# CYCLOADDITION Rxn.

It involves the combination of two unsaturated moiety & form a cyclic transition state under thermal condition or photochemical condition. Cycloaddition Rxn are two types-

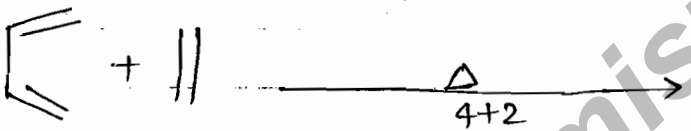
i) Intermolecular Cycloaddition Rxn:-



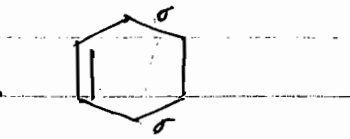

2+2 = 4n Syst. 2+2 Cycloaddition



Two New σ bond formation.

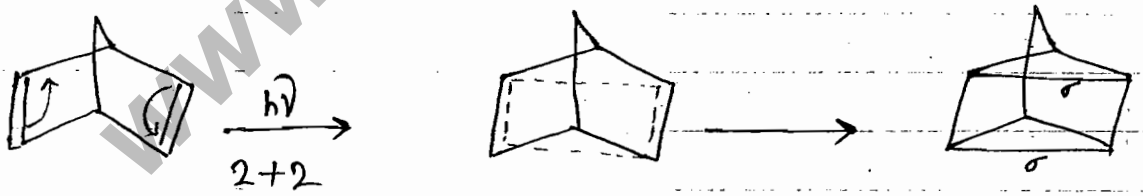



4 + 2 = 4n+2 Syst. 4+2 Cycloaddition



Two New σ bond formation.

ii) Intramolecular Cycloaddition Rxn.




2+2 Cycloaddition

Two New σ bond formation

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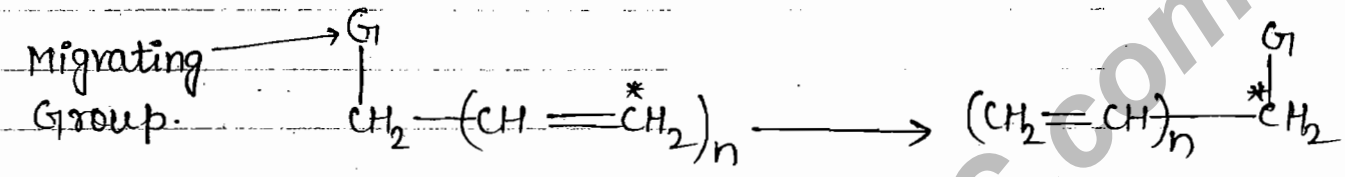
# SIGMATROPIC Rxn.

Sigma ⇒ Sigma bond , atropic ⇒ migration.

It involves the migration of σ-bond within the π- framework.



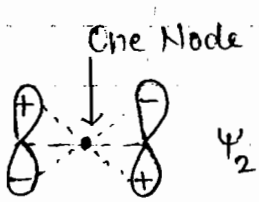

# THEORIES FOR EXPLANATION OF PERICYCLIC Rxn.

Three theories has been proposed for explanation of pericyclic Rxn.

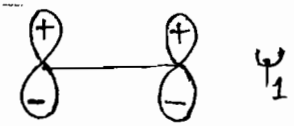
1) FMO Approach (Fukey Frontier Molecular Orbital)
2) Woodward Hofmann Corelation Diagram.
3) Dewar's PMO Approach.
   ↳ Peterbation Molecular Orbital.

Some π-Electronic systems for the Explanation of Pericyclic Rxn:-

1) Ethene $CH_2=CH_2$




No. of Node = n-1

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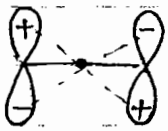
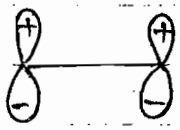
$\psi_{odd}$ ⇒ At terminal lobes same sign.

$\psi_{even}$ ⇒ At terminal lobes opposite sign

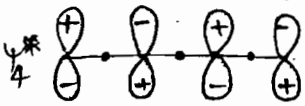
$\psi_2$  — LUMO — 1 HOMO $C_2$ (Asymmetric)

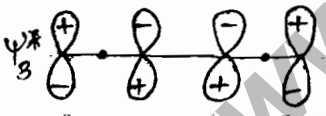
$\psi_1$  1 HOMO (A) — 1 ($h\bar{\nu}$) m (Symmetric)

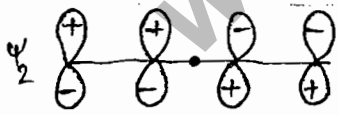
$\psi_{odd}$ ⇒ mirror (m) ⇒ Symmetric (S)

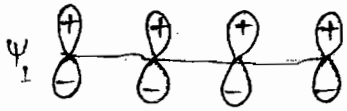
$\psi_{Eeven}$ ⇒ $C_2$ ⇒ Asymmetric (A).

2) 1, 3 Butadiene.

$\psi_4^*$  — LUMO S A

$\psi_3^*$  LUMO — 1 HOMO A S

$\psi_2$  1 HOMO — 1 S A

$\psi_1$  1 (A) — 1 ($h\bar{\nu}$) A ($C_2$) S (m)

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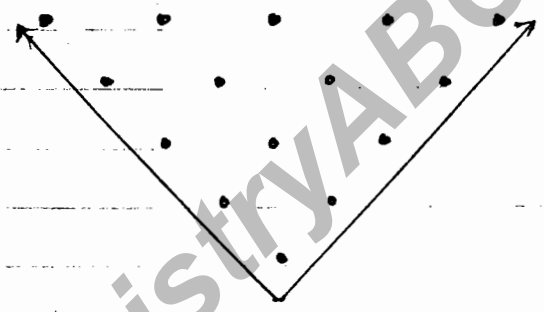
Note

* There must be present one node in middle if system is - $\psi_2, \psi_4, \psi_6, \psi_8 \cdots \psi_{even}$.

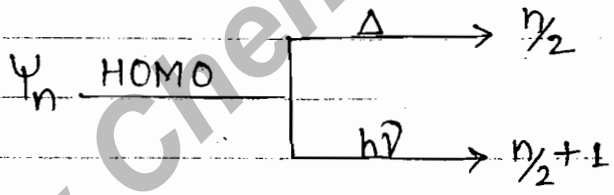
* There must not be present node in middle if system is $\psi_5, \psi_7, \psi_9 \cdots \psi_{odd}$.

* LUMO of thermal condition becomes HOMO of photo cond$^n$.
* No. of Carbons = No. of lobes.

* Representation of nodes in a system must be in such manner. ⟶



For HOMO




Q. HOMO of 1,3 butadiene system under photochemical cond$^n$. ?

$$HOMO = \frac{n}{2}+1 = \frac{4}{2}+1 \Rightarrow 3 \Rightarrow \psi_3 \text{ is HOMO.}$$

Q HOMO of 1,3,5 Hexatriene system under thermal cond$^n$. ?

$$HOMO = \frac{n}{2} = \frac{6}{2} = 3 \Rightarrow \psi_3 \text{ HOMO.}$$

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For LUMO $\psi_n$ LUMO

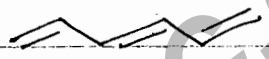
$\Delta \rightarrow \frac{n}{2}+1$

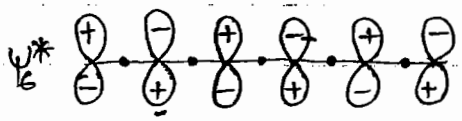
$h\nu \rightarrow \frac{n}{2}+2$

Ques. LUMO of 1,3,5 Hexatriene system under photo condⁿ. ?

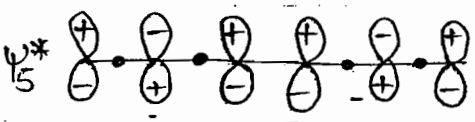
$LUMO = \frac{n}{2}+2 \Rightarrow \frac{6}{2}+2 \Rightarrow 3+2=5 \Rightarrow \psi_5$ LUMO

3) 1,3,5 - Hexatriene System:-

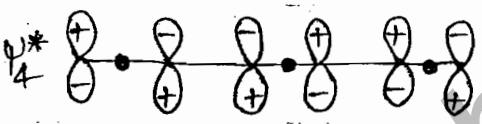




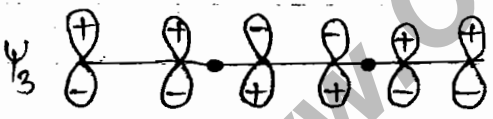
$\psi_6^*$ — — S A



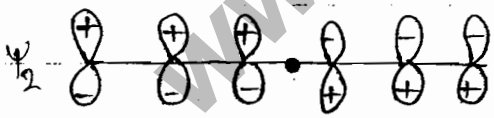
$\psi_5^*$ — LUMO A S



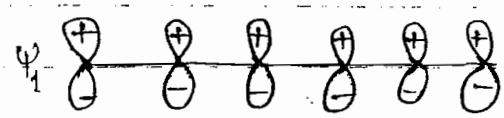
$\psi_4^*$ LUMO ↿HOMO S A



$\psi_3$ HOMO ↿↾ ↿ A S



$\psi_2$ ↿↾ ↿↾ S A



$\psi_1$ ↿↾ ↿↾ A S

Δ $h\nu$ $C_2$ m

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## Element of Symmetry in Pericyclic Rxn:-

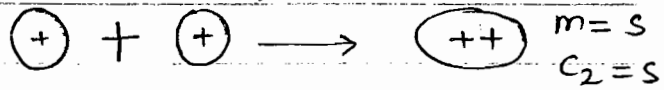
In pericyclic reaction two types of element of symmetry use -

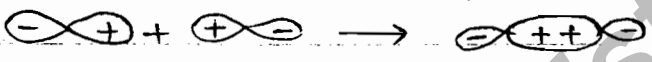
1. Mirror plane
2. $C_2$ - axis symmetry

## Element of Symmetry in $\sigma$-bond and $\pi$ bond :-

$\sigma$

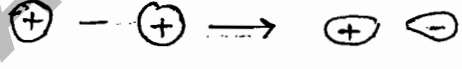
By addition ↑ ↓ $\sigma$ - Bonding

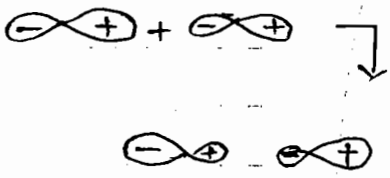



$\sigma$ - Bonding is Symmetric for both $C_2$ & m.

By Subtraction. ↓ ↑ $\sigma^*$ Antibonding

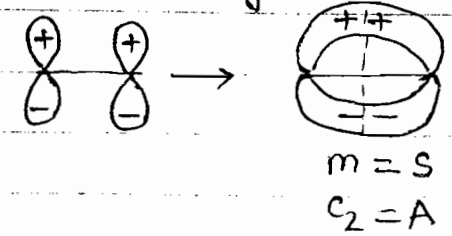


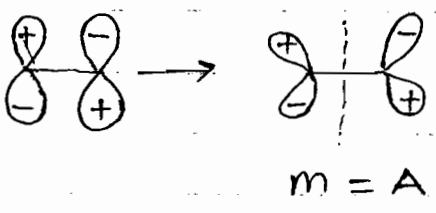

$\sigma^*$ - Antibonding is Asymmetric for both $C_2$ & m.

$\Pi$

$\pi$ - Bonding




$\pi^*$ - Antibonding




Acc. to Woodward apply $C_2$ diagonally.

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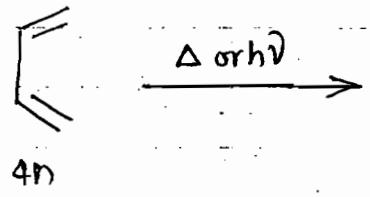
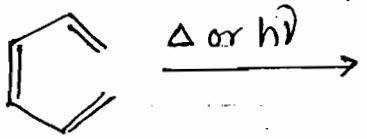
# ELLECTROCYCLIC Rxn.

In involve the intramolecular cyclization of conjugated polyene under Δ or hν condition.




4n




4n+2

In order to formation of a new σ-bond p-orbital rotate in two ways-

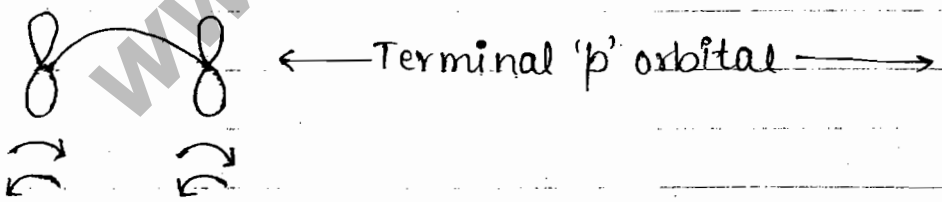
1.) Conrotatory 2.) Disrotatory

Just like Car wiper

Rotation of 'p' orbital.

'Con rotatory way

Disrotatory way




## SELECTION RULE

| System | Δ | hν |
|---|---|---|
| 4n | Con | Dis |
| 4n+2 | Dis | Con |

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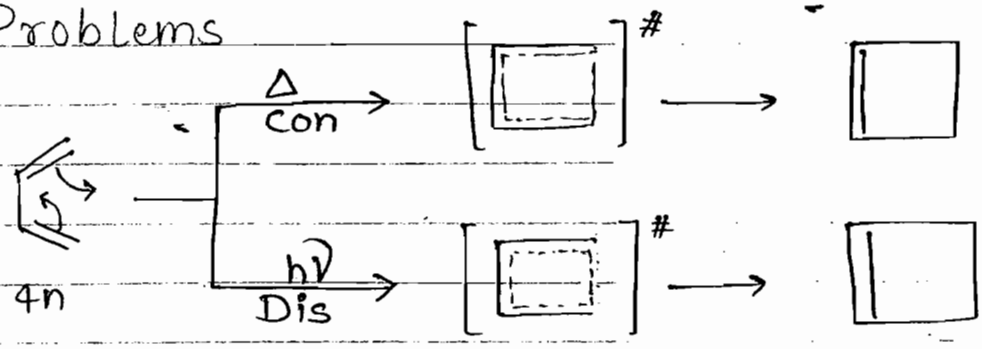
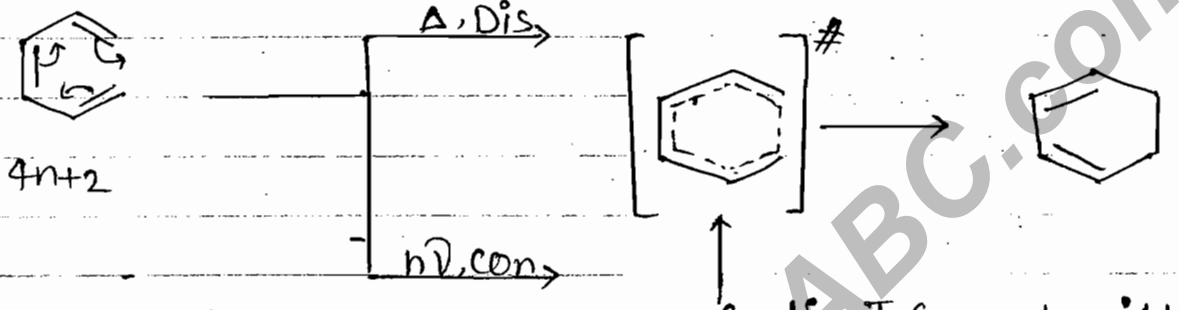
Problems

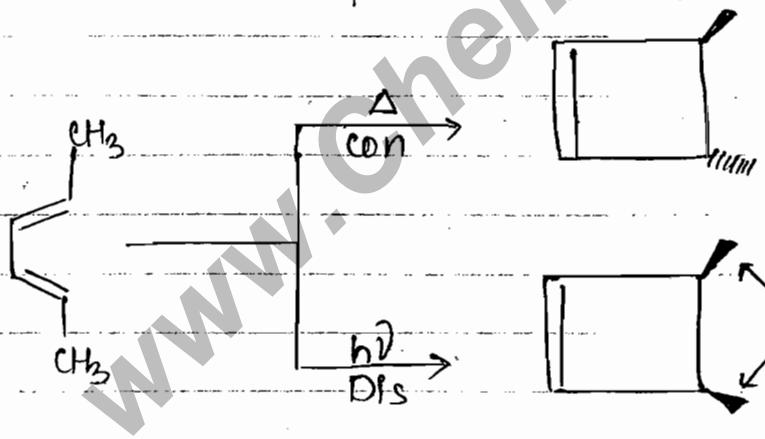


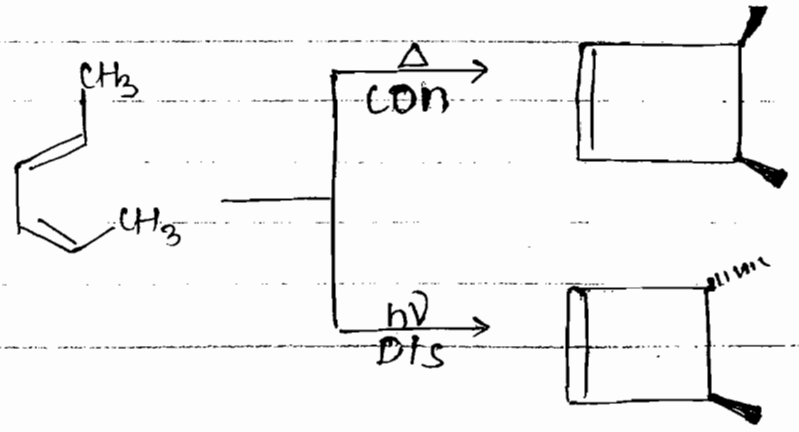

Cyclic T.S. on periphery

Pericyclic Rxn.

Stereochemistry of electrocyclic reaction:-




Above or below the plane.

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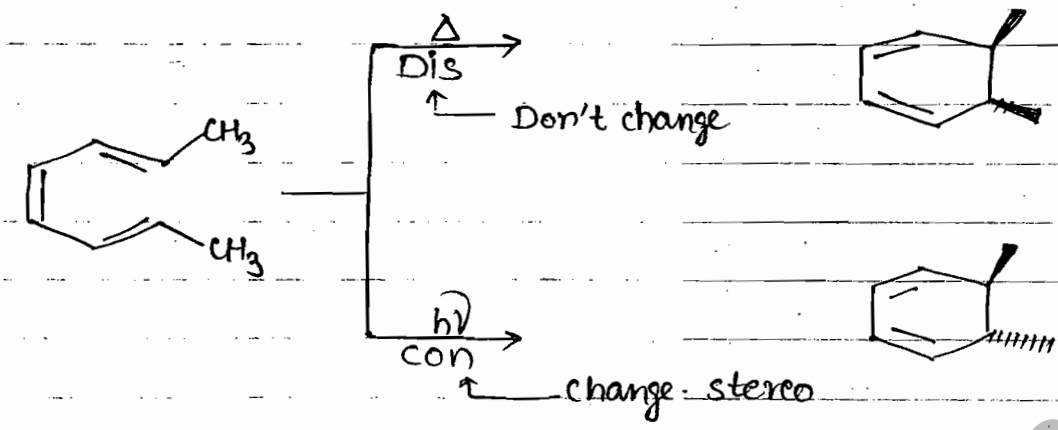
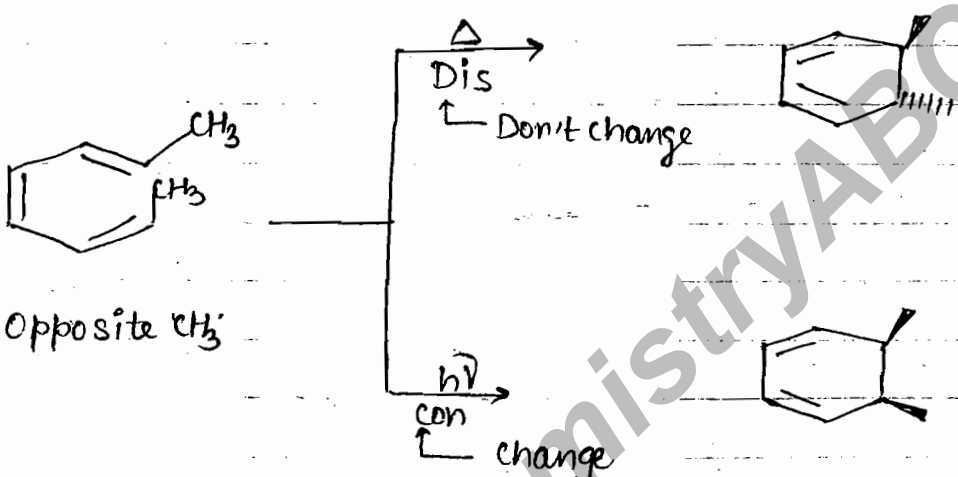
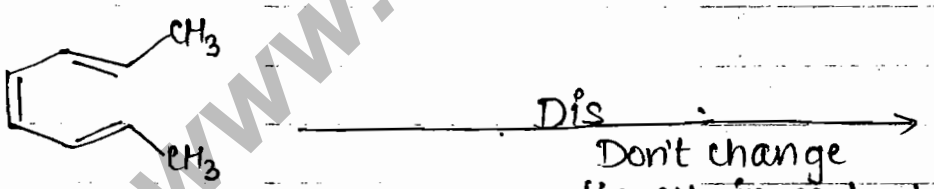
Dis = D ⇒ Don't change } Tricks




Opposite $CH_3$

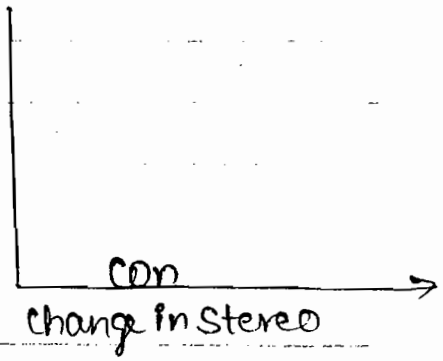
SHORT TRICK :- Con = C ⇒ Change Stereo
Dis = D ⇒ Don't change Stereo

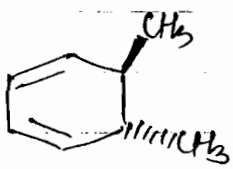



Both $CH_3$ groups outside i.e. same in nature

(i.e. $CH_3$ in reactant same then, should be same in prod.)

Both $CH_3$ above (ie. same in nature)



Both $CH_3$ not same in nature i.e changed.

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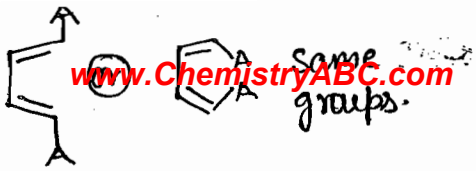
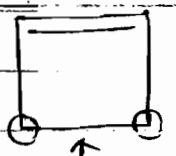
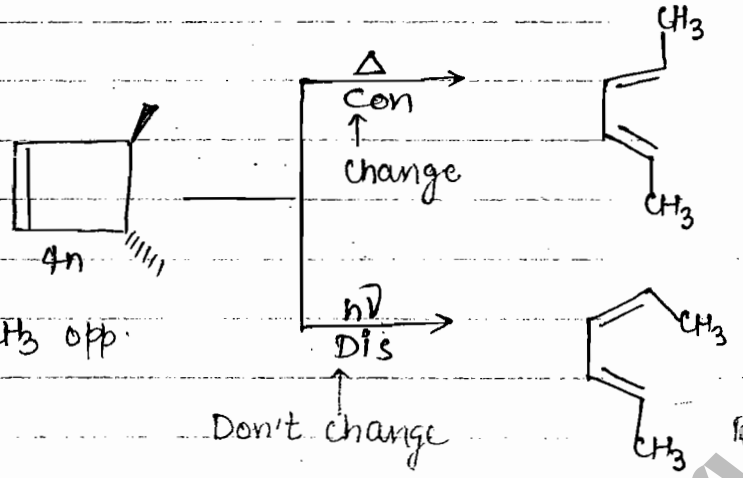



# Ring Opening :-



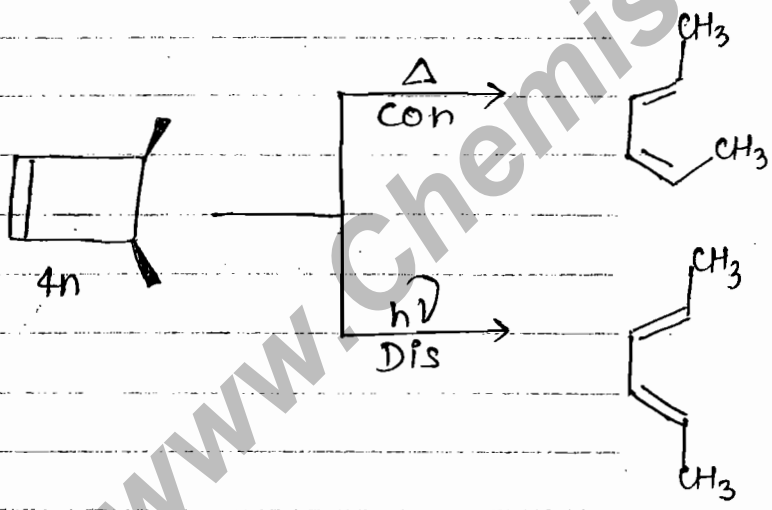
Terminal Double bond के adjacent carbon पर अगर σ bond है तो वह Ring opening में participate करेगा।



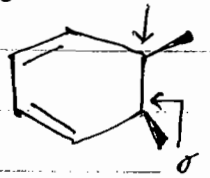

both $CH_3$ opp.

Both $CH_3$ similar (changed)

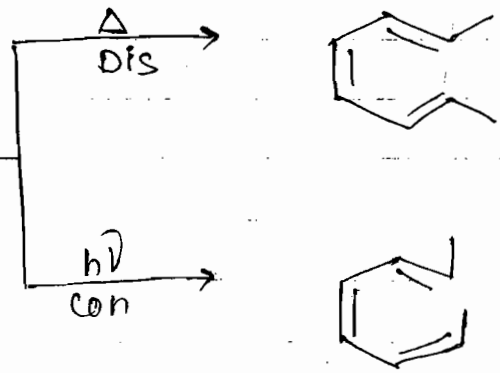
Both $CH_3$ opp. (Don't change)




Adjacent 'C' of double Bond.



σ bond on adjacent 'C'

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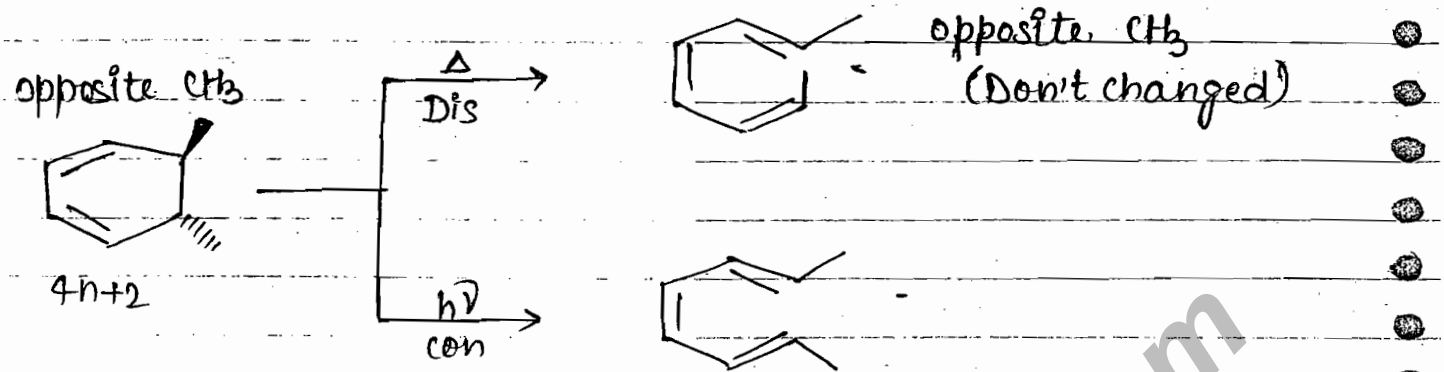
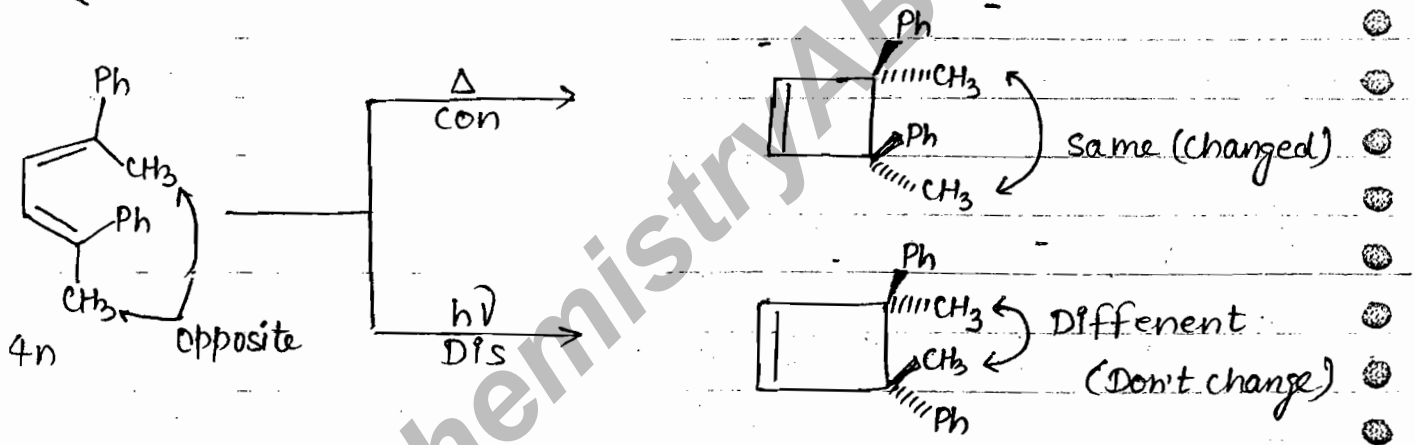



* ⇌ Valence isomerization




A common statement for electrocyclic Rxn—

The given system belong to 4n or 4n+2. Acc. to Woodward Hofmann co-relation diagram under Δ or hν condition con., dis. way mation will be takes place and the given product is formed. Driving force for this rxn. is formation of σ-bond at the expance of π-bond. ⓜ re second deriving force is release in ring strain (in case of ring opening).

Q. The following rxn. takes place via free radical mech at high temp. explain why?

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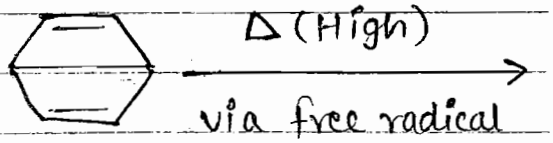
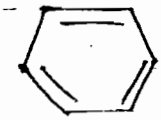
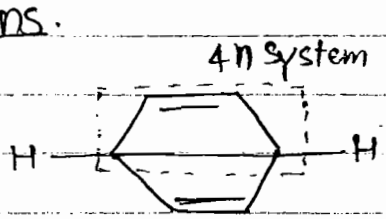
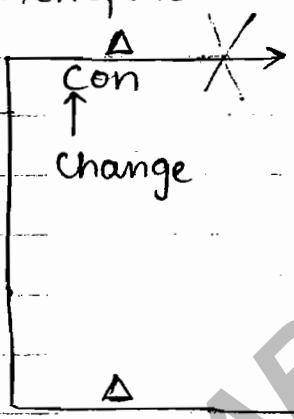


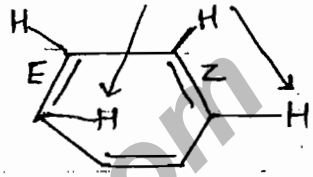
Ans.



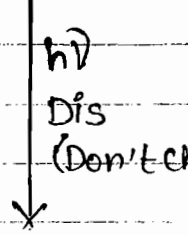

Pericyclic

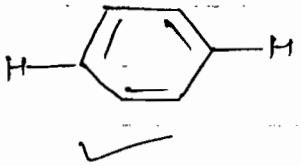


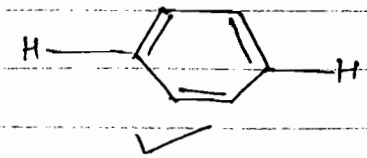

Both 'H' Diff. (Changed)



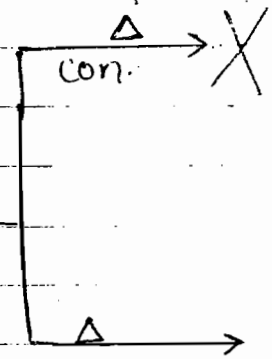

Impossible such Stereo in Benzene



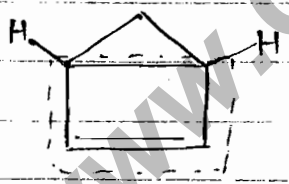



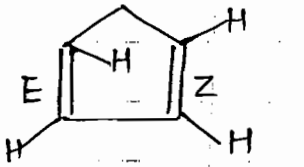




Pericyclic

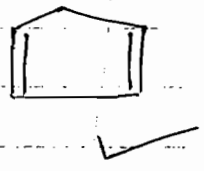



Q

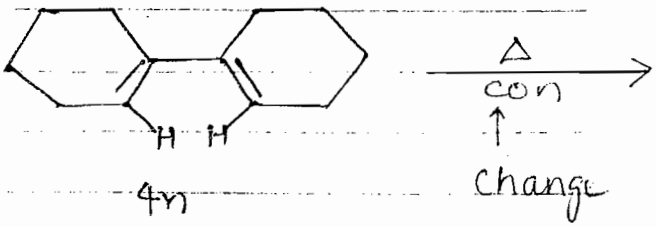



Impossible



Q.

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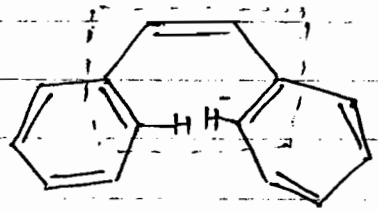
GATE 2014
M. Imp

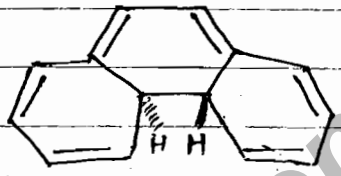
Q. cis Stilbene $\xrightarrow{h\nu}$ (A) $\xrightarrow[\text{or } [O]]{air/I_2}$ (B)



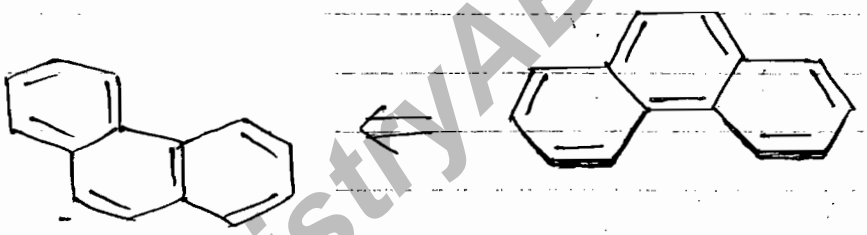
4n+2

$\xrightarrow[\text{con}]{h\nu}$

↑ change (Stereo of H)

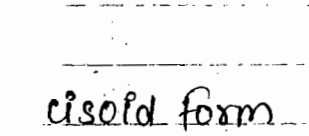


$\downarrow$ $Air/I_2$ or [O]



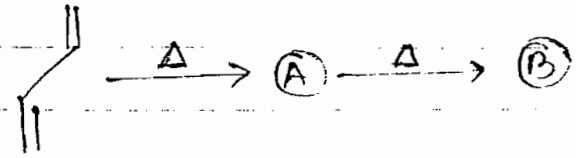
Conjugated polyene exist in two form

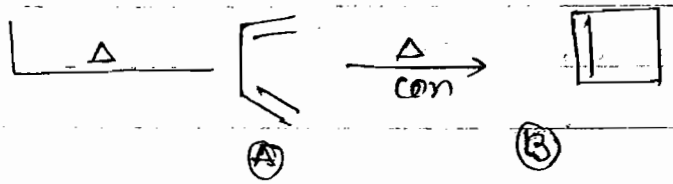
Transoid form



cisoid form

* for electrocyclic Rxn conj polyene must be present in cisoid form for the overlapping of terminal p-orb.

Q 



(A) (B)

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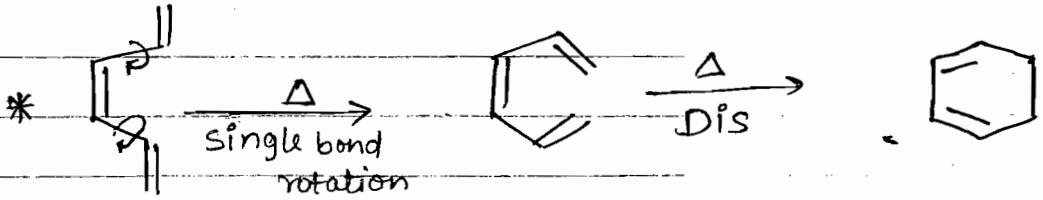
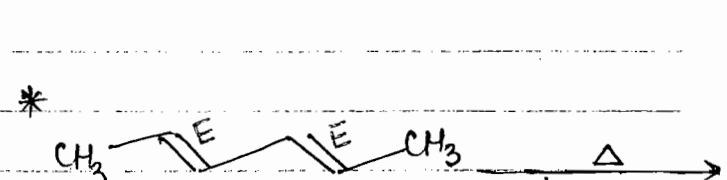
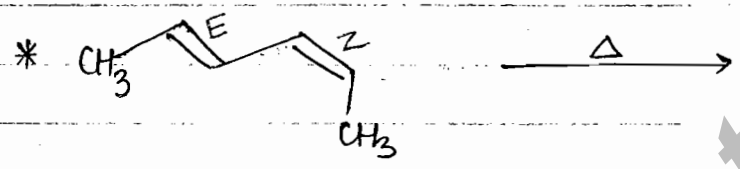
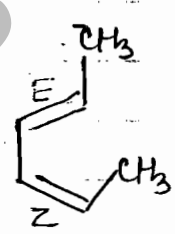
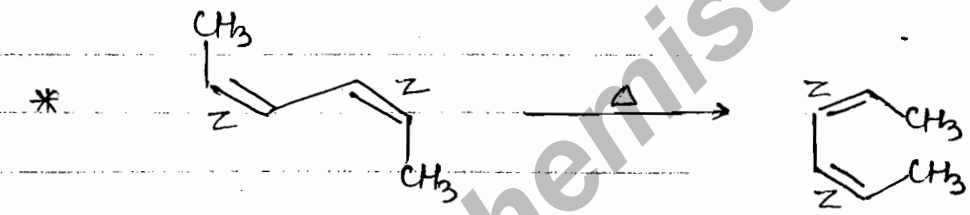



Transoid cisoid

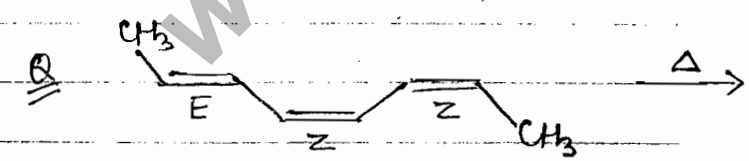


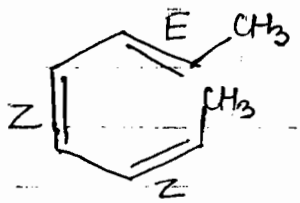


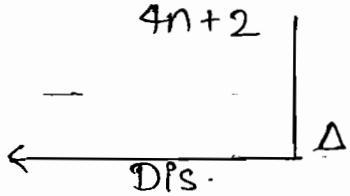




Note :- Due to Single Bond rotation No change in E, or Z alkene.



4n+2

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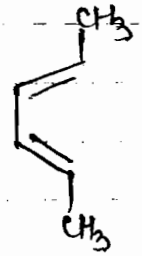
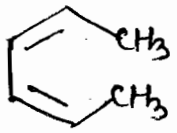
Q Rate of Rxn. will be faster in - - ?

(A)  $\xrightarrow{\Delta}$ Fast

Less repulsion b/w $CH_3$ gps. more existance in cisoid form.

⇓

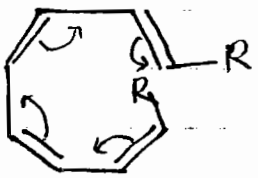
Rxn. fast.

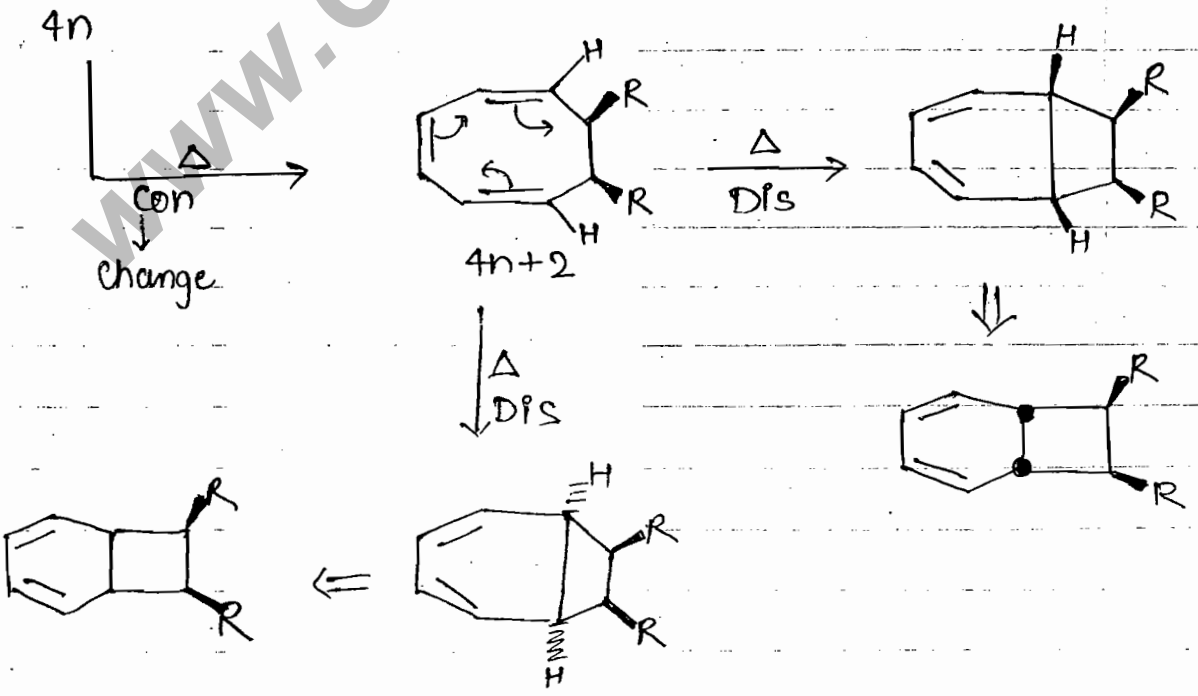
(B)  $\xrightarrow{\Delta}$ slow

More repulsion b/w $CH_3$ gps, less existance in cisoid form i.e. transoid form more favourable.

⇓

Rxn slow.

Q.  $\xrightarrow{\Delta}$ (A) $\xrightarrow{\Delta}$ (B)

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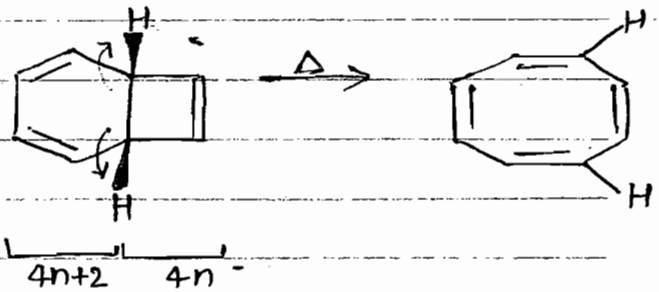
Q Which mechanism involve in the following reaction




✓ X

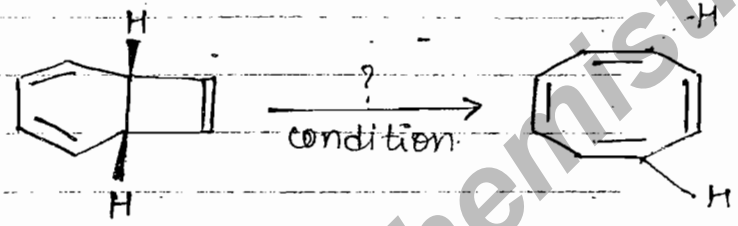
Both H may out side only by Dis rotation. Dis + Δ

⇓

4n+2

Hence 4n+2 ring opening in Δ condition with Dis. rotatory way.

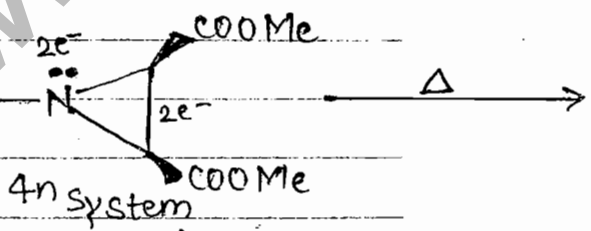
If we do the opening of 4n system then, in thermal condition con rotatory possible, hence both 'H' changed in stereo - so desired product is impossible.

Q 


only possible by Dis rotation.

4n + Dis ⇒ hν condition.

(A) 4n+2 + Dis ⇒ Δ condition.

Q 


* e⁻ which participate in concerted mechanism are include in a particular system.

⇒ Here (In ques.) l.p. of N also participating in mech. so we will count these electron in system, i.e. why system is 4n instead of 4n+2.

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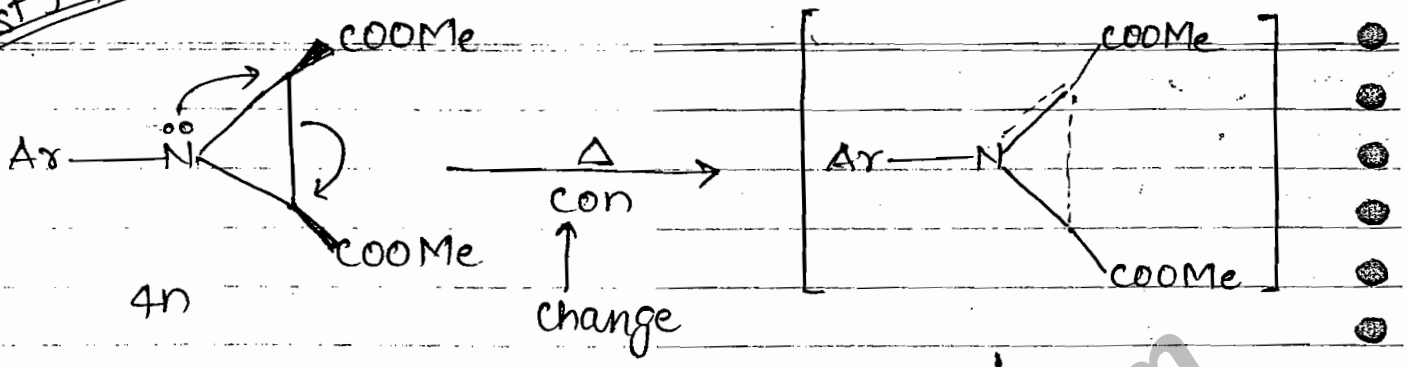
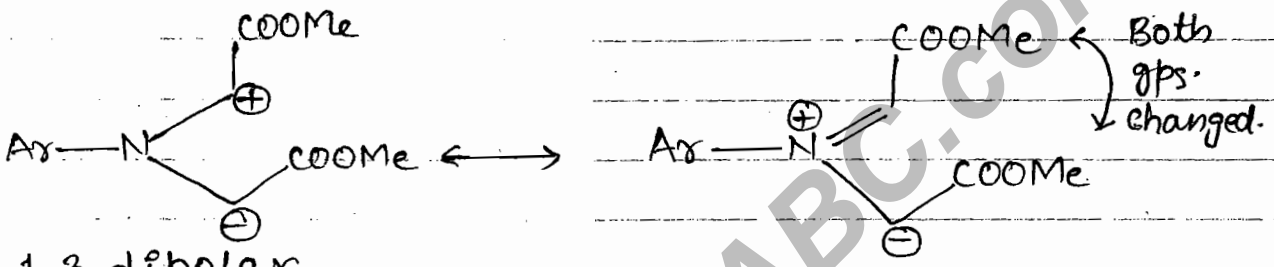
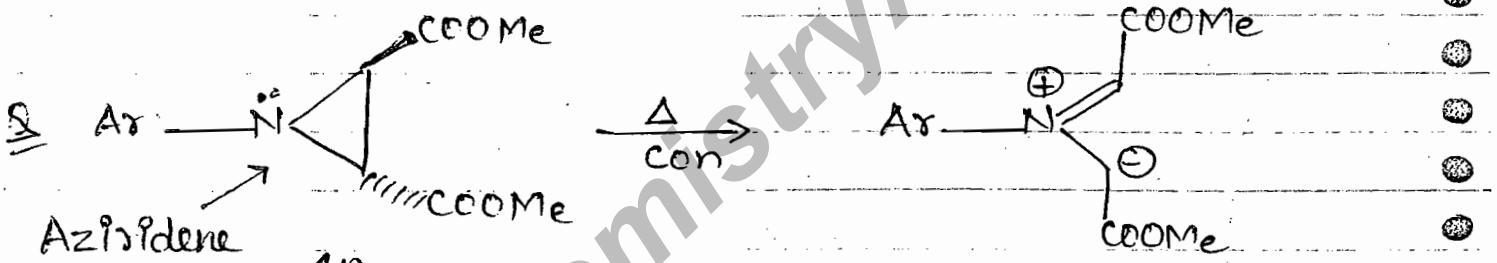
Most Imp:




*In pericyclic Rxn. Aziridene ring behave as a 4n system.

Electrocyclic Rxn. of Cyclopropane Cation:-

Cyclopropane cation behave as 4n+2 system

2 $e^-$ System $\Rightarrow$ 4n+2

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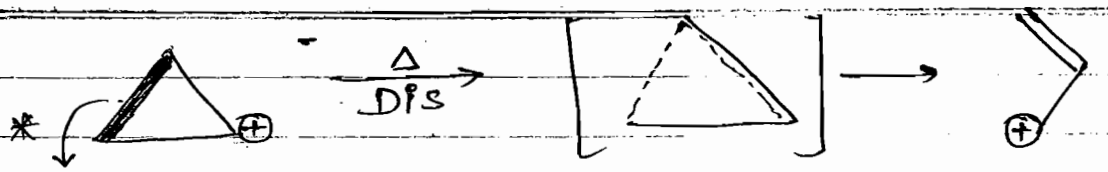
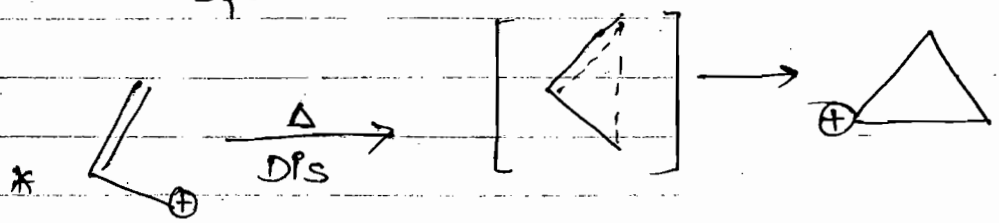
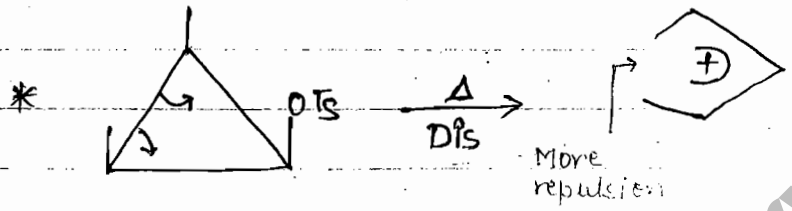


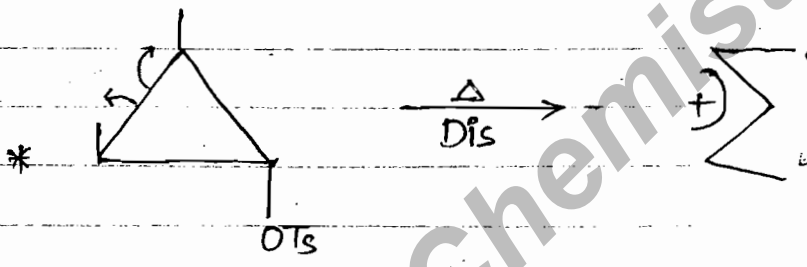

$2e^- \Rightarrow 4n+2$ System




$4n+2$




U-shape carbocation
Less stable.

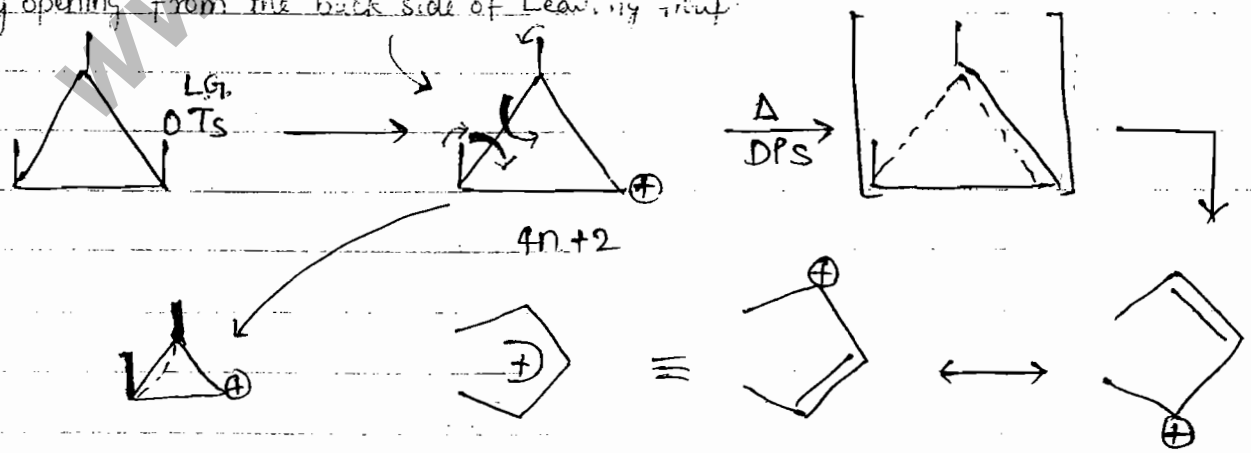



W-shaped carbocation
more stable

Rate of formation

W shape > U-shape.

Ring opening from the back side of Leaving group




U Shape

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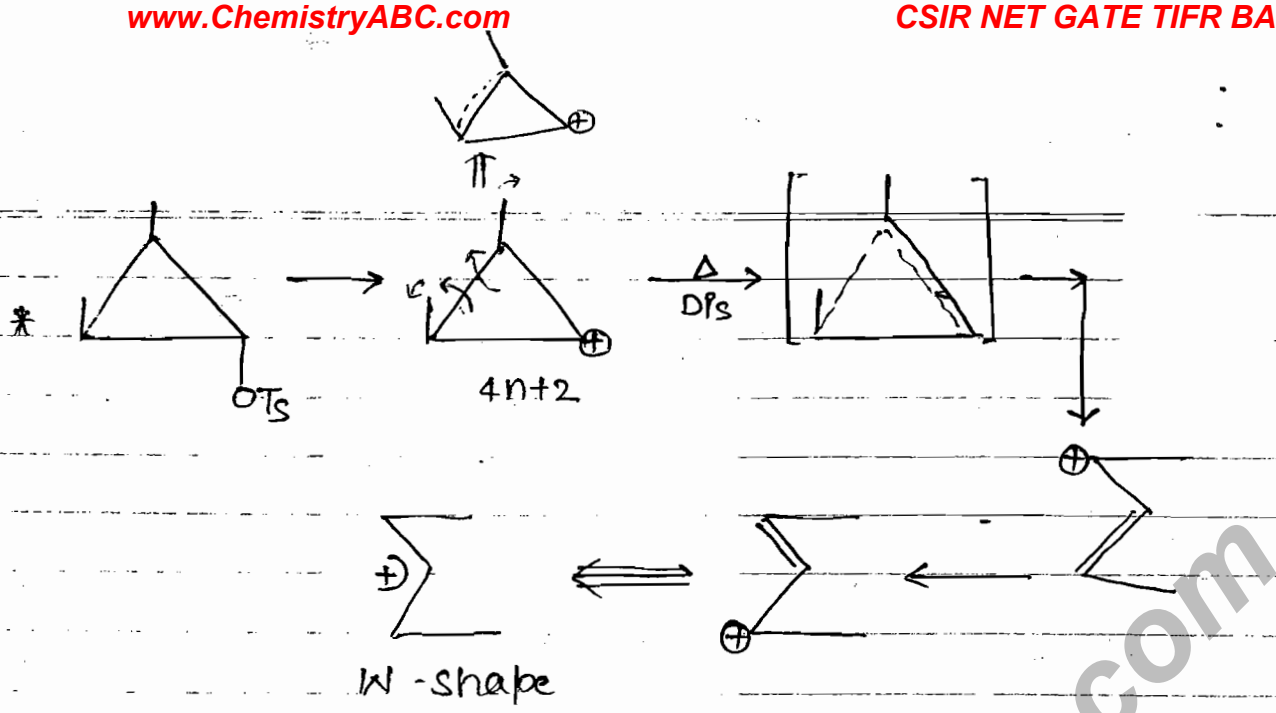
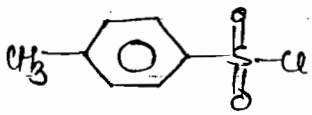
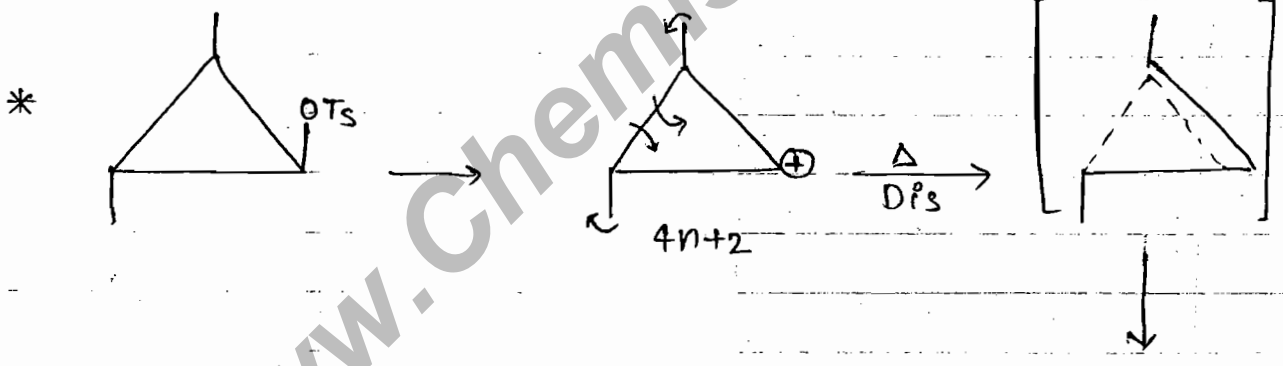
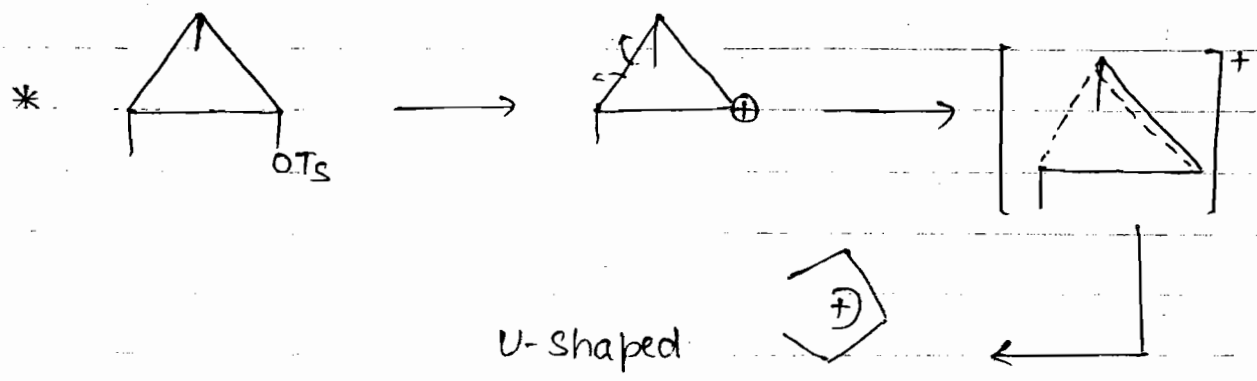



**Note:-** Ring opening will be takes place from the back side of the leaving group



Tosyl sulphonyl chloride

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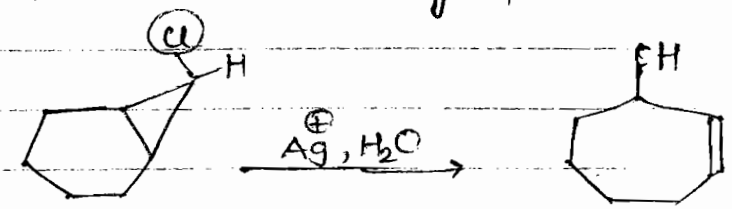
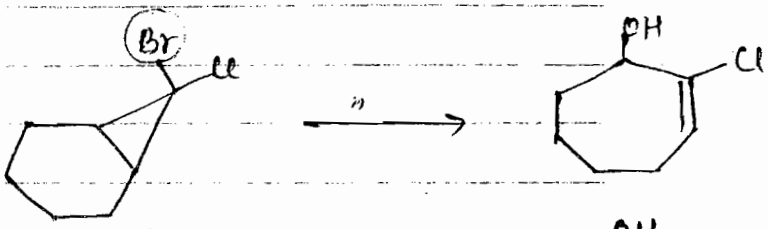
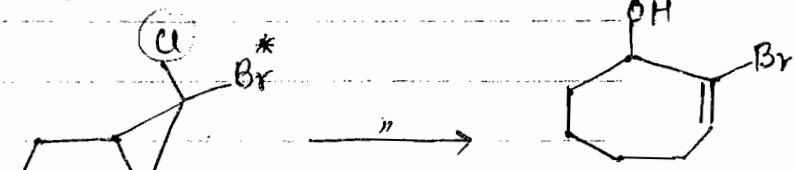
M.Imp

* Explain the following problems:-



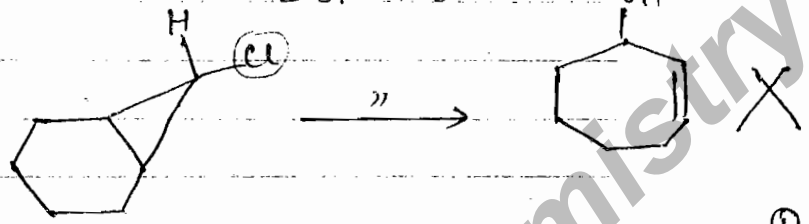

L.G SHOULD BE ENDO SIDE

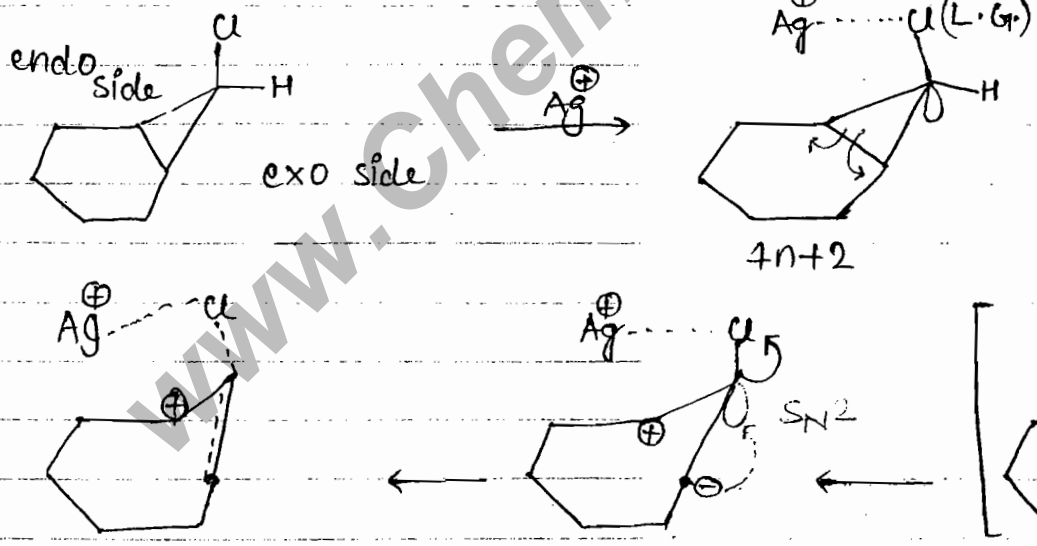



* In this case Br is good. L.G. even Cl⁻ leaves becoz Cl is endo side. and endo L.G. only can leave

L.G. exo (No Rxn.)

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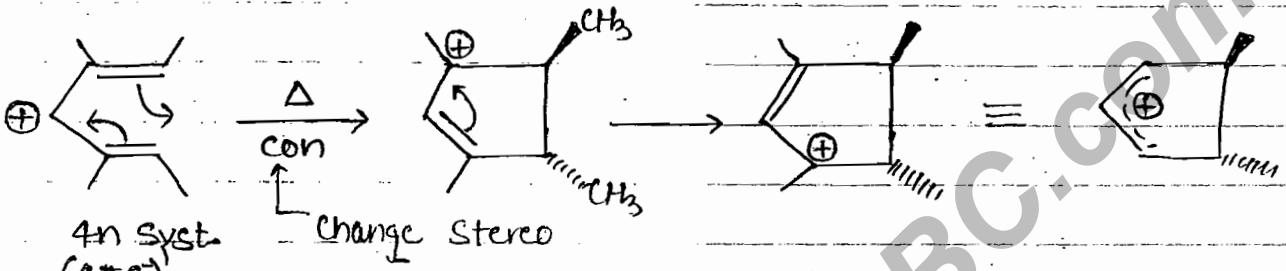
L.G. must be present at endo side for such type ~~rxn~~ rxn. Rxn takes place in two step.

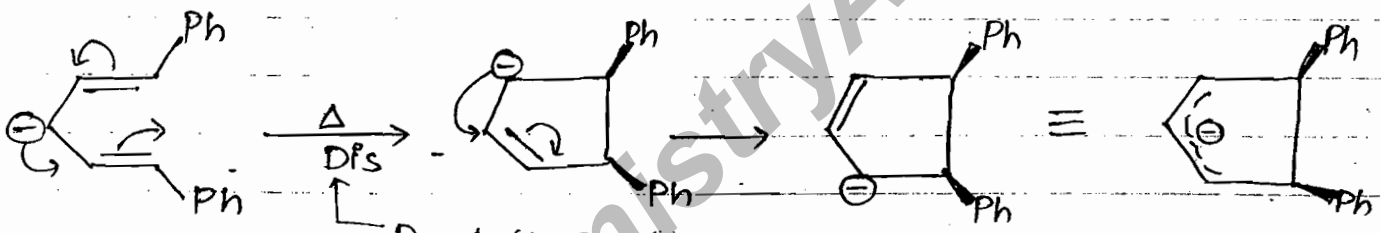
i) Electrocyclic Rxn ii) $S_N2$.

## ELECTROCYCLIC Rxn of Carbcation/Anion :-



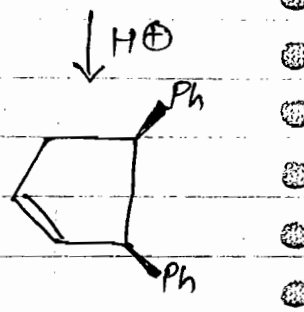

4n Syst. ($4\pi e^-$)

Change Stereo




4n+2 Syst. ($6\pi e^-$)

Don't Change Stereo




## WORK UP :-

Work up.

- Water (Solvent)
- Organic Solvent

$CHCl_3$, $CH_3COEt$, DCM, $C_2H_5OC_2H_5$ etc.

density $H_2O$ > $CH_3COEt$, Et-O-Et

DCM, $CHCl_3$ > $H_2O$

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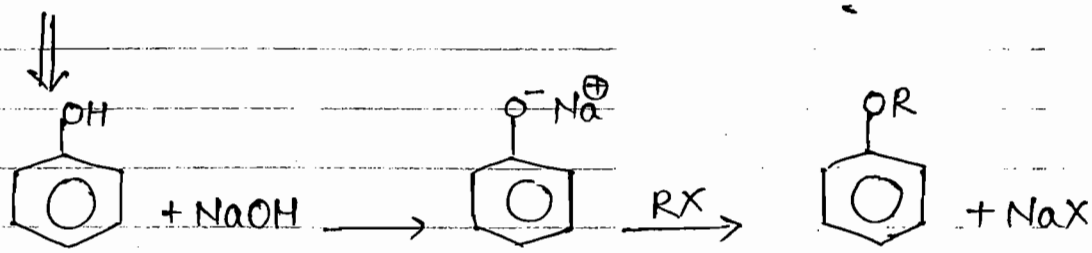
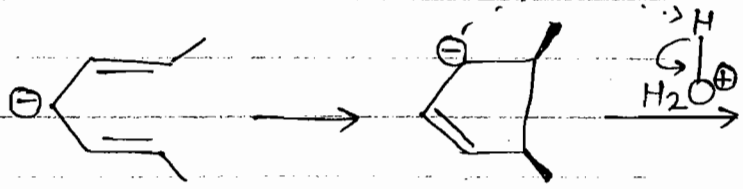
Work up is of three types -

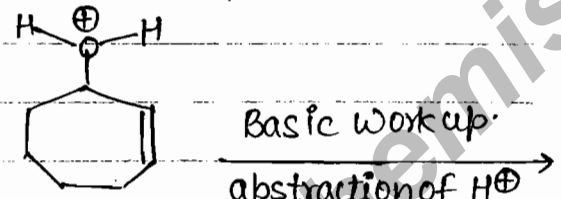
i) Neutral ii) Acidic iii) Basic



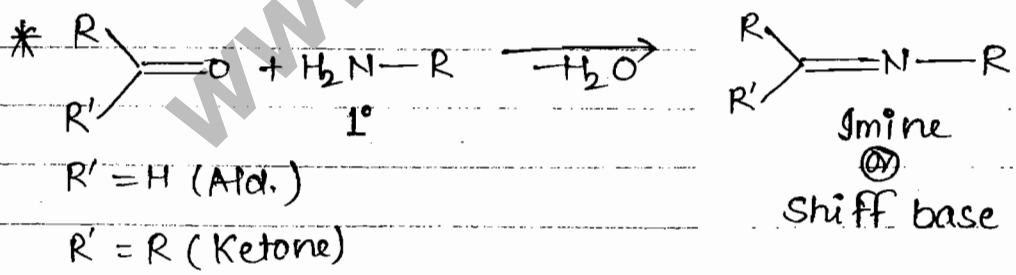

ii) Acidic Work up:-

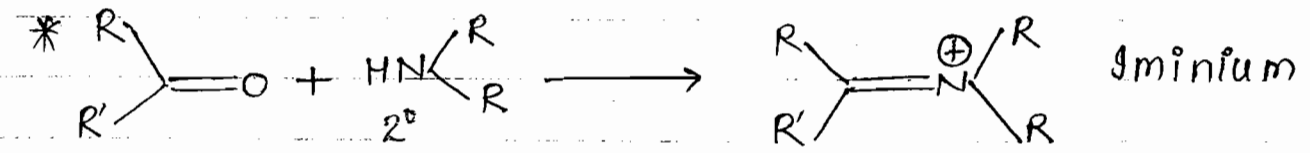


iii) Basic Work up:-




Rxn of CARBONYL Comp. with 1° and 2° Amine

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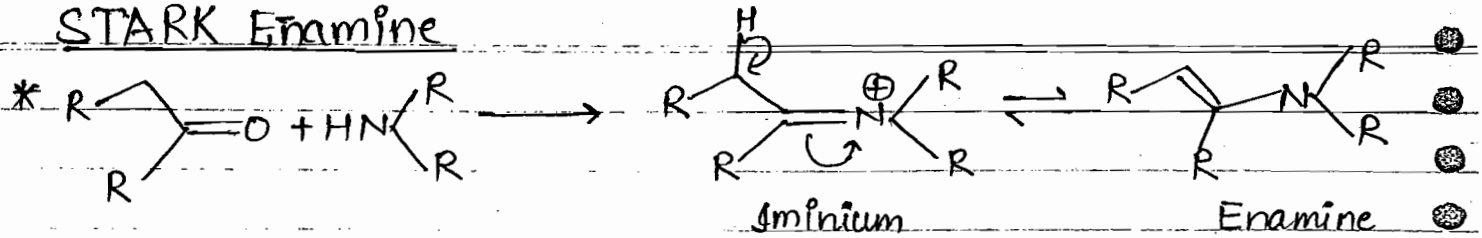
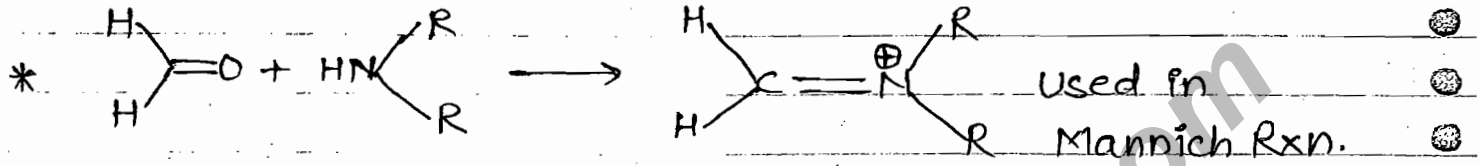
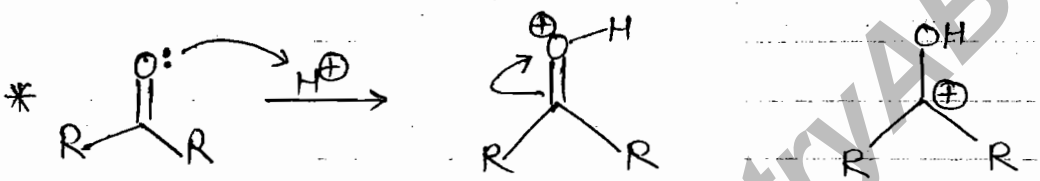
New bond is always stronger than old bond.

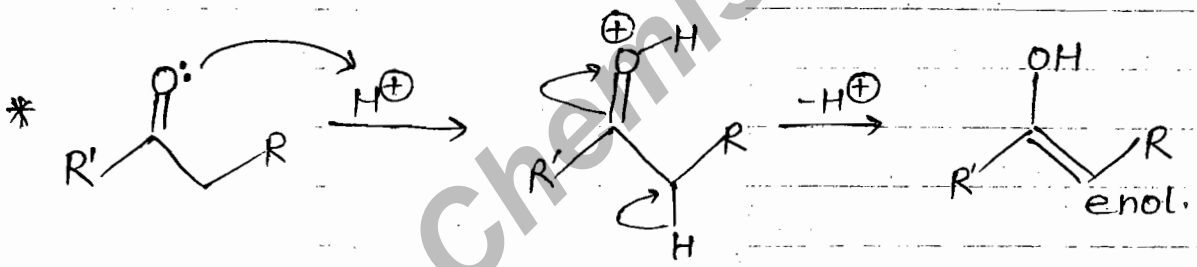
## STARK Enamine

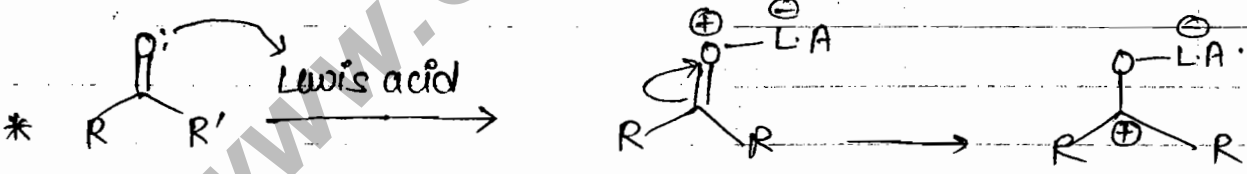


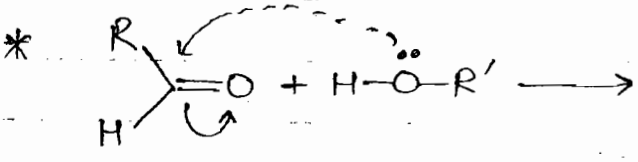

## Rxn of CARBONYL Comp with Lewisacid or Acid :-






## Rxn of Carbonyl comp with ALCOHOLs :-



Hemiacetal.

H = R (Hemi Ketal)

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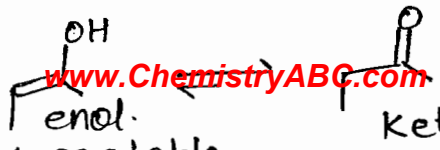
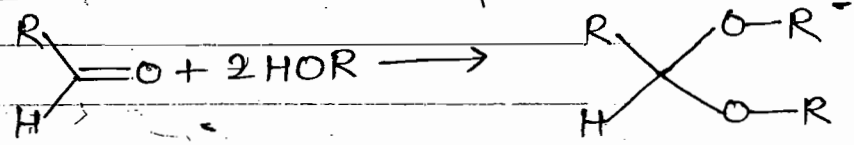
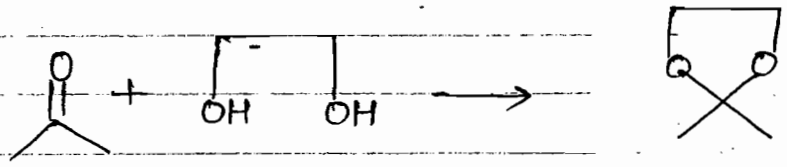



↳ stable only if System is gaining aromaticity or H Bond.

* 


Acetal

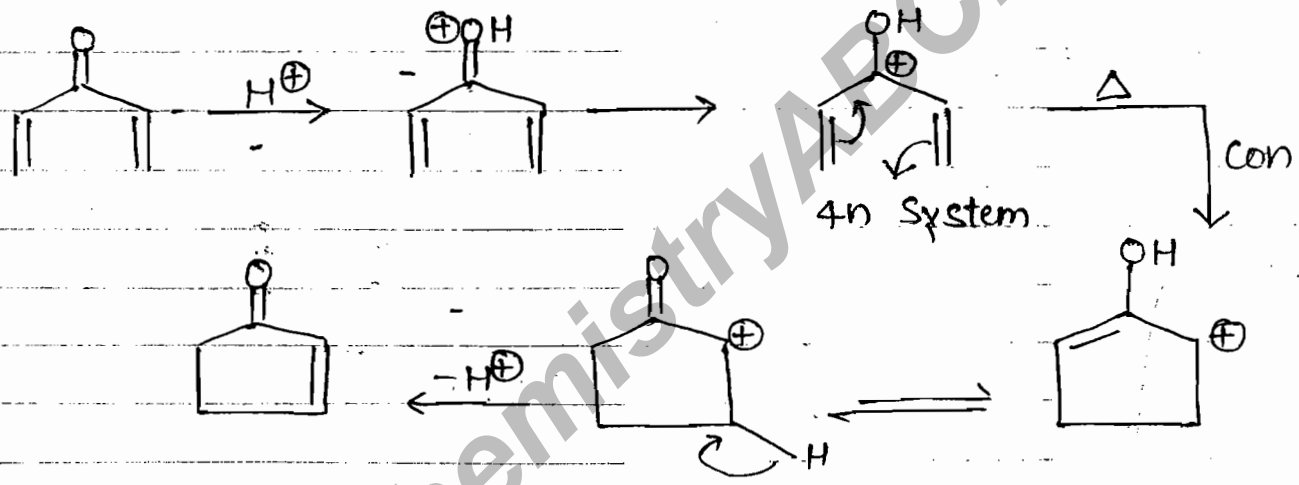
H = R (Ketal).

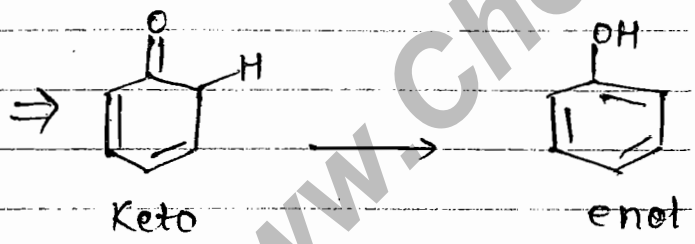
* 



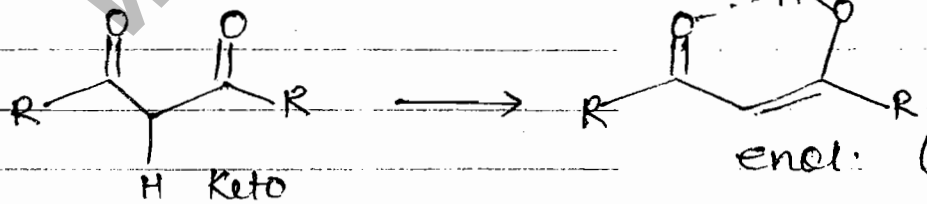

Ketal.

## NAZAROV CYCLIZATION :-




(More stable becoz system Gaining aromaticity)




enol: (More stable due to H.B.)

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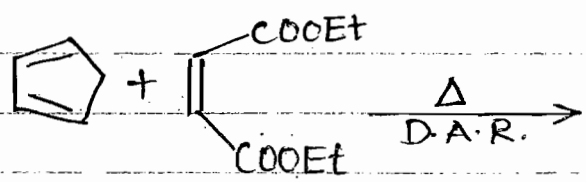
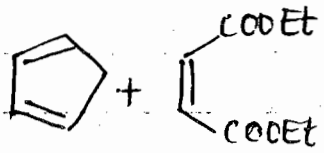
22/Sept/2014

# RETRO DIEL's ALDER Rxn.

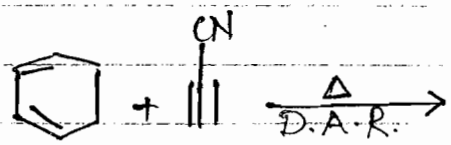
* Required high temp. (400~600°C)
* When Rxn. takes place at low temp then generally catalyst required

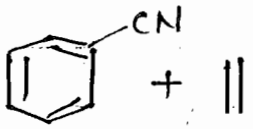
Q.



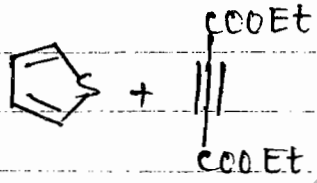


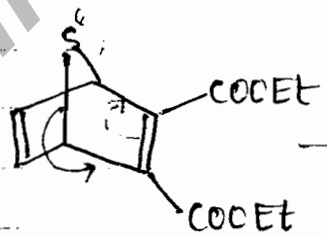

Q



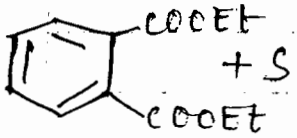



Q.

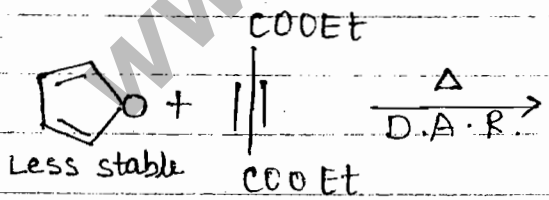


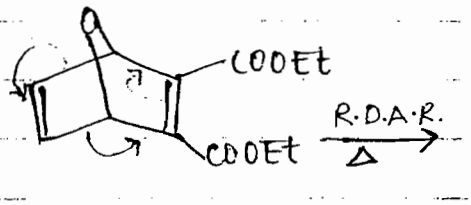



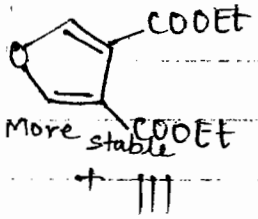

* Desulphination (S stable in atomic form).




Q




* Here oxygen can't release in form of atom because it is unstable.

+R/−R or −I/+I substituted Pyrrole, Furon, Thiophene are more stable than non substituted.

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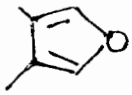
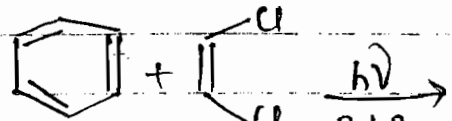


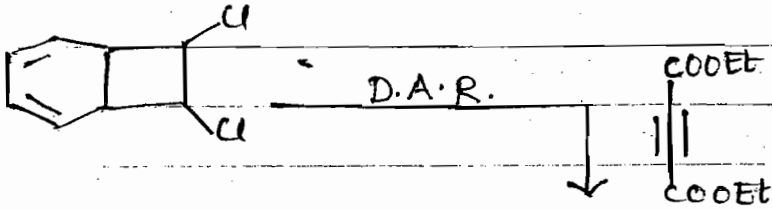
Two sites blocked for substitution (More stable)

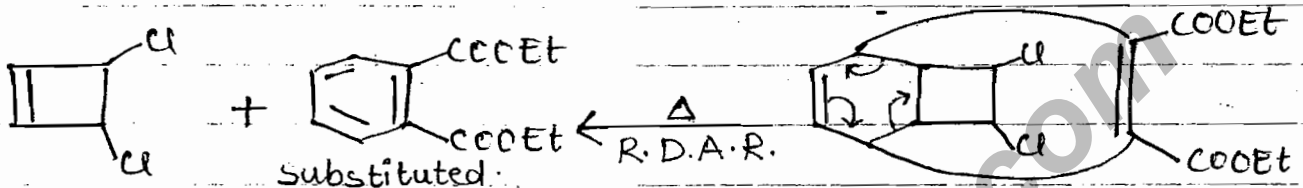
All sites are free to react other molecules. (Less stable)

Q.



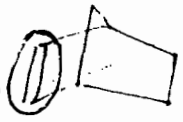
Non substituted. (Less stable)




* If such comp is given with temp. then R.D.A.R may take place -

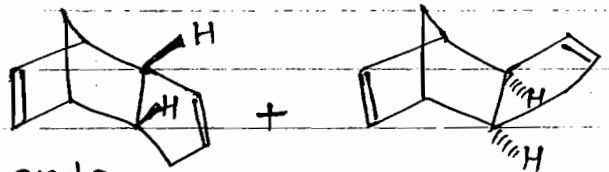
This double bond should be present →



* If after R.D.A.R. there is possibility of forming aromatic comp. then make always Aromatic comp.
* After R.D.A.R. if product is more stable than reactant then process that follow mechanism and form more stable product.

Q Cyclopenta dienyl exist in dimer form, why?

Due to DA.R. It dimerises.



endo (Major) + exo (minor)

Refluxion. | High Temp.
R.D.A.R. ↓

2.

* Cyclopentadienyl exist in dimer form at Room temp.

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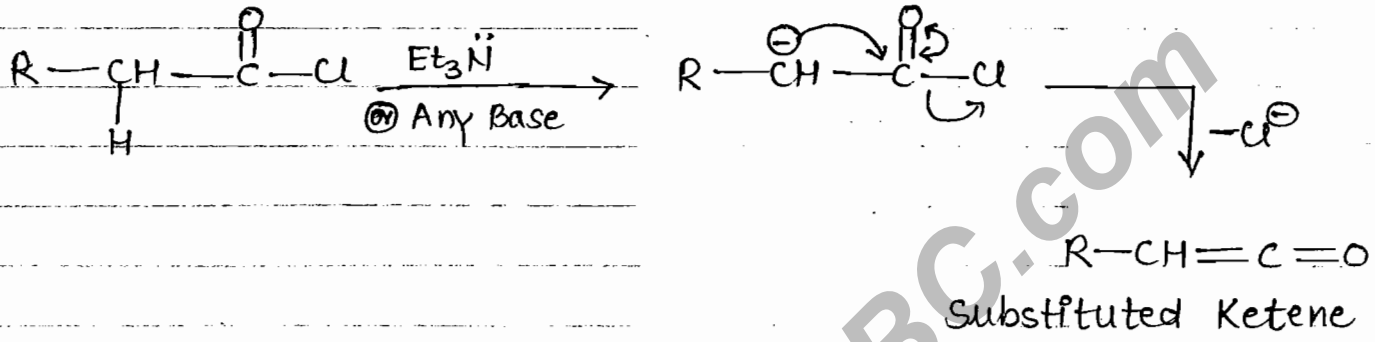
M.Amp.

# CYCLOADDITION Rxn. of KETENE or ISOCYANATE

Ketene ($CH_2=C=O$) Isocyanate ($R-N=C=O$)

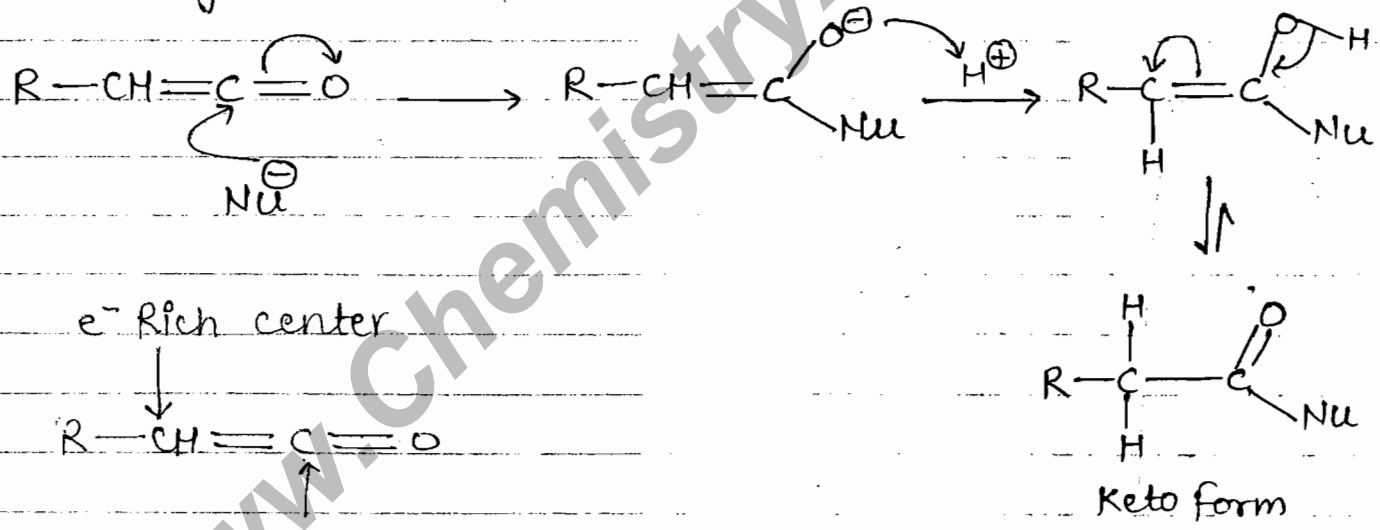
* Formation of Ketene:-




$R-CH=C=O$

Substituted Ketene

* Ketene gives Nucleophilic Addition Rxn.




e⁻ Rich center

⇒ $R-CH=C=O$

e⁻ deficient centre

## 2+2 CYCLOADDITION Rxn. of KETENE under THERMAL CONDITION:-

* Ketene gives 2+2 cyclo-addition Rxn. under thermal condition.
* These thermal 2+2 cycloaddition Rxn. do not work in b/w two alkene because the HOMO & LUMO

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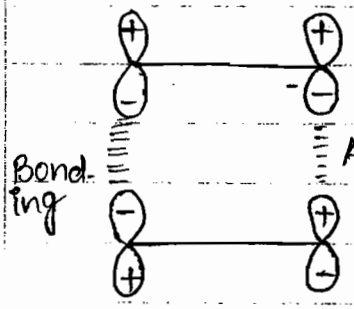
combination is antibonding at one end, it means supra - antara interaction takes place under thermal condition.



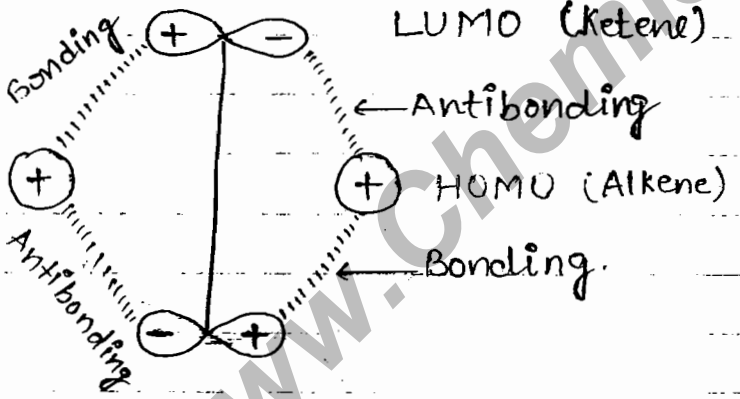

HOMO ($\psi_1$) Alkene.

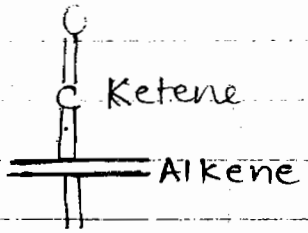
LUMO ($\psi_2^*$) Ketene (e⁻ deficient)

i.e. why LUMO of Ketene

S - A interaction.

but in the case of ketene 2+2 cycloaddition Rxn takes place under thermal condition. In this rxn. one alkene rotate at 90° w.r.t. other alkene.




One alkene rotated at 90° w.r.t. other alkene.

In the above diag. two Bonding interaction & two antibonding interaction takes place so according to above representation No. Rxn. will take place. But ketene have extra p-orbital and this orb interact with HOMO of the alkene.

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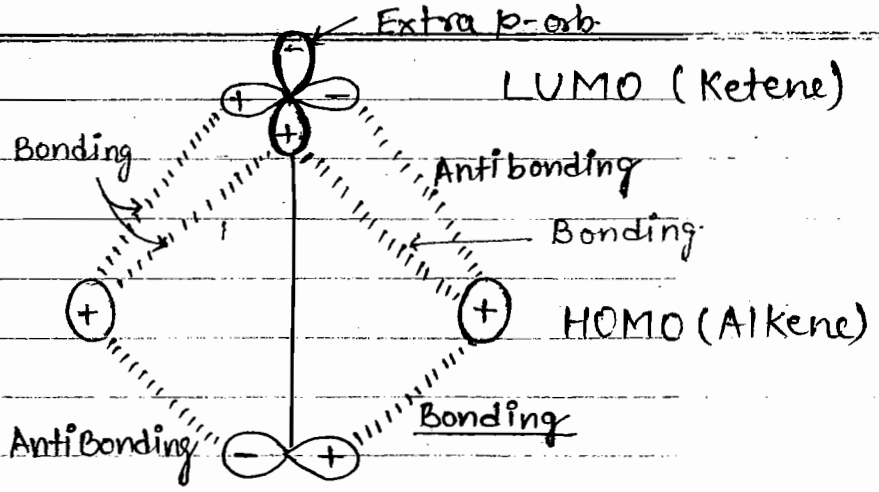
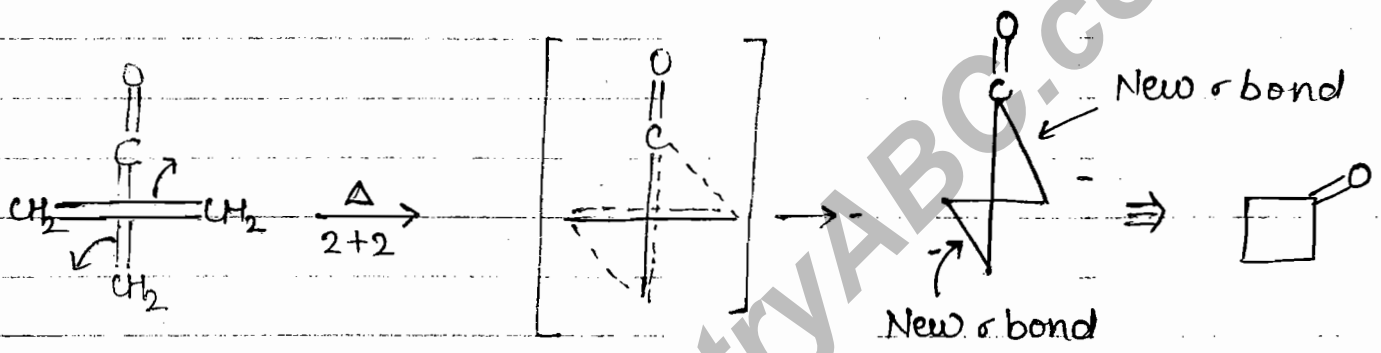



In this diagram - Net bonding interaction are Two.

Net B. = (4 - 2) = 2

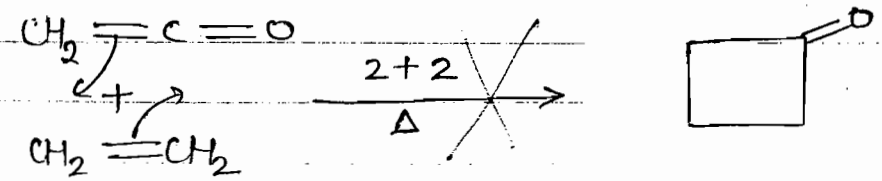
B A. Net B.




In the above diagram four bonding interaction and two anti bonding interaction takes place. The net bonding interaction are (4 - 2 = 2) two which is favourable for Rxn.

The above reaction takes place via concerted mechanism no ionic mechanism involved.

* Problems of Ketene :- Ketene gives 2+2 cycloaddition Rxn under Δ condition via concerted Mechanism.

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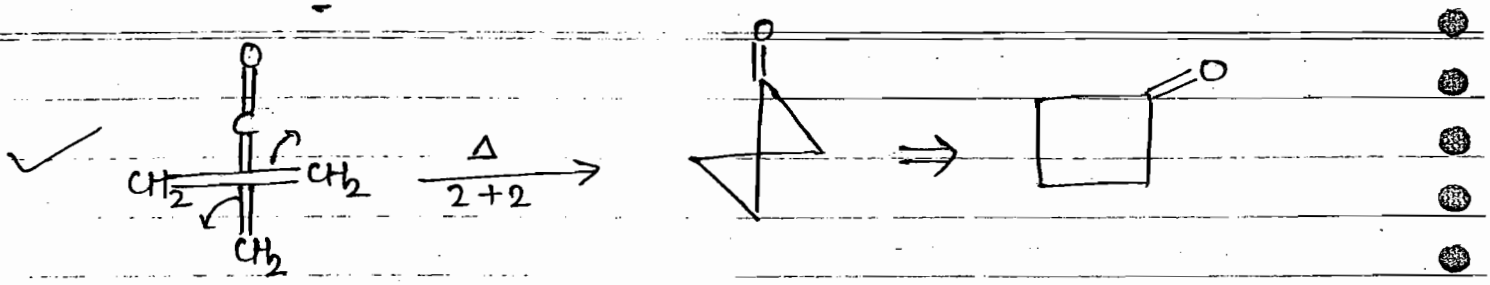
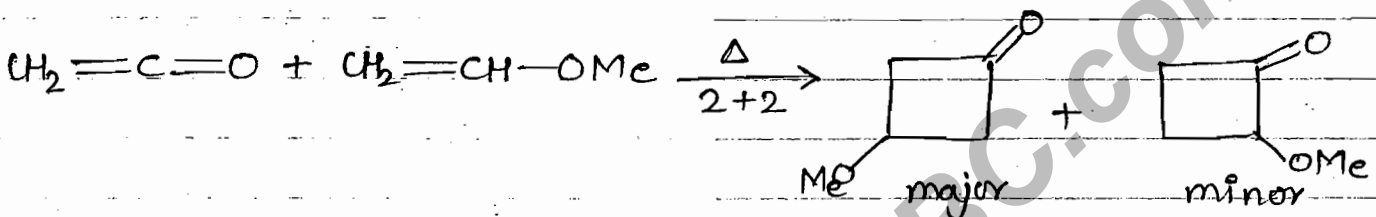
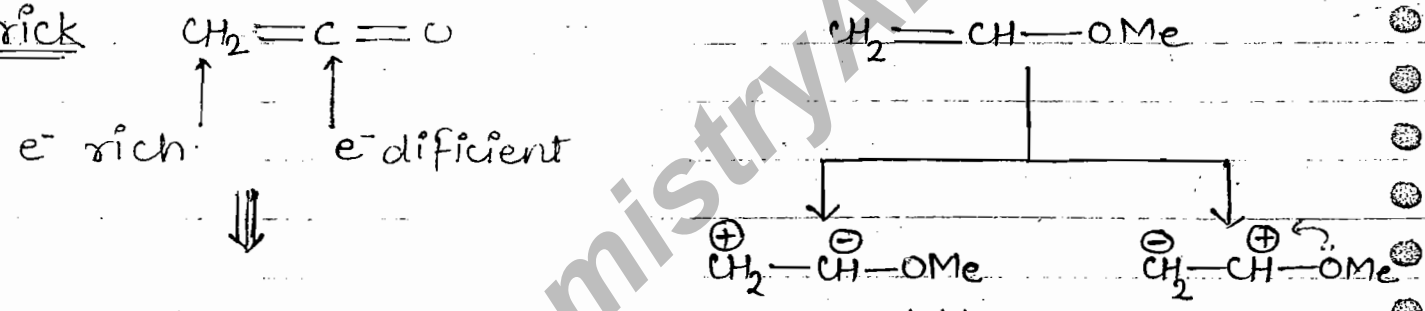
$CH_2-\overset{\oplus}{X}$ Substituted Carbocation (More stable ⇒ Stabilized by I.P.)



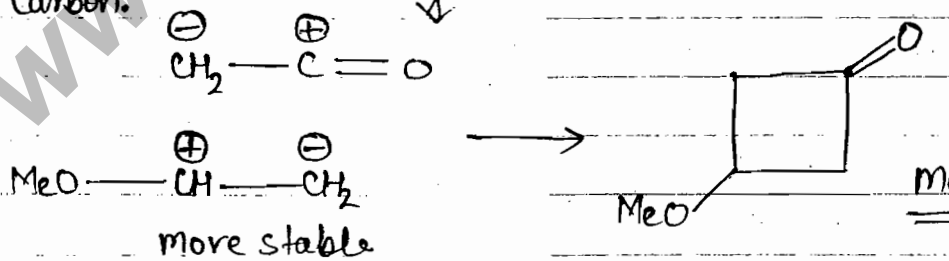
## Cycloaddition Rxn. of Ketene with Asymmetric Alkene:-




**Trick**




Always break Alkene double bond in such manner (+ve) charge on carbonyl carbon.

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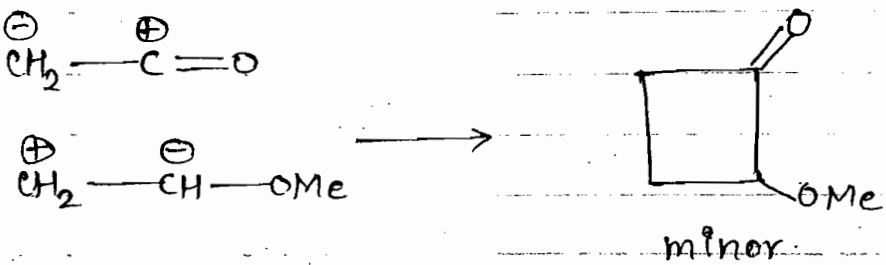


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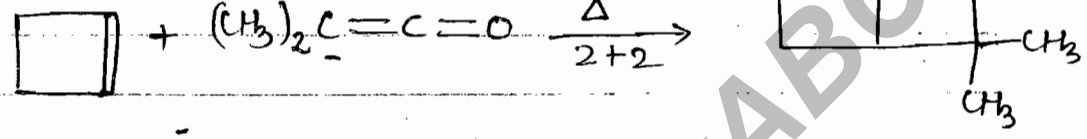
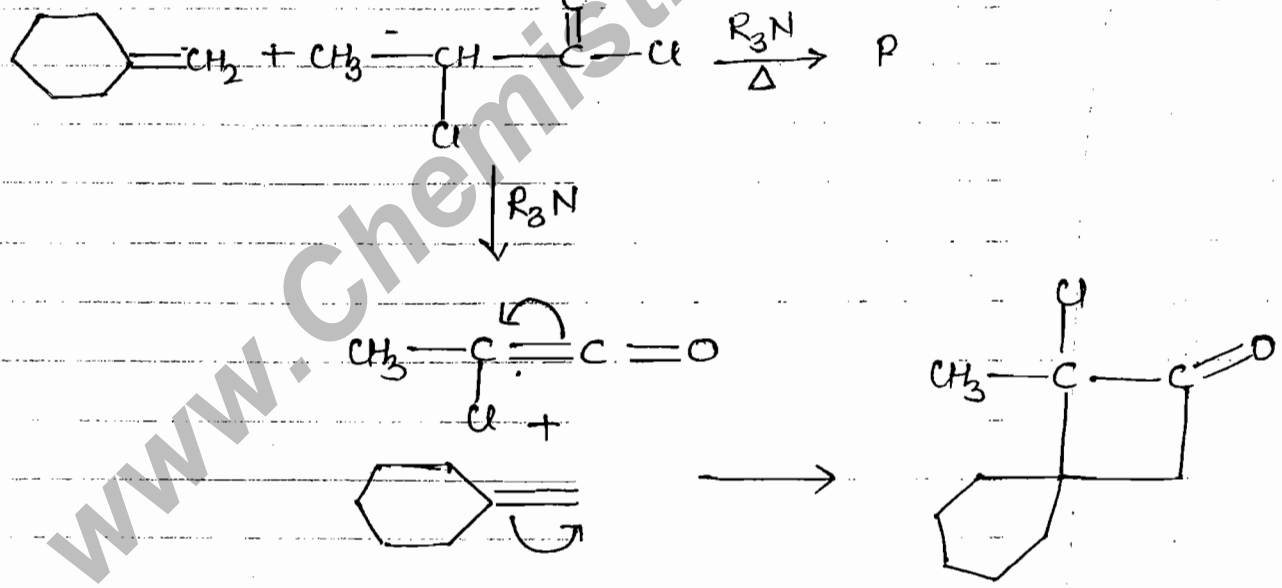
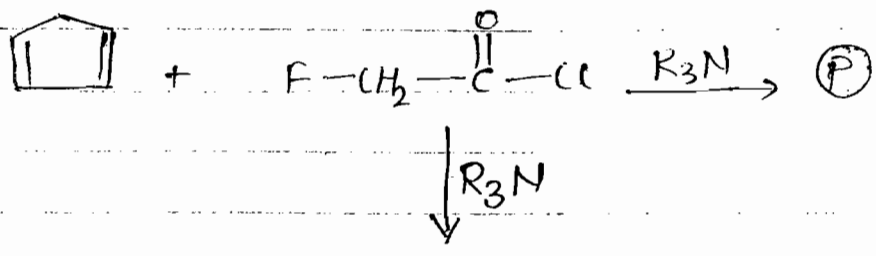
* No ionic mechanism involve in ketene cycloaddⁿ Rxn. the given trick is only to solve questions in exam this is wrong method to represent mechanism. Actually mechanism is concerted mechanism. and the regioselectivity is proceed by the polarization of alkene, with the more e⁻ rich end of the alkene following forming a bond with the e⁻ deficient centre carbon atom of the ketene.

Prob. 

Prob. 

Imp.

Prob. 

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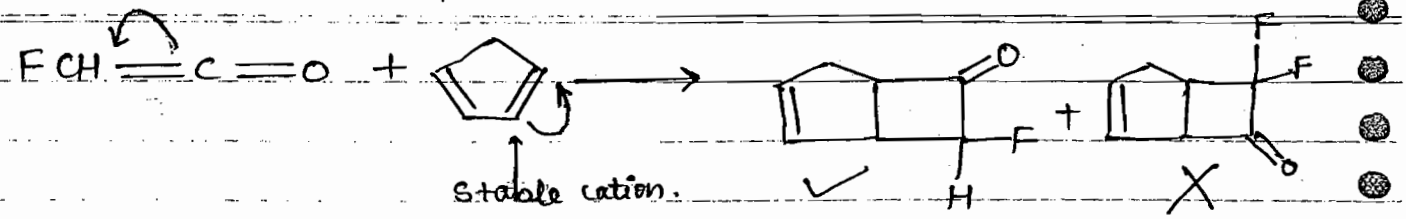
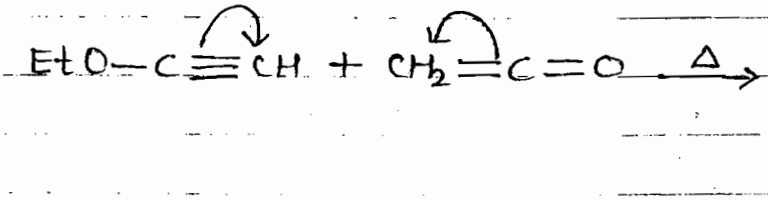
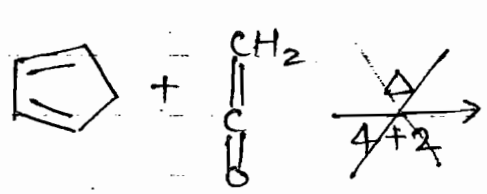
We always see the stability of carbocation not the stability of anion in cycloaddition Rxn. (Only for Trick).




Prob.

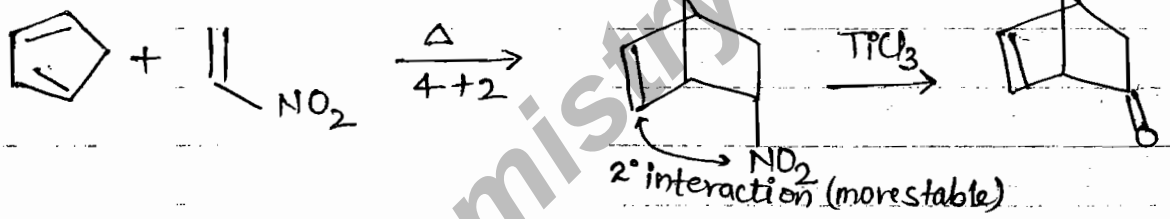


Prob.



Ketene always gives 2+2 cyclo addition Rxn.

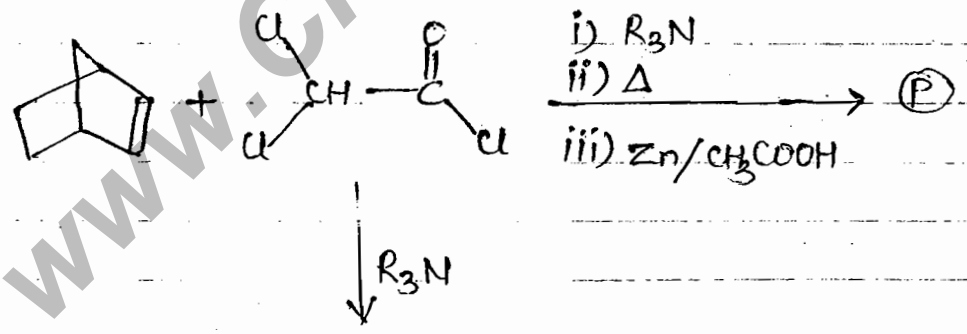
Prob.

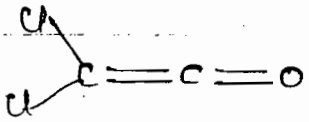


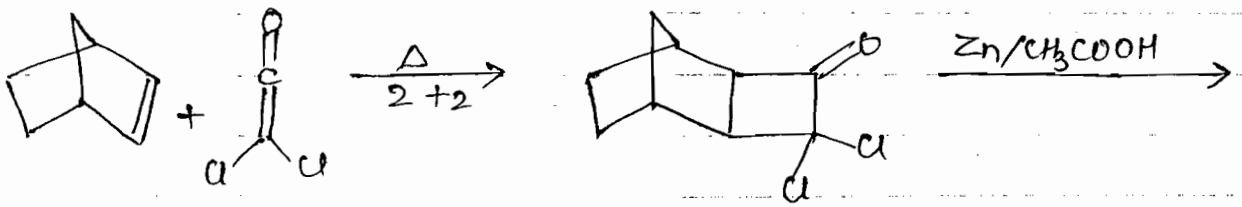

* $TiCl_3$ convert $-NO_2$ group into carbonyl group.

M.Imp.

Prob.



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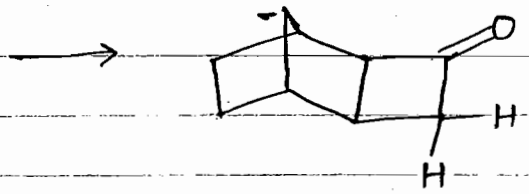
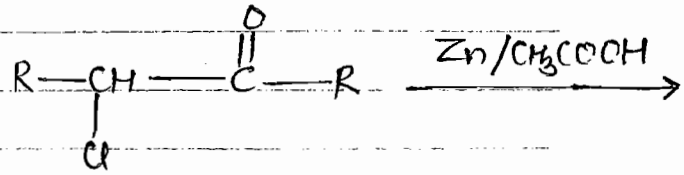
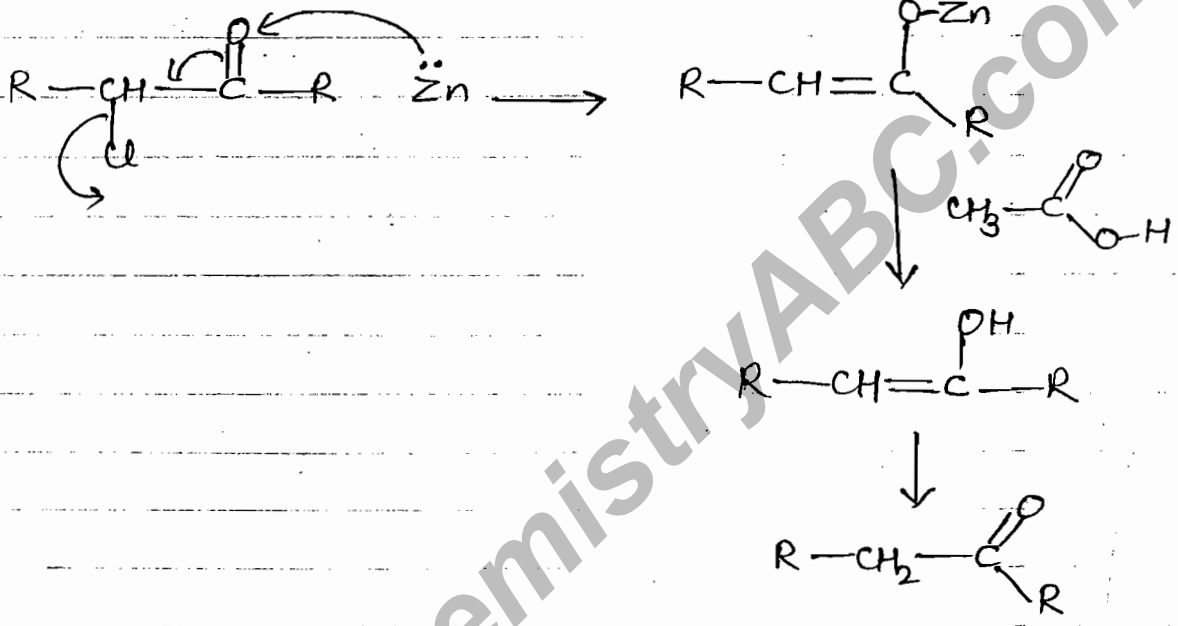


M.Imp.

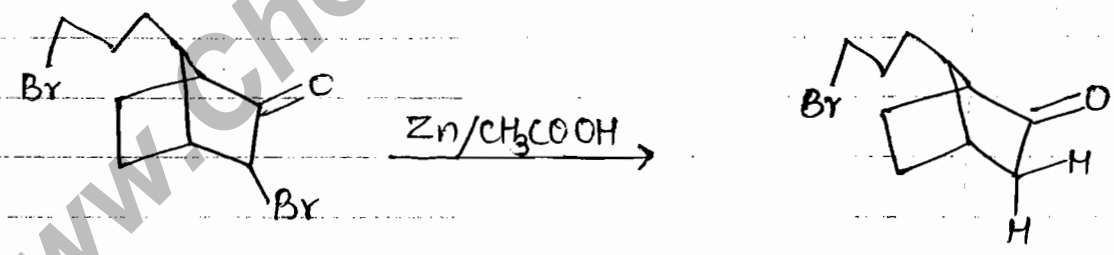
Prob.





Imp.

Prob



* $Zn/CH_3COOH$ remove the halogen which is present on $\alpha$- position of carbonyl group.

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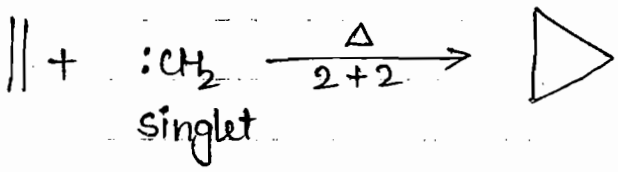
# CHELEOTROPIC CYCLOADDITION Rxn.

Rxn b/w singlet carbene and alkene is k/a cheleotropic cycloaddition Rxn. Cheleotropic Rxn is the case of 2+2 cycloaddⁿ Rxn.

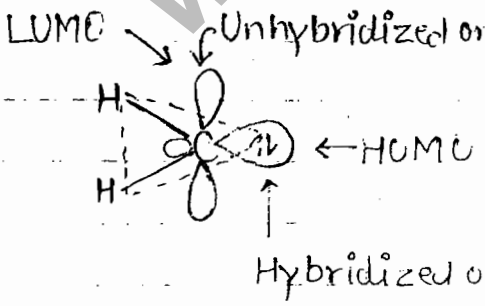


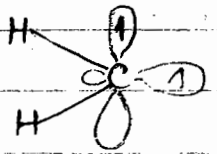

On the basis of atom this rxn is k/a 2+1 cycloaddition Rxn. & on the basis of e⁻ this rxn is k/a 2+2 cycloaddition Rxn. Cheleotropic Rxn (2+2) is thermally alowed. Supra-supra addition will take place, concerted mechanism follow.

Orbital representation of cheleotropic Rxn.

Carbene

Singlet ($^1CH_2$) | Triplet ($^3CH_2$)




It gives Stereospecific Product.

It gives stereoselective Product.

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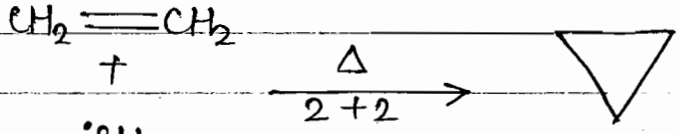
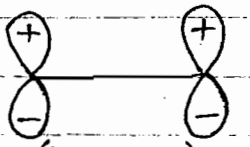
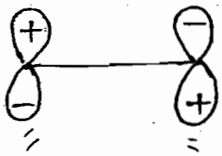
* $CH_2=CH_2$ + $:CH_2$ $\xrightarrow[2+2]{\Delta}$

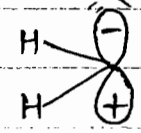




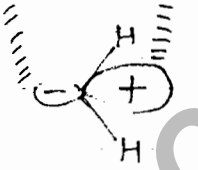
HOMO ($\psi_1$)



LUMO ($\psi_2^*$)

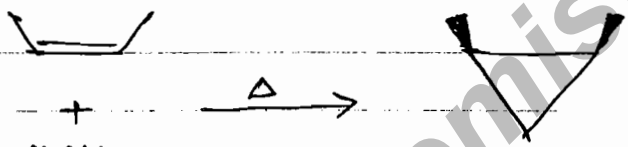


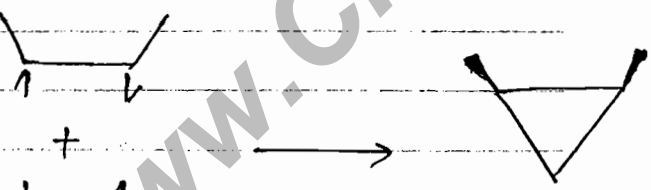
LUMO ✓



HOMO ✗

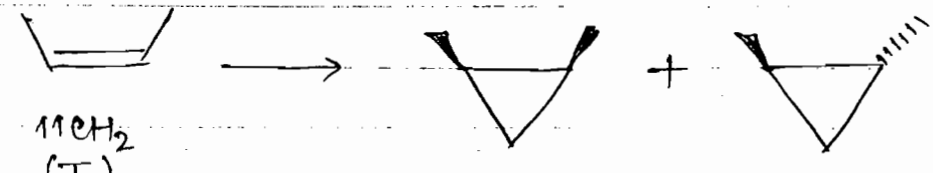
Always take LUMO of carbene because carbene is $e^-$ dificient

* 



Stereospecific pdt.

(Singlet)

* 

(T)

Stereo selective pdt.

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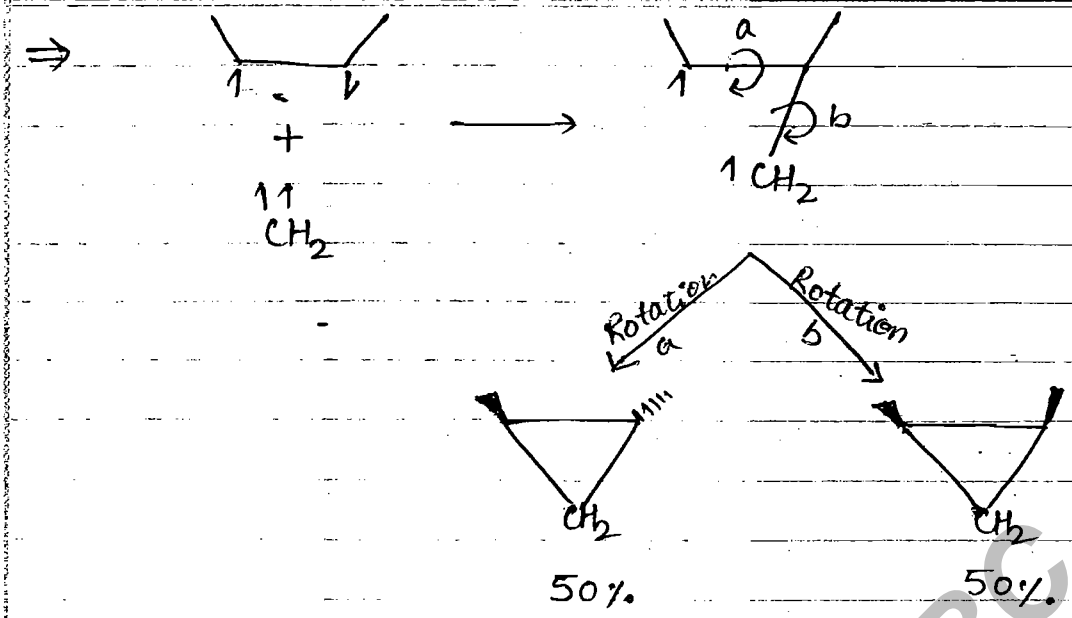
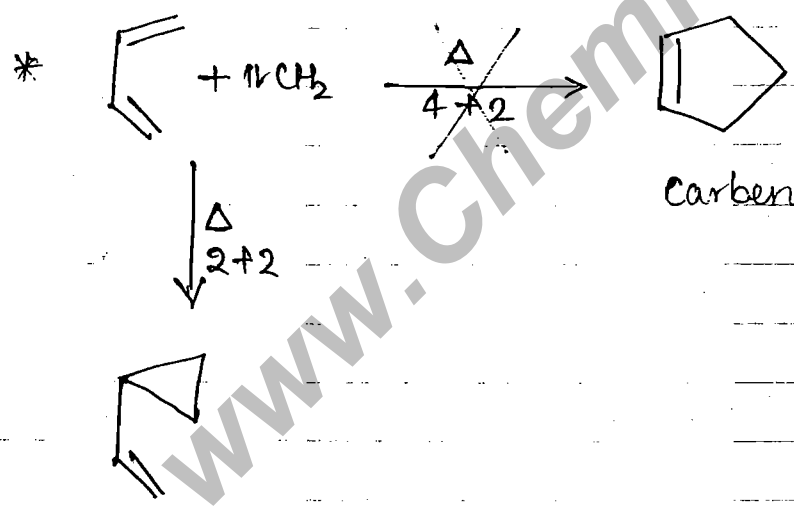



* Initially singlet carbene form but in the presence of Nitrogen, argon, $CCl_4$, Benzophenone, singlet carbene convert into triplet carbene.

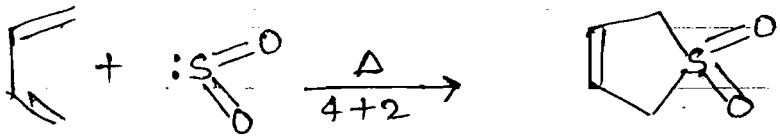



Carbene never gives 4+2 Rxn.

M.Imp.

## CYCLOADDITION Rxn. OF $SO_2$ :-

This also type of cheleotropic rxn.



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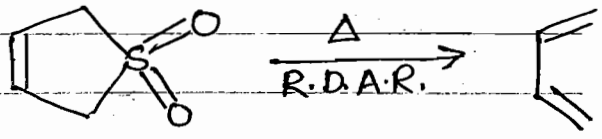
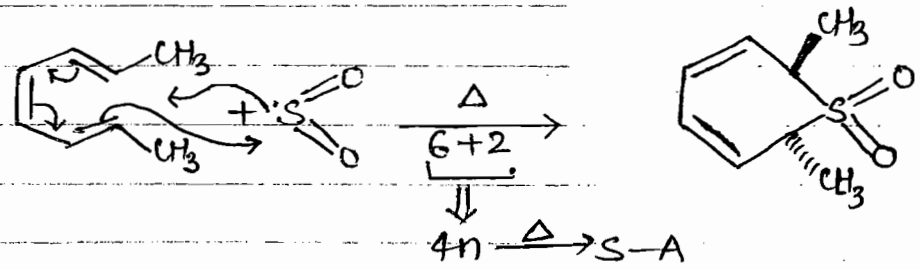



M.Imp. Prob.

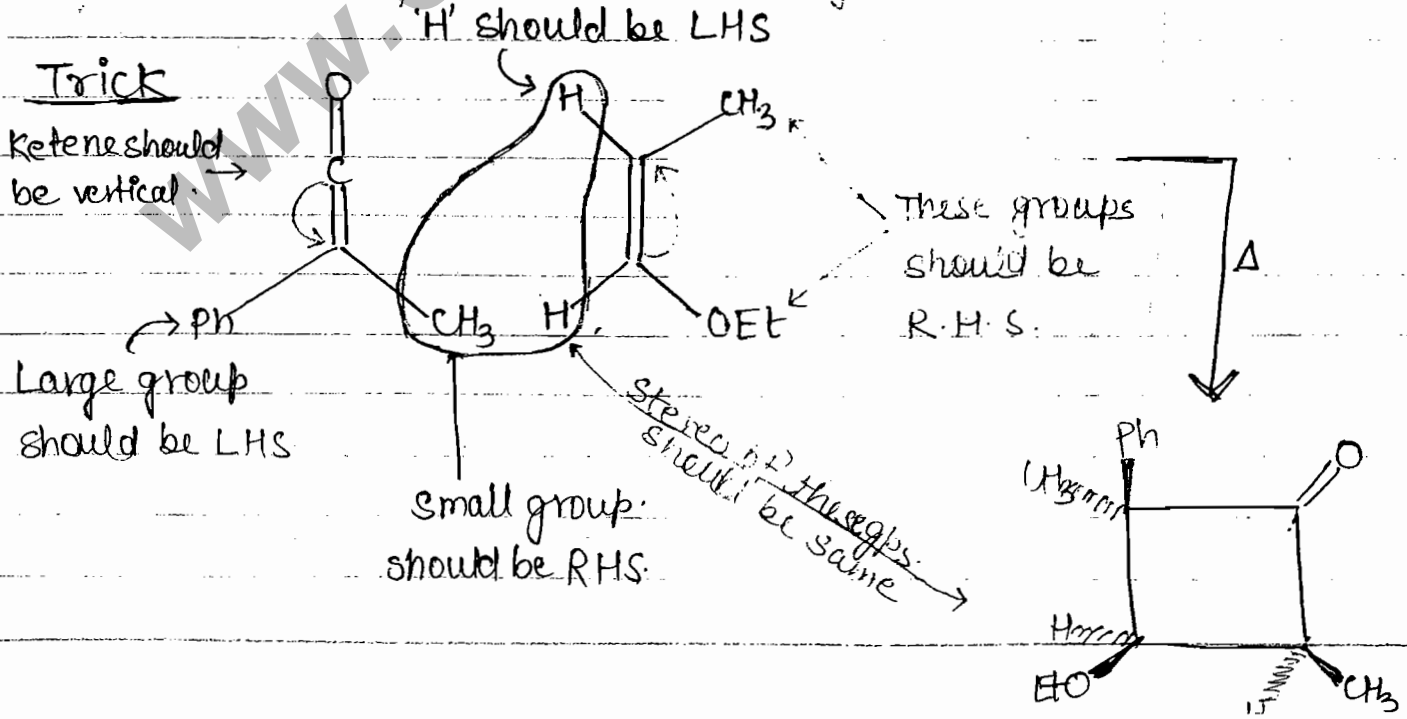



Generally s-s interaction is favourable over s-A interaction. In large system s-A interaction may be take place ~~because of~~ under thermal condition or photochemical condition because of flexibility.

In this case system rotate at 180° to form a bond via bonding interaction. due to this rotation stereochemistry change at one end.

Note. System having 6 C or more C may be ~~fste~~ form s-A bonding because of flexibility.

* Stereochemistry of Ketenes in Cycloaddition Rxn.

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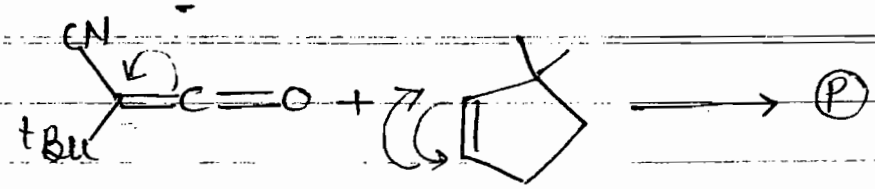
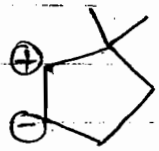
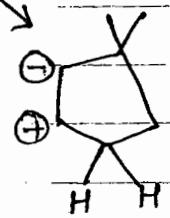
Q.



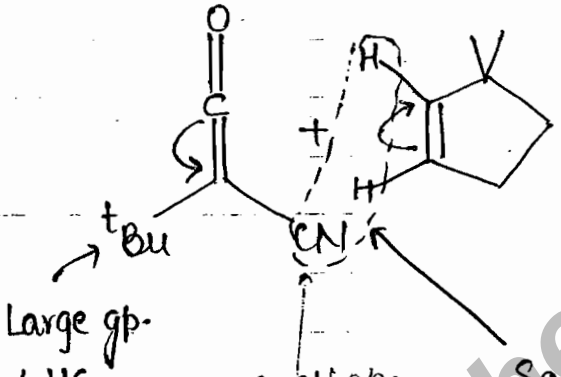


$C^{\oplus}$ stabilise by Inductive effect. (Less stable $C^{\oplus}$)



2 Hyperconjugation str. stabilize to $C^{\oplus}$ (More stable $C^{\oplus}$)

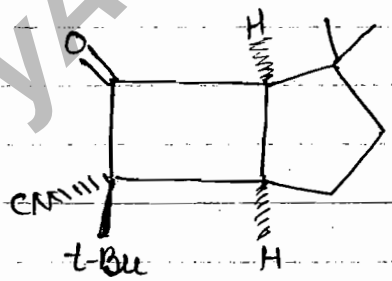
Mech.



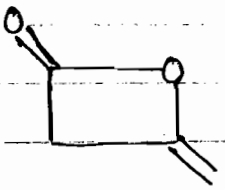
Large gp. LHS

small gp R.HS.

Same stereochemistry

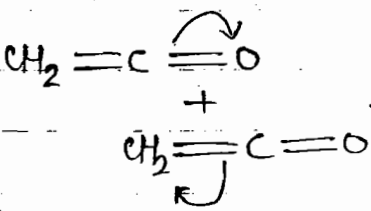


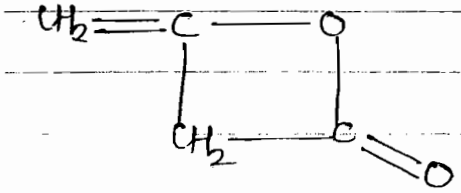
* 2 $CH_2=C=O$ $\xrightarrow{550°C}$



Dimer of ketene

*





Dimerisation of Ketene.

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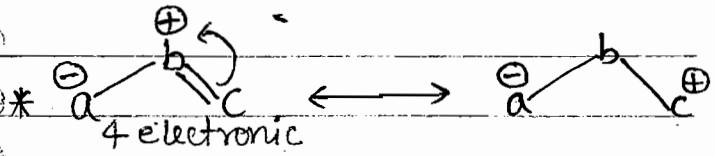
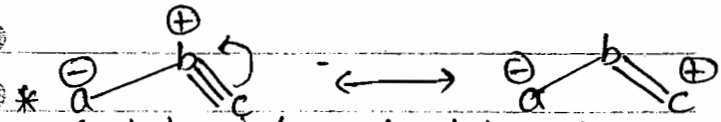
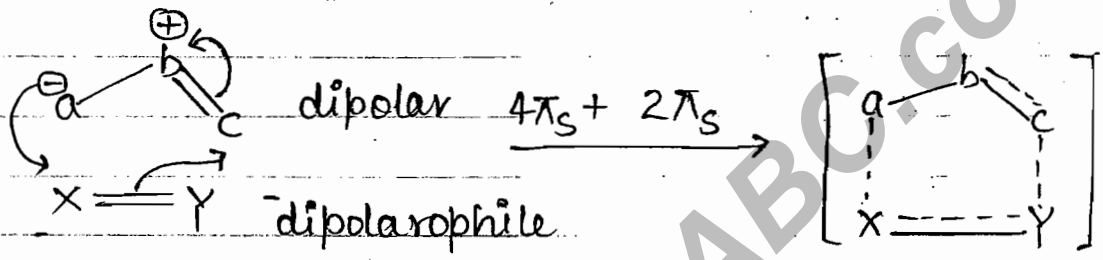
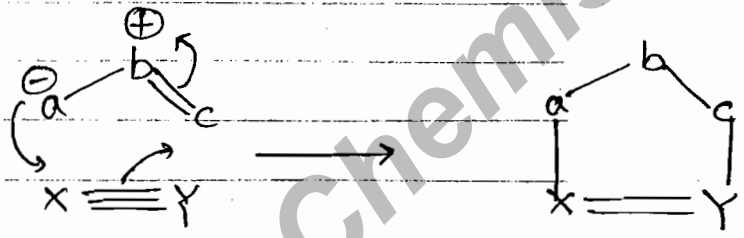
M.Imp

# 1,3-DIPOLAR CYCLOADDITION Rxn.




* Ex. 


Ex. 

* 1,3 dipolar spp. act as an e⁻ rich spp.
* 1,3 dipolar mol. are isoelectronic with allyl carbanion and have four π-e⁻ in system.

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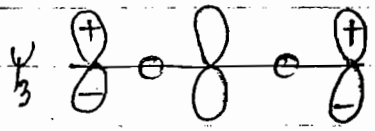
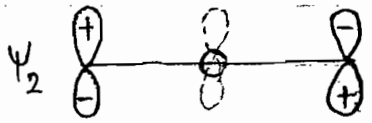
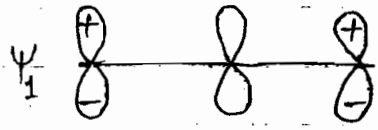
# ORBITAL REPRESENTATION OF 1,3 DIPOLAR CYCLOADDITION Rxn.




2 — LUMO




1 ↿ HOMO




0 ↿↾

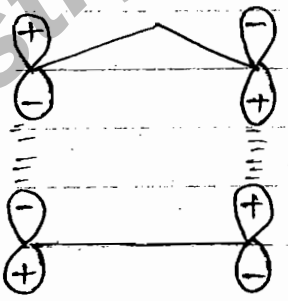
mode Δ

Ex.

HOMO ($\psi_2$)

+

X=Y LUMO ($\psi_2$)

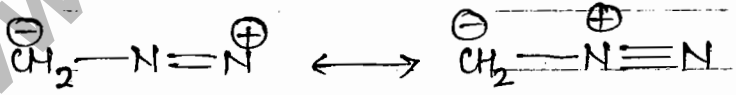


HOMO

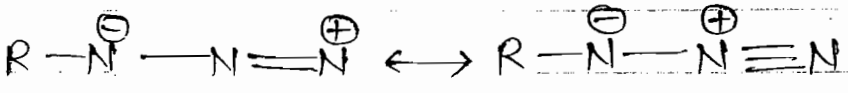
LUMO

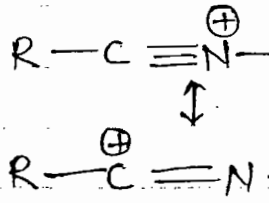
Sol.

1,3 dipolar spp may be ① $CH_2N_2$ (Diazomethane)



② $RN_3$ (Alkyl azide)



③ 

(Alkyl nitrile oxide)

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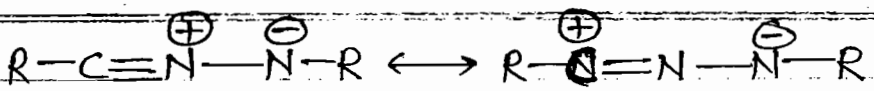
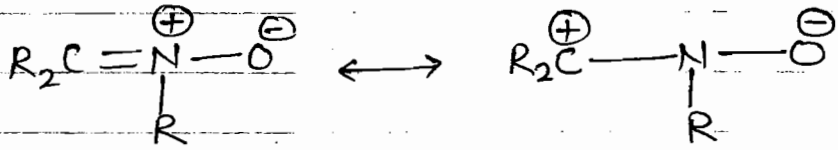
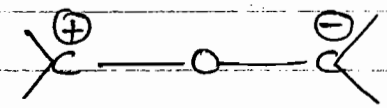
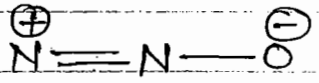
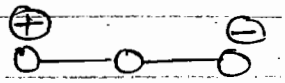
④ Nitrile imine 

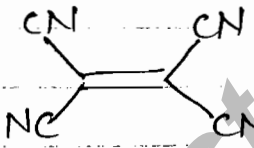
imp.
⑤ Nitrone 

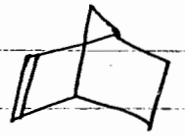
⑥ 

⑦ 

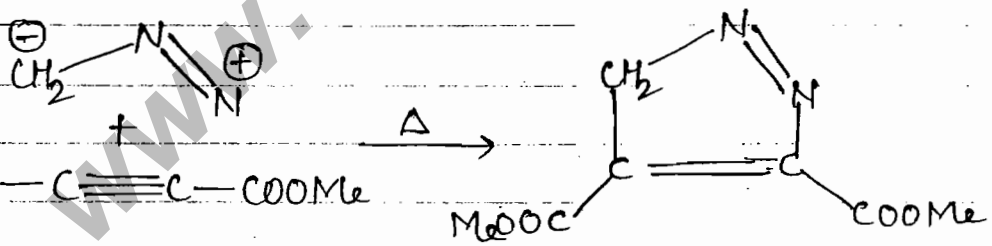
⑧ 

Dipolarophile may be-

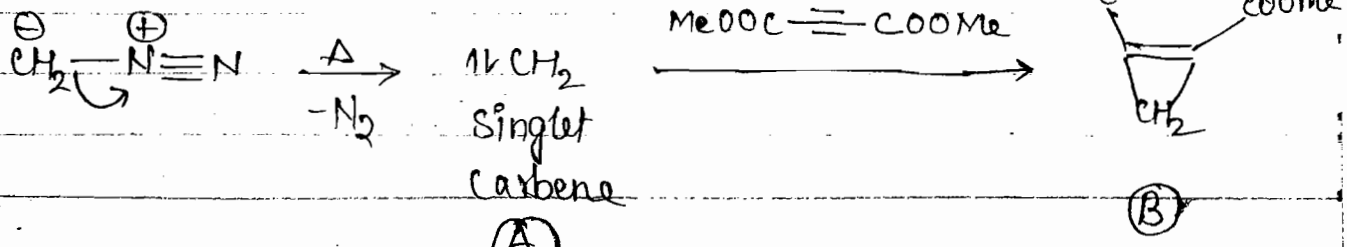
C=C, C≡C,  , MeOOC–C≡C–COOMe,



imp
Prob. $CH_2N_2$ + MeOOC–C≡C–COOMe $\xrightarrow{\Delta}$ (P)



M. imp.
Prob. $CH_2N_2 \xrightarrow{\Delta}$ MeOOC–C≡C–COOMe (A) → (B)



(A)

(B)

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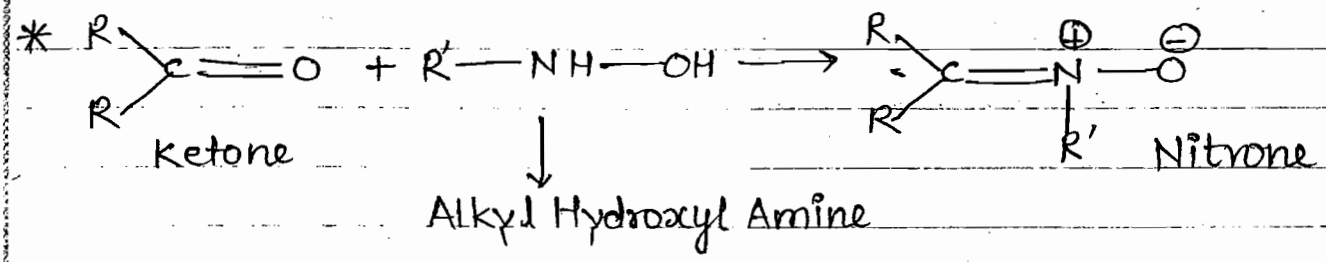
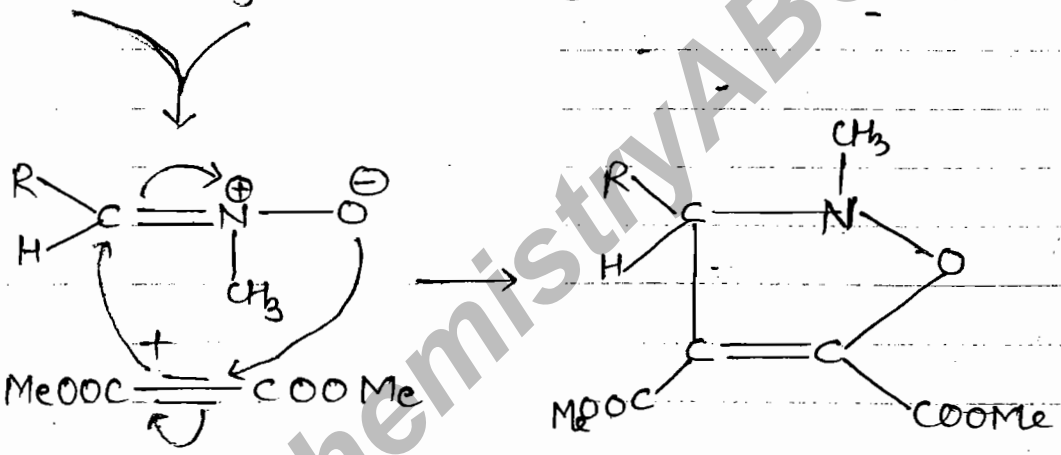
Alkyl Nitrile $R-C\equiv N$

Alkyl Nitrile oxide $R-C\equiv\overset{\oplus}{N}-\overset{\ominus}{O}$

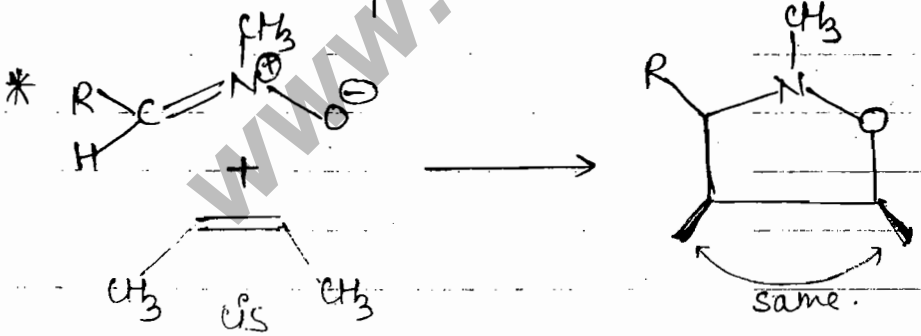


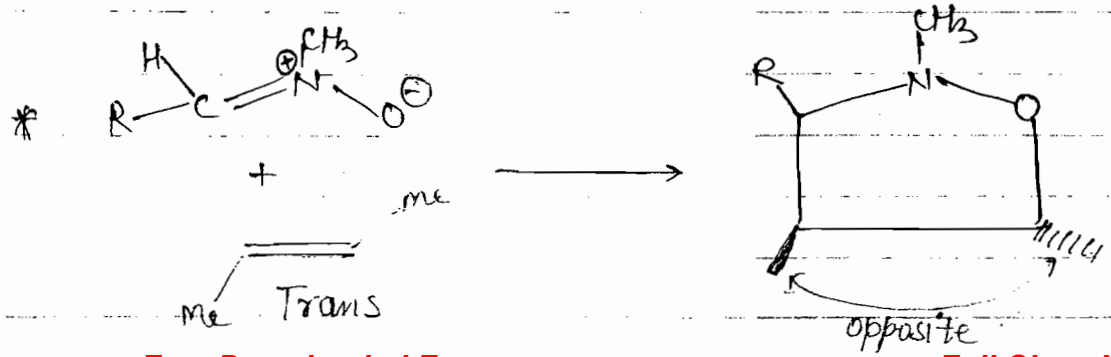

* If $e^-$ withdrowing groups are attached with dipolarophile then H-L gap decreases hence Rate of Rxn. increases. (Just like Diel's Alder).

Prob. $R-CHO + CH_3NHOH \longrightarrow$ (A) $MeOOC-\equiv-COOMe$ (B)




Stereochemistry.

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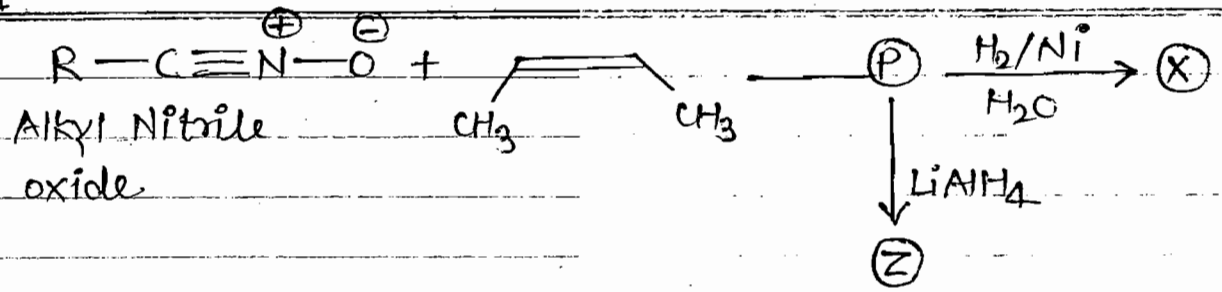
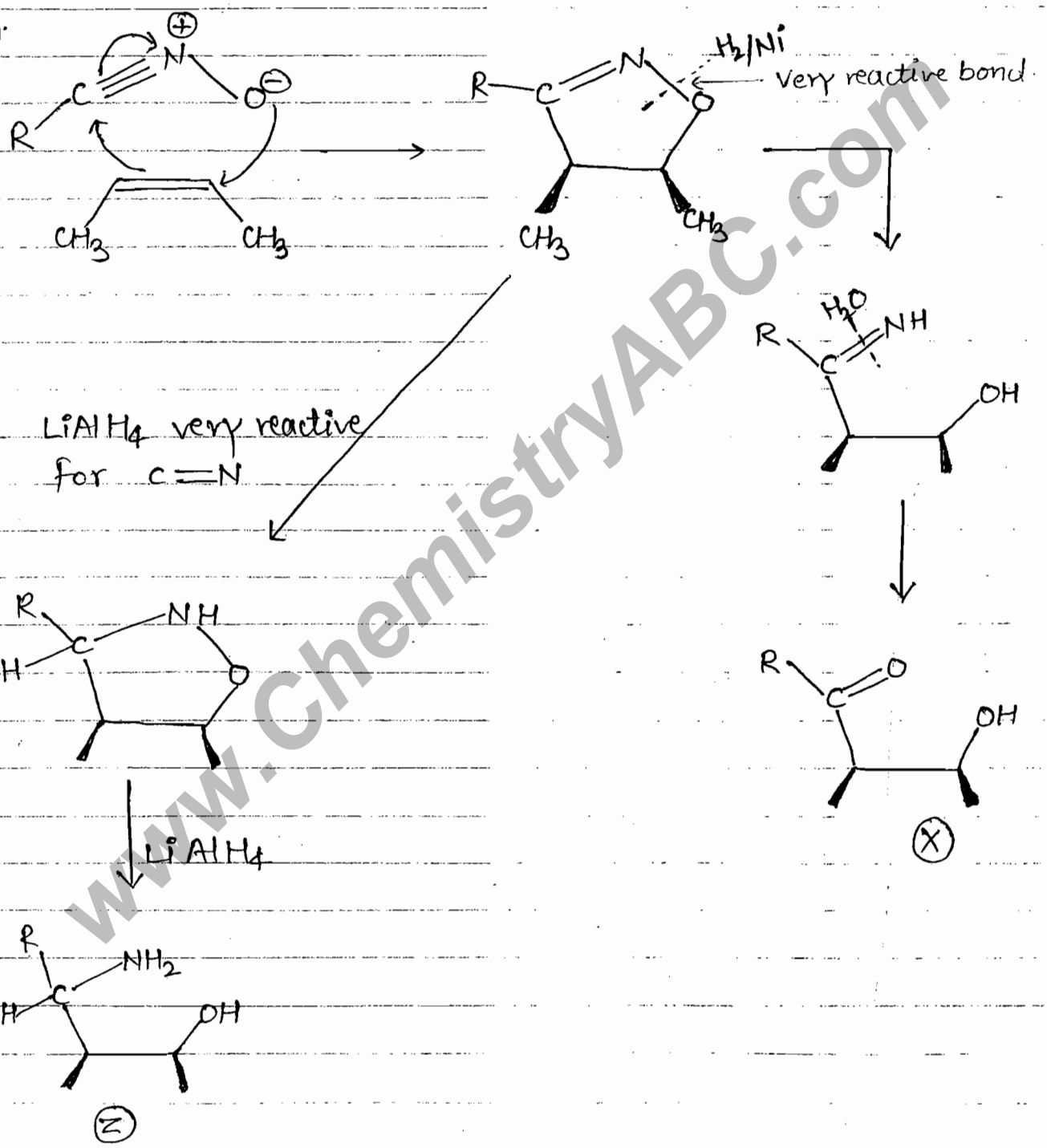
M.Imp.

Prob.




Soln.

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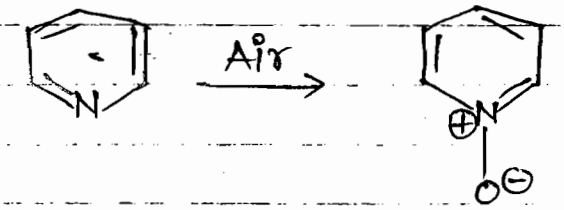
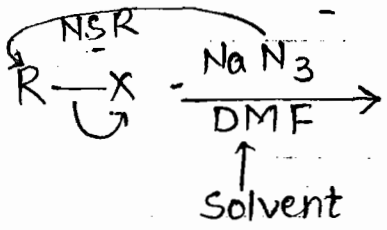
* 

* $R-C\equiv N \xrightarrow[\text{m-CPBA (or) } H_2O_2]{[O]} R-C\equiv\overset{\oplus}{N}-\overset{\ominus}{O}$

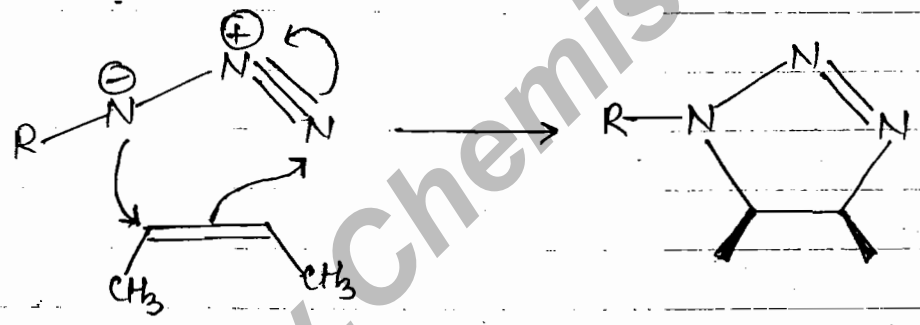
Imp.

## 1,3 DIPOLAR CYCLOADD$^{n}$ OF ALKYL AZIDE :-




$RN_3 + NaX$

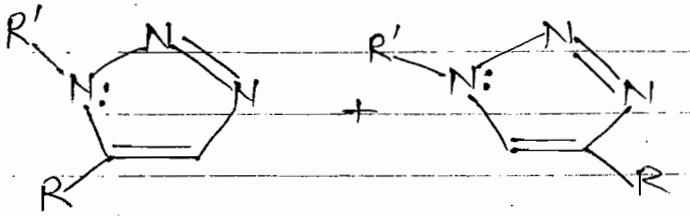
↑ Alkyl Azide

* 

Alkyne (or) alkene

* Rxn. of unsymmetrical alkene with 1,3 dipolar Spp.

When 1,3 dipolar ⊖ react with unsymmetrical alkene then mix of product form.

$R'N_3 + R-C\equiv CH \xrightarrow{\Delta}$ 

Mix of Product found.

1,5 isomer + 1,4 isomer

Regioisomers

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Sodium Ascorbate NaAs

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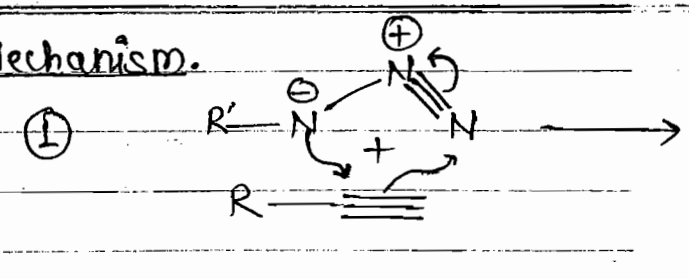
R—C≡C—R Internal Alkyne.

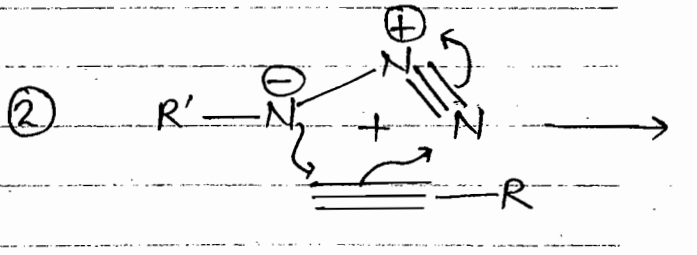
R—C≡CH Terminal alkyne

Mechanism.



1,5 isomer

Trizole



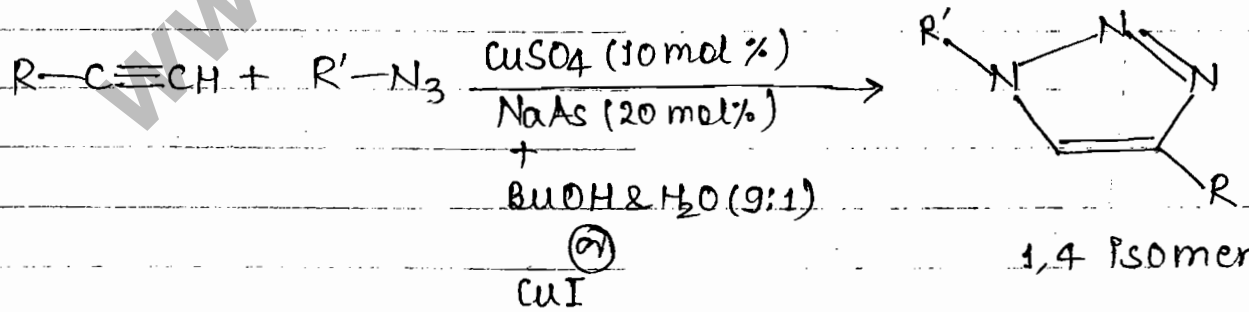
1,4 isomer

* Both products are aromatic (6πe⁻)
* All 1,3 dipolar gives 5 memb. heterocyclic comp. on reacting with dipolarophile.

# CLICK REACTION :-

Rxn. b/w terminal alkyne and alkyl azide in the presence of $CuSO_4$ (10 mol%) & NaAs (20 mol %) in tertiary Butanol and $H_2O$ (9:1) yield only 1,4 isomer. Click Rxn. is 100% regioselective or regiospecific. Click Rxn. is (Cu I) catalysed Rxn.

Imp.




* $Cu^{II}SO_4$ + NaAs ⟹ $Cu^{I}I$

↑ It changes $Cu^{II}$ into $Cu^{I}$.

↑ We can take CuI in place of $CuSO_4$ & NaAs.

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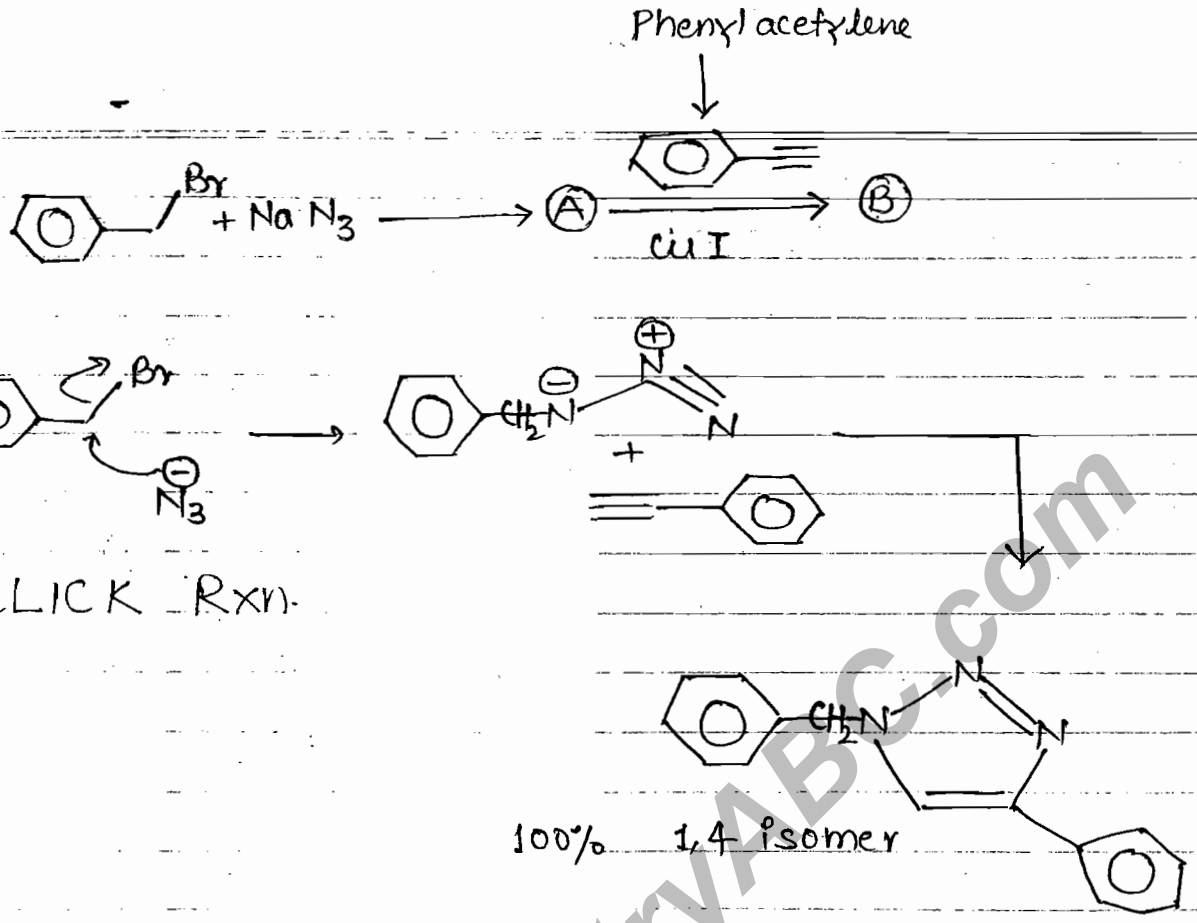


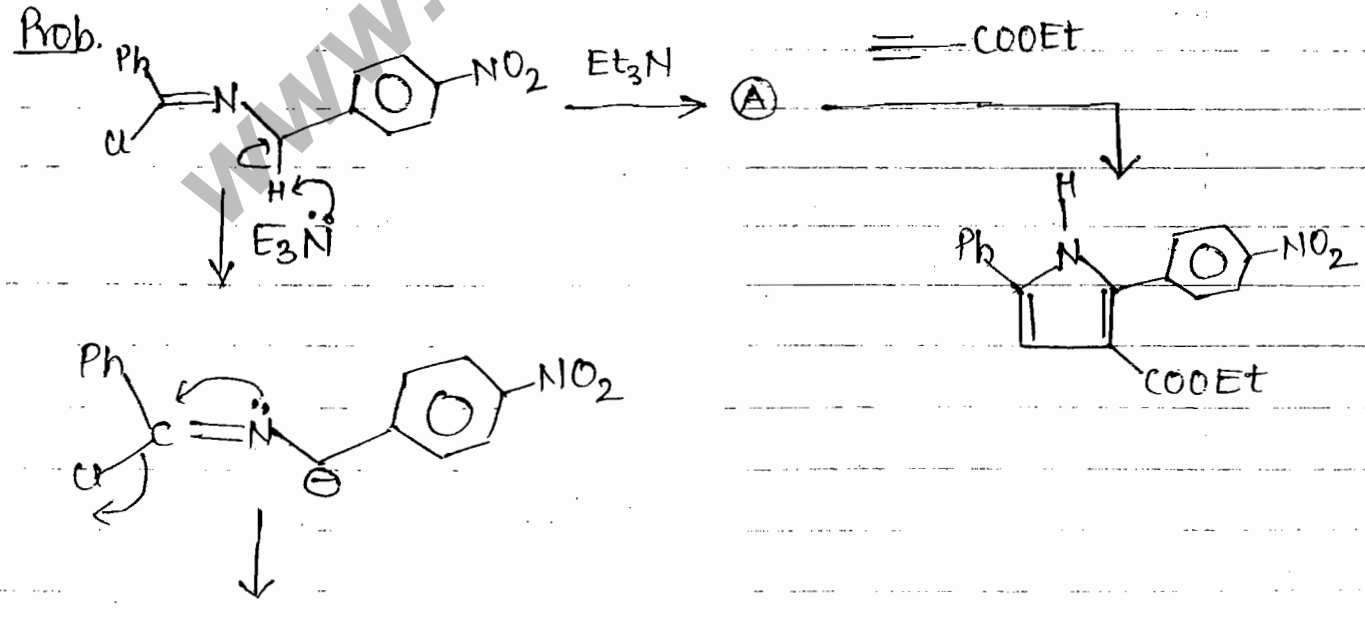

CLICK Rxn.




100% 1,4 isomer

## Application of CLICK Rxn.

* In polymer chemistry.
* In drug chemistry
* In peptide chemitry
* In Green chemistry
* In Supramolecular chemistry

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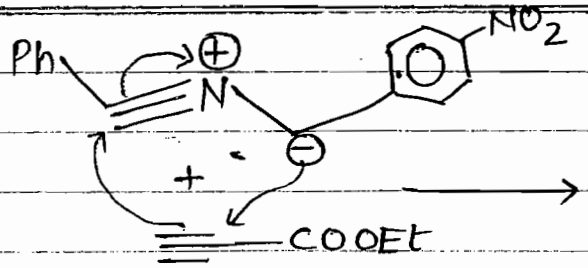
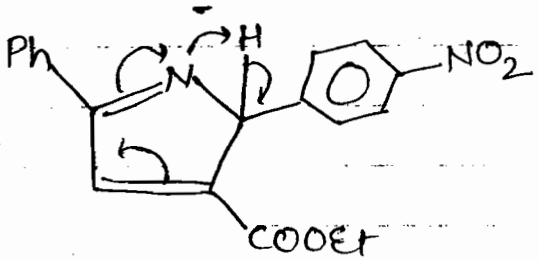
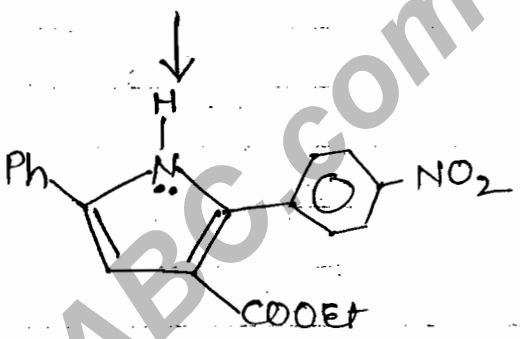


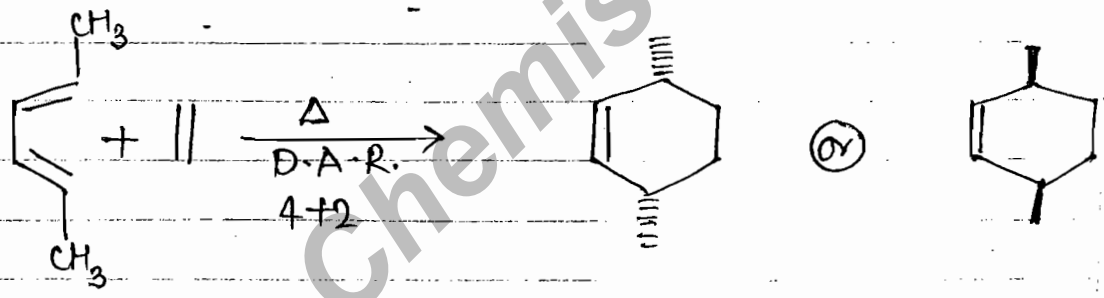




Unstable

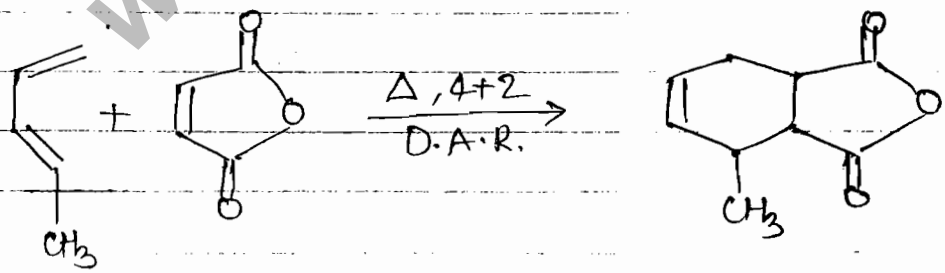



Stable (Aromatic)

Q trans, trans 2,4 hexadiene + ethene $\xrightarrow{\Delta}$ P




Q trans 1,3 pentadiene + Maleic Anhydride $\xrightarrow{\Delta}$

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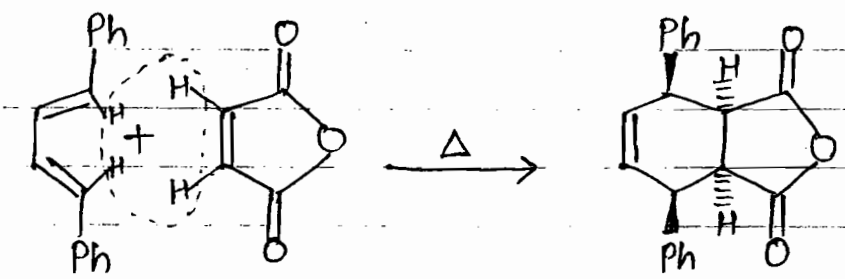
Q trans, trans 1,4 diphenyl 1, 3 Butadiene + Maleianhydride

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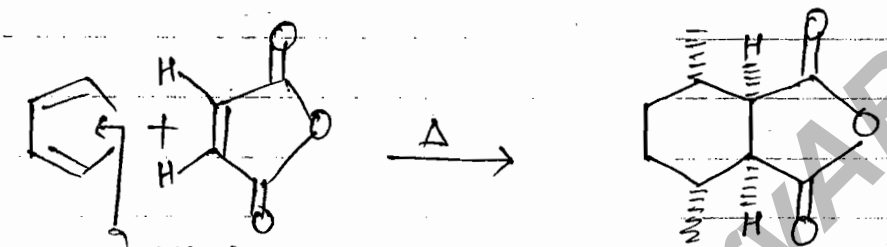
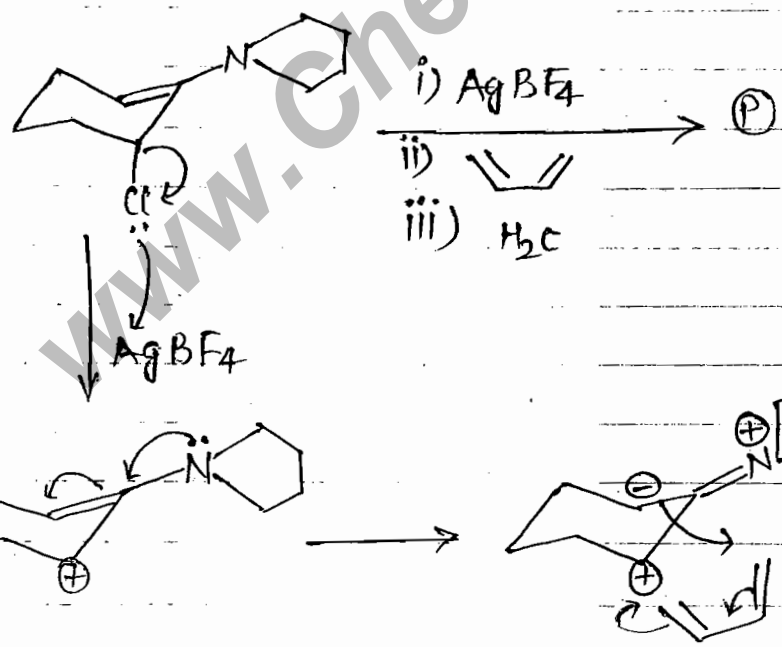



अगर ये Alkyl
Cavity में हैं तो anhydride के H और इनकी Stereo same होगी।

## CYCLOADD$^n$ Rxn. OF CATION & ANION

Imp. Prob.

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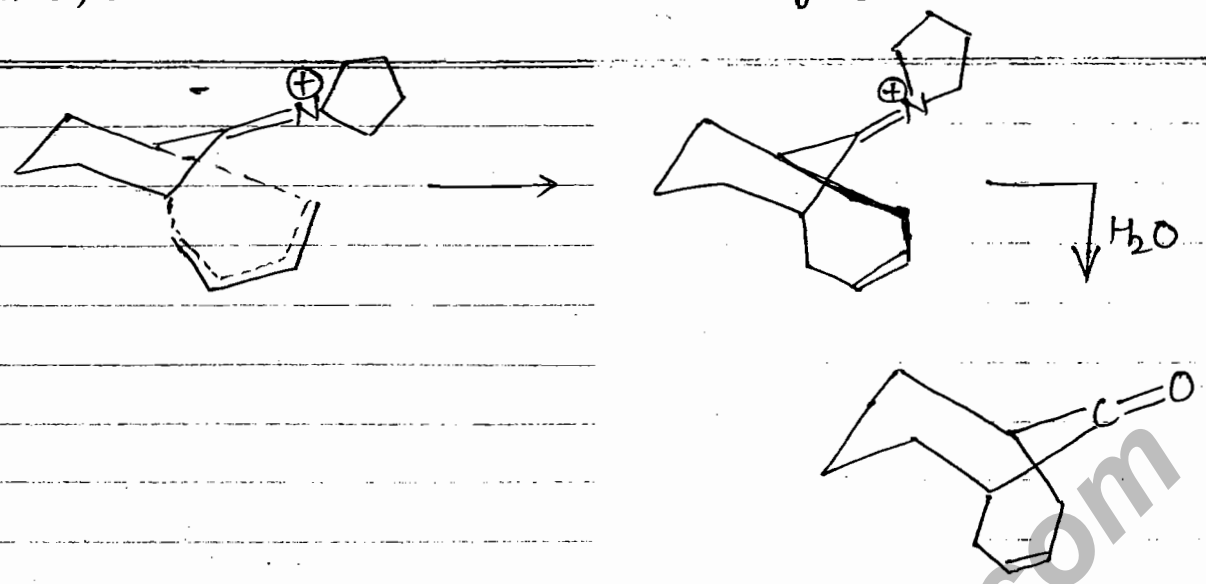
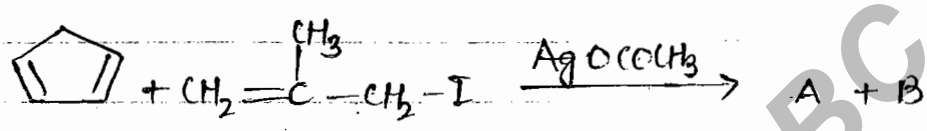
25/09/2014

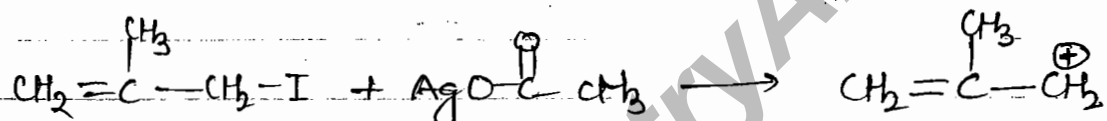
- Generally
- If Cl, Br, I not in substrate and silver is given as catalyst
- then Cl, Br or I will be remove as Leaving group.

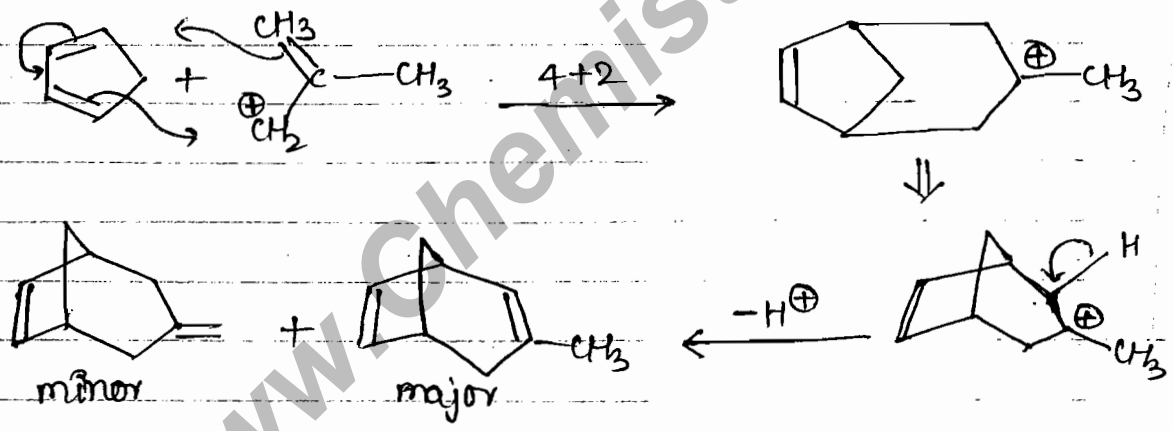



Imp.

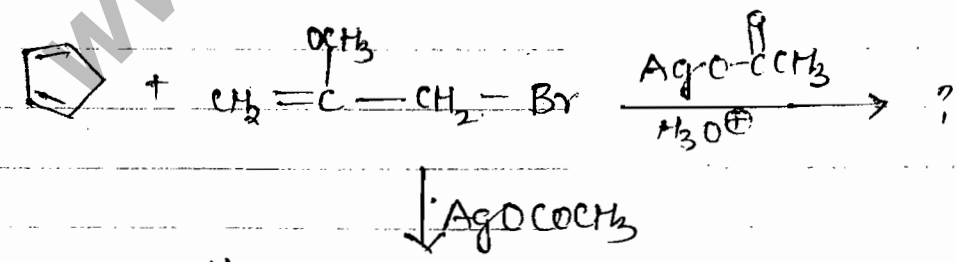
Prob.




Prob.

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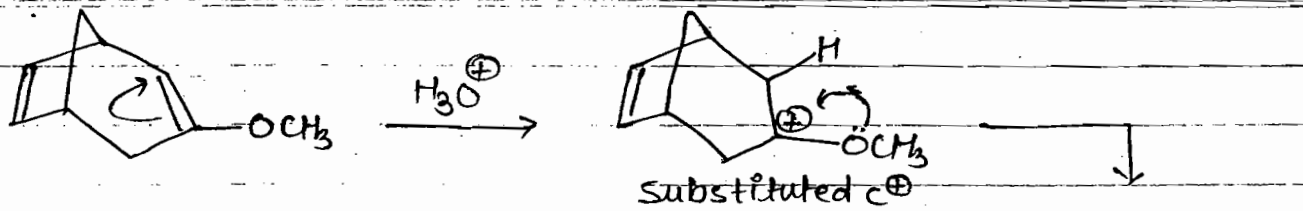
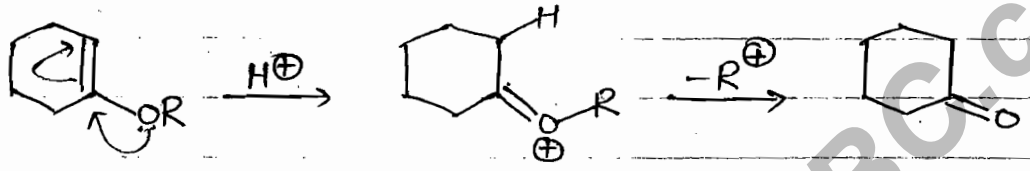
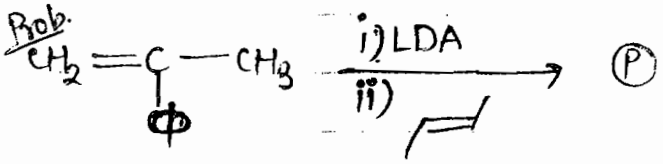
to break.

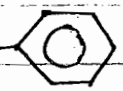


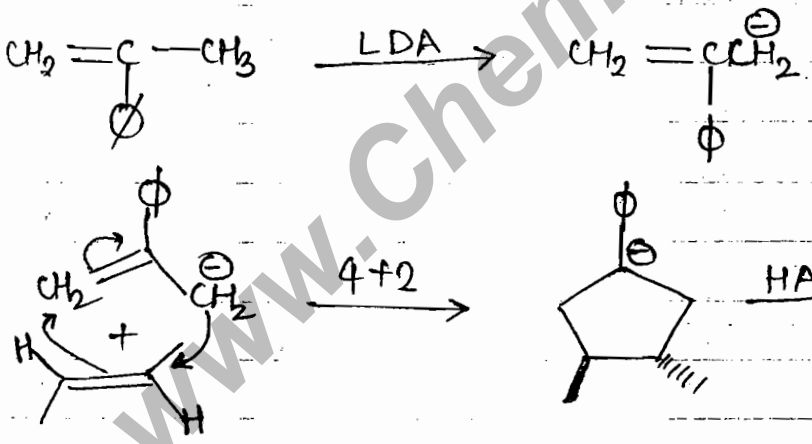

* 


Imp.

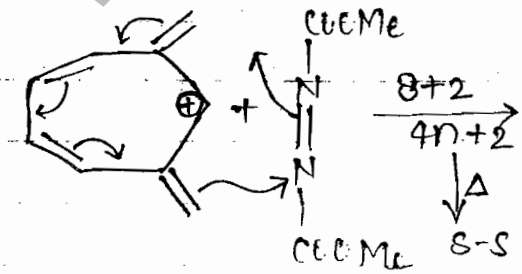
Rob.

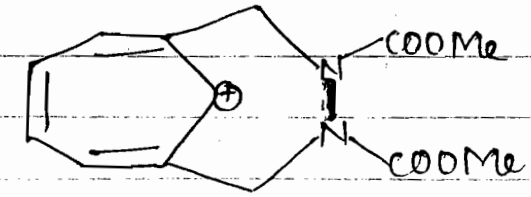



∴ $\phi \Rightarrow Ph^- \Rightarrow$ 




Rob.




* If rxn. condⁿ is not given then assume thermal condⁿ.

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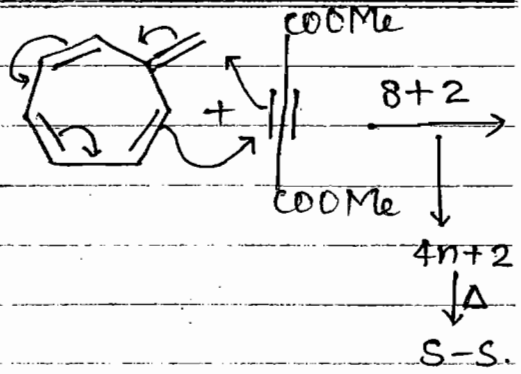
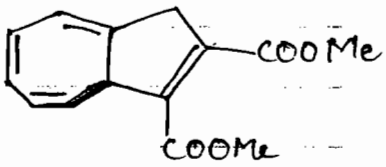
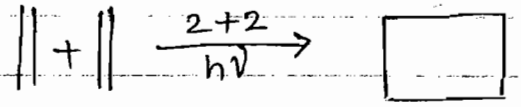
Prob.




# 2+2 CYCLOADDITION Rxn.

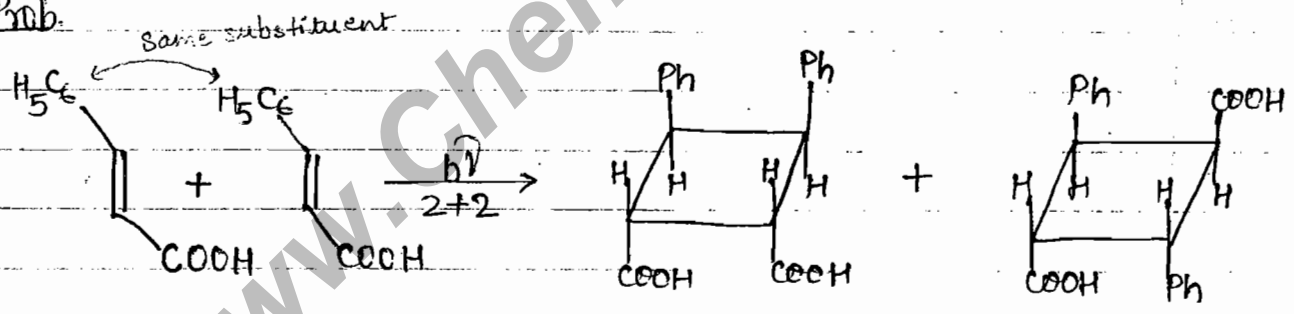
* 2+2 Cycloaddition rxn: photochemically allowed and thermally forbidden. S-S addition in ~~Δ~~ hν condⁿ.

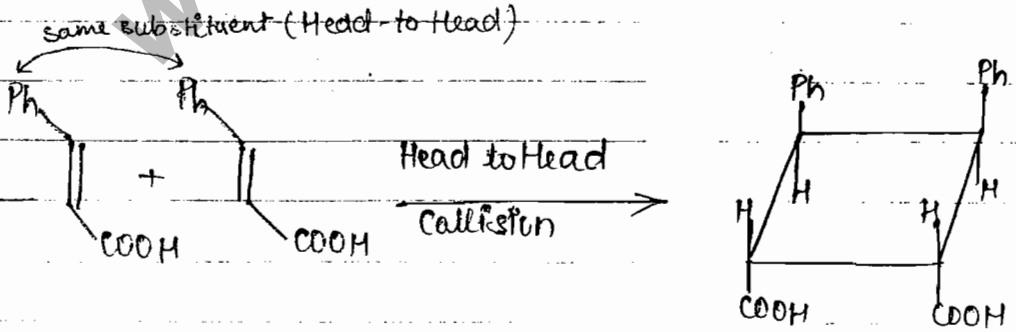



Imp

* HOMO - HOMO interaction in 2+2 cycloadⁿ Rxn in hν condⁿ

Prob.

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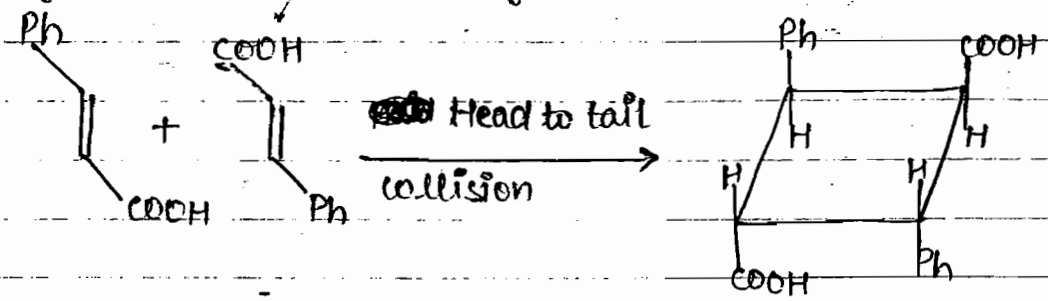
Head to tail

substituent functional gp.

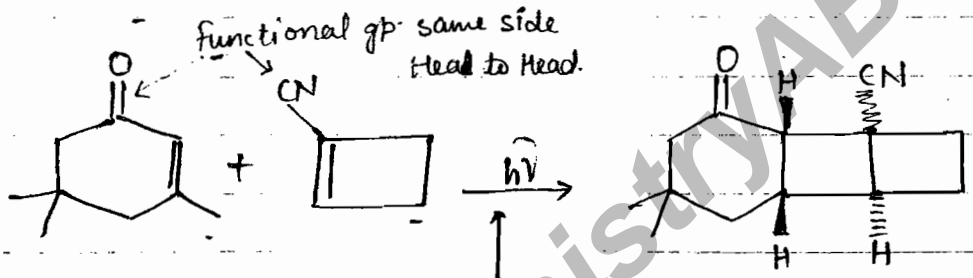



Collision

Head to Head
if EWG present

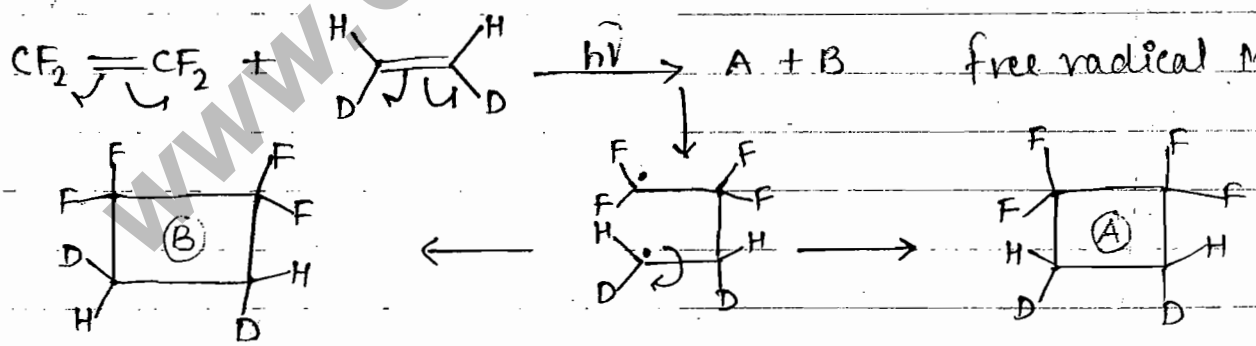
Head to tail
If ERG present

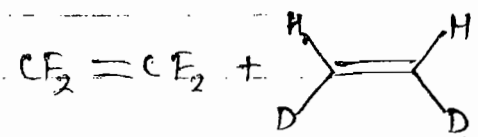
Q.

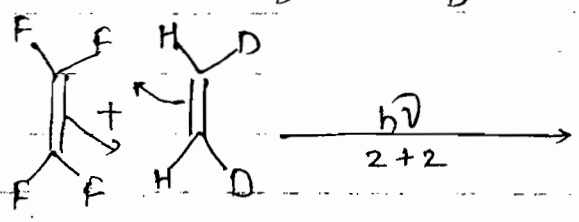



Head-Head
Collision.

Q. Which mechanism involve in the following reaction.




Q.  $\xrightarrow{h\nu}$ (A) Pericyclic Mech.

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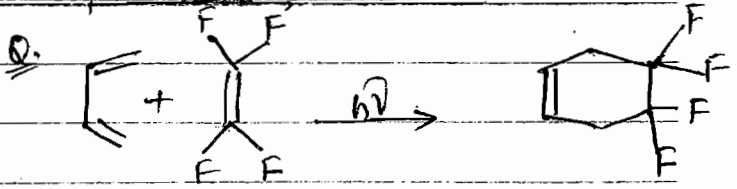
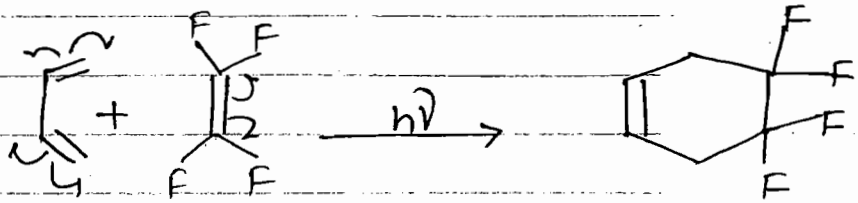
4+2 Cycloadd$^{n}$ impossible in hν cond$^{n}$ so it will follow free radical mech.

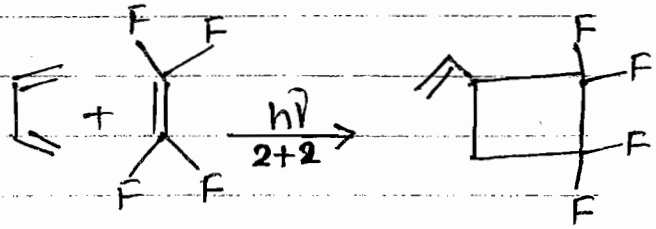
Q.



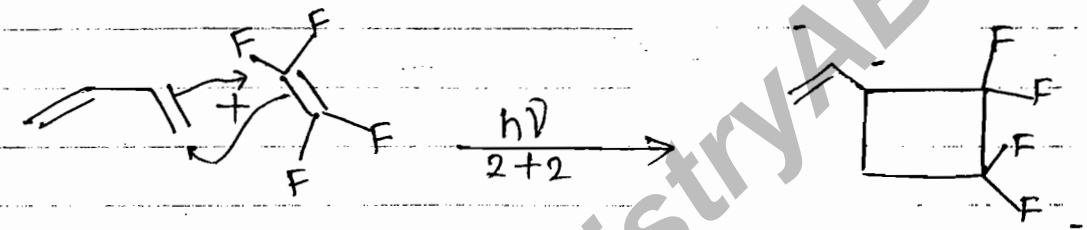
Free radical Mech.



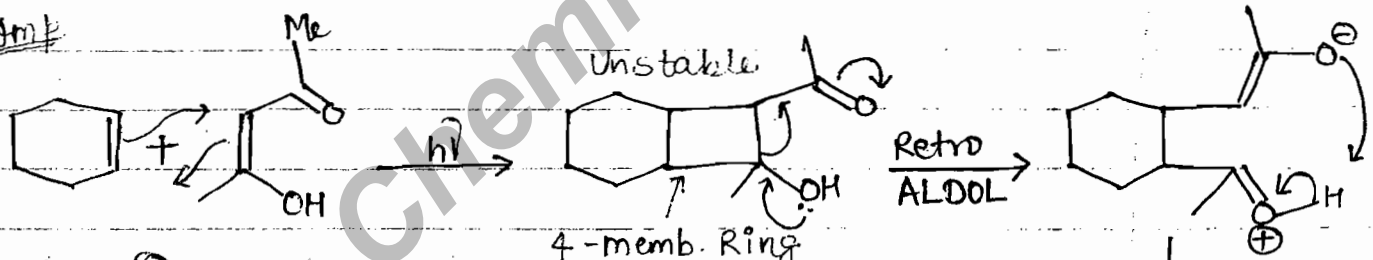
Q



Pericyclic Mech.



M.Imp

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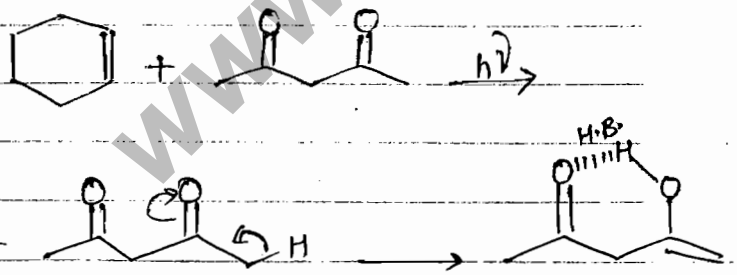


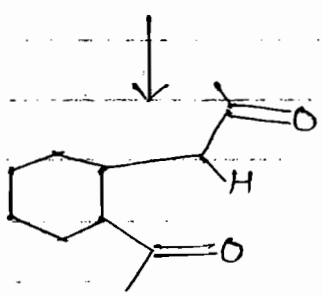

Stable

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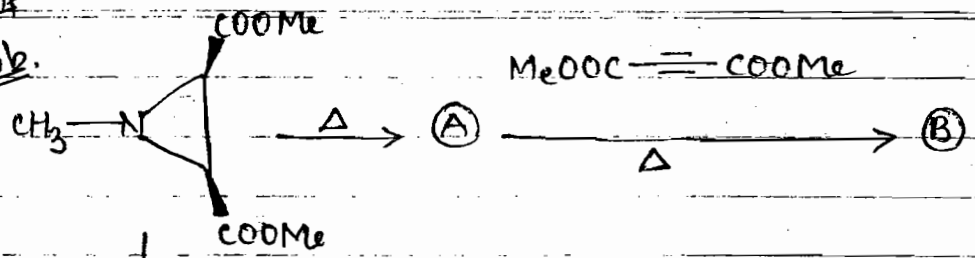
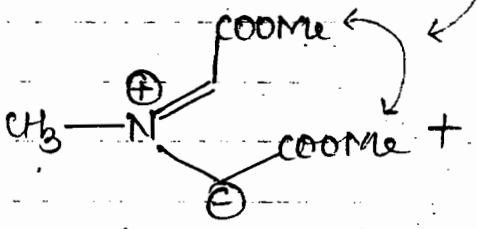
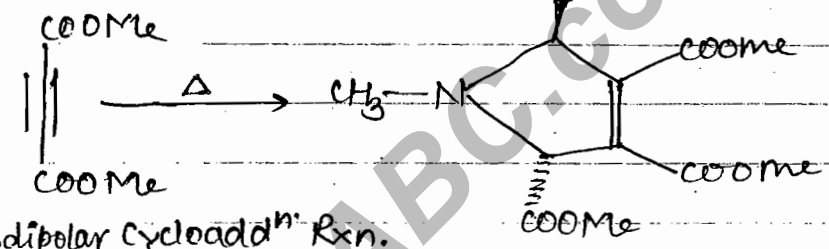
Prob.




Δ 4n con → Stereo change




1,3 dipolar




1,3 dipolar Cycloaddⁿ Rxn.

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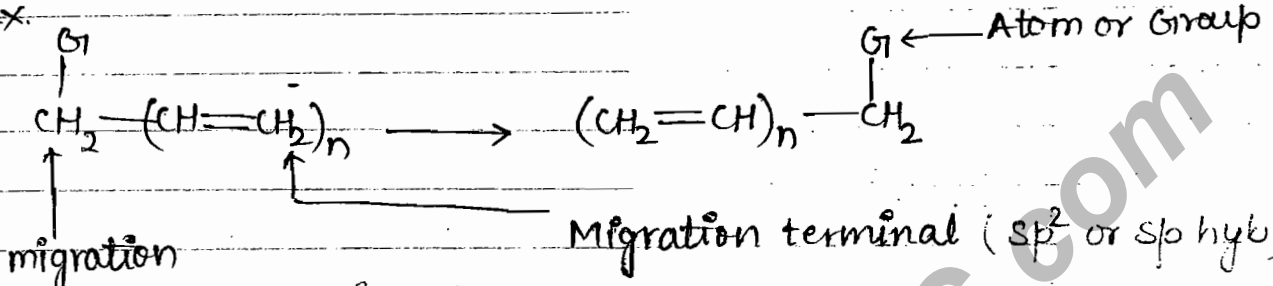
# SIGMATROPIC REACTIONS

It involve the migration of sigma bond within the π-framework.

Ex.




↓

just adjacent to π-frame work

⇒ After reaction, migration origin becomes $sp^2$ & migration terminal becomes $sp^3$ or $sp^2$ hyb.

NAMING OF SIGMATROPIC Rxn:

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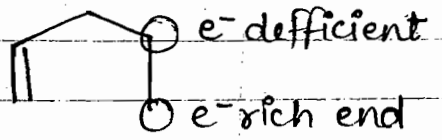
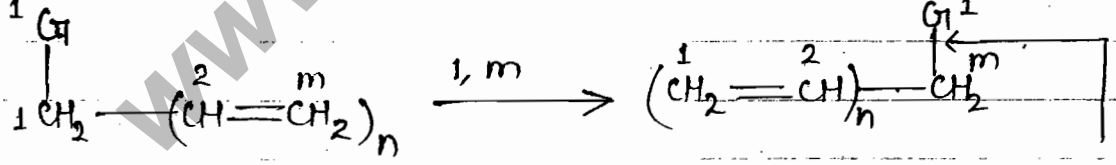
# Sigmatropic Rxn

- 7,7 sigmatropic
- 1,m sigmatropic Rxn.
  - 1,3 — One double bond present
  - 1,5 — Two double bond present
  - 1,7 — Three double bond present
  - 1,11 — Five double bond present
- 3,3 sigmatropic (In 1,5 diene)
  - Cope rearrangement
  - Claisen cope rearrangement
  - Azza cope rearrangement
  - Claisen rearrangement
- 5,5 sigmatropic
  - oxy cope rearrangement
- 2,3 sigmatropic

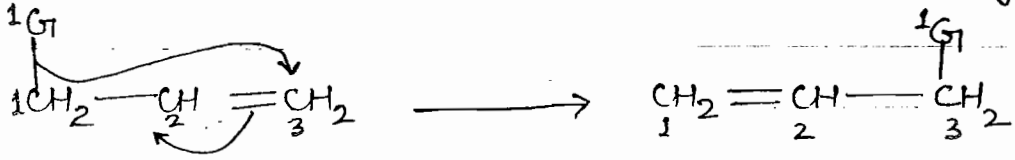



Ex.




New bond forming b/w 1 & m so 1,m sigmatropic Rxn.

Ex.




1,3 sigmatropic Rxn.

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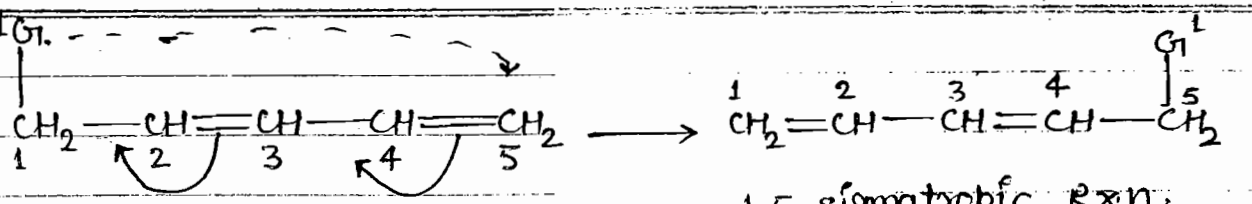
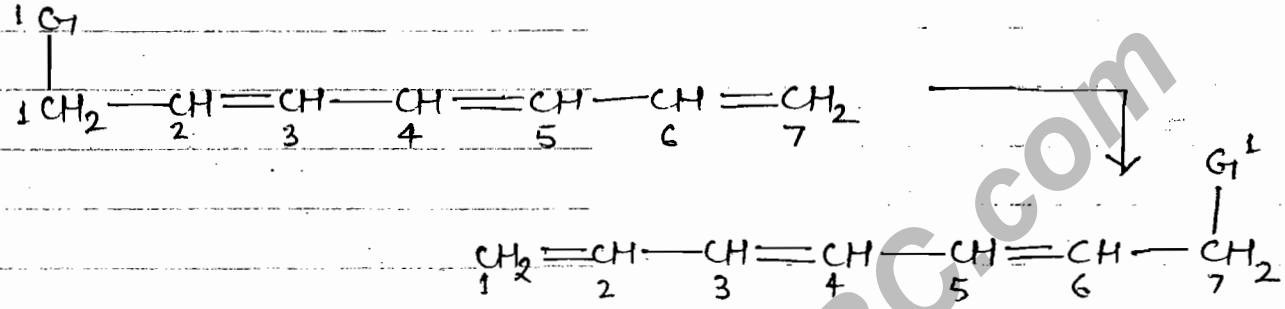
Ex.



1,5 sigmatropic Rxn.

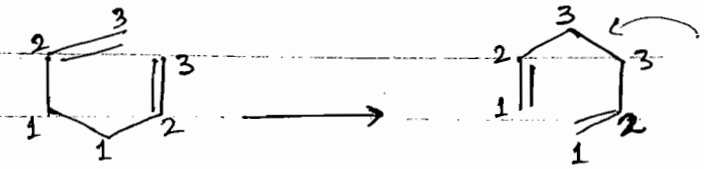
Ex.



1,7 sigmatropic Rxn.

| | |
|---|---|
| Alkene double bond in conj | Rxn. |
| 1 double bond. | 1,3 sigmatropic |
| 2 " " | 1,5 " |
| 3 " " | 1,7 " |
| 4 " " | 1,9 " etc |

3,3 Sigmatropic Rearrangement:



New sigma bond bpw 3 & 3. i.e. 3,3 sigmatropic rearrangement.

1,5 diene

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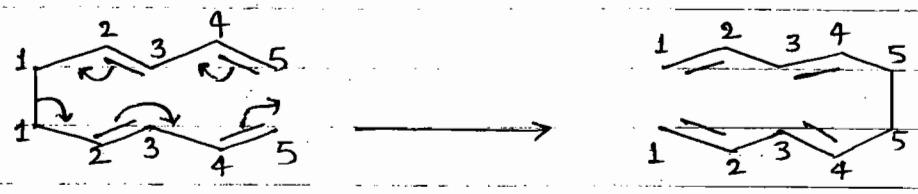
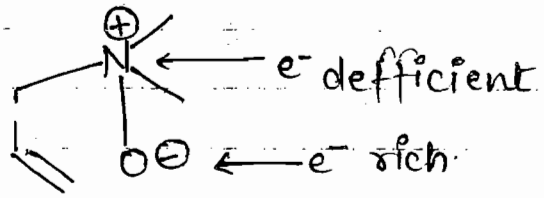
## 5,5 sigmatropic Rearrangement

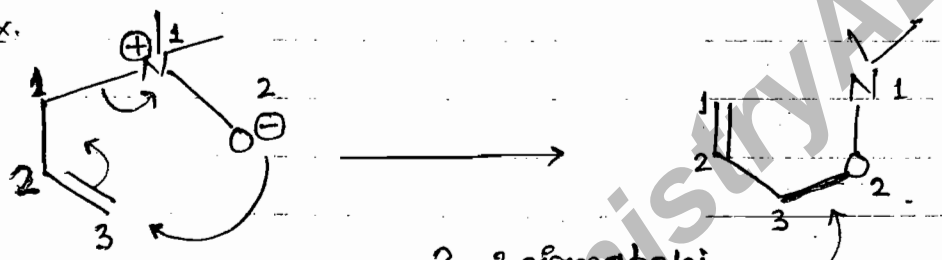


M. Imp.

## 2,3 Sigmatropic




Ex.




System

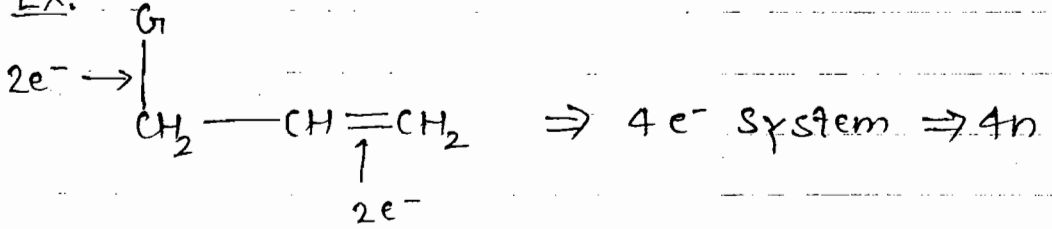
4n

4e⁻, 8e⁻, 12e⁻, 16e⁻

4n+2

6e⁻, 10e⁻, 14e⁻, 18e⁻

Ex.

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Ex. $CH_2(2e^-)-CH=^{2}CH-CH=^{2}CH_2$ $\Rightarrow 6e^- = 4n+2$ system.

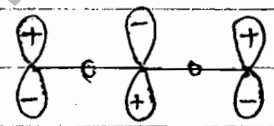
Trick

Sigmatropic rearrangement (Most Imp.)

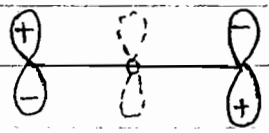
| | | | | |
|---|---|---|---|---|
| 1,3 | 1+3 | = 4 $e^-$ | $\Rightarrow$ | 4n |
| 1,5 | 1+5 | = 6 $e^-$ | $\Rightarrow$ | 4n+2 |
| 1,7 | 1+7 | = 8 $e^-$ | $\Rightarrow$ | 4n |
| 1,9 | 1+9 | = 10 $e^-$ | $\Rightarrow$ | 4n+2 |
| 3,3 | 3+3 | = 6 $e^-$ | $\Rightarrow$ | 4n+2 |
| 5,5 | 5+5 | = 10 $e^-$ | $\Rightarrow$ | 4n+2 |
| 2,3 | 2+3 | = 5 $e^-$ | | add 1 $e^-$ extra = 6 $e^-$ (4n+2) |

## M.O. Diagram of Allylic System

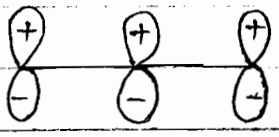
$CH_2(\cdot)-CH=CH_2 \xrightarrow{\text{Homolytic}} \dot{C}H_2-CH=CH_2$ (Allylic Radical)



2 $\psi_3^*$ — LUMO — 1 — HOMO



1 $\psi_2$ — HOMO — 1



0 node $\psi_1$ — 1↓ — 1↓

$\Delta$ $h\nu$

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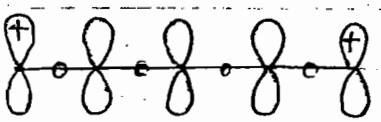
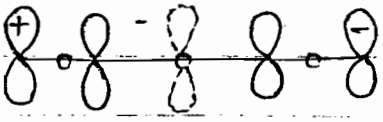
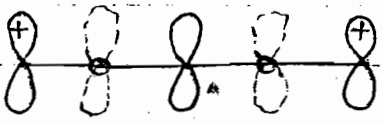
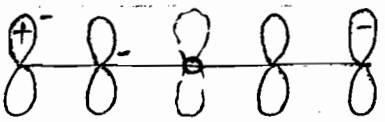
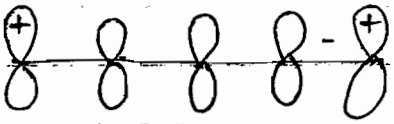
# M.O. Representation of Pentadienyl System :-

4 $\psi_5^*$  ——— ——— LUMO

3 $\psi_4^*$  LUMO ——— 1 ——— HOMO

2 $\psi_3$  1 HOMO ———

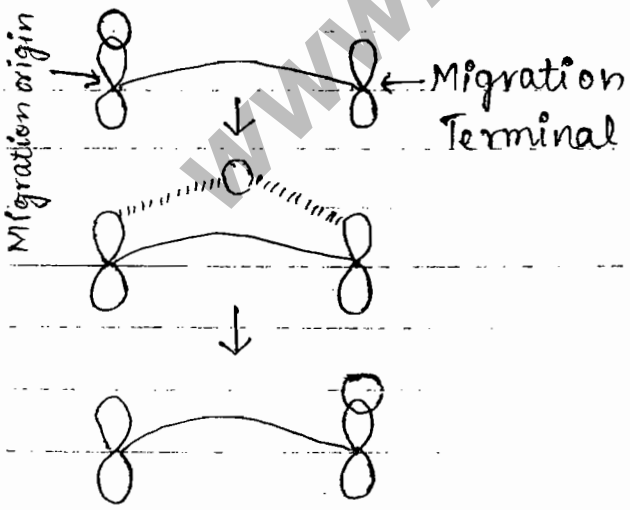
1 $\psi_2$  ↿⇂ ——— ↿⇂

0 $\psi_1$  ↿⇂ ——— ↿⇂

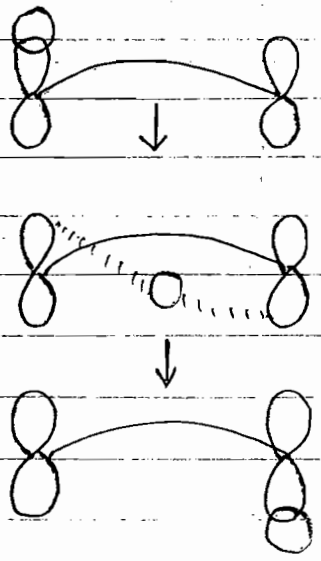
Node Δ hν

## Migration of atom (H or D)

### Suprafacial




### Antarafacial



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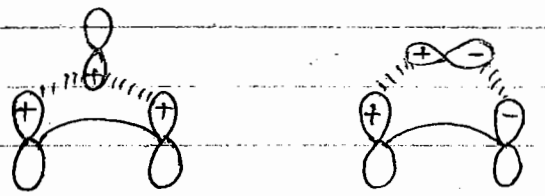
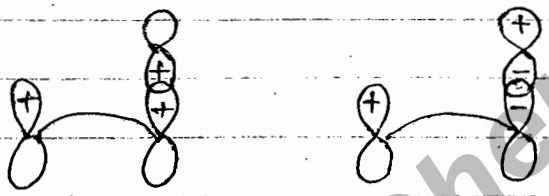
# Migration of group of Atom (Alkyl)

- Suprafacial
  - Retaintion
  - Inversion
- Antara facial
  - Retainsion
  - Inversion





Migration of alkyl groups always takes place via Suprafacial with retention or inversion.

In the atom migration (H or D) suprafacial migration favouble than Antrafacial. In small systems always ~~antrafac~~ suprafacial migration takes place but never atrafacial.

In large system antrafacial migration may take place because of system flexibility.

## Migration of HYDROGEN atom:-

### 4n System:-

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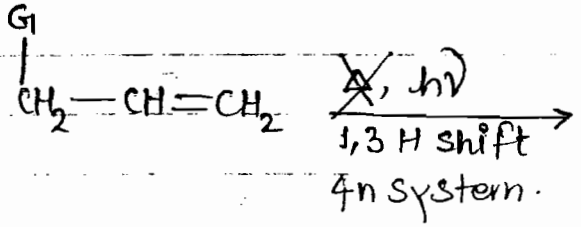
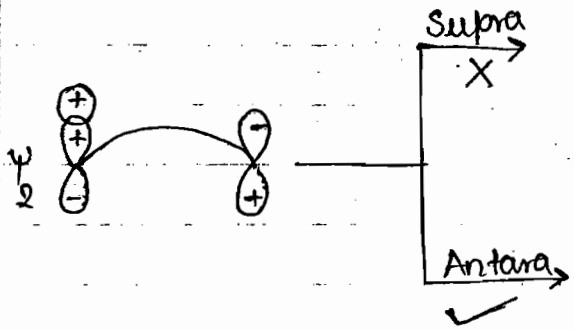
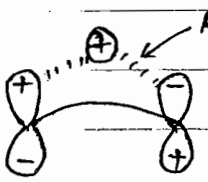



## Thermal Condition

HOMO $\psi_2$



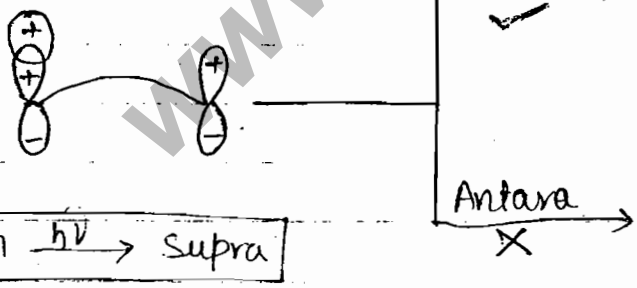

Geometrically allowed but symmetrically forbidden.

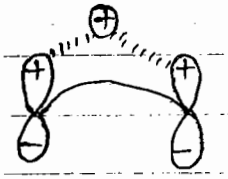
Geometrically forbidden but symmetrically Allowed.

* 4n $\xrightarrow{\Delta}$ Antara System

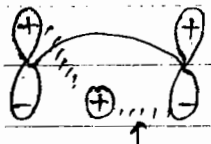
## Photochemical Condition

HOMO $\psi_3^*$



Geometrically & symmetrically allowed.




Geometrically & symmetrically forbidden.

4n $\xrightarrow{h\nu}$ Supra

1,3 H shift NEVER takes place under thermal condition because of Antarafacial migration. while 1,7 H shift can take place in Δ condⁿ. even it is antarafacial migration, the

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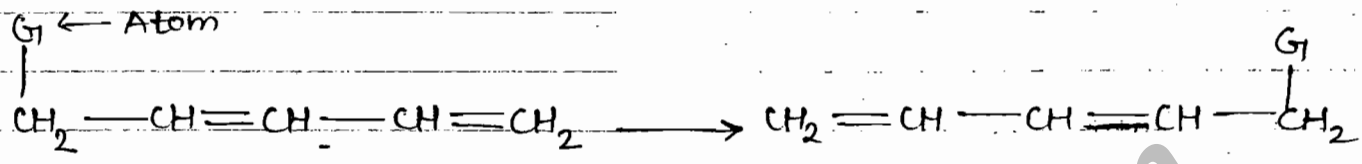
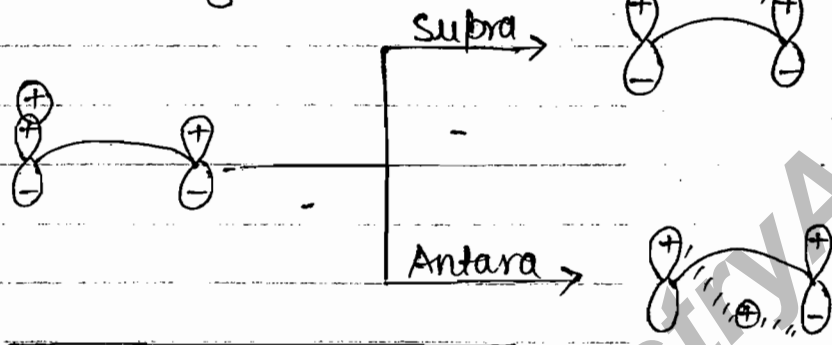
reasion is flexibility of system.

4n+2 System :-




* Thermal Condition.

HOMO $\psi_3$



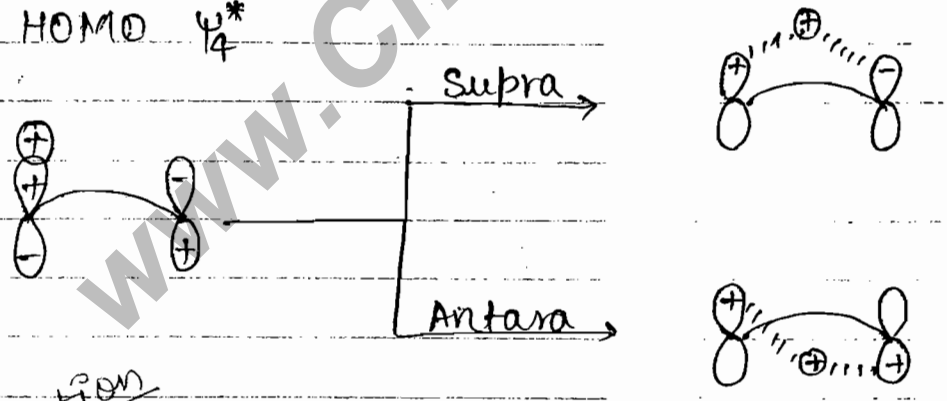

G. & S. Allowed.

G. & S. For bidden

4n+2 $\xrightarrow{\Delta}$ Supra

* Photochemical Condition

HOMO $\psi_4^*$




G. allowed.
S. forbidden.

G. forbidden.
S. Allowed.

Selection Rule

| System | Δ | hν |
|---|---|---|
| 4n | Antara | Supra |
| 4n+2 | Supra | Antara |

⇒ As ↓

Remember by Arsenic

An Su अंश्

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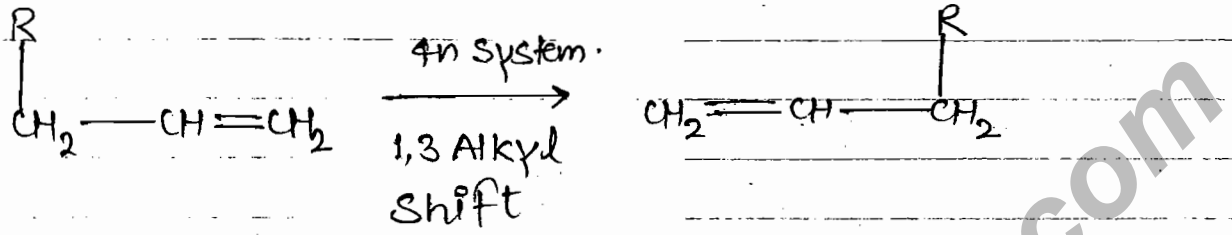
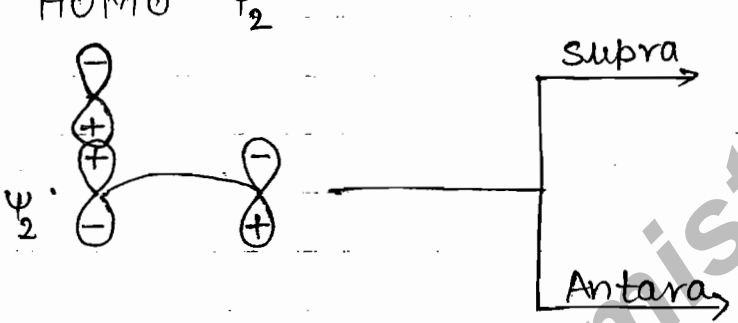
# Migration of ALKYL Group.

## 4n System.



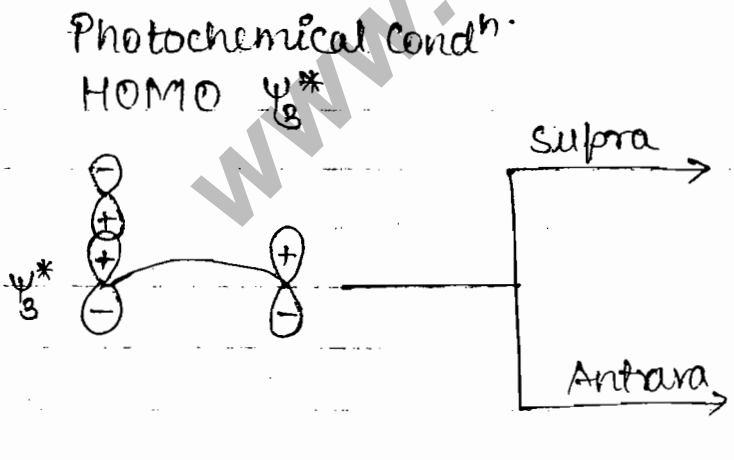

## Thermal condⁿ.

HOMO $\Psi_2$




## Photochemical condⁿ.

HOMO $\Psi_3^*$




→ Migration of alkyl group take place via Supra Facial way with Retention or Inversion. When inversion take place, then stereochemistry

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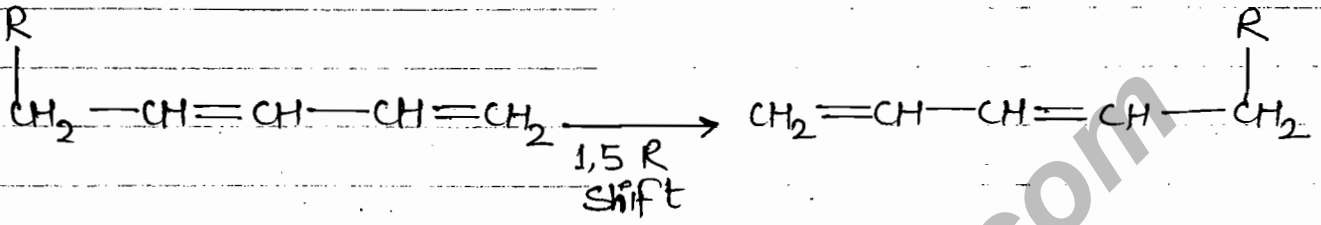
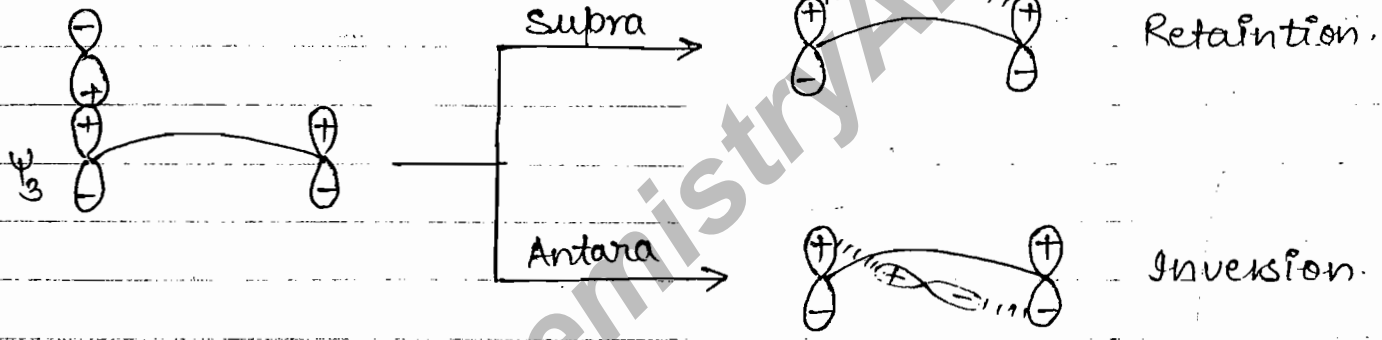
change and when Retaintion take place then stereo chemistry maintain.

4n+2 System.



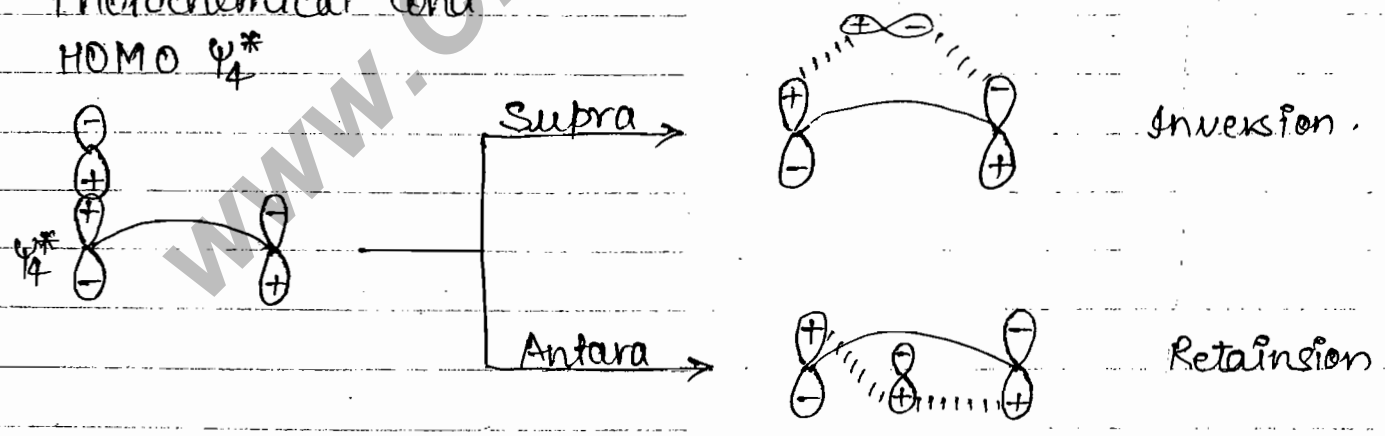

Thermal Condⁿ.

HOMO $\psi_3$




Photochemical Condⁿ.

HOMO $\psi_4^*$

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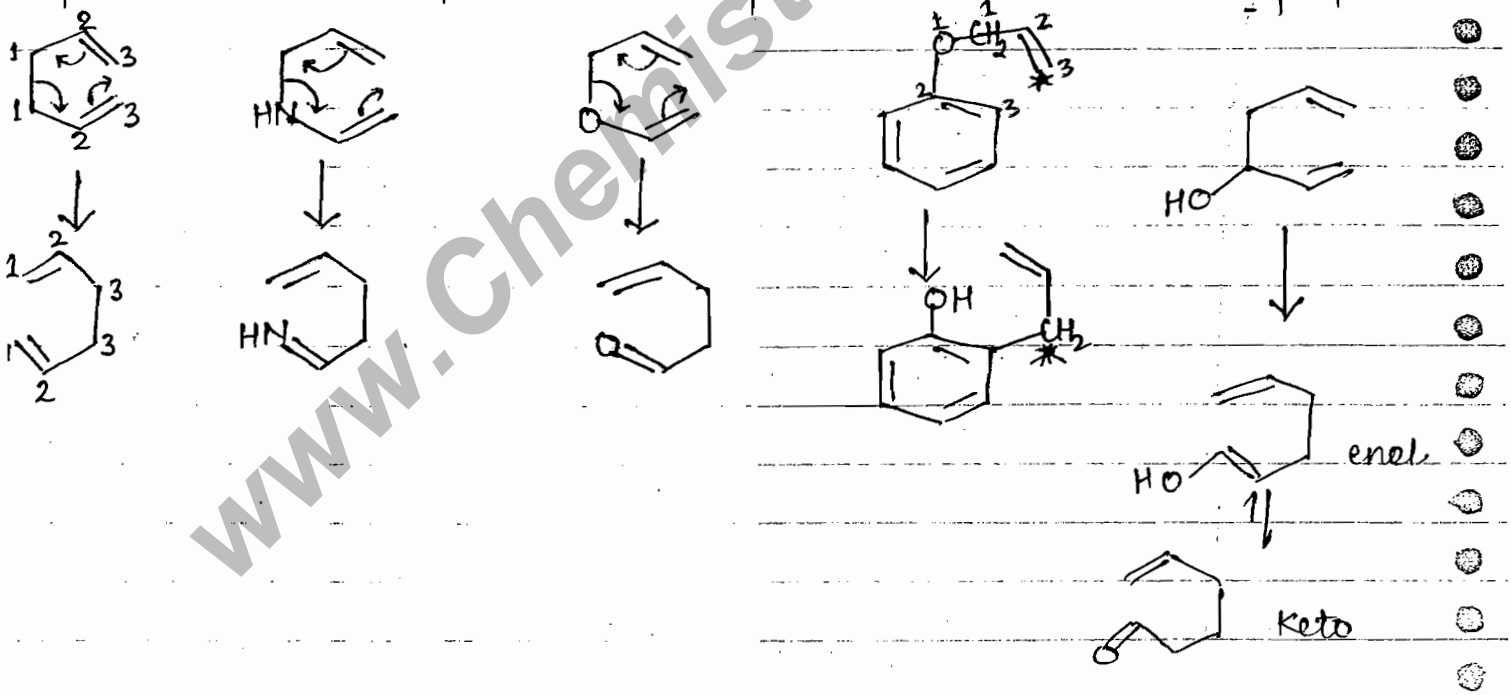
Claisen, ... comp.

| | ✓ Supra | | Antara ✗ | |
|---|---|---|---|---|
| | Δ | hν | Δ | hν |
| 4n | Inversion | Retaintion | Retaintion | Inversion |
| 4n+2 | Retaintion | Inversion | Inversion | Retaintion |

Remember by I.R. radiation

## 3,3-SIGMATROPIC Rearrangement

Cope | Azza-Cope | Claisen Cope | Claisen | Oxy Cope




# COPE REARRANGEMENT

* Exist in 1,5 diene.
* Case of 3,3-sigmatropic i.e. 4n+2 system.

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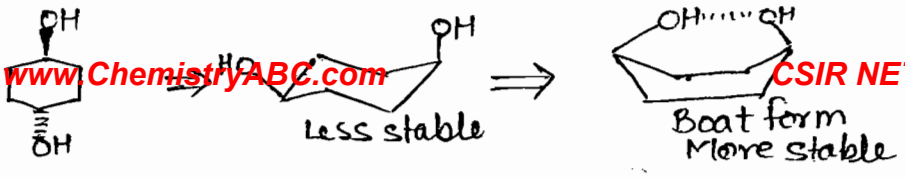
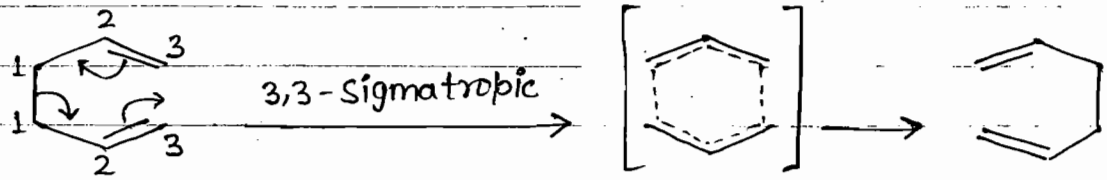
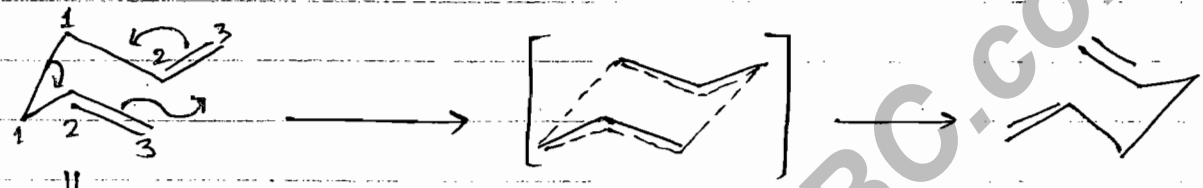



* Thermally allowed.
* 4n+2 System Δ condⁿ. Retaintion in stereo.

Ex.

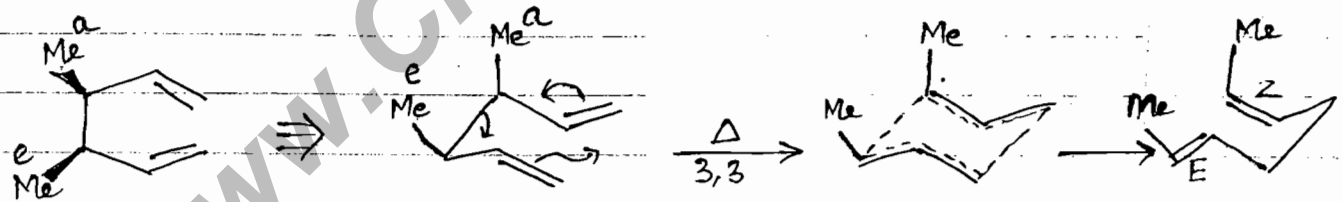


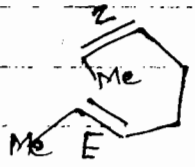
Trick
Here movement of three bonds i.e. three arrow ⇒ Odd
If odd arrow then Thermally allowed.
If even arrow then photochemically allowed.

M.Imp.

## STEREOCHEMISTRY of COPE Rearr-t.




Trick Axial Alkyl forms ⇓ 'Z'-alkene.
Equatorial Alkyl forms ⇓ 'E' alkene

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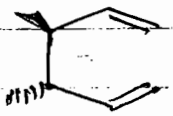
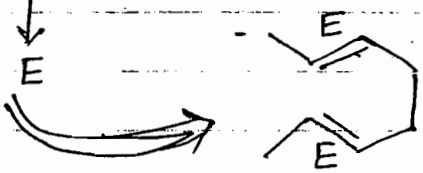
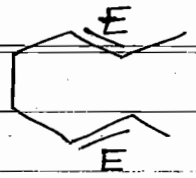
Ex. 

1,2 trans

e, e or a, a

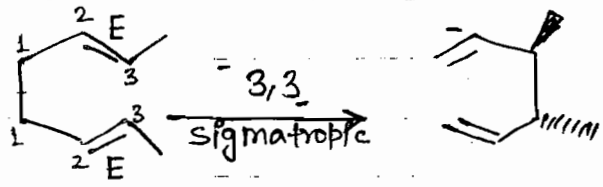
E E

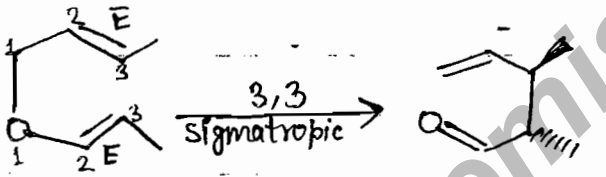


Ex. 

E, E Alkene

e e

Q. 

Q 

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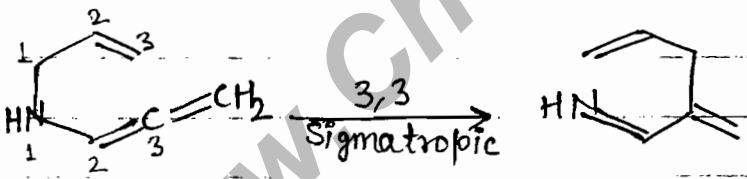
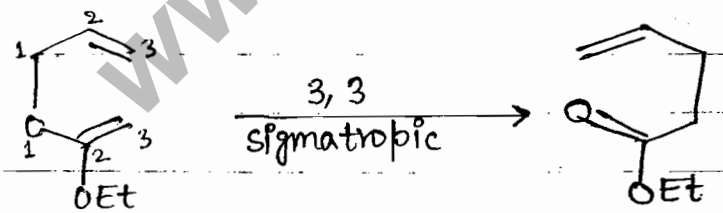
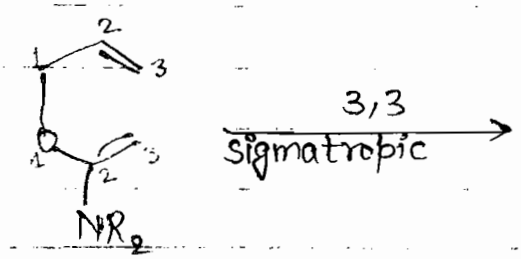
Q 

Q 

Q 

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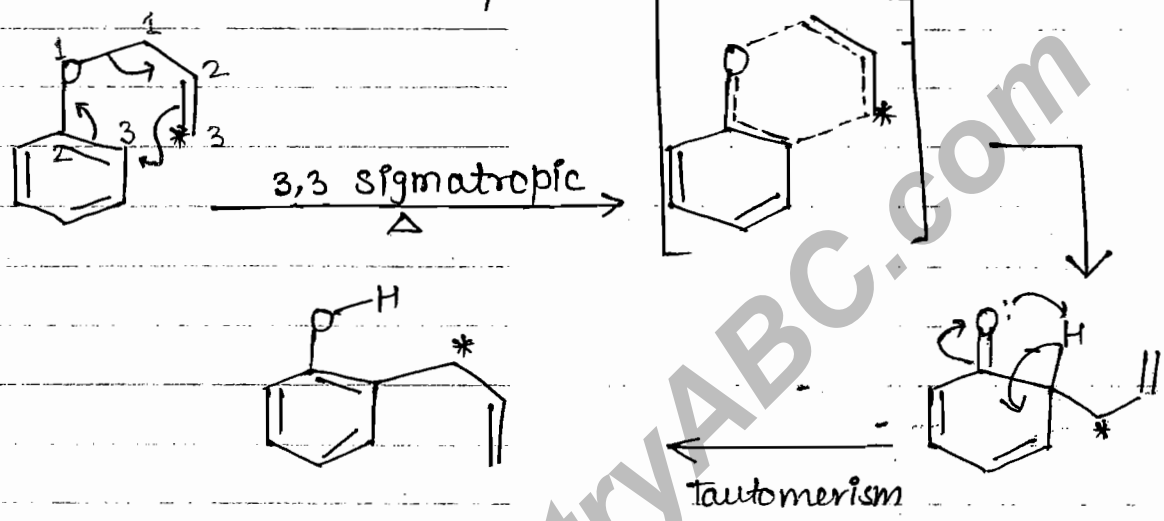
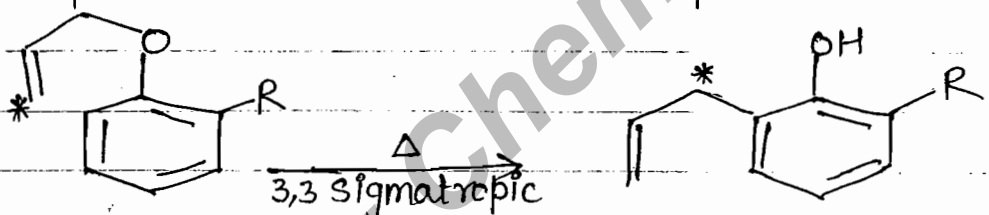
# CLAISEN REARRANGEMENT

Case of 3,3 sigmatropic rearrangement, takes place under Δ cod$^{n.}$, exist in aryl, allyl ether, ~~Retain~~ Retention in conf$^{n.}$

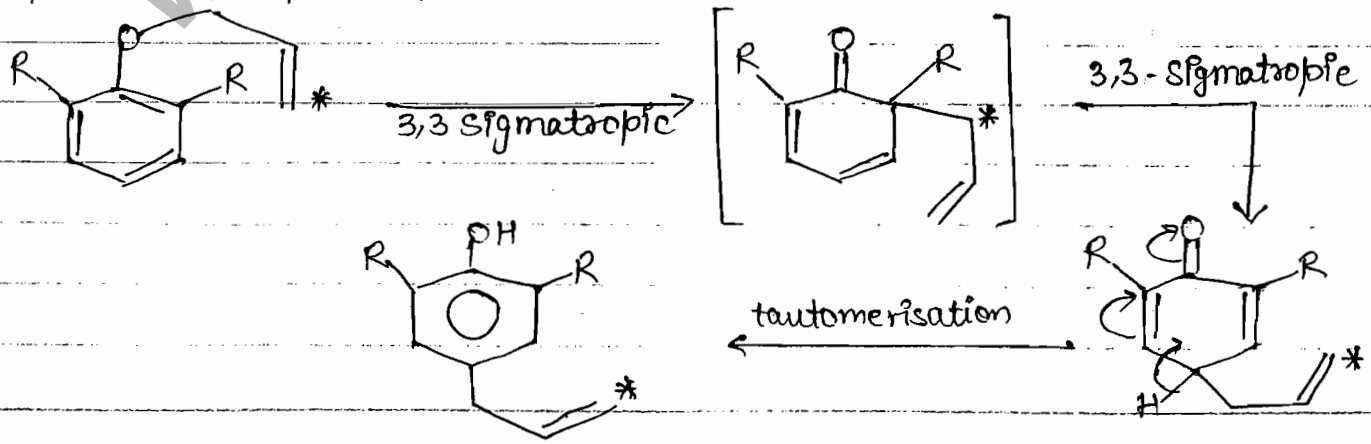
Ex.




When one ortho position occupied, the rxn. takes place at another ortho position.




When both ortho positions occupied then rxn. takes place at para position.

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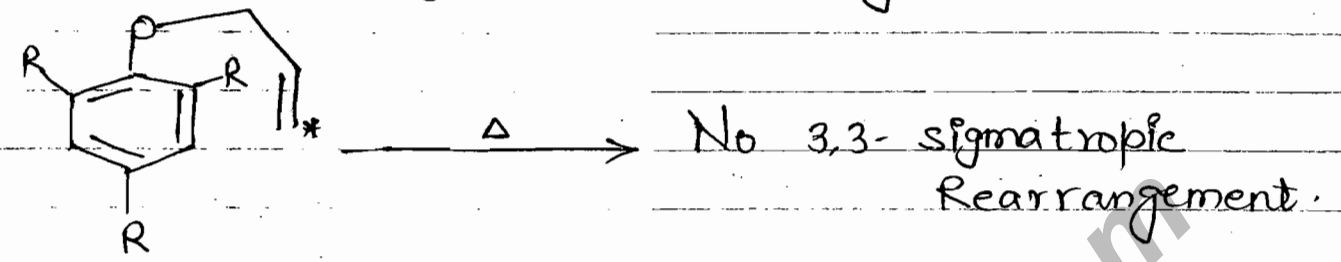
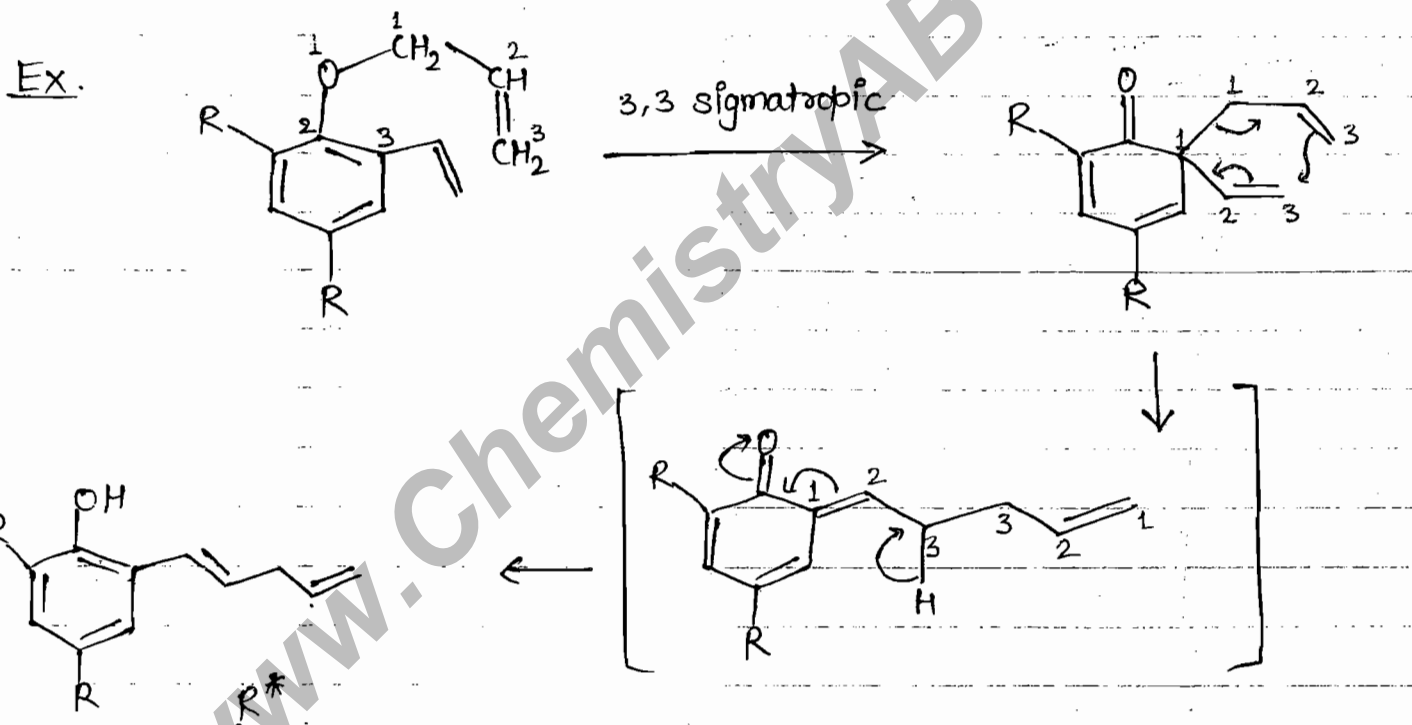
When both ortho and para positions are occupied then no, 3,3-sigmatropic rearrangement take place.




Note: But, at one ortho position vinyl group present then r.n. can take place.

Ex.

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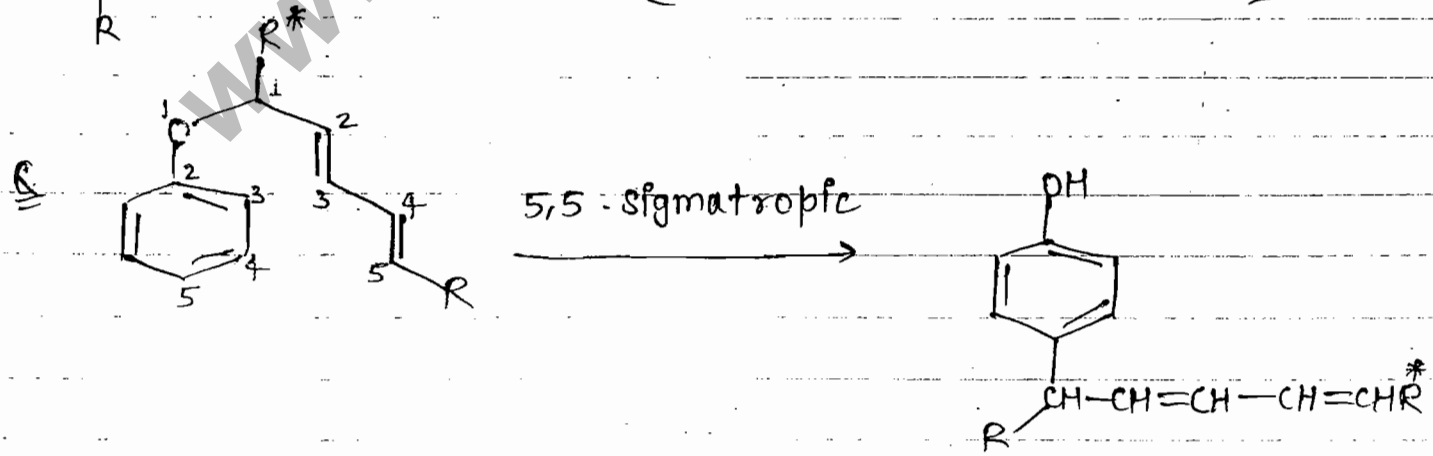


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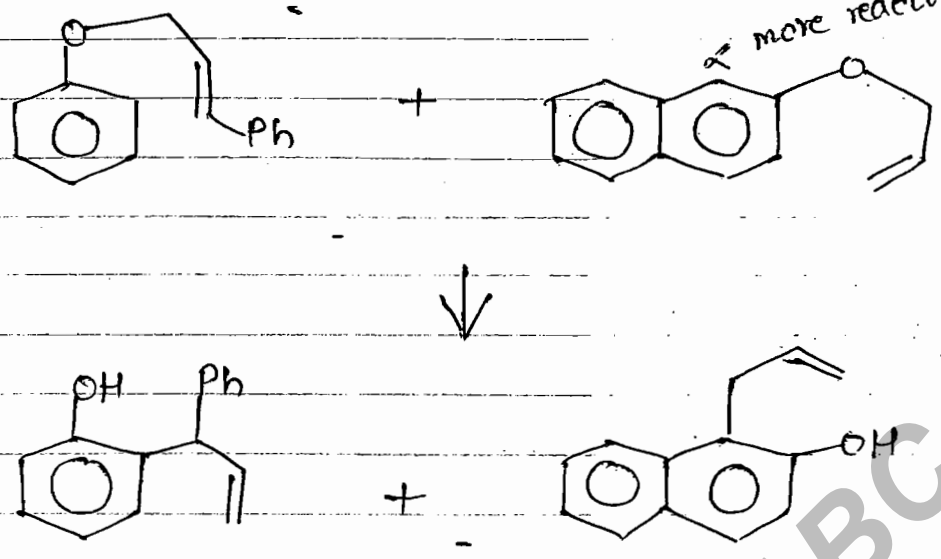
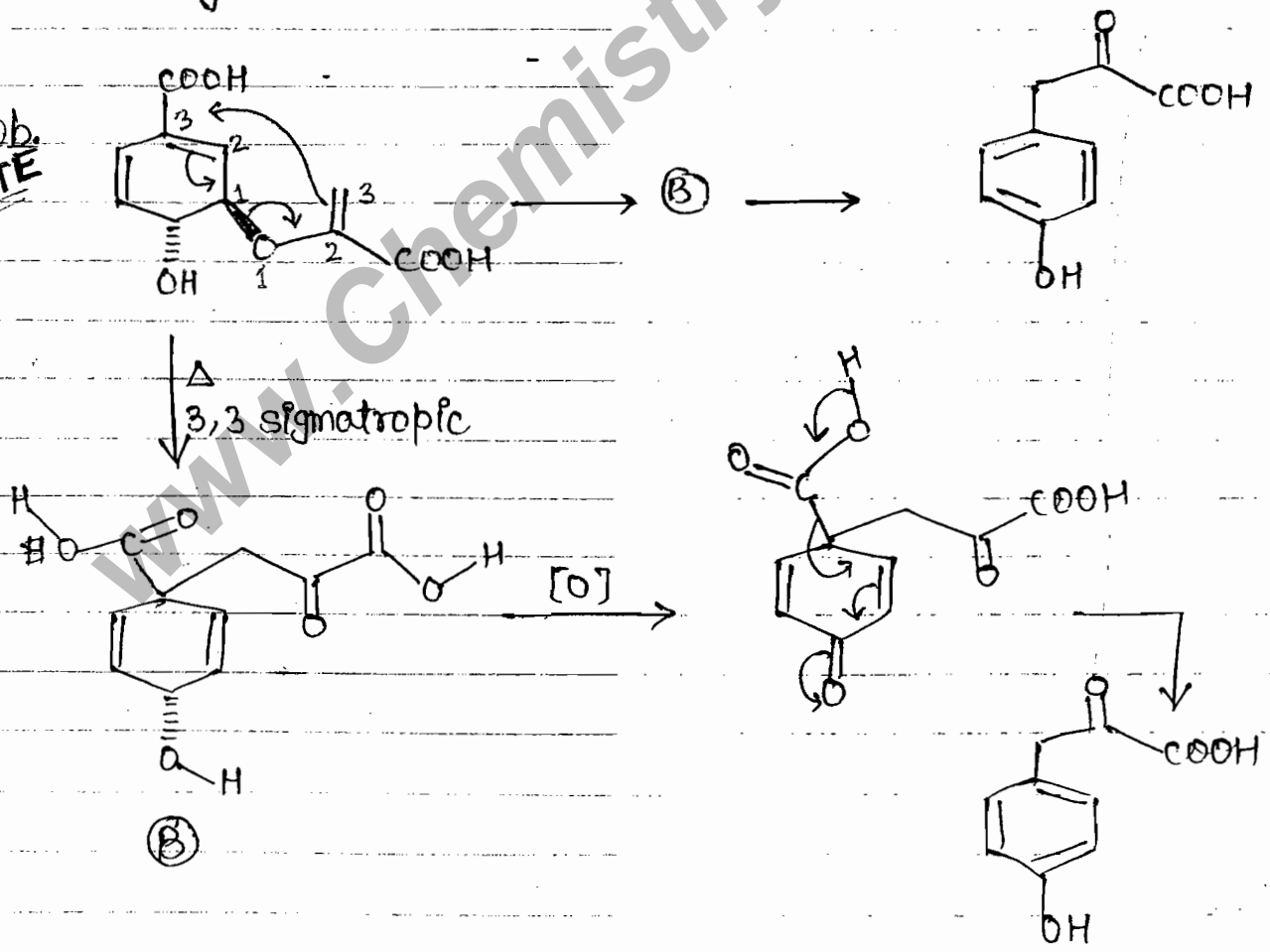
* In Claisen Rearrangement No Cross over Pdt. Formation :-




* Cope rearrangement or all type 3,3 sigmatropic rearrangement are Intramolecular

Prob. GATE

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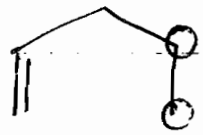
# 2, 3 - SIGMATROPIC REARRANGEMENT

* 2,3 - Sigmatropic rearrangement is Δ allowed.
* 5- memb. cyclic T.S. will form.
* electronically rich and electronically deficient centre +nt.
* electronically deficient centre +nt at allylic position.

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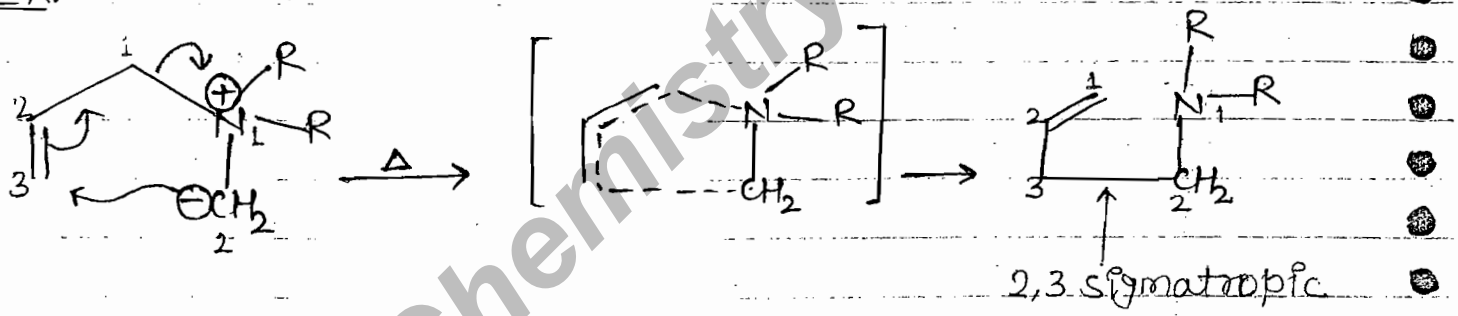


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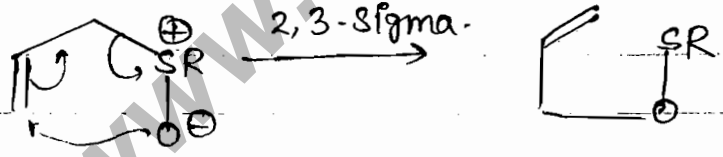


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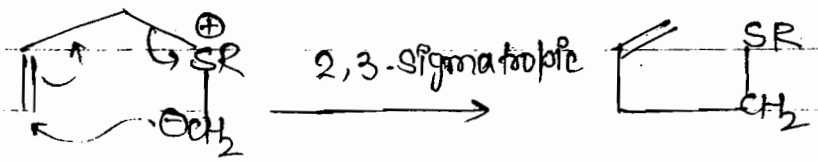
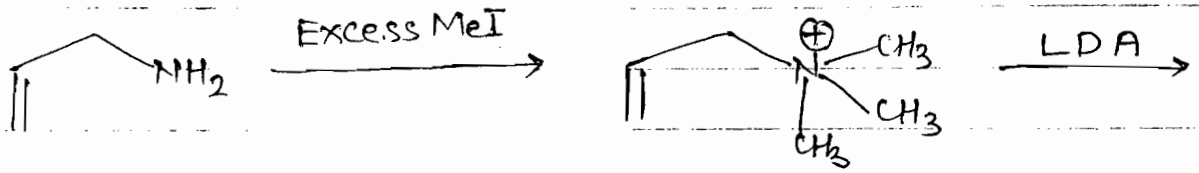



⇒

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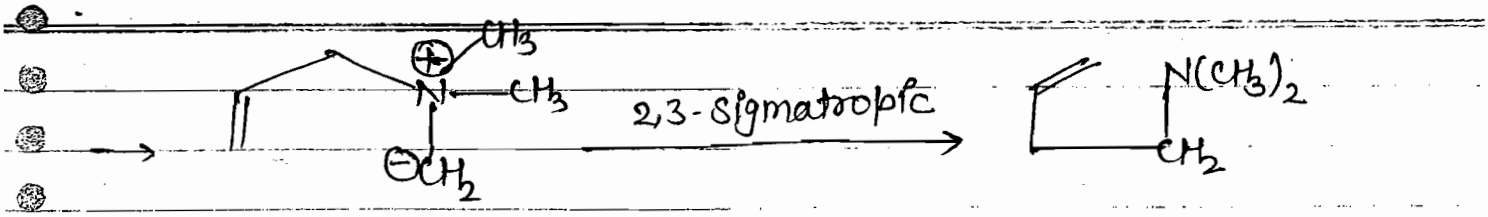
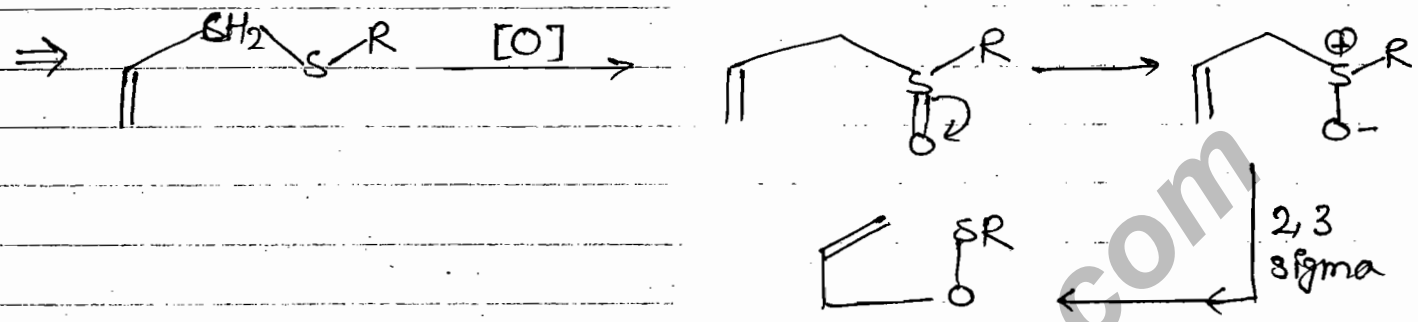
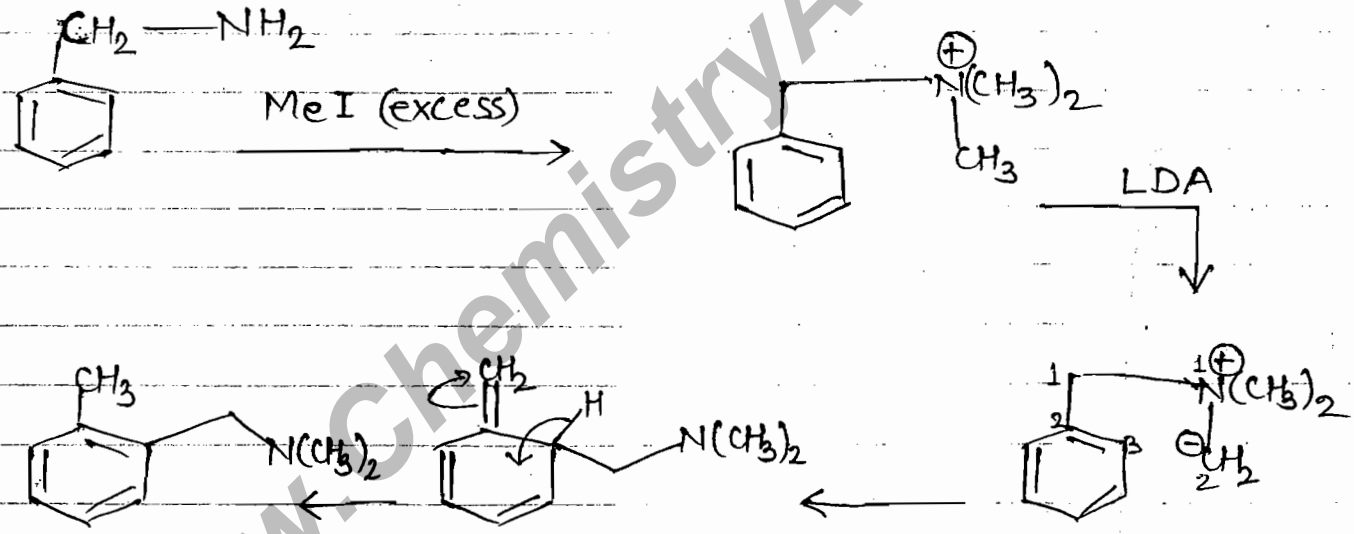
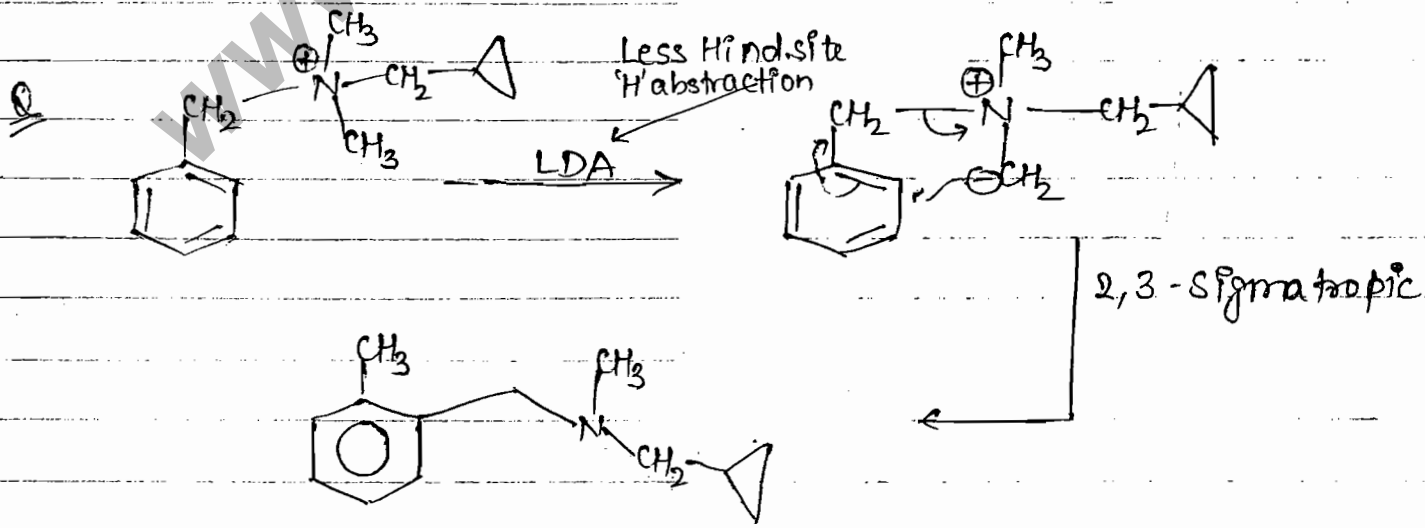



## SUMMLET HAUCHER Rxn.

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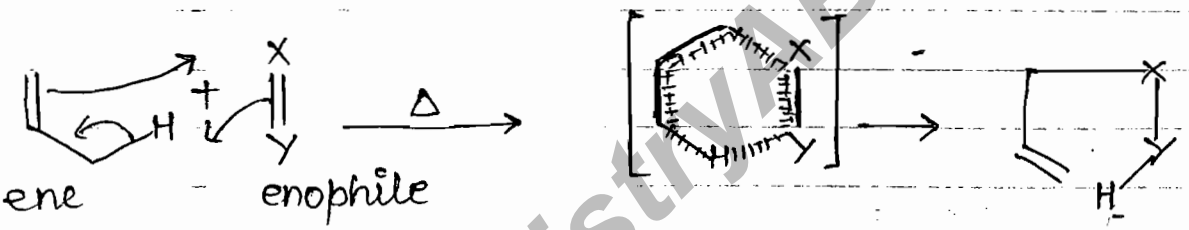
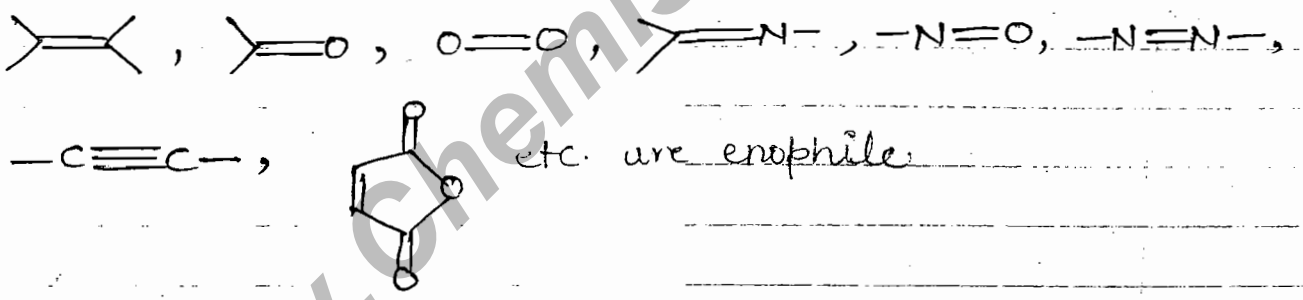
# ENE OR GROUP TRANSFER Rxn.

* It involve the transfer of 'H' atom from one molecule to the other molecule.
* In ene rxn. the alkene ~~wit~~ which have allylic 'H' transfer to the enophile then two new σ bond formed.
* In ene rxn. 6 memb. T.S. form.
* Ene rxn. are thermally allowed.
* Total 6 $e^-$ involve in the rxn. ($4\pi + 2\sigma$ $e^-$)

Ex.




etc. are enophile

⇒ One alkene ~~stti~~ should have allylic H & cond$^n$ should be Δ.

* M. C. Diagram of Ene Rxn.

Generally HOMO of Alkene & LUMO of enophile interact during the rxn.

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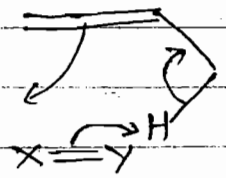
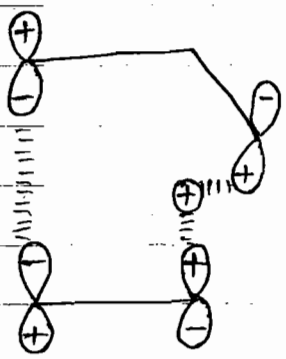
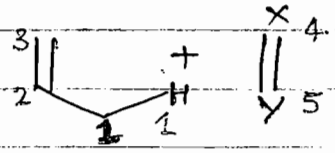




$\psi_2$ HOMO in $\Delta$ condⁿ.

$\psi_2$ LUMO

* Generally ene rxn. are also designated as cycloaddition rxn. because in this rxn two unsaturated moity involve.
* Generally ene reactions are also designated as a 1,5 sigmatropic rearrangement



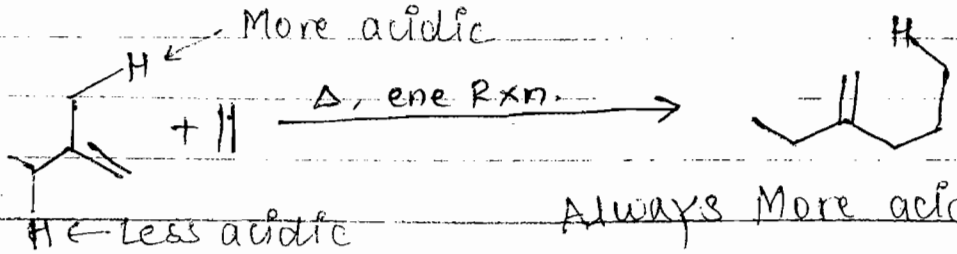
But both above designation are not correct actually it is group transfer case.

ene Rxn.

Intramolecular Intermolecular

* Ene Rxn. are also Lewis acid catalysed Rxn. Rate of Rxn. increases in the presence of lewis acid.

Q




Always More acidic 'H' transf.

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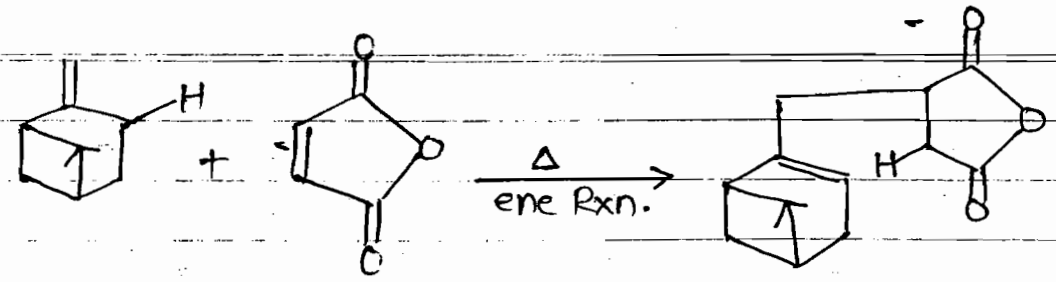
Imp.
Q

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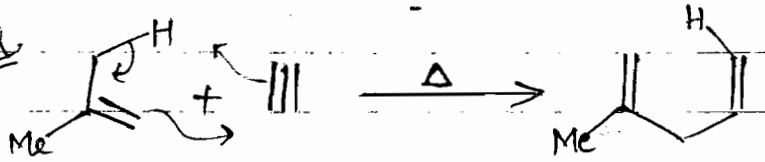
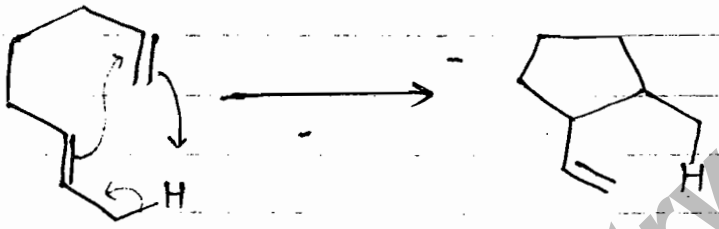



Intra molecular ene Rxn.

Imp.
Q




Intra molecular ene Rxn.

Imp.
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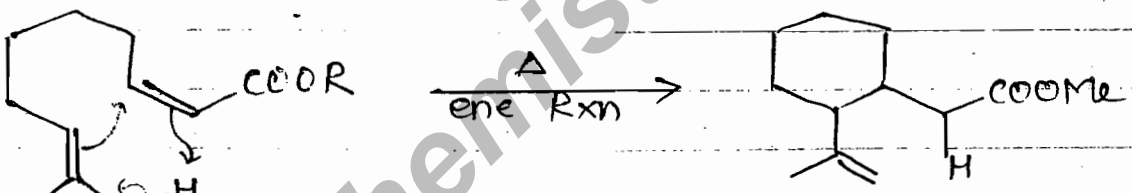
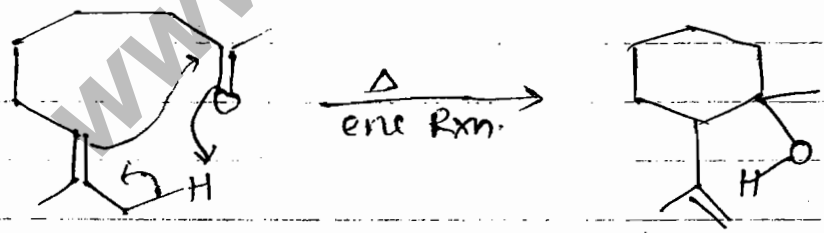



Lewis acid.
Rate of Rxn. fast.

Imp.
Q




ZnBr Rate of Rxn. fast

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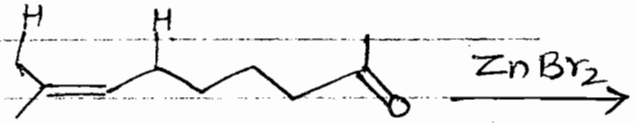
Prob:

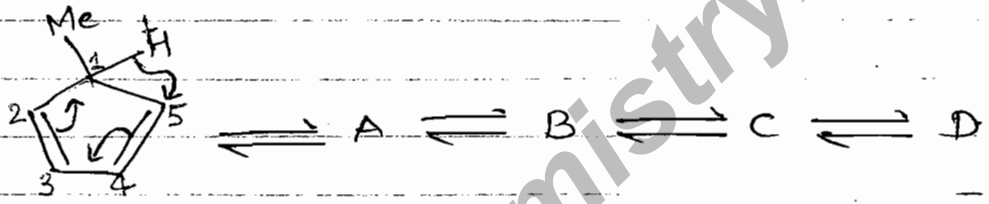

* Two double bond (one having allylic H') + Δ ⇒ ene Rxn.

Prob. 

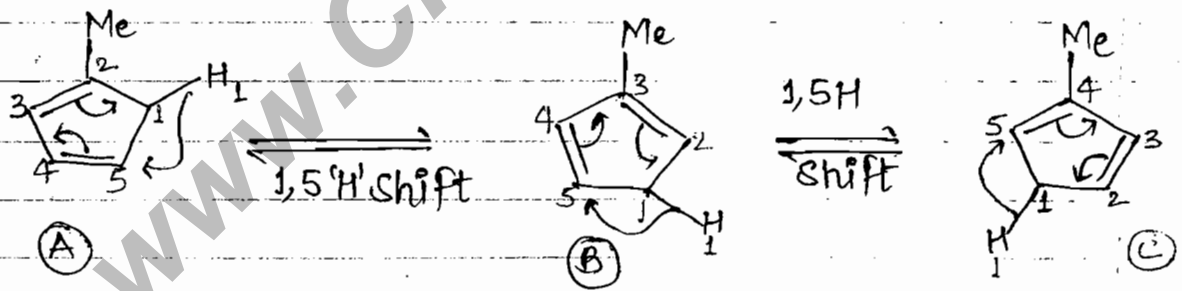

* Two double bond + Δ ⇒ ene Rxn.
↑ one having Allylic H'

V.V. Imp.

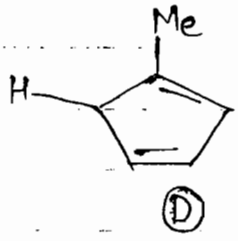
## SCRIMBLING of H-Atom




1,5 'H' shift




If Methyl & 'H' both shift possible then shift 'H' first.

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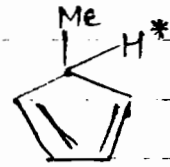
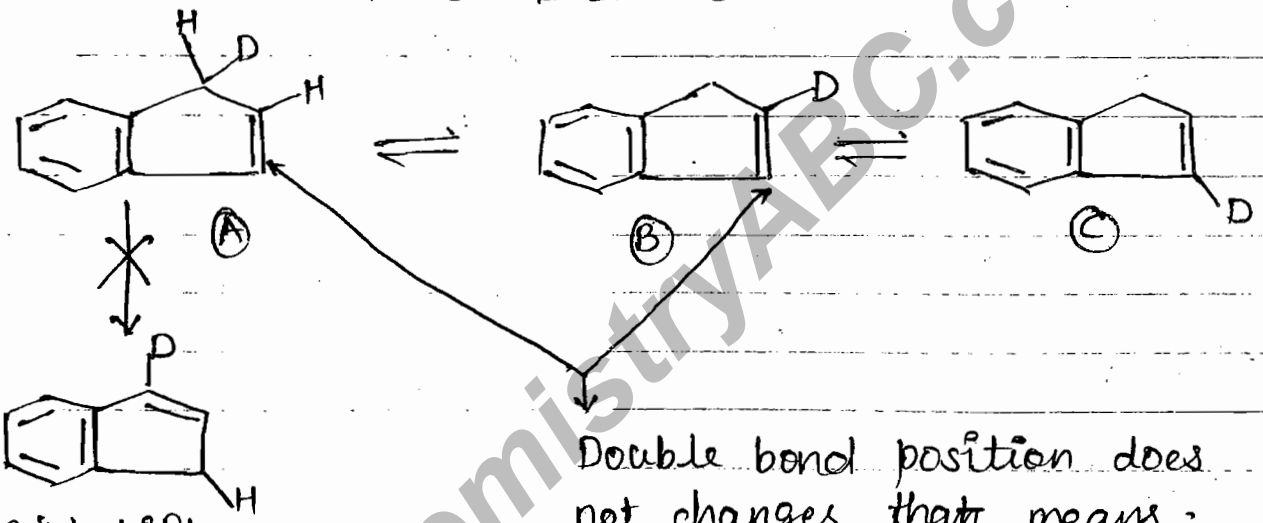
Explain the splitting of the Methyl proton in the following ~~pro~~ comp.




Methyl protons gives singlet due to scrimbling of H*

# PROBLEMS

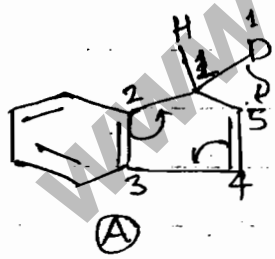
1)



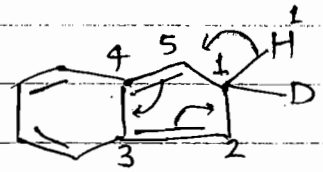

1,3 'H' shift in Δ cond$^{n}$ doesn't take place

Double bond position does not changes that means - double shifting (Arrangement)

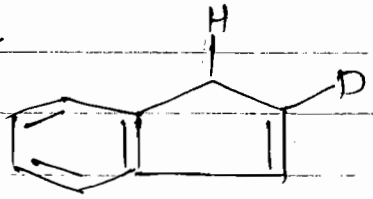
(B)




1,5 'D' shift →




1,5 'H' shift ↓




1+5 = 6 ⇒ 4n+2

↓Δ

Supra

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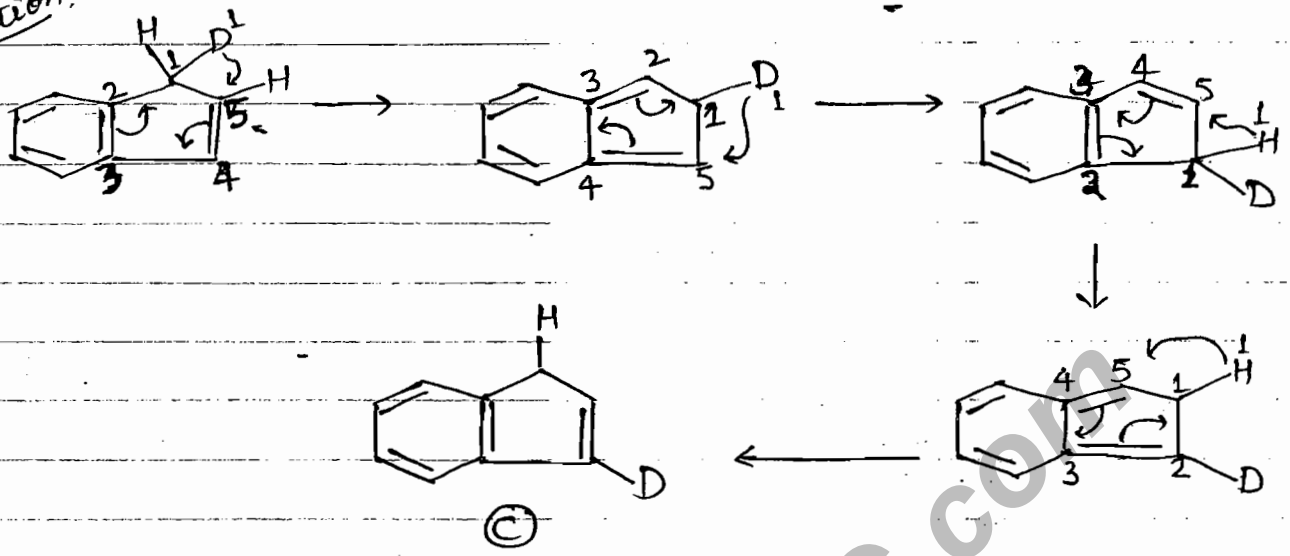
© Explanation.



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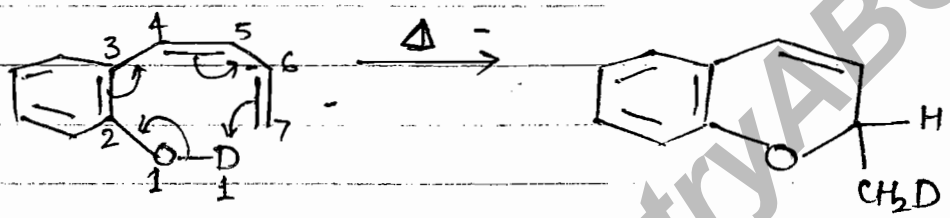
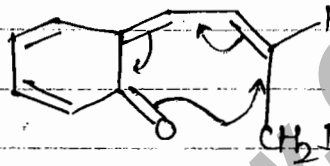
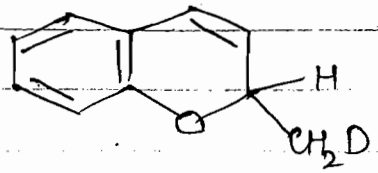


1,7, D Shift

1+7 ⇒ 8 ⇒ 4n $\xrightarrow{\Delta}$ Antara (Here Rxn take place due to fluxionality in Big system.



4+2 Cycloaddition, Δ, Dis



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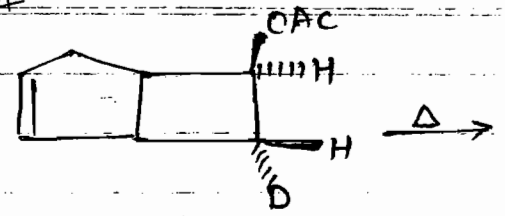
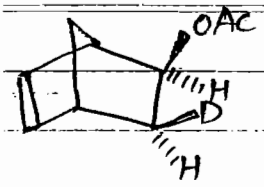
M.Imp.

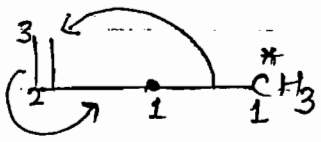
3)




$\xrightarrow{\Delta}$




Note:-




$\xrightarrow{\Delta}$ 1,3 methyl shift

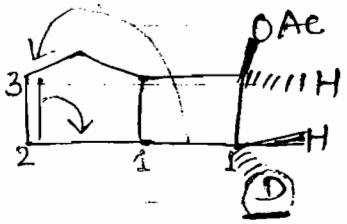
Stereo inverted.

$4n + \Delta \Rightarrow$ Supra

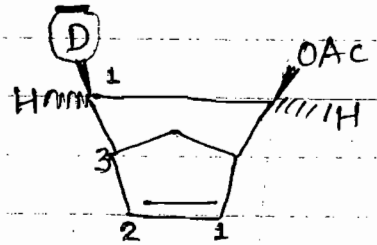
$\Downarrow$

Stereoinversion.

Soln:




$\xrightarrow{\Delta}$ 1,3 Alkyl shift



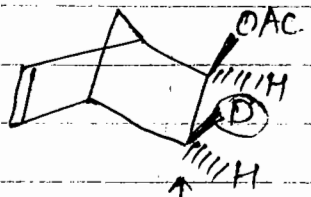

$\Downarrow$

$4n + \Delta \Rightarrow$ Supra

$\Downarrow$

Inversion

$\downarrow$




Stereo Inverted

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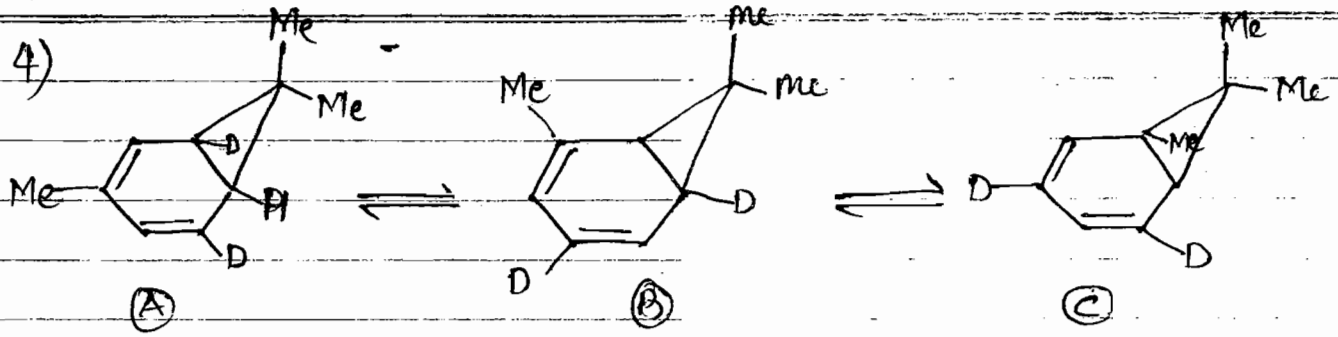
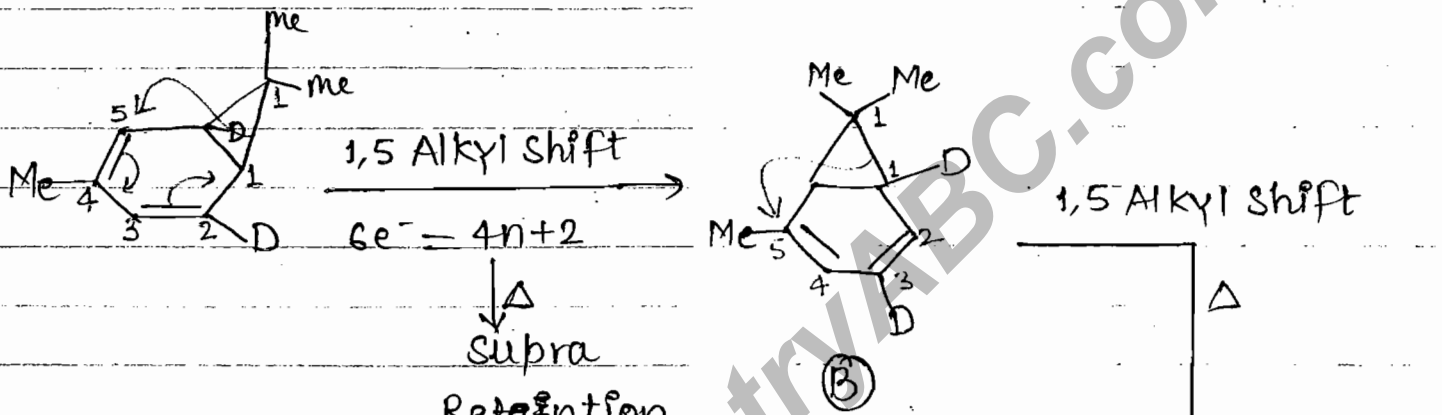
4)




* 2 double bonds present => 1,5 sigmatropic may take place

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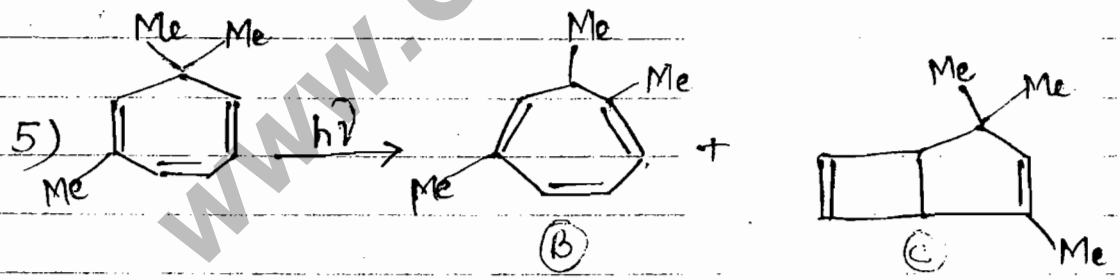
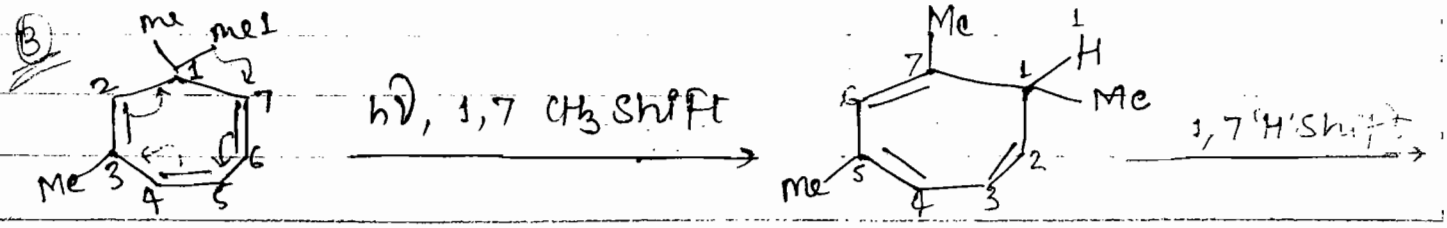



When double bond position not changes ~~ise~~ after rex. i. means two time rearrangement.

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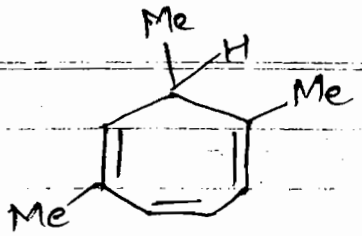
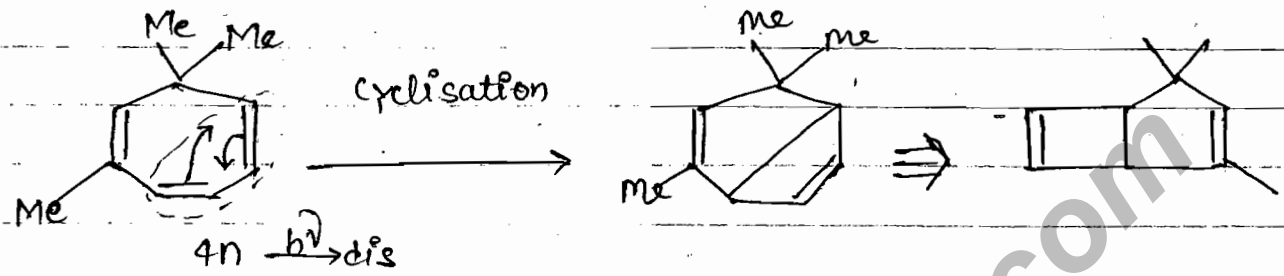
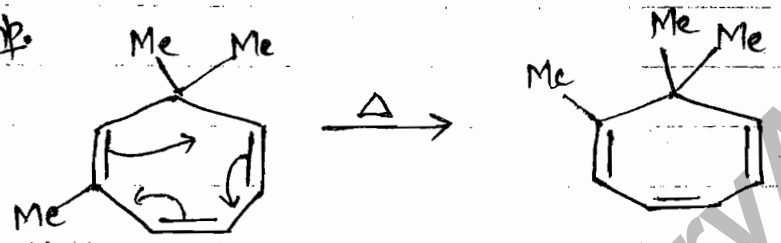


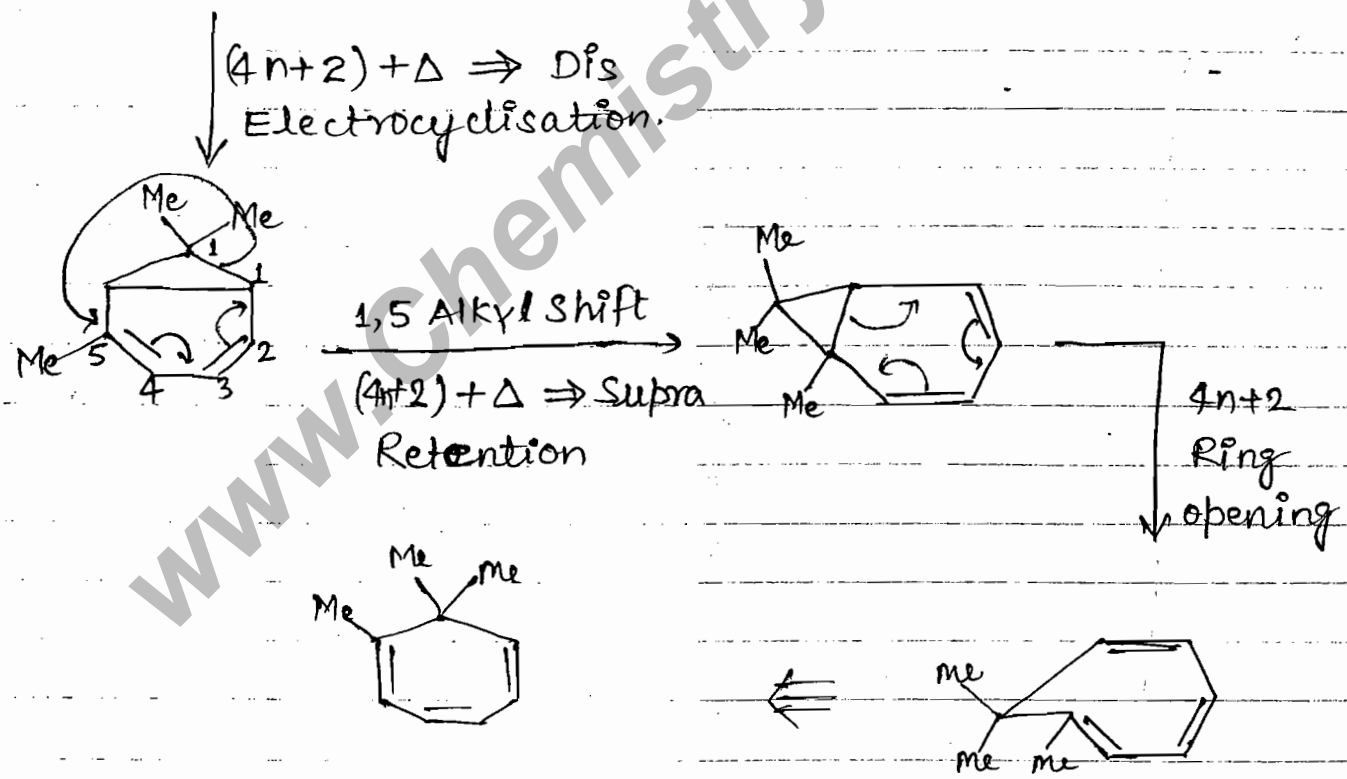
(c)




M. Imp.

6)



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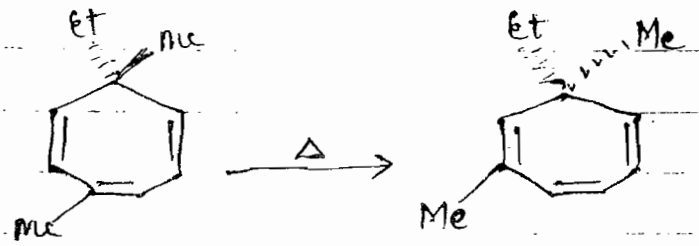

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Explain Stereochemistry of Me & Et

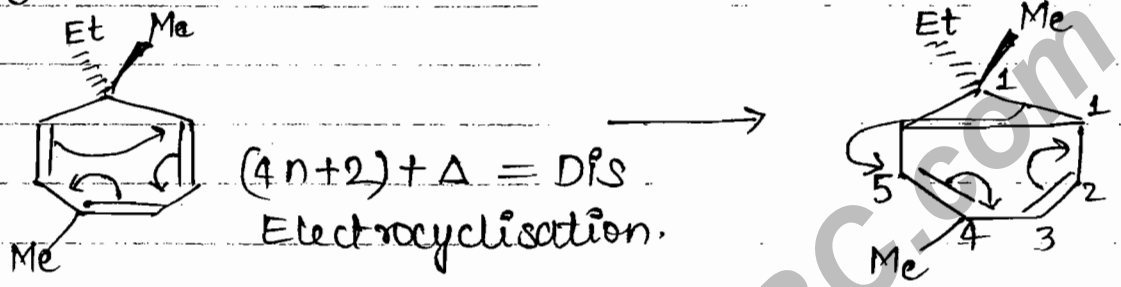
Electrocyclization

1,5 Alkyl shift

$(4n+2)+\Delta \Rightarrow$ supra $\Rightarrow$ Retention.

Ring opening.

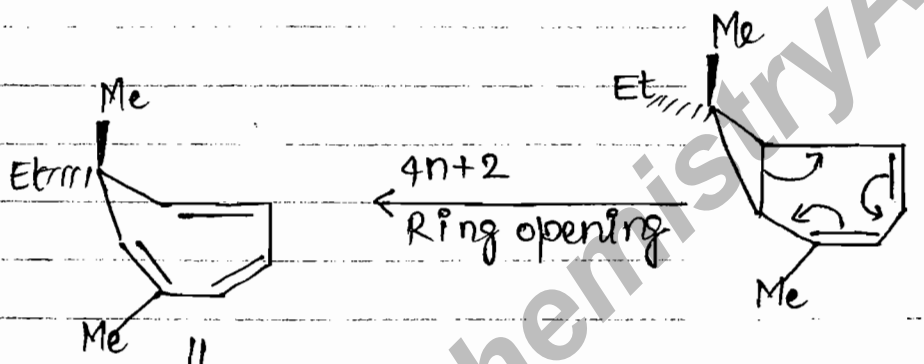
Soln.

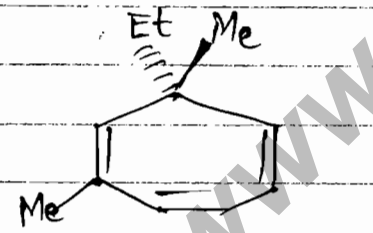



1,5 Alkyl shift

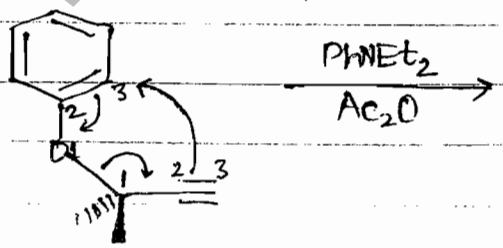
$(4n+2)+\Delta \Rightarrow$ Supra

Retention



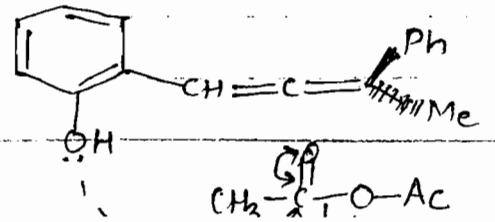

Prob. 8




3,3 sigmatropic

$(4+2)+\Delta \Rightarrow$ supra

Retention

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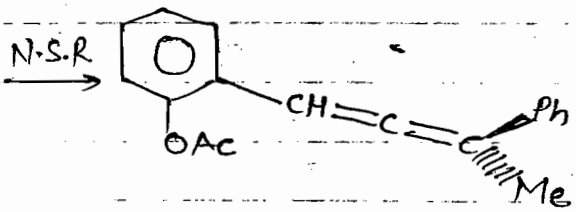
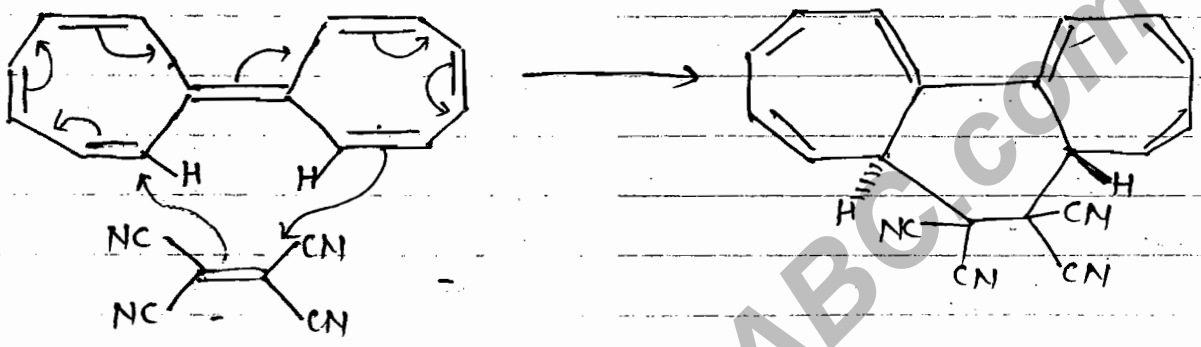



Q9




14 + 2 = 16 π e⁻

⇓

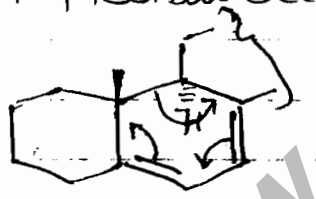
4n

⇓ Δ

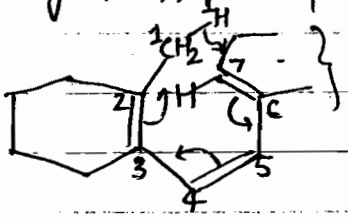
S – A

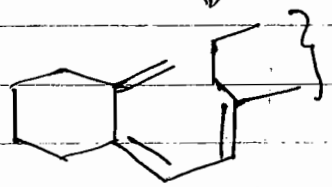
S-A fissible becoz system bfg Rxn: may proceed S-A.

Q10



$\xrightarrow[4n+2]{h\nu}$



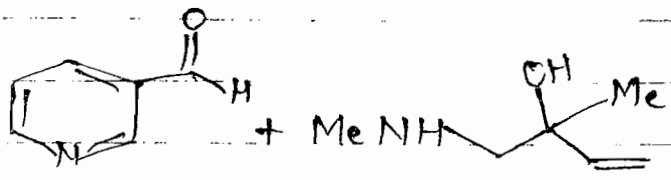



$\xrightarrow{h\nu}$

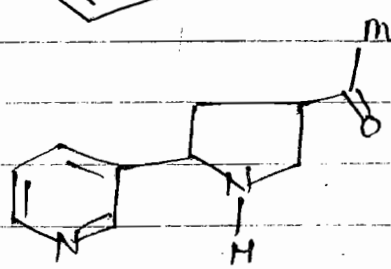
CD

Stereo of $CH_2$ & H → change

Q11




$\xrightarrow{H^{\oplus}}$

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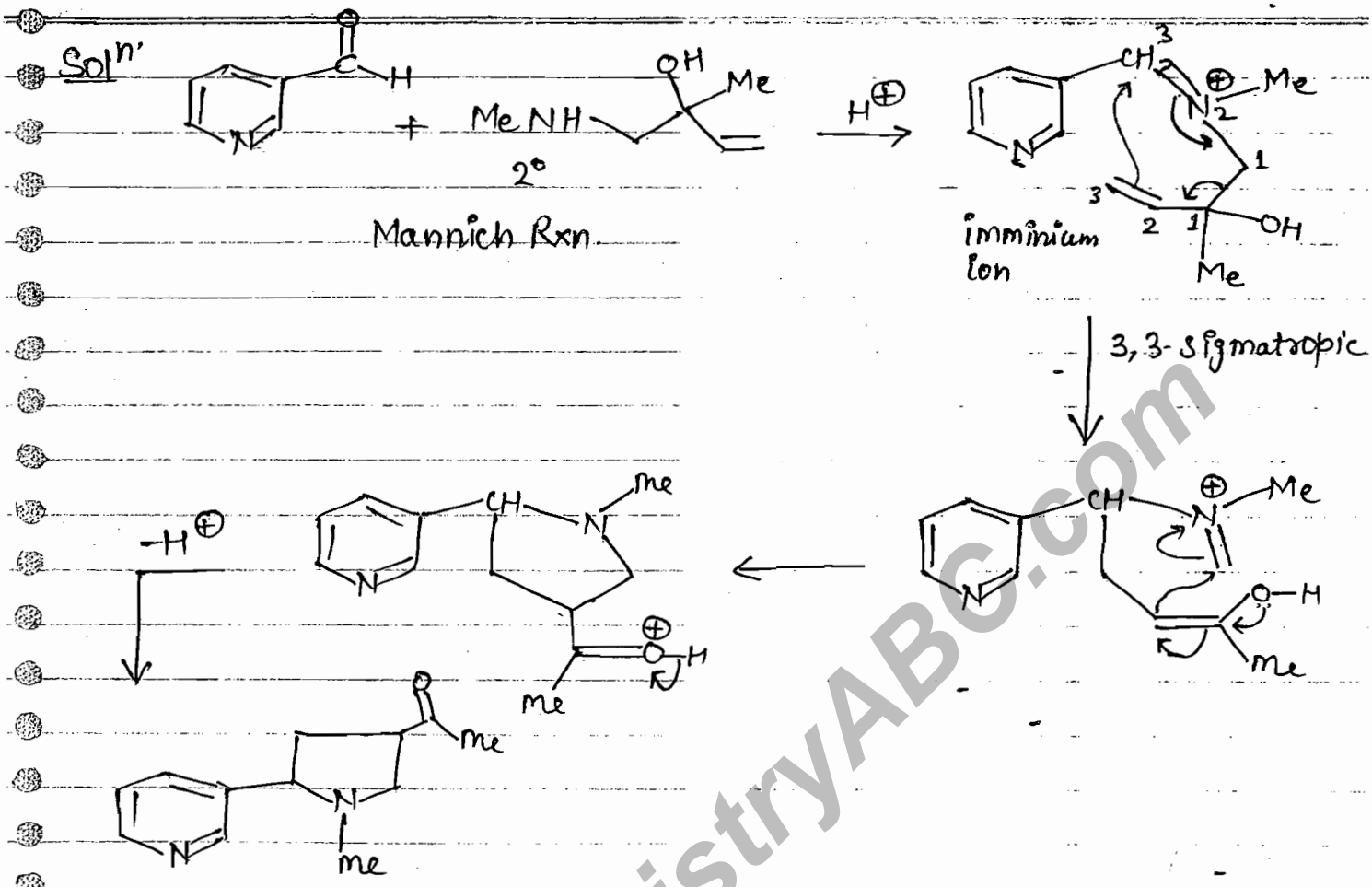
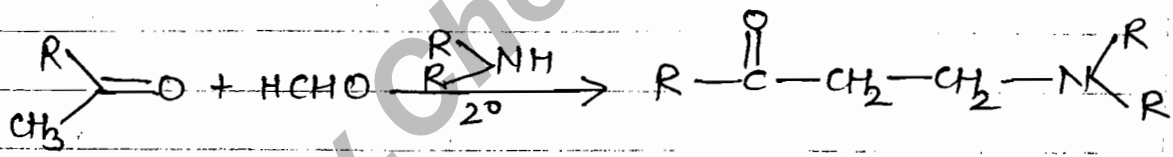
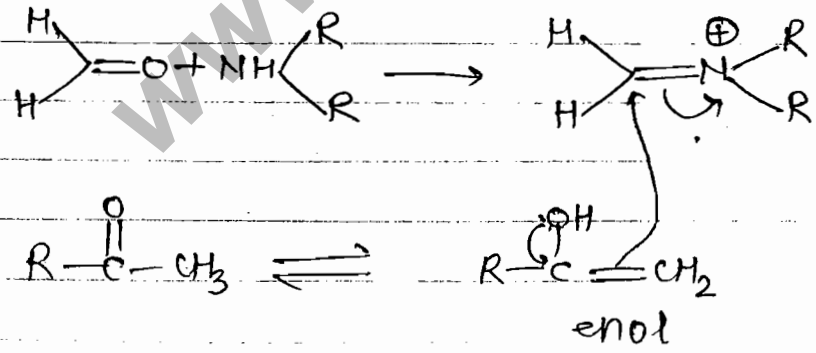
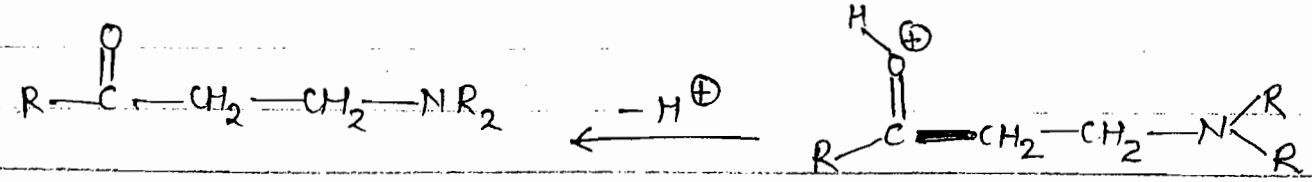



Mannich Rxn.

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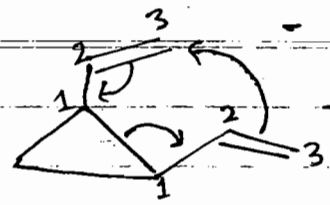
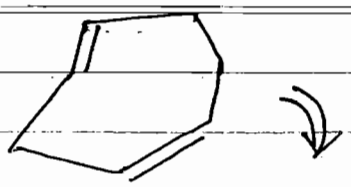
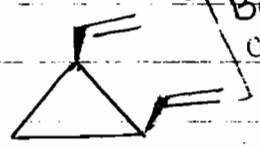
Q12



$\xrightarrow{\Delta}$ 3,3 sigma.

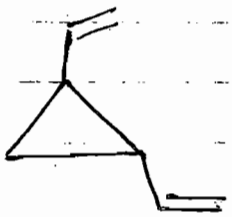


(or)

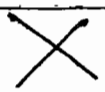


Both cis can form bond.

Q13



3,3 - Sigma

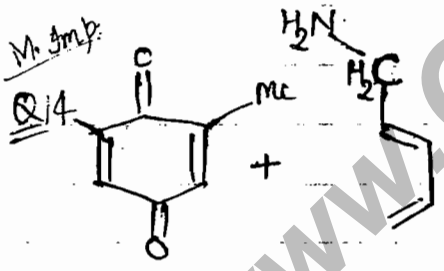


(or)

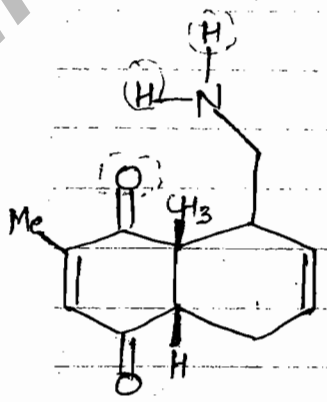
Both trans can't form bond.

M. Imp.

Q14



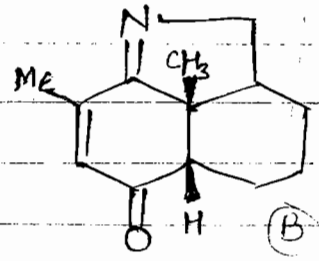
$\xrightarrow{\Delta}$ 4+2



Shift Base

$\downarrow -H_2O$

(A)



(B)

Final product is (B) not (A) but in exam both option will be given so remember this point.

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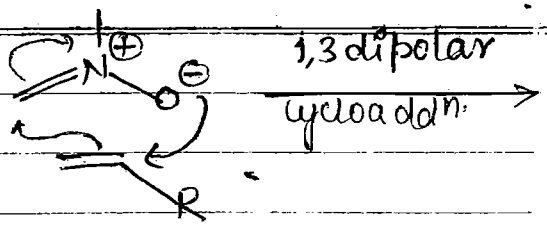
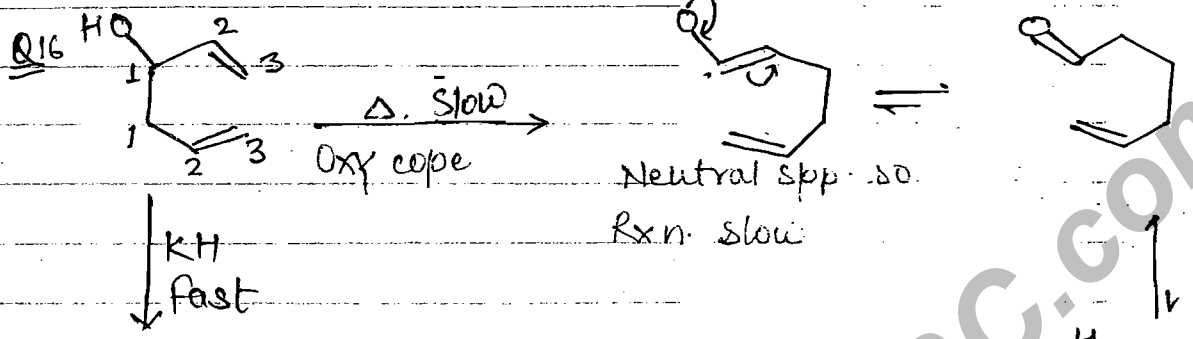
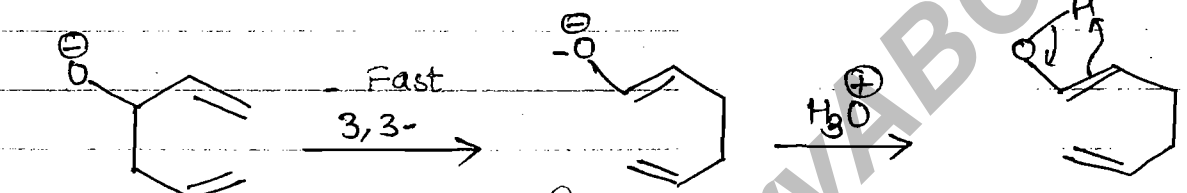
Q15



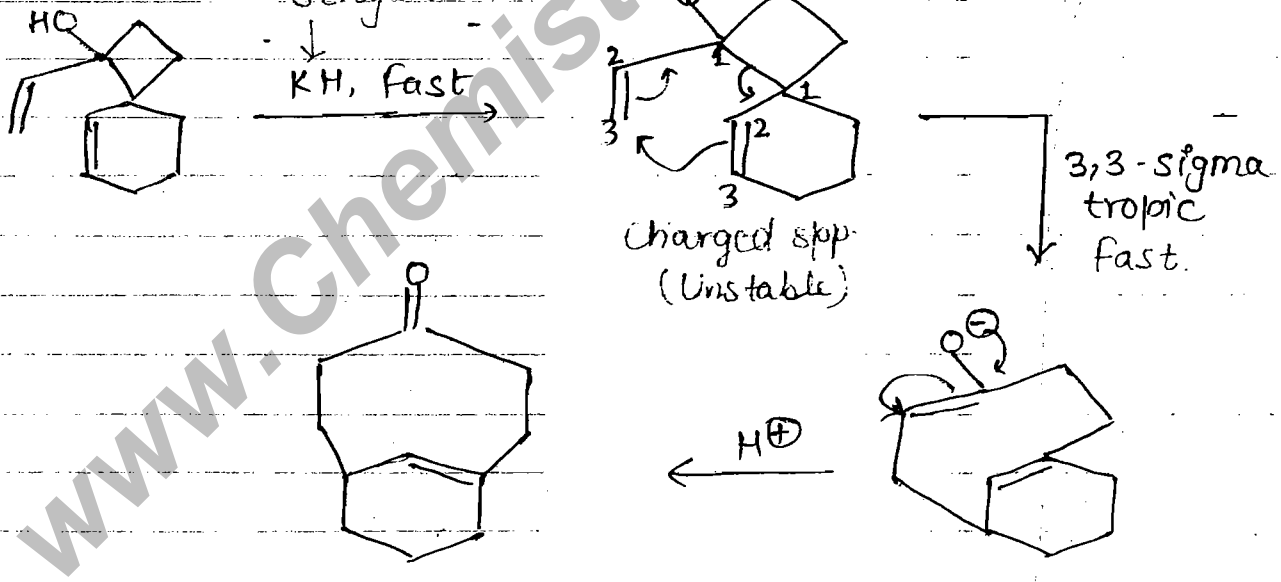

Q16




charged spp unstable so rxn fast

Q17




KH, NaH ⇒ Strong Base ⇒ Very easily Alcoholic 'H' abstraction or abstration of very less acidic

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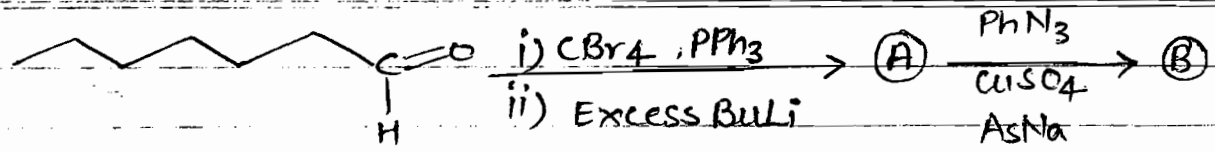
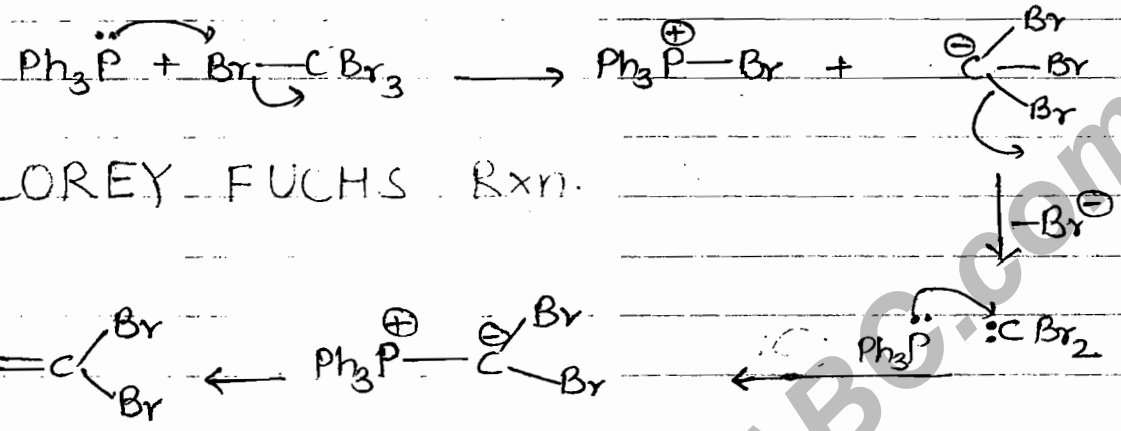
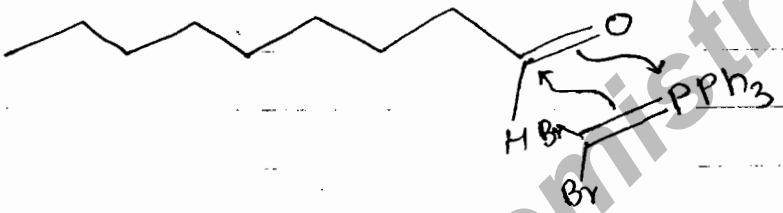
Q18 

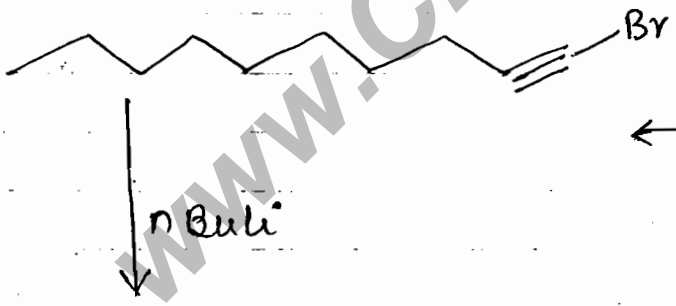

Soln

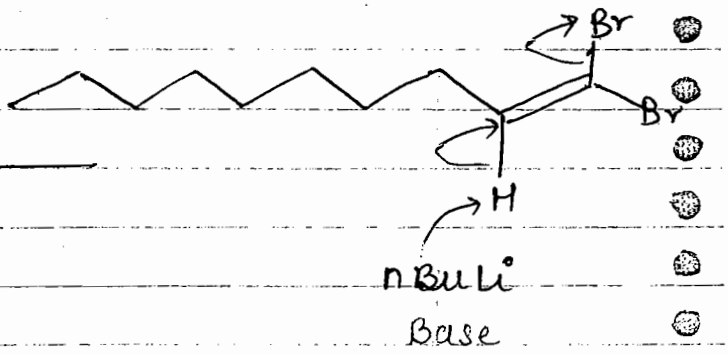


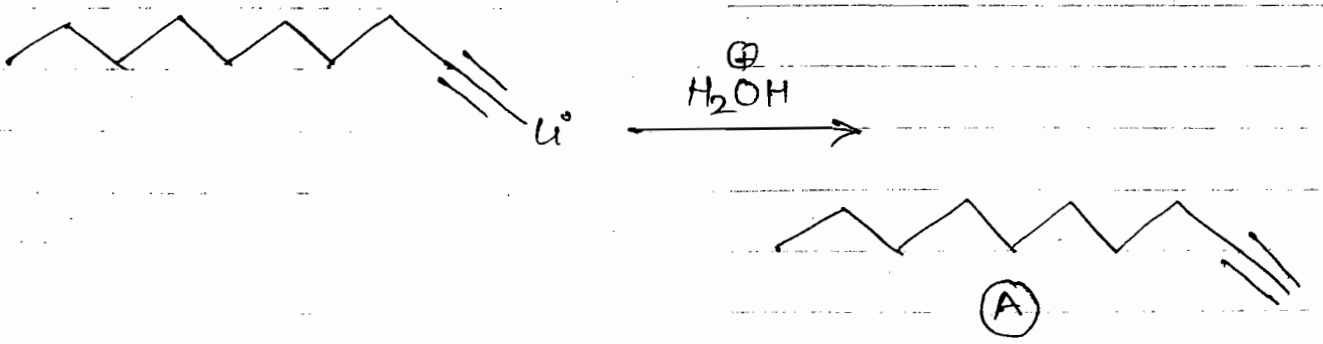

COREY FUCHS Rxn.




Witting Rxn.

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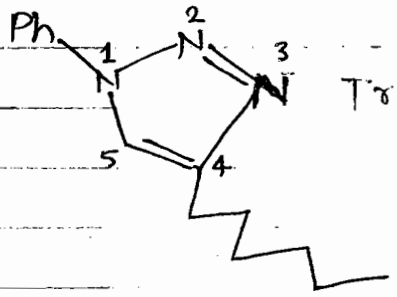
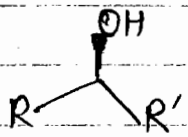
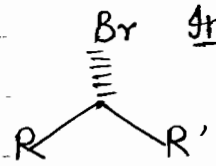
(A) $PhN_3$, $CuSO_4$, AsNa → 

Triazole

CLICK Rxn.

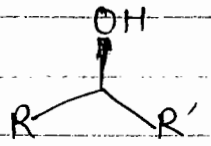
In click Rxn.. 1,4 isomer only

Apple Rxn.

*  $PPh_3$, $CBr_4$ → 

Apple Rxn. $S_N2$

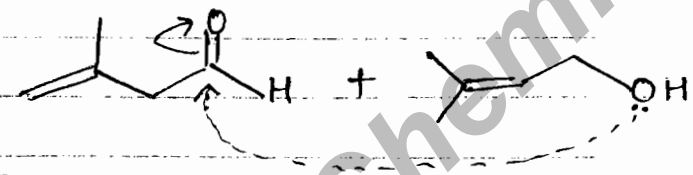
Imp. Inversion.

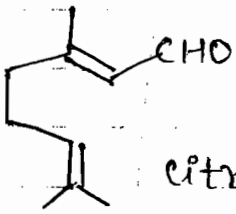
*  $PCl_5$ or $PCl_3$ or $SOCl_2$ →

Retention

M. Imp.

Q.19

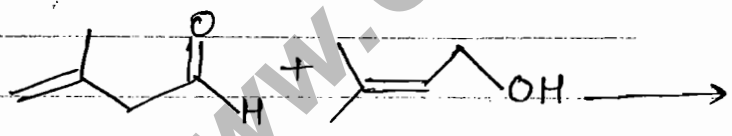




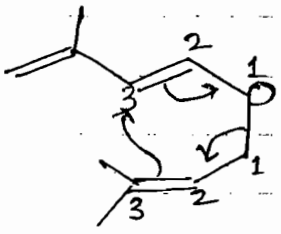
citral.

Natural prod.

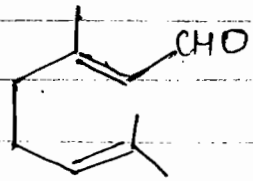
Soln.



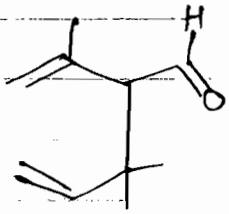
Mechanism see on next page



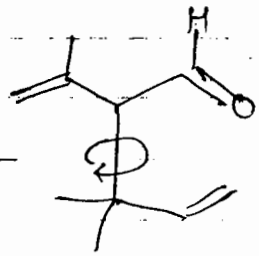
3,3, Claisen Cope



3,3 sigma Cope



Rotation



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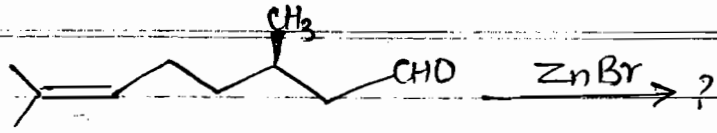
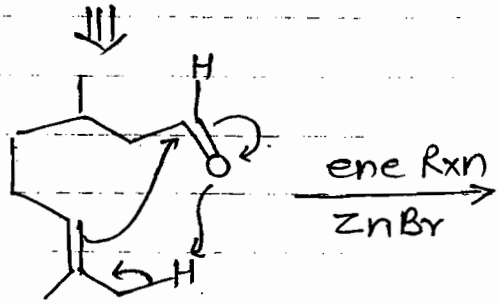
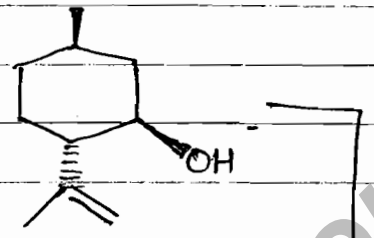
M. Imp

Q20



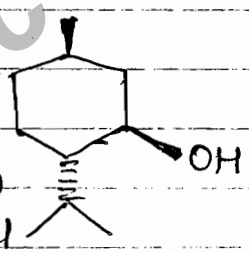




ene Rxn
ZnBr

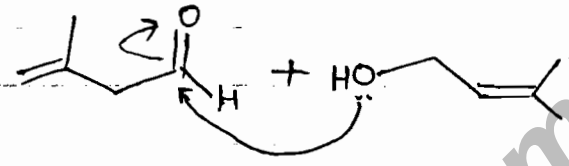


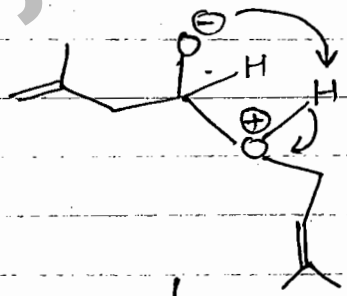

$H_2/Ni$

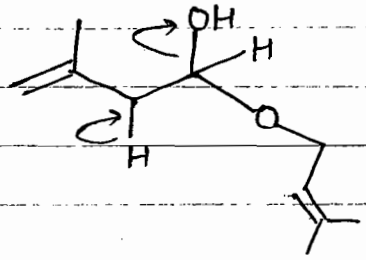
Natural prod.




(−)
Menthol

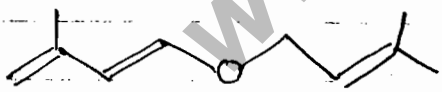


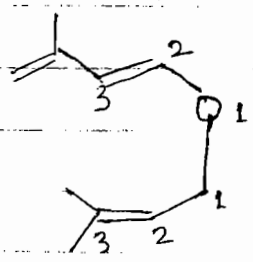




Hemiacetal

Dehydration
$-H_2O$






Claisen cope

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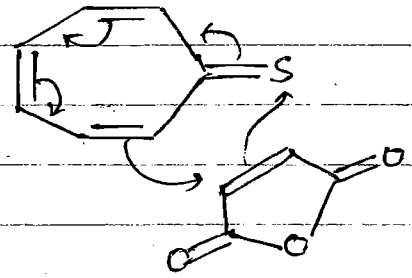
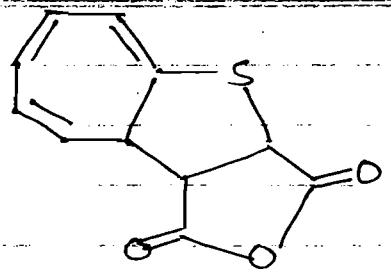
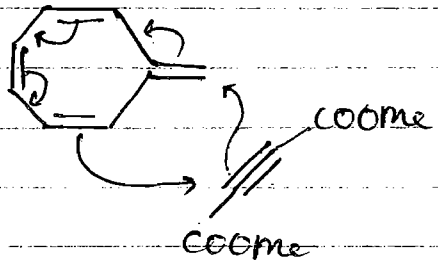
Q21



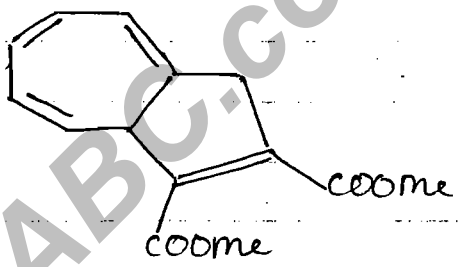
$\xrightarrow[8+2]{\Delta}$ $4n+2 \xrightarrow{\Delta}$ S-S



Q22

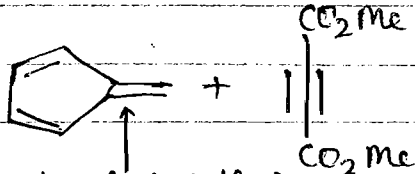


$\xrightarrow[4n+2]{\Delta}$ S-S



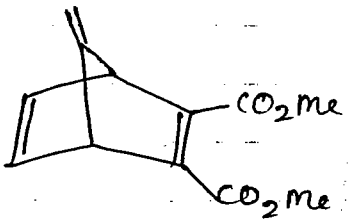
Grop.

Q23

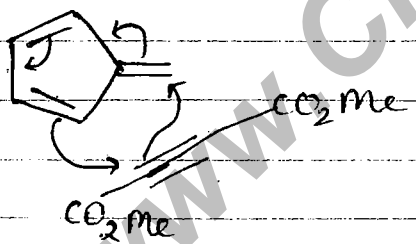


This bond not included in Rxn, becoz then system becomes 4n which is in Δ condition S-A (Impossible for small system).

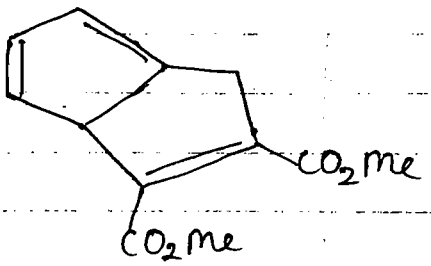
$\xrightarrow[4+2]{\Delta}$ 4n Syst. D.A.R.



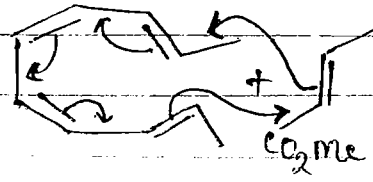
Q24



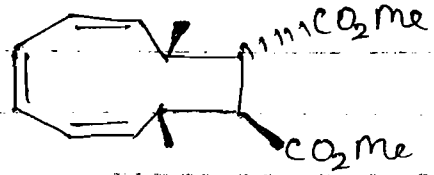
$\xrightarrow[6+2]{h\nu}$ 4n Syst S, S



Q25



$\xrightarrow[8+2]{\Delta}$ 4n+2 Syst. S-S



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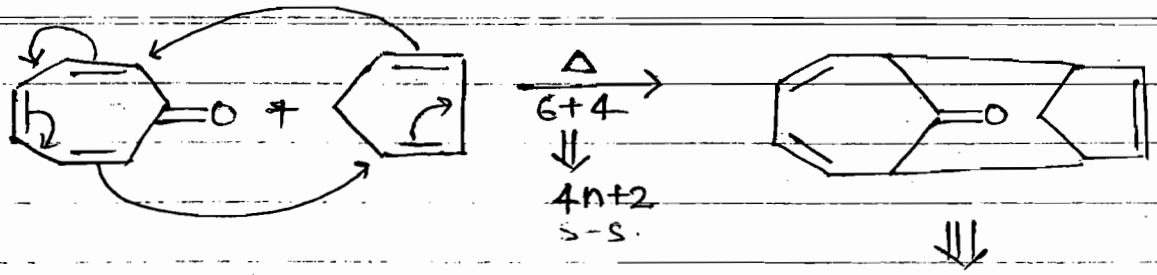
If S-S & S-A both possible then preferred will be S-S

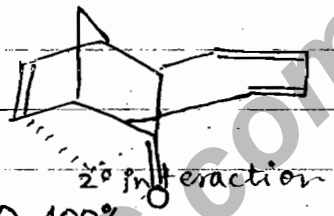
M.Imp.

Q.26




Here 8+4 also can take place but that will be S-A

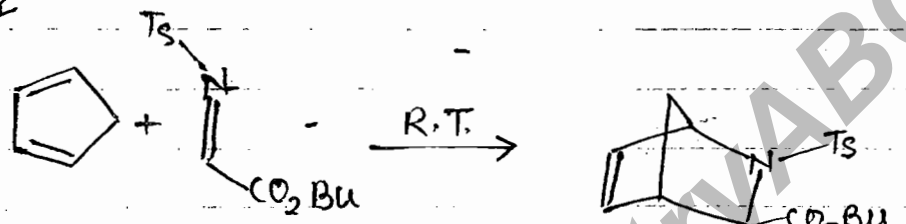
We know S-S is more favourable than S-A.




only exo 100%

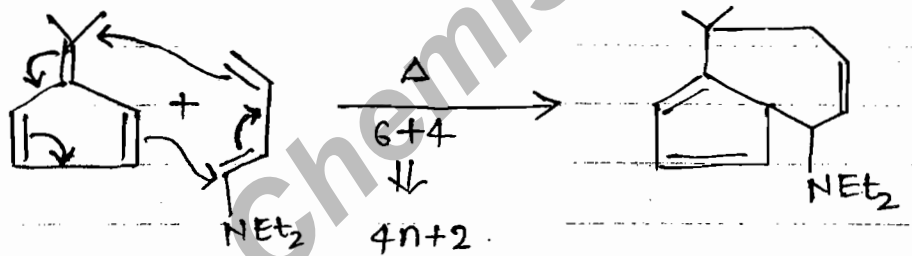
M.Imp

Q.27

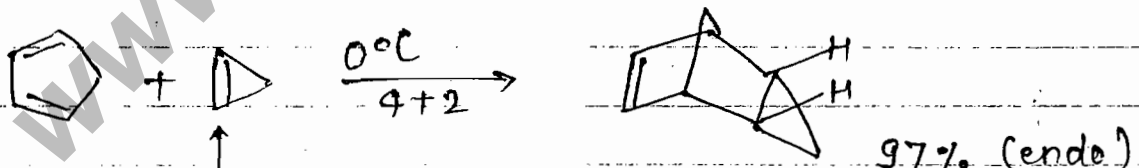



only exo

Q.28




Q.29




97% (endo)

Highly reactive that's why Rxn. proceeds easily at 0°C.

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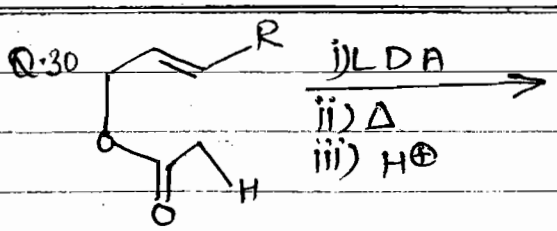
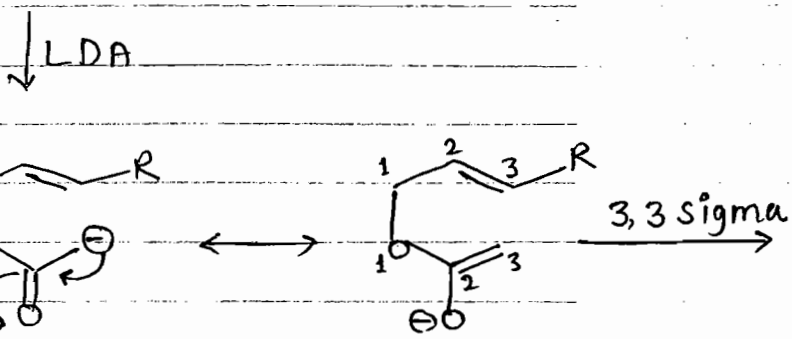
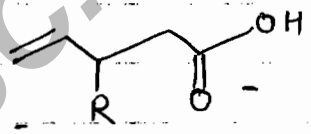
Q.30

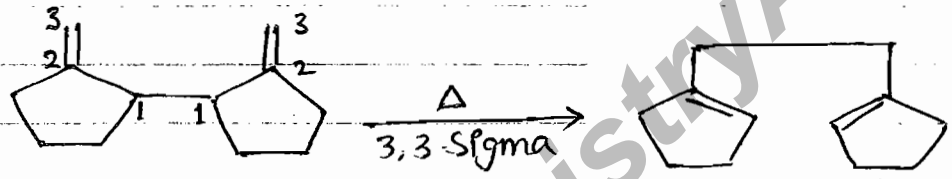


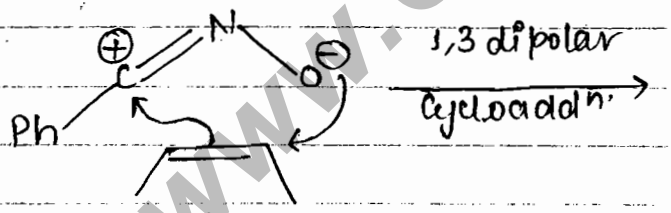

Ireland claisen Rearrangement

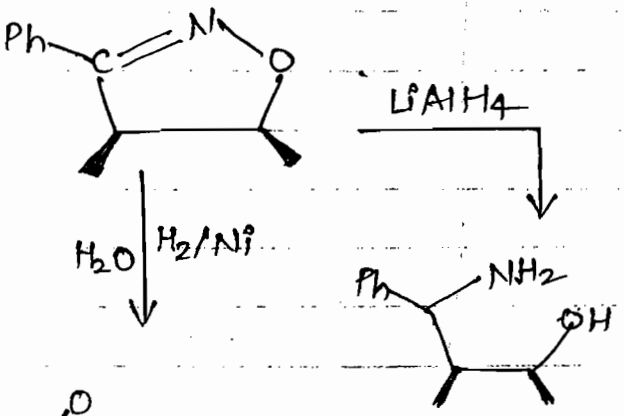


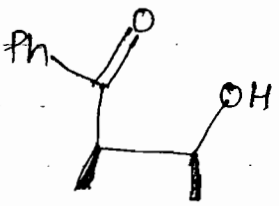

Q.31




Q.32

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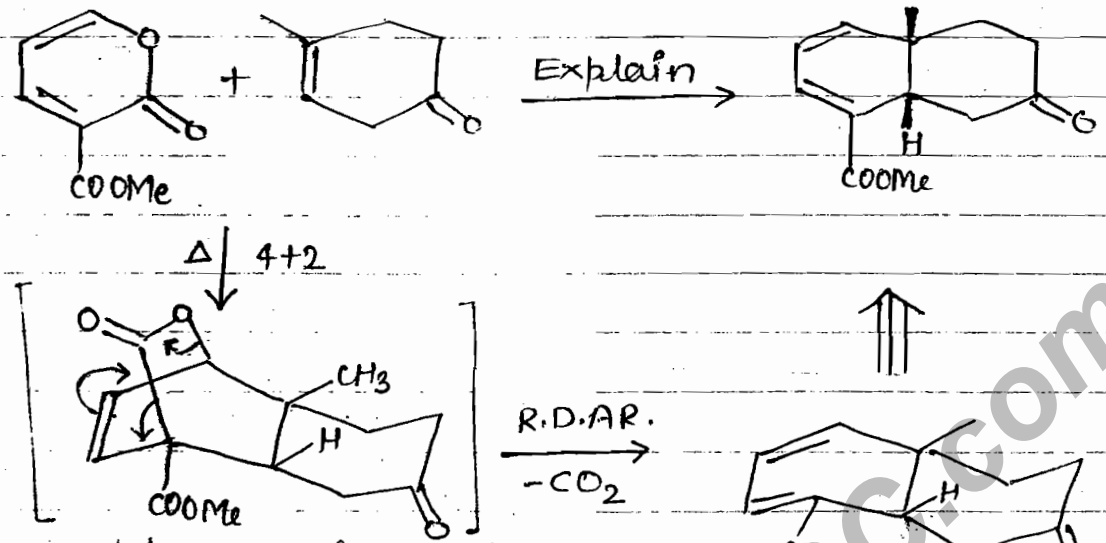
In such type of System R.D.A.R. will take place, to decar. of compound (Product after D.A.R.)

M.Imp

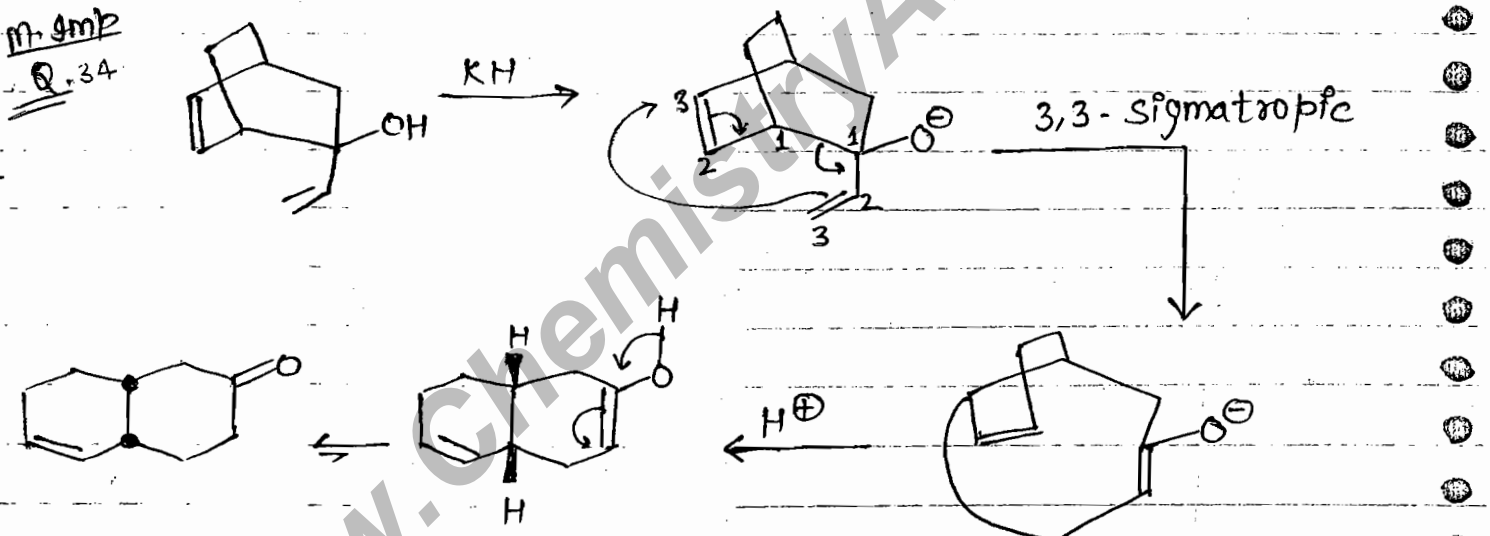
Q.33



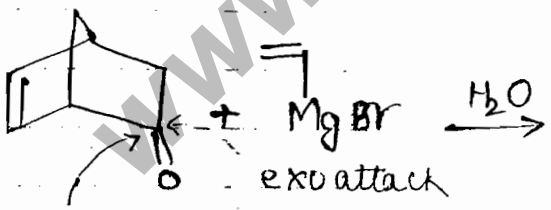

Unstable (Heat is already present so decarboxylation

M.Imp

Q.34

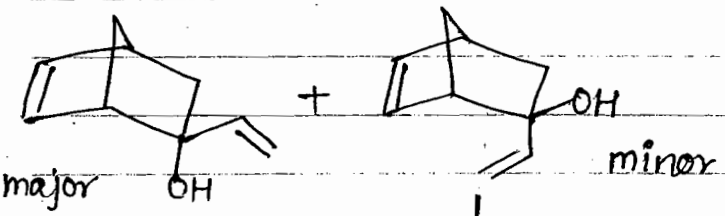



Q.35




Endo attack
More Hind
(due to cavity)

exo attack
Less Hind




Δ

No 3,3 Sigmatropic

Δ

It can give 3,3-sigma tropic Rxn.

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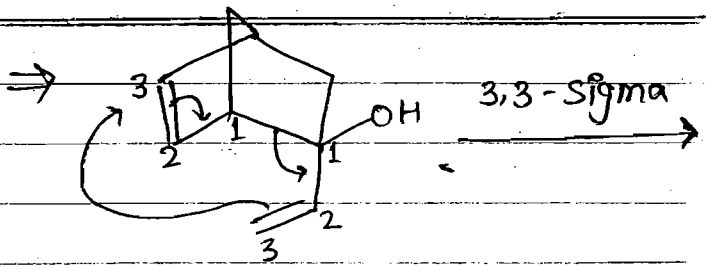
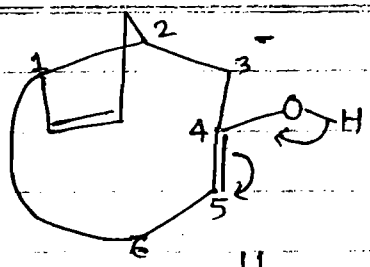
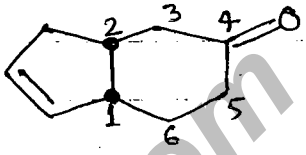
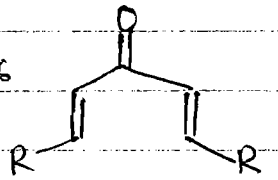


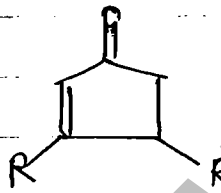




Q36

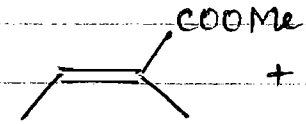



$H^{\oplus}$

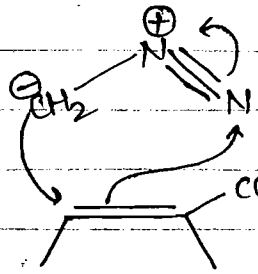
Nazarov cyclization

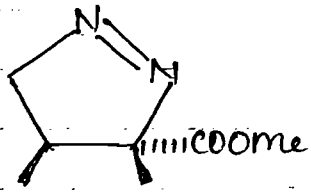



Q37

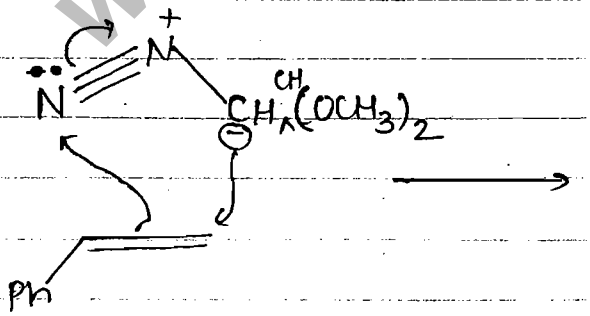


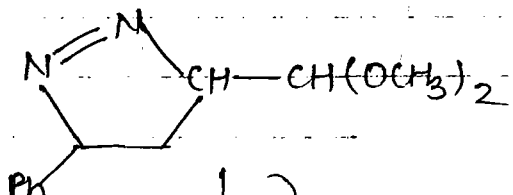

+ $CH_2N_2$ ⟶

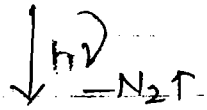


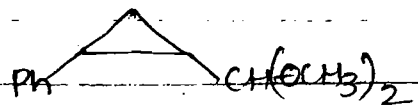




Q38 $Ph-CH=CH_2 + N_2CHCH(OCH_3)_2$ ⟶

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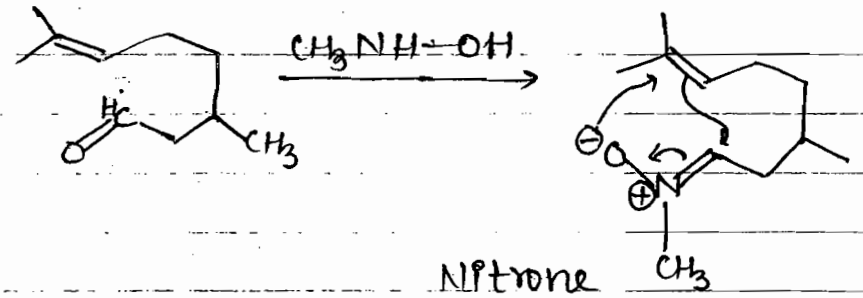
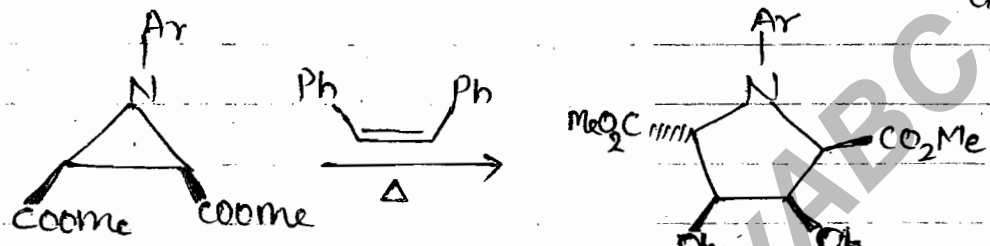
Q39

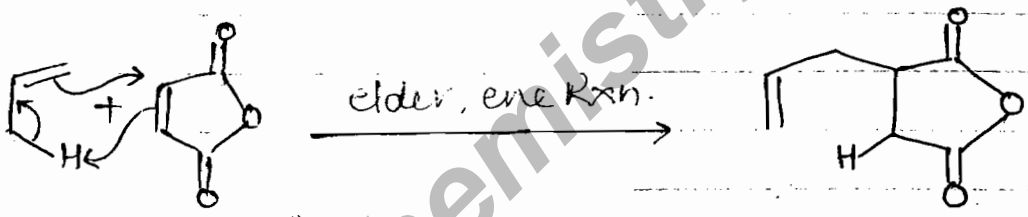



Q40



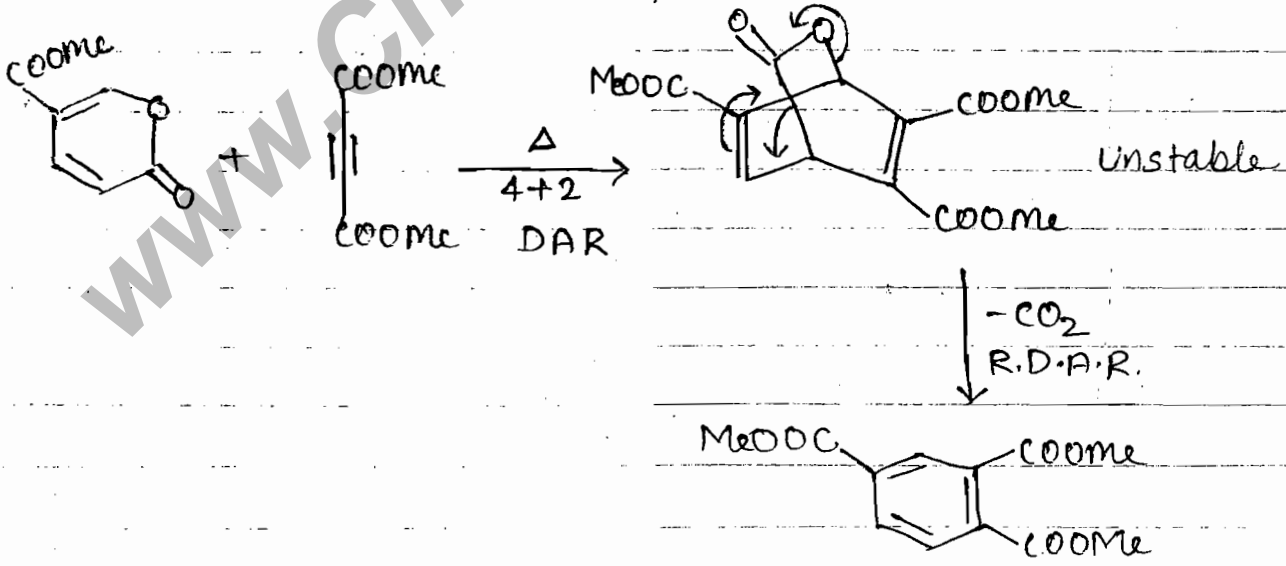

Ring opening(con in Δ) then 1,3 dipolar cycloaddition.

Amp.
Q41




↳ if ~~elder~~ malic anhydride rxt then elder ene Rxn.

Q42

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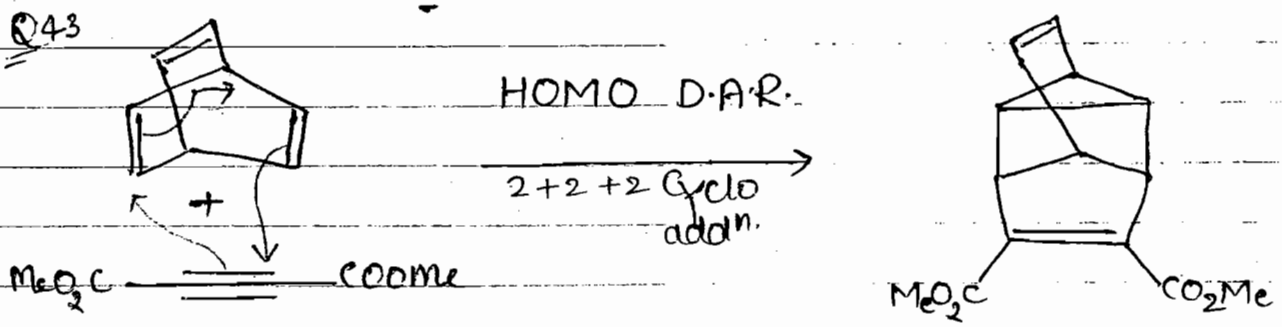
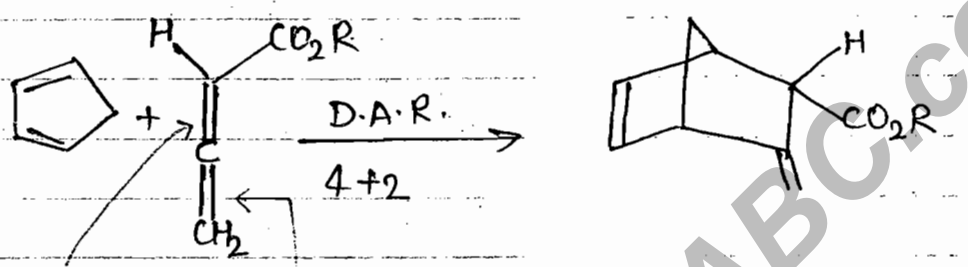
Q43



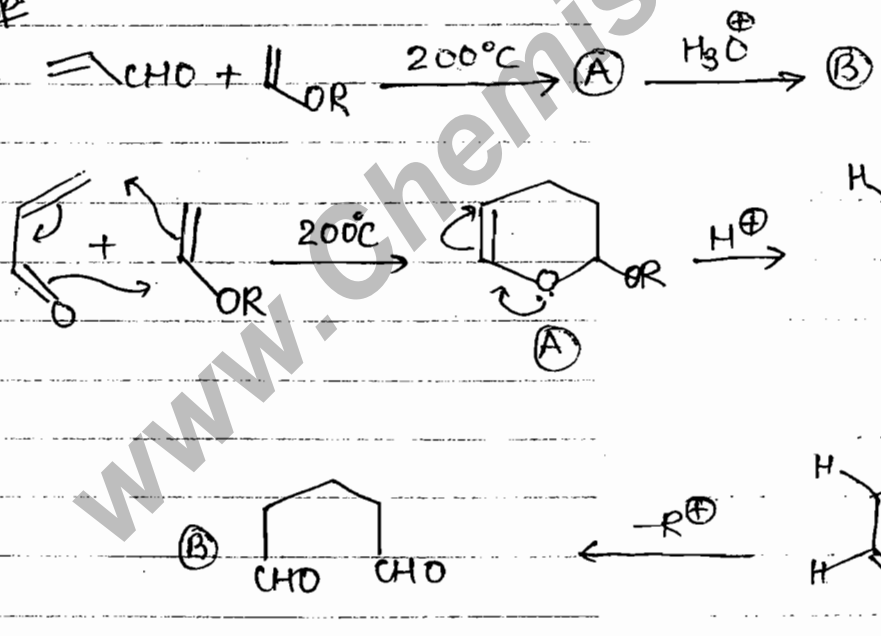

M.Imp.
Q.44



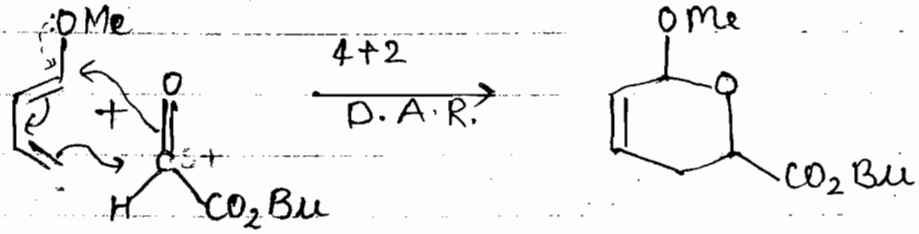

e⁻ deficient dienophile

e⁻ rich dienophile

M.Imp.
Q45




Q46

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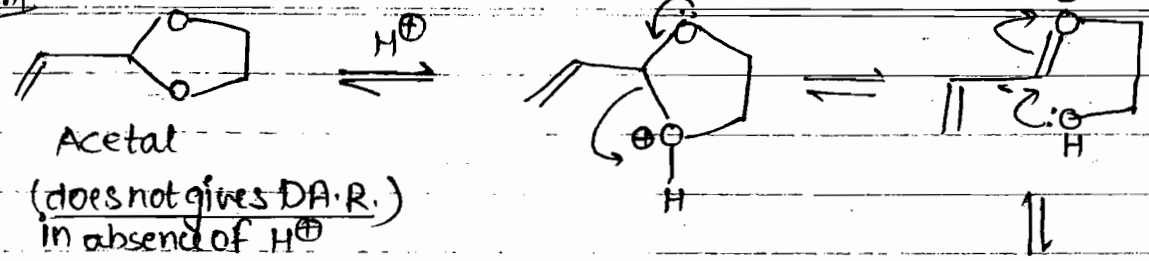
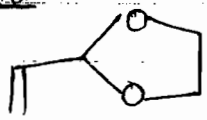
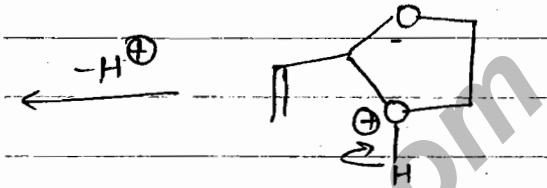
Q47 M.Imp.



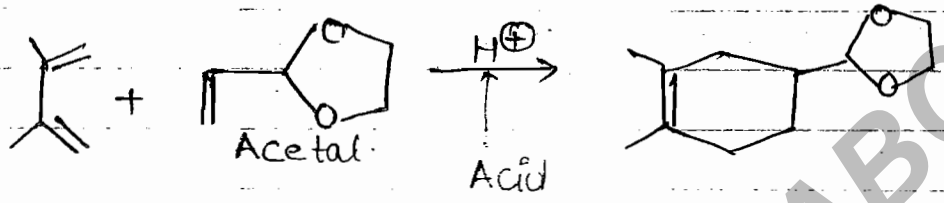

(does not gives DA·R.) in absence of $H^{\oplus}$

But in the presence of Acid Acetal can give Rxn.

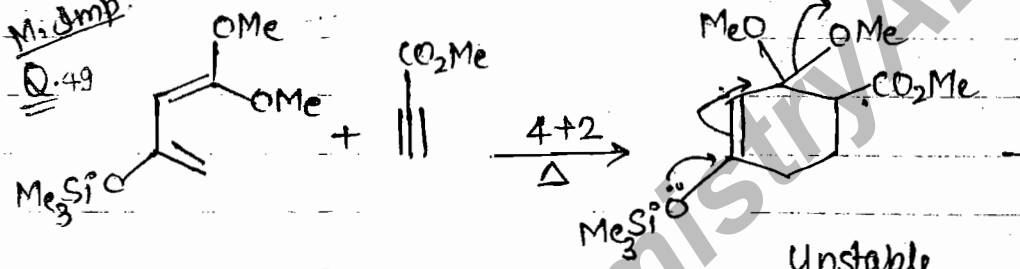




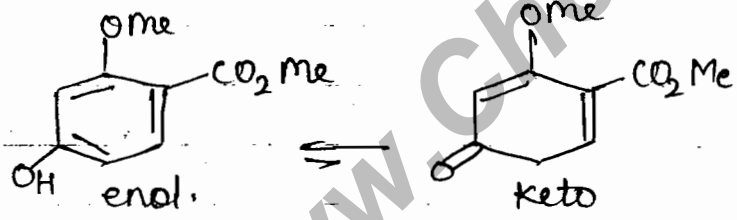

Q48

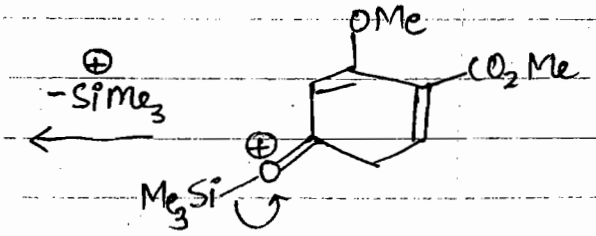



Q.49 M.Imp

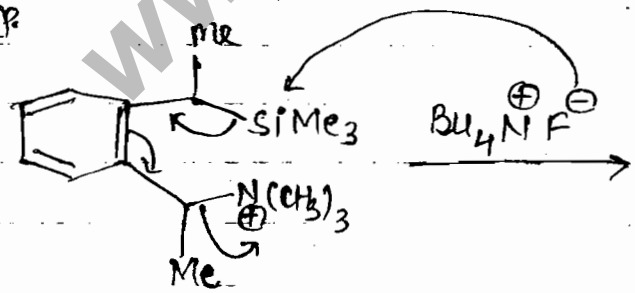


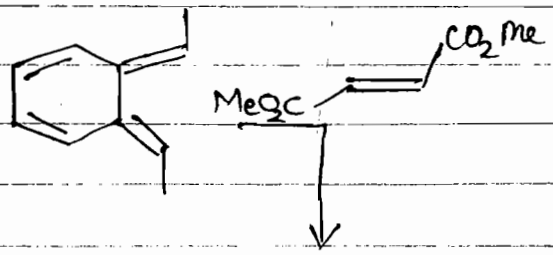

Unstable

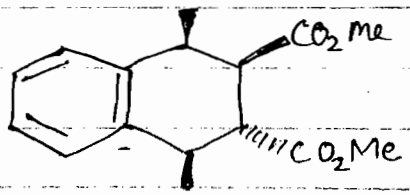



Q50 M.Imp

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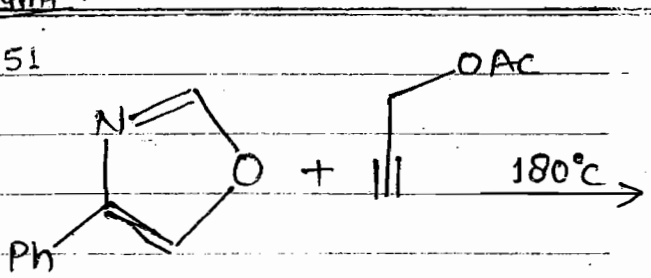
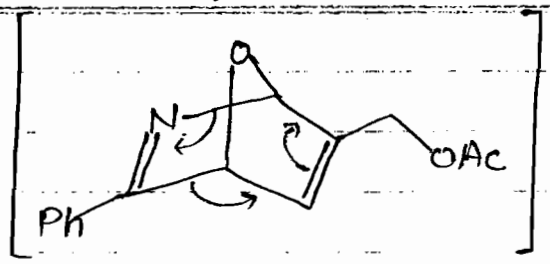
If such system is given with acid, do always like this.

M.Imp.

Q 51

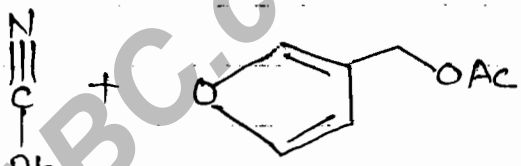


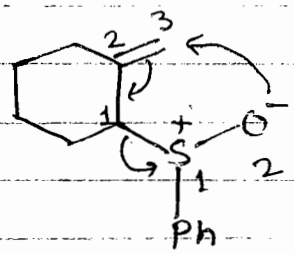

unstable

R.D.A.R.

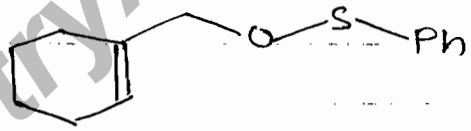
Δ




Q52

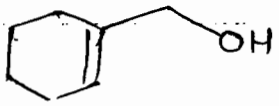



Δ

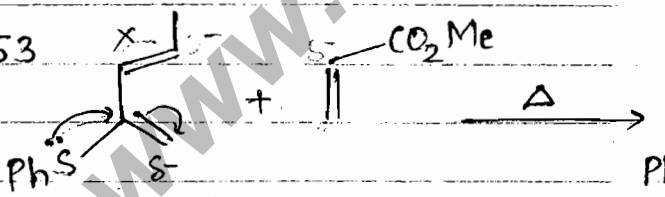



$P(OEt)_3$

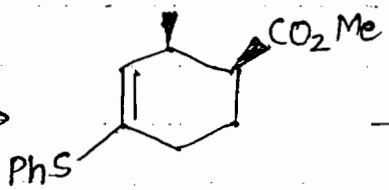
This Reagent breaks O=S bond.



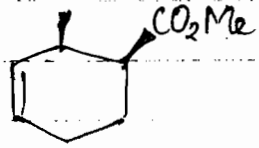

Q.53




Δ




Raney Ni




Raney Ni

↳ Best reagent for desulphurination

Breaks C–S bond

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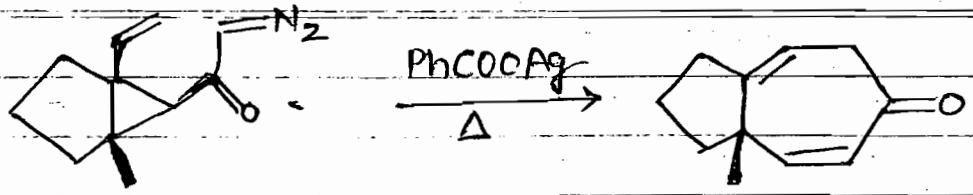
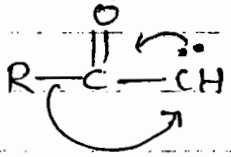
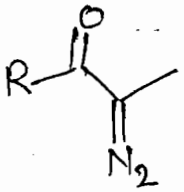
Q54 


Soln.

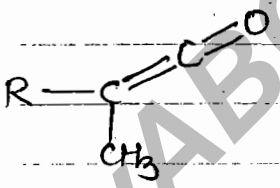
Trick 


Wolf Rearrangement → R—CH=C=O

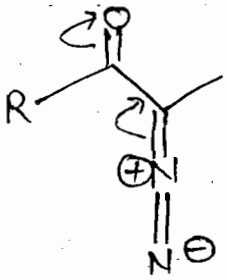
Acyl carbene



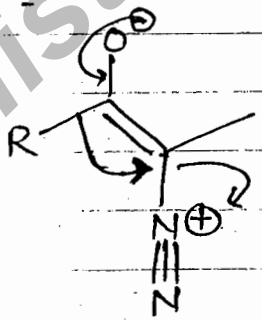

hν or Ag(I) or Δ →




⇓

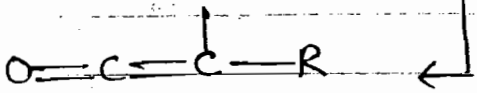



$Ag^{I}$ or hν or Δ →

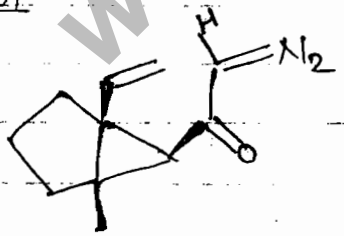



Wolf Rearrangement

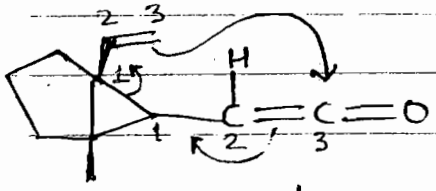
$-N_2$




Prob. Soln.

* 


$Ag^{I}$ / wolf →




Δ 3,3 Sigma

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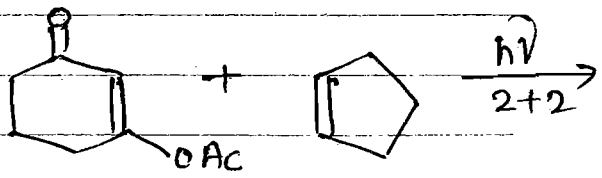
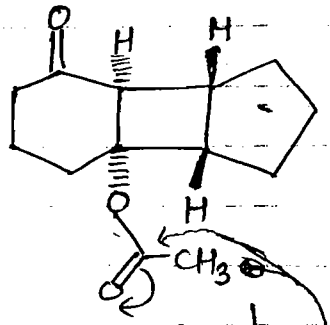
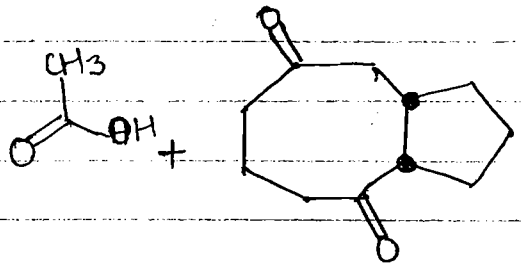
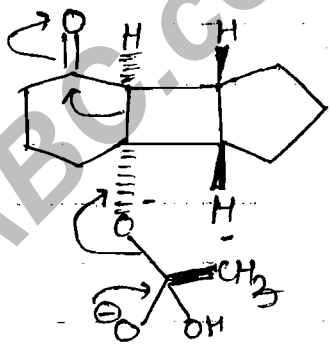
Imp

Q.55



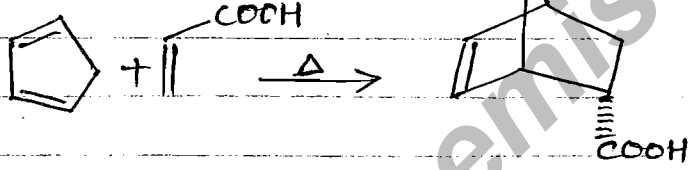



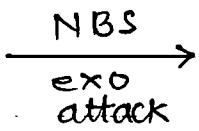



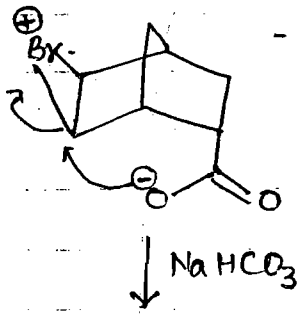



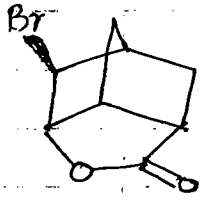

Imp

Q.56

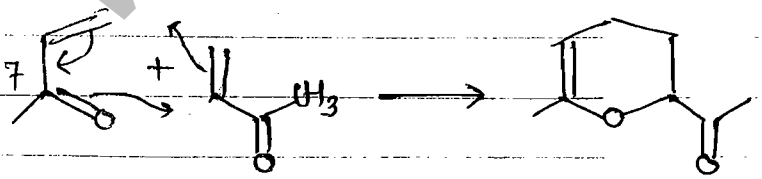


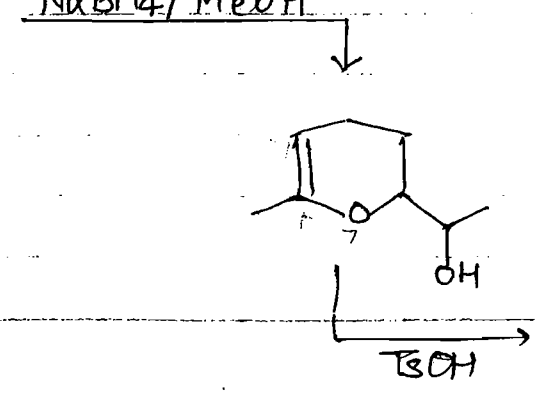




Q.57

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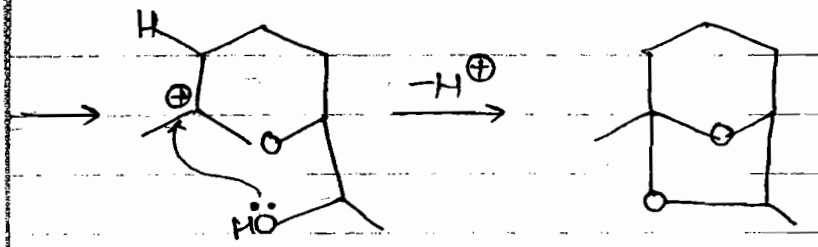
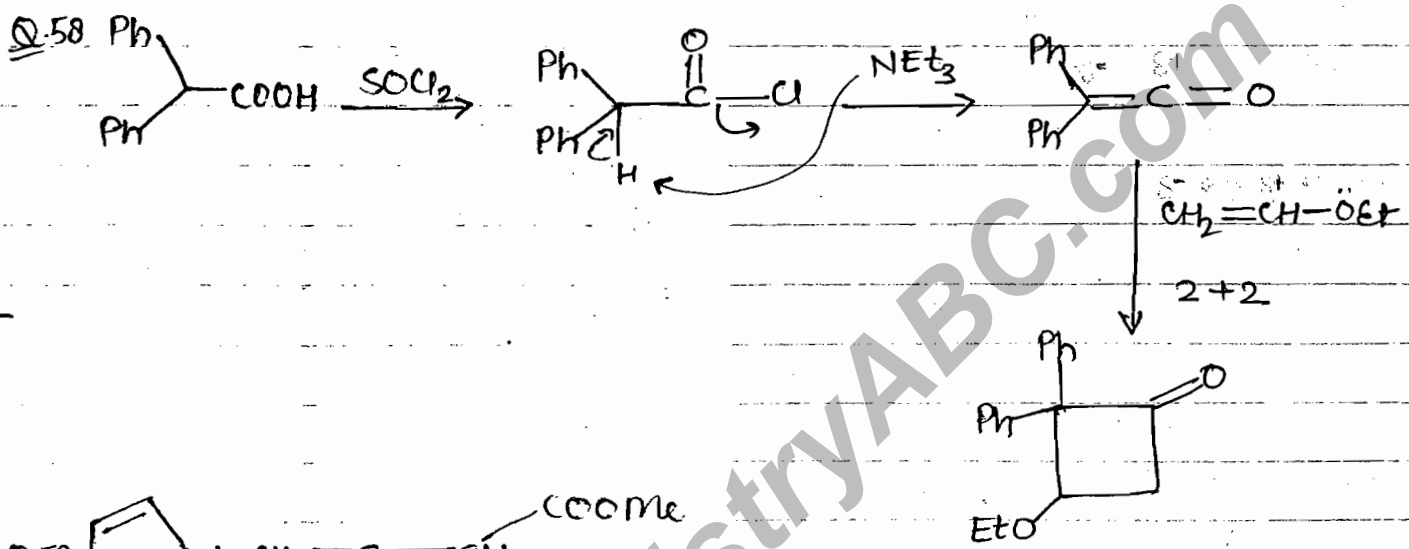


Q.58

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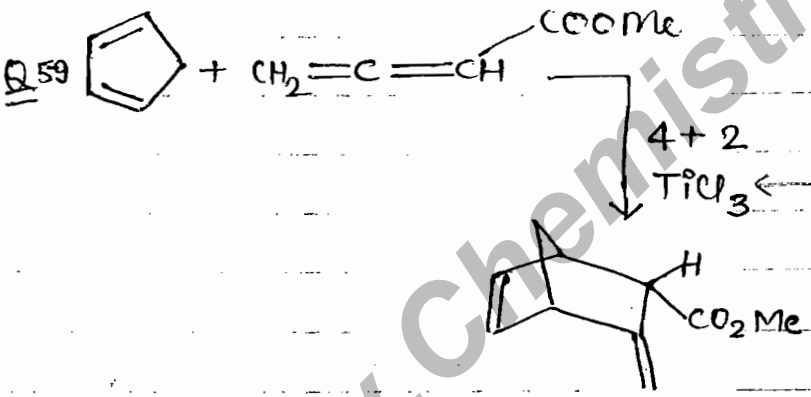
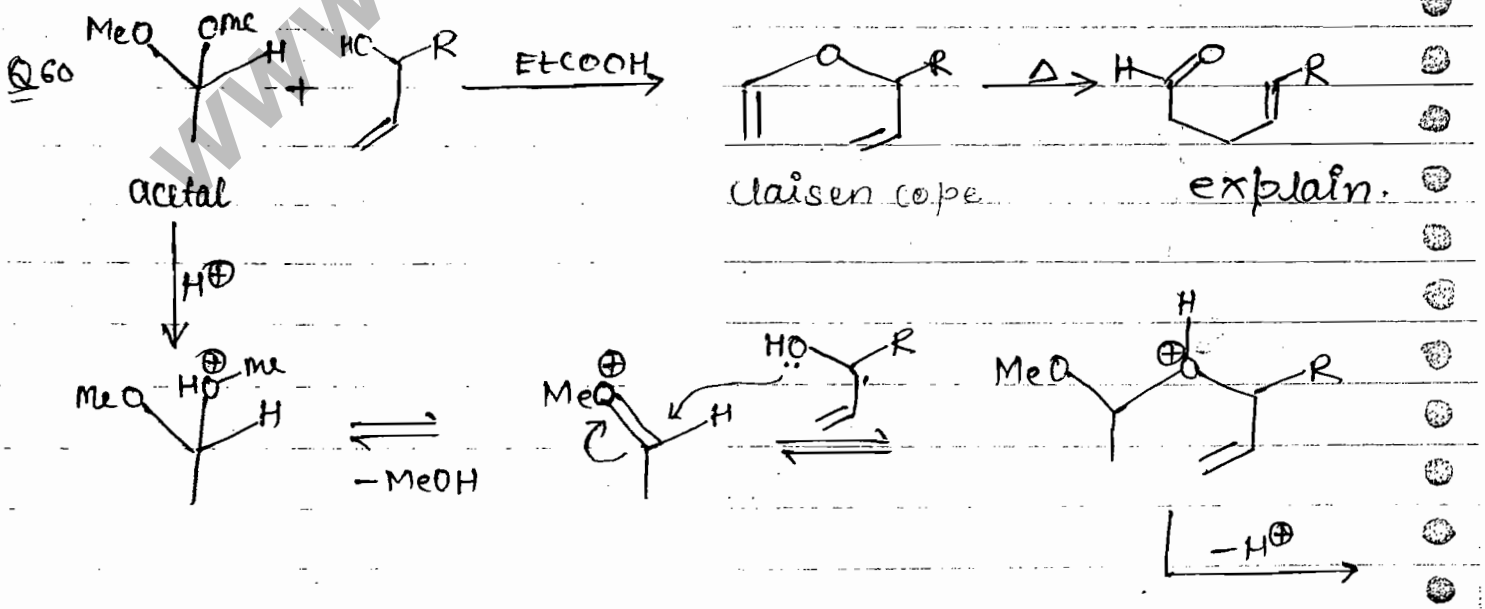



← Rate of Rxn. Increases.

Q.60

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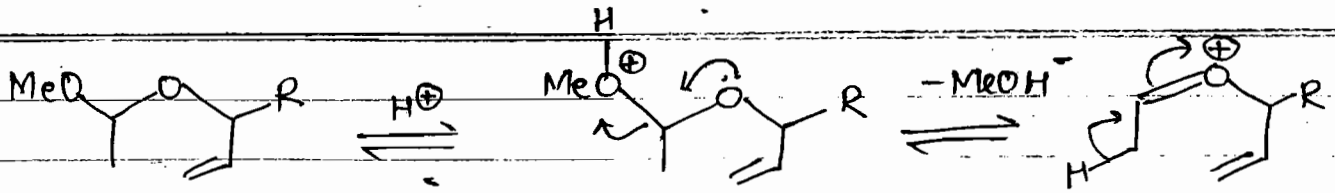
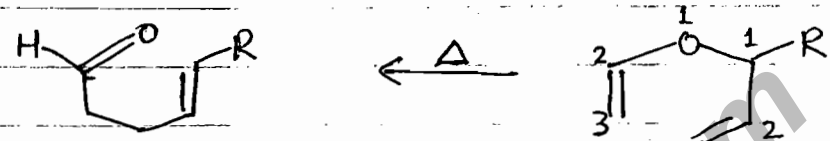
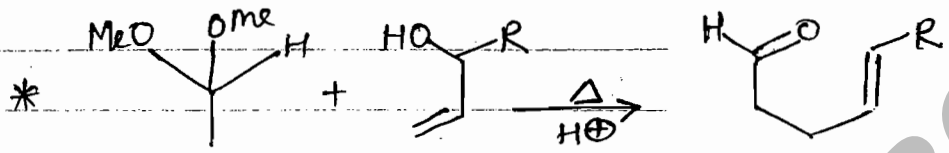
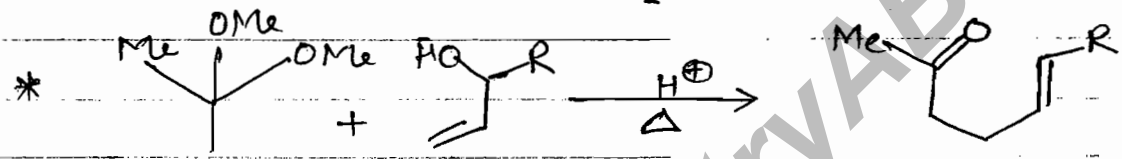
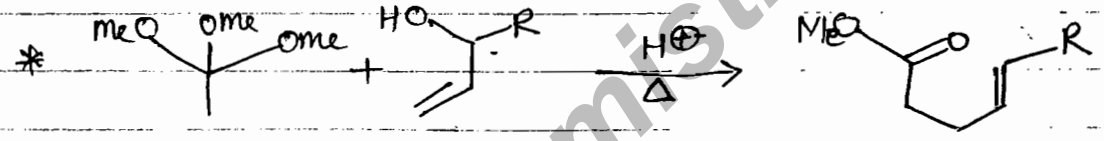


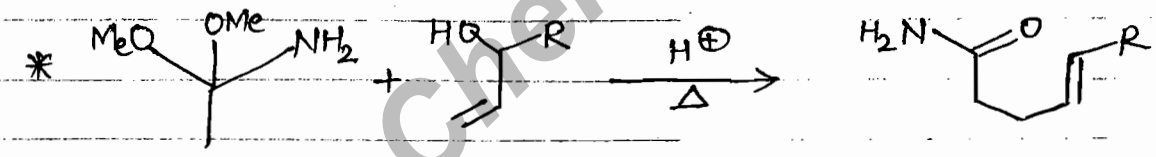

Claisen Cope



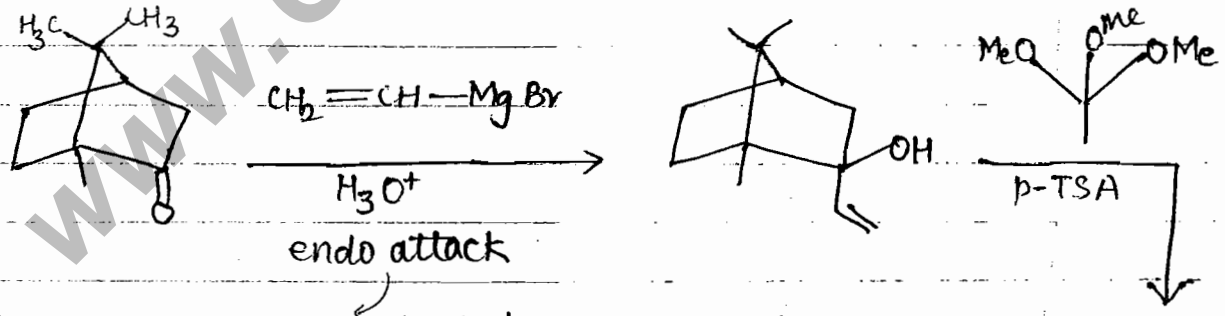



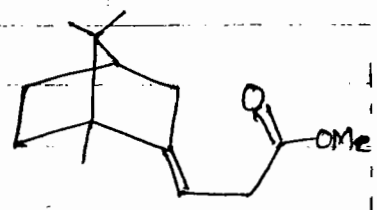

M.Imp

Q.61




endo attack

Because on exo attack two $CH_3$ groups are creating hindrance




para toluene sulphonic acid ⇒ p-TSA

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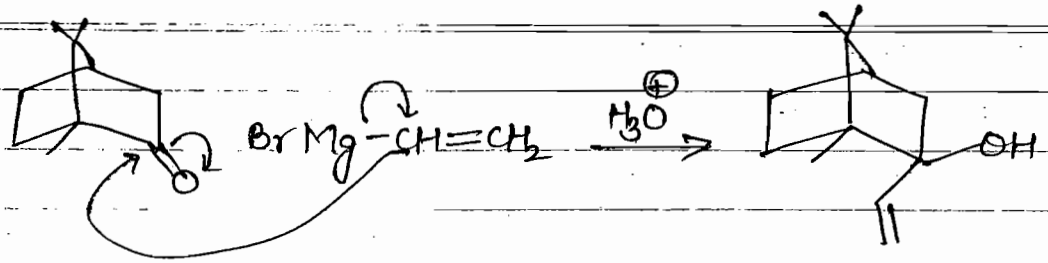
Mechanism.

1)

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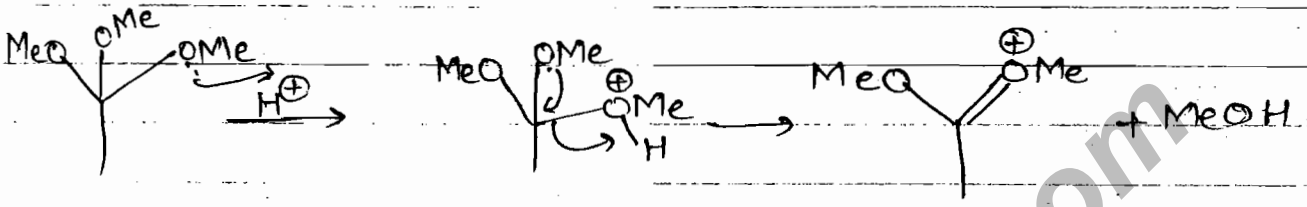
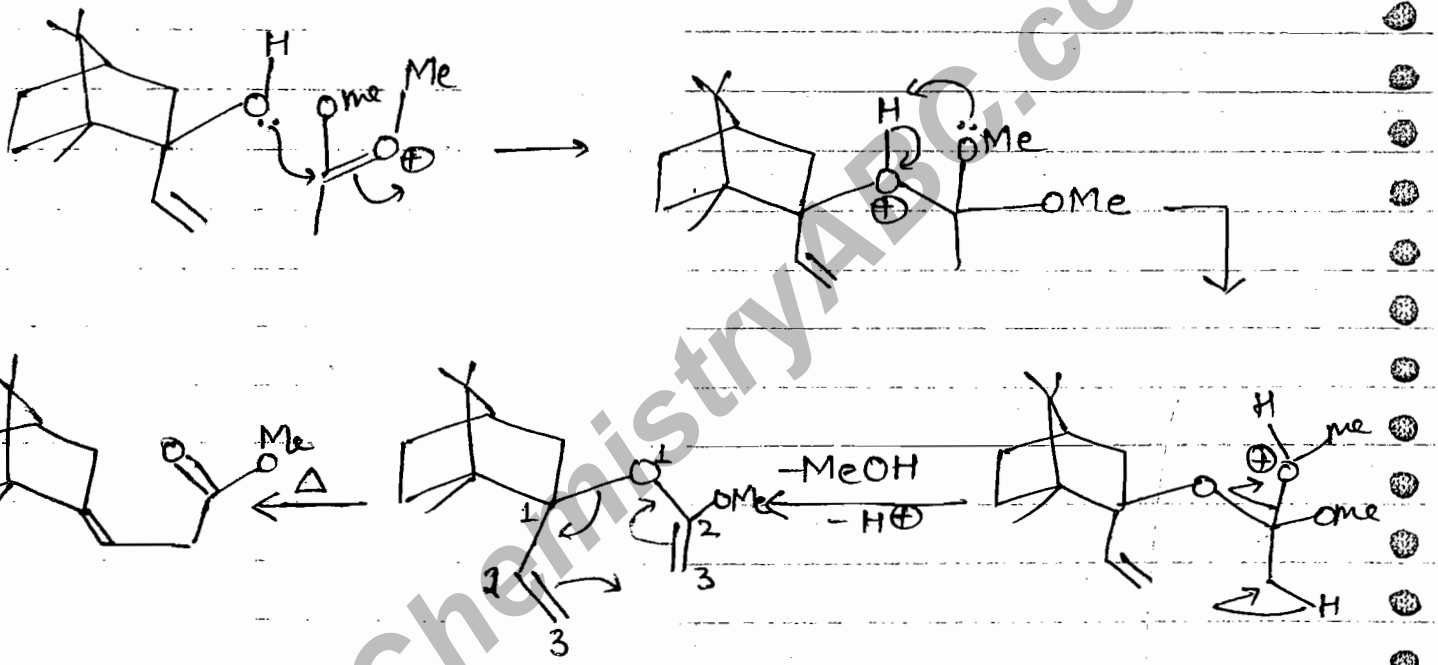



3)

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# PHOTOCHEMISTRY

Photo ⇒ Photon  Chemistry

Chemical rxn. which shows chemical changes by the absorption of light called photochemical rxn. The branch of chemistry which deals photochemical rxn. are called photochemistry.

Photochemical rxn. absorbe a light radiation in the region of 200nm to 800 nm

200 — 400 nm ⇒ U.V. Region

400 — 800 nm ⇒ Visible "

Diff. b/w photochemical Rxn. & Thermal Rxn.

| Photochemical Rxns. | Thermal Rxns. |
|---|---|
| Rxn. takes place by the absorption of light radiation | During Rxn. heat may be absorbe or emitted. |
| Most of photochem. Rxn. are independent on temp. | On increasing temp. rate of rxn. increase. $K = Ae^{-Ea/RT}$ |
| for spontaneous photochem. Rxn. $\Delta G$ may be +ve or -ve, $\Delta G$ +ve for photosynthesis, ozone depletion, Natural decomposition of HCl. | for spontaneous system. $\Delta G$ must be negative. |

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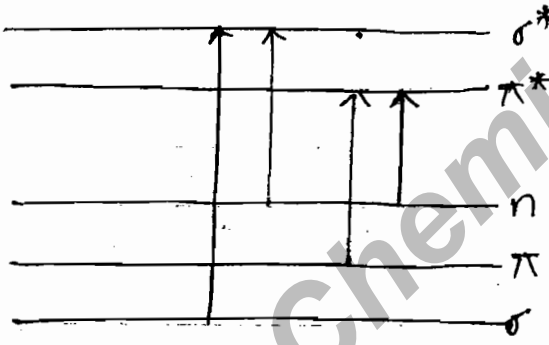
By the absorption of quantum particular molecule get excited. (1 molecule = 1 photon concept)

By the absorption of heat whole molecule get excited.

## Law of photochemistry

1) Grawthus & Drawper Law
2) Einstein Law of photochemical Equivalance.

## Electronic Transitions:




Energy order.

$\sigma-\sigma^* > n-\sigma^* > \pi-\pi^* > n-\pi^*$

Energy order for Carbonyl.

$\sigma-\sigma^* > \pi-\pi^* > n-\sigma^* > n-\pi^*$

## Effect of Solvent :-

Solvent

- Polar solvent
- Non polar solvent

The order of stability by polar solvent of

**non bonding > $\pi^*$ bonding > $\pi$ bonding.**

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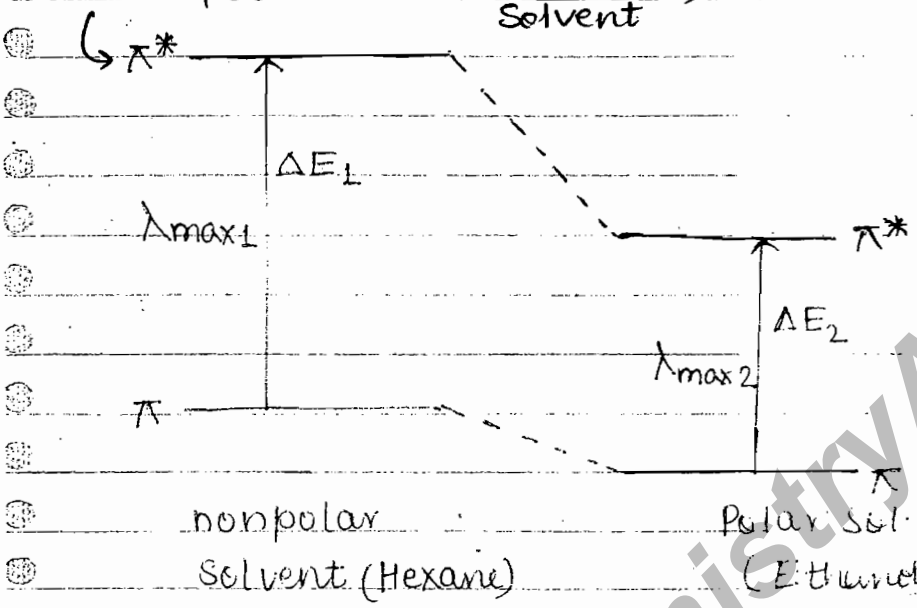
For $\pi - \pi^*$ ⇒ Polar Solvent increases Rate of Rxn.
For $n - \pi^*$ ⇒ Non polar Solvent " " " "

Increasing the polarity of the solvent, $\lambda_{max}$ increase in allowed transition ($\pi - \pi^*$ transition) In $\pi - \pi^*$ transition the dipole interaction wh with the solvent molecule lower the energy of the excited state more than ground state

More polar orb. $\xrightarrow[\text{Solvent}]{\text{Polar}}$ More E ↓

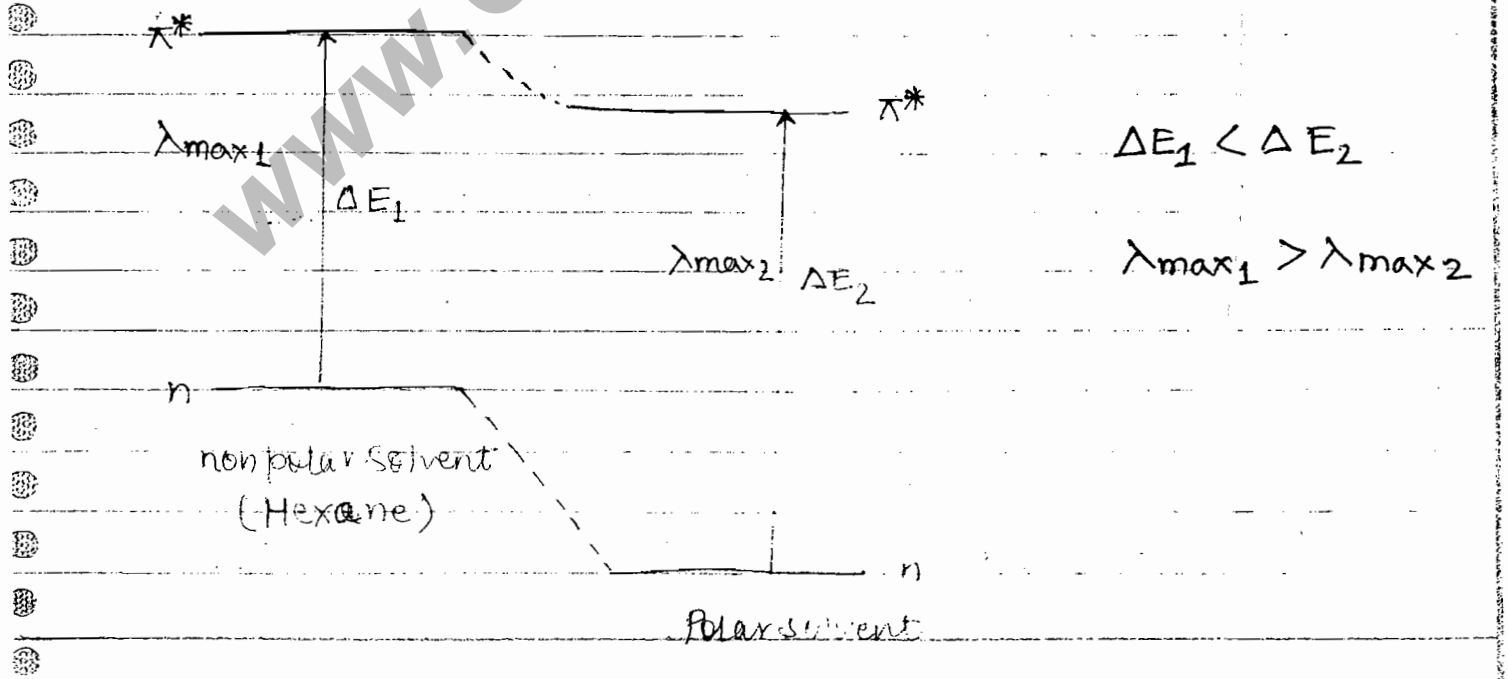



$\Delta E_1 > \Delta E_2$

$\lambda_{max_1} < \lambda_{max_2}$

$E \propto \frac{1}{\lambda}$

Increasing polarity of solvent $\lambda_{max}$ decreases in $n - \pi^*$ transition.




$\Delta E_1 < \Delta E_2$

$\lambda_{max_1} > \lambda_{max_2}$

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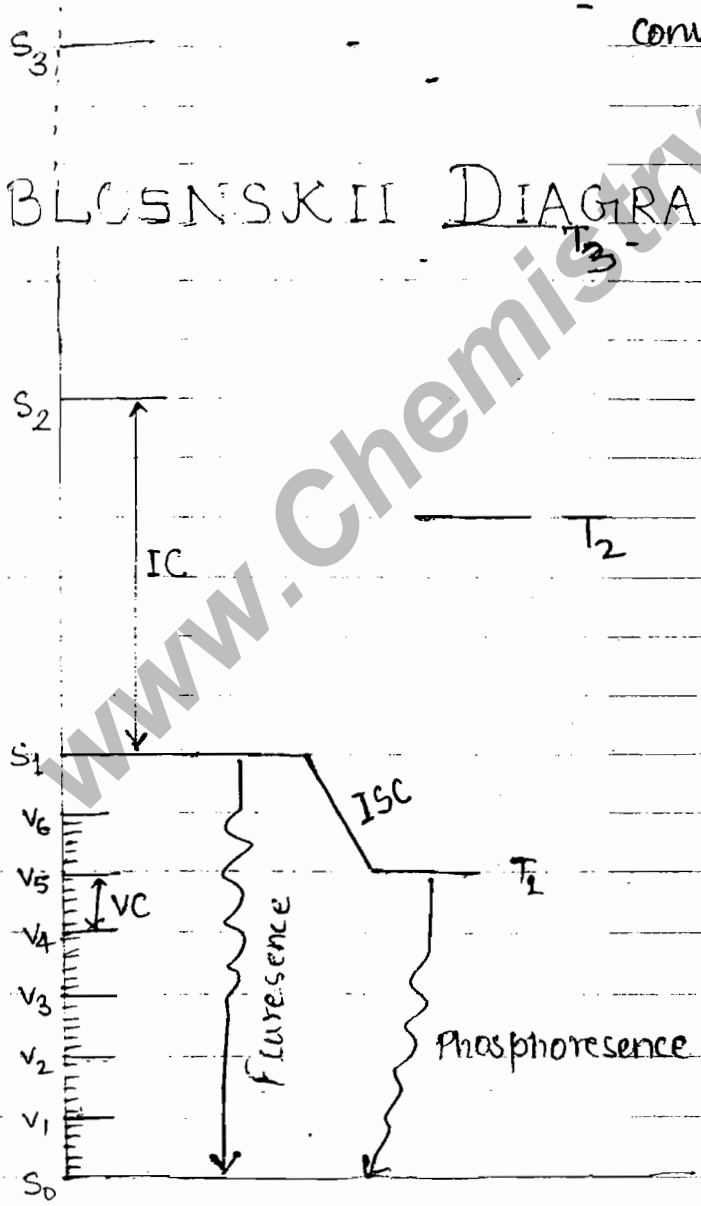
# Fate of Excited e⁻ or Future of Excited e⁻ :-

Physical Process

- Radiative Process
  - Fluresence
  - Phosphoresence
- Non Radiative process
  - I.C. — Internal conversion
  - ISC. — Inter System crossing
  - V.C. — Vibrational cascade

## JABLONSKII DIAGRAM




Fluorosensence

$S_1 \longrightarrow S_0 + h\bar{\nu}$

Phosphoresence

$T_1 \longrightarrow S_0 + h\bar{\nu}$

I.C.

$S_3 \longrightarrow S_2 + \Delta$

$S_2 \longrightarrow S_1 + \Delta$

ISC.

$S_2 \longrightarrow T_2 + \Delta$

$S_1 \longrightarrow T_1 + \Delta$

V.C.

$V_2 \longrightarrow V_1 + \Delta$

$V_n \longrightarrow V_{n-1} + \Delta$

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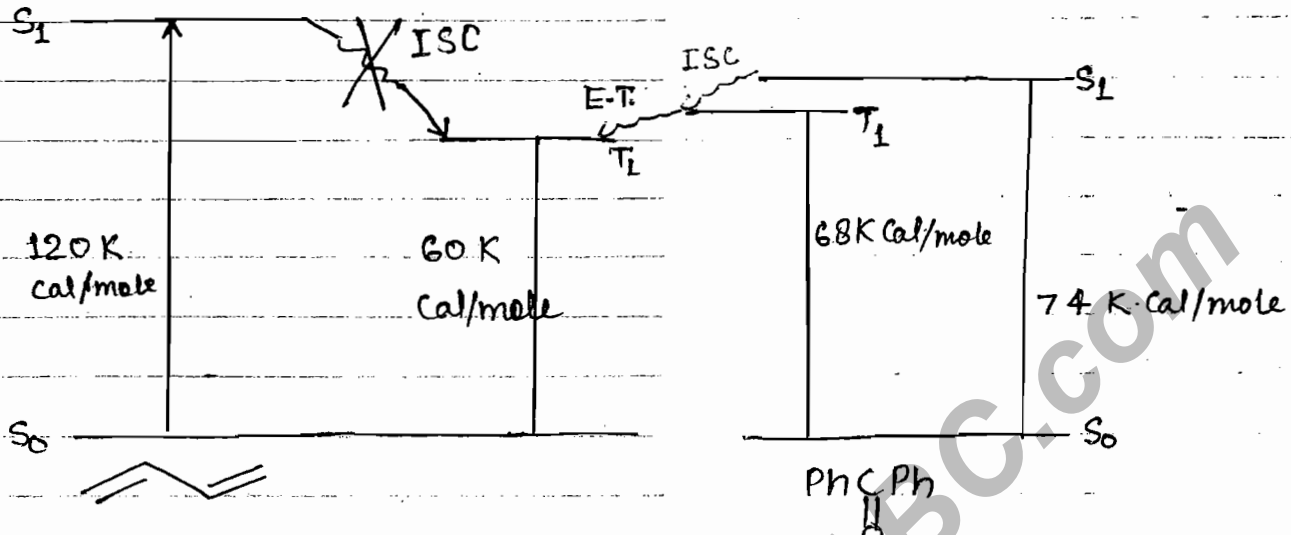
E.T.R. ⇒ Energy trans for Rxn.

Sensitizer is just like catalyst for photochemical Rxn.

# ENERGY TRANSFER or PHOTOSENSITISATION



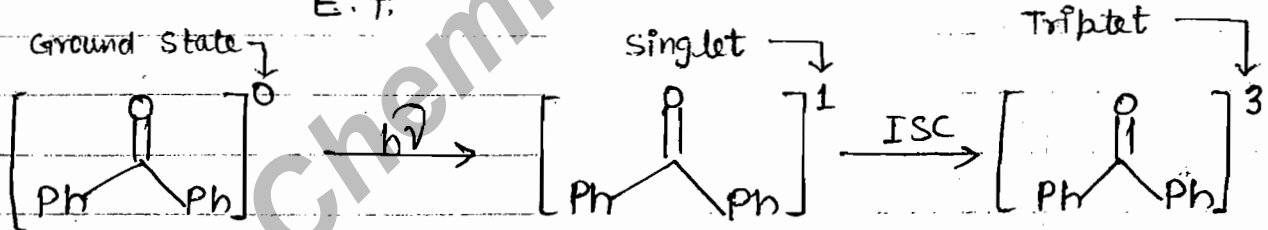

D = Donor

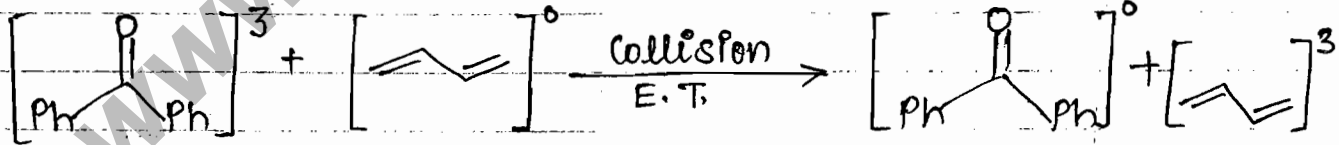
A = Acceptor

$$[D]^0 \xrightarrow{h\nu} [D]^1 \xrightarrow{ISC} [D]^3$$

$$[D]^3 + [A]^0 \xrightarrow[E.T.]{\text{collision}} [D]^0 + [A]^3$$

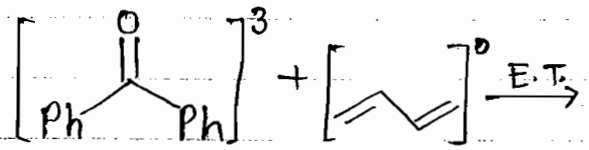
Ex.



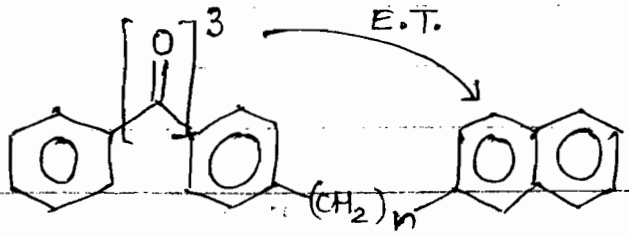




E.T.R.

Intermolecular




Intramolecular

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# ORGANIC PHOTOCHEMISTRY

ORG. CHEMISTRY

- Photochemistry of Carbonyl compounds.
  - Norrish type I (N-I) — α-bond cleavage
  - Norrish-type II (N-II)
  - Paternobuchi
  - Photoreduction of Carbonyl
- Photochemistry of olefin
  - cis-trans isomerism
  - Di-π-methane rearrangement
  - Oxo di-π-methane rearrangement
- Photochemistry of aromatic compound
- Photochemistry of singlet oxygen
- Barton Rxn.
- Hafmann Lofler Frentage rearrangement

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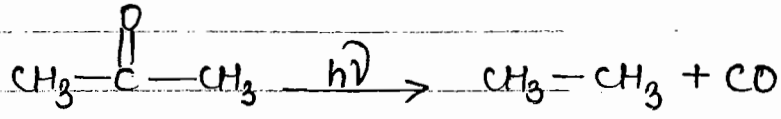
# PHOTOCHEMISTRY OF CARBONYL Compound

Norrish type I : 1) Both, singlet & triplet ~~rxn~~ state takes part in the rxn.

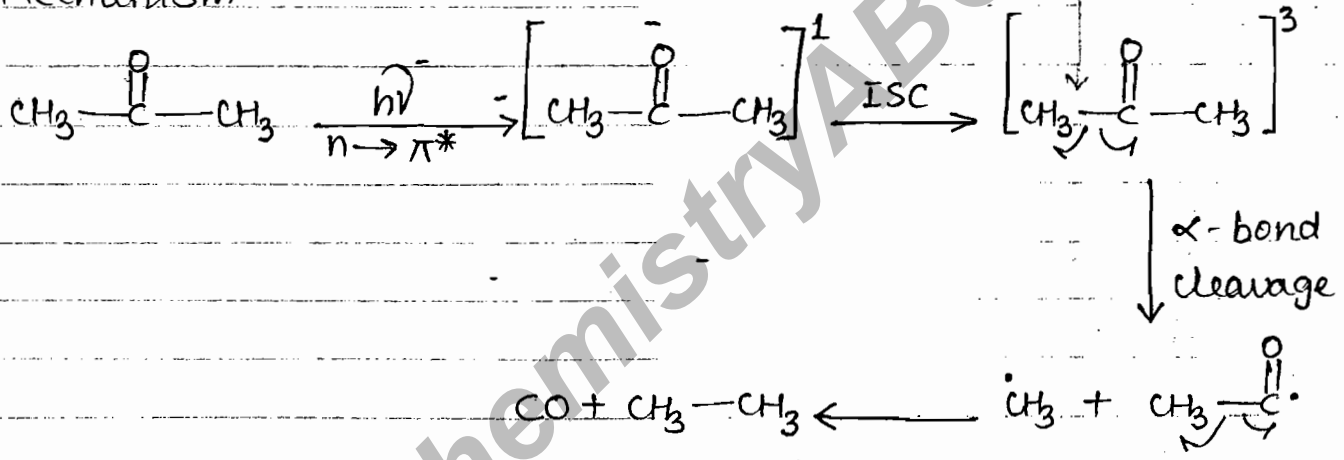
2) $n \rightarrow \pi^*$ transition take place

3) $\alpha$ - bond cleavage and mostly reactions CO eliminate

Ex.



Mechanism

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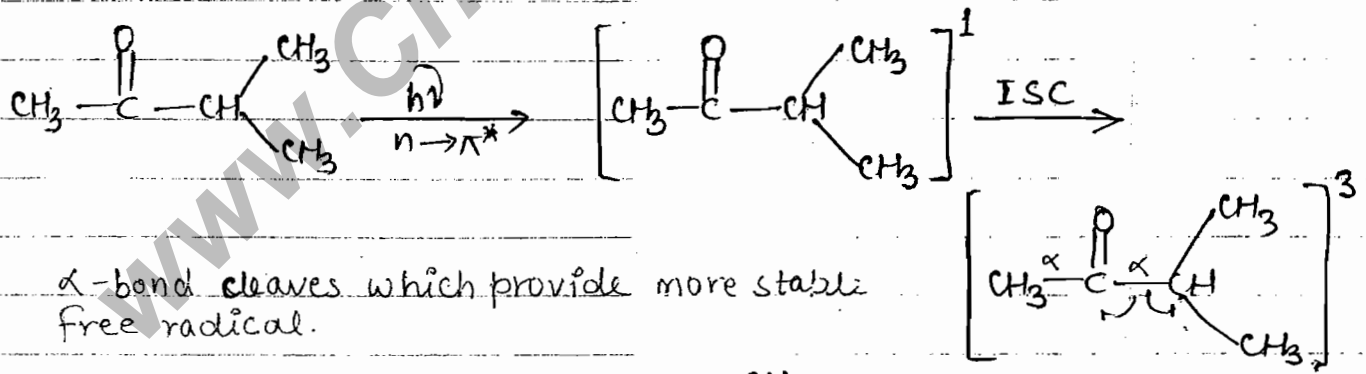


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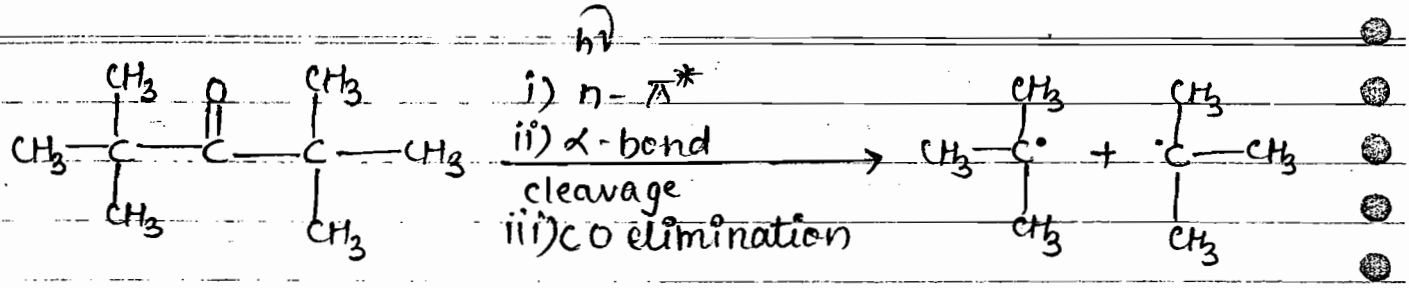
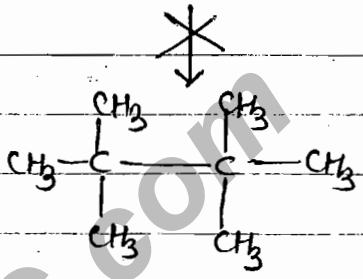
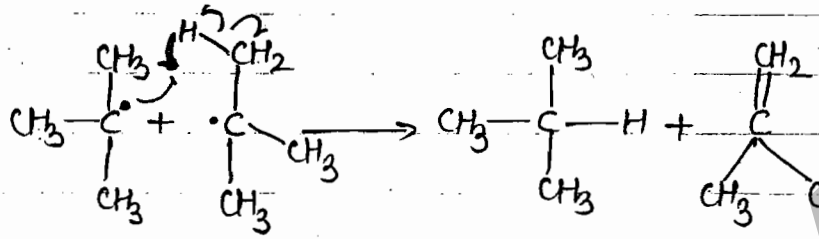
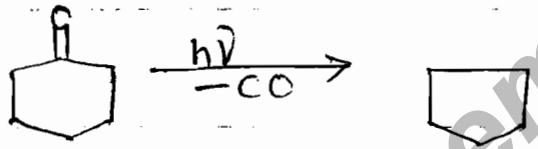
Free radical stability increases by both ENG, ERG due to captodative effect.

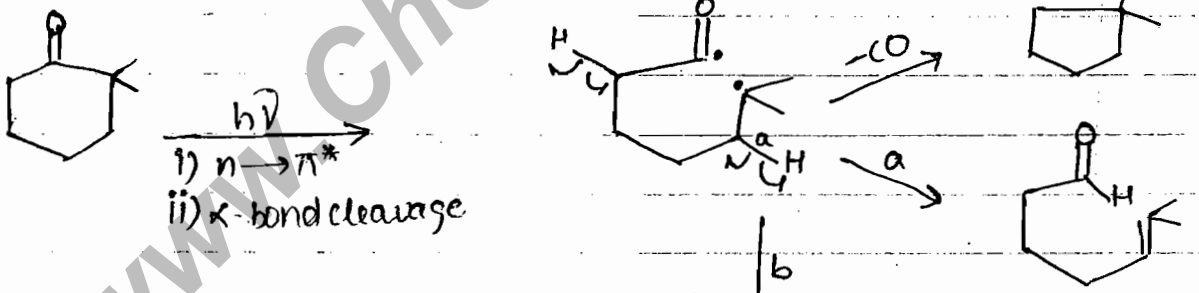
Q 

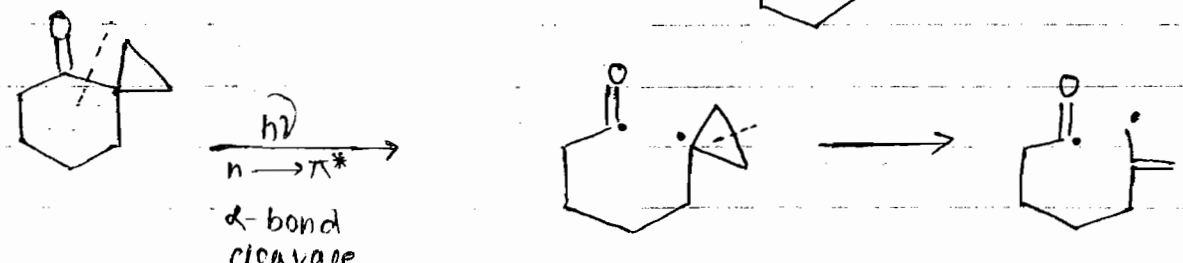




* 

3° free radical ⇒ Elimination of H• in competition with alkyl free radicals addition).

Q 


Q 


Q 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H• (Radical) can't be isolated.

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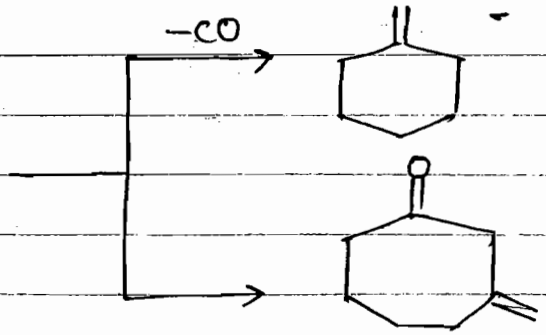
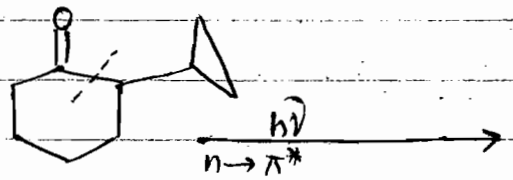
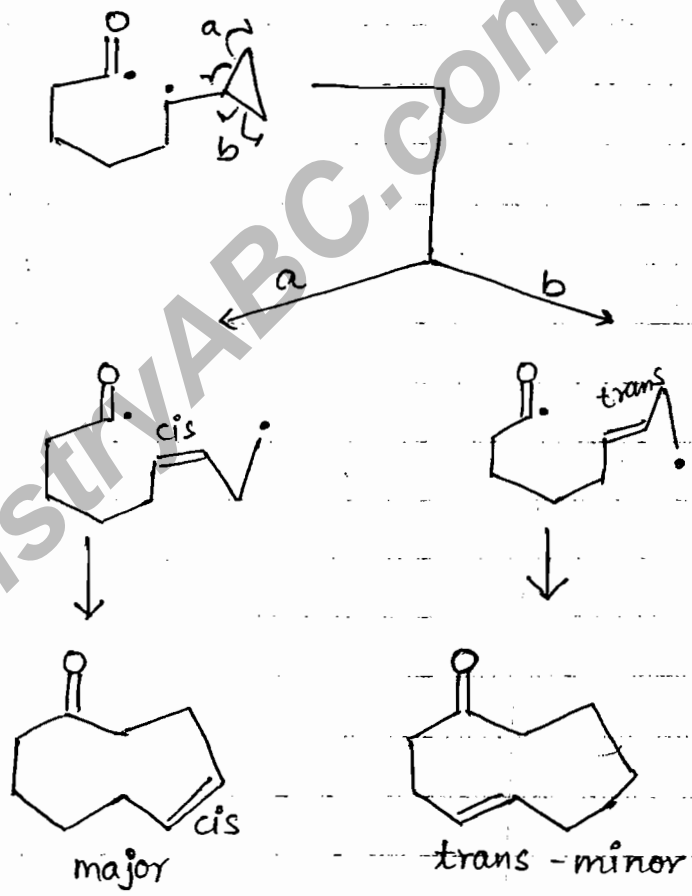



M. Imp.

Q



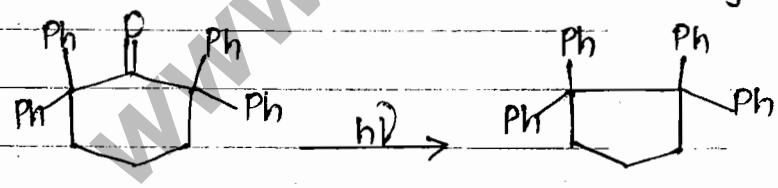

α- bond cleavage



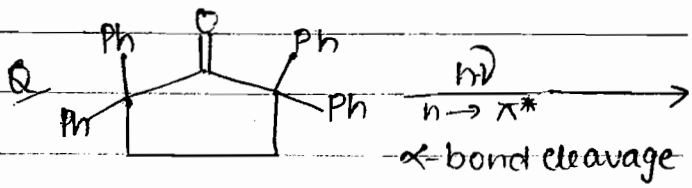

major

trans - minor

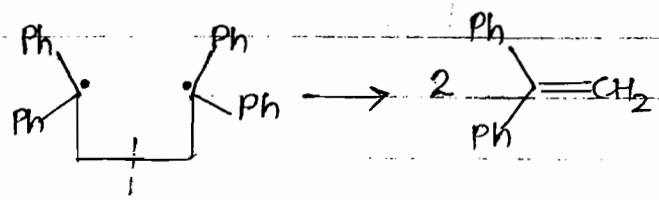
Q




Q




α- bond cleavage




If SU(1) type condⁿ then always C—C bond breaks

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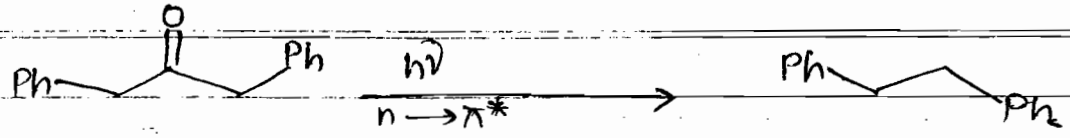
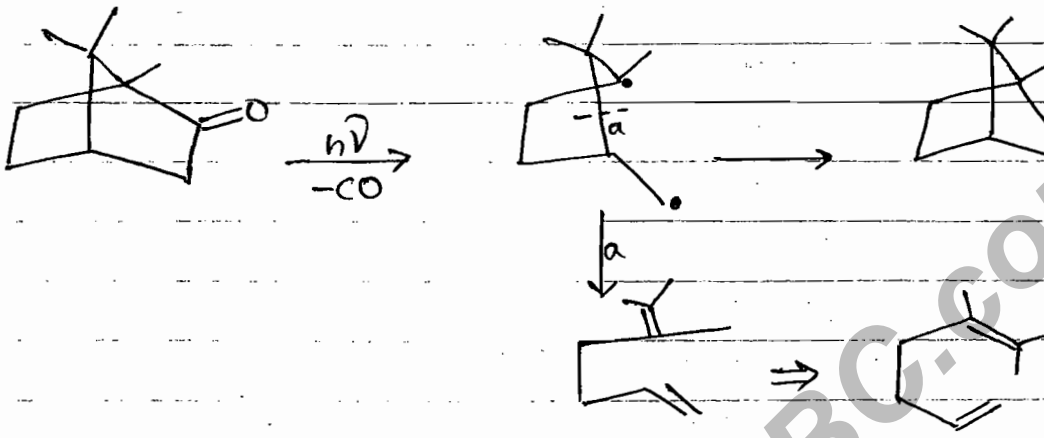
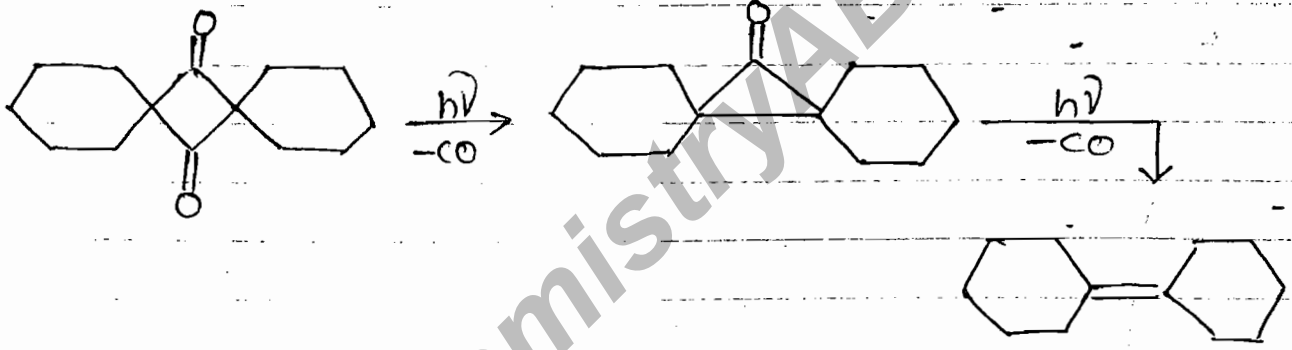
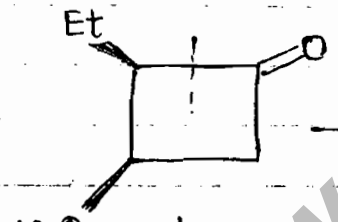
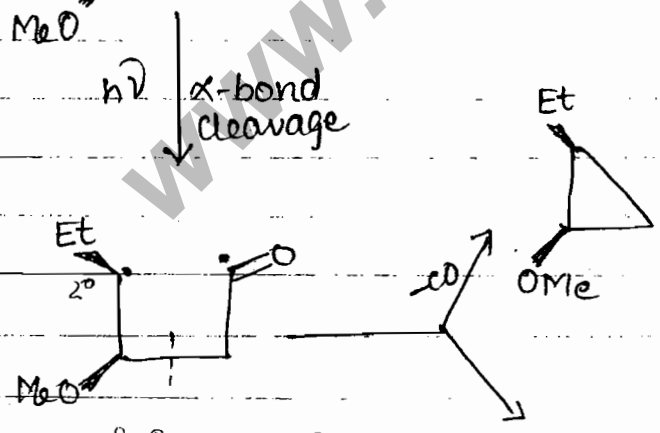
Q 


α bond cleavage
CO elimination

Q 


Q 


Q 




1,4 position radical always C—C bond breaks

+ $CH_2=C=O$

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Except α-bond cleavage, remaining all type carbonyl rxn. are Norrish type II.

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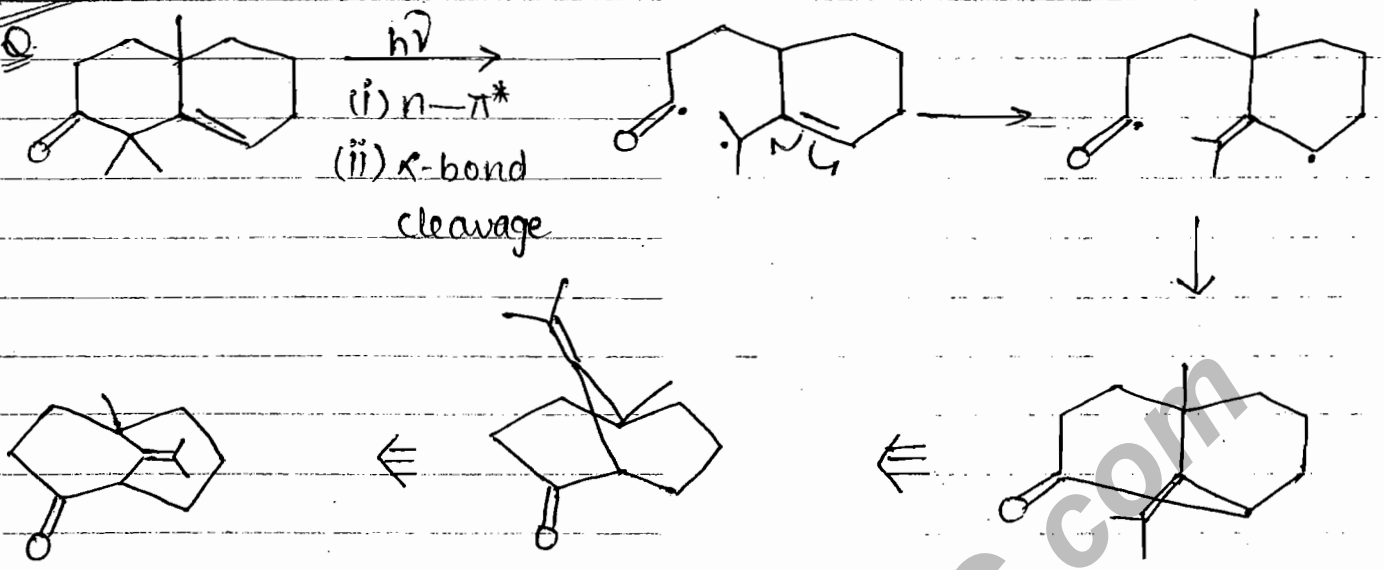
NET 2008

Q.

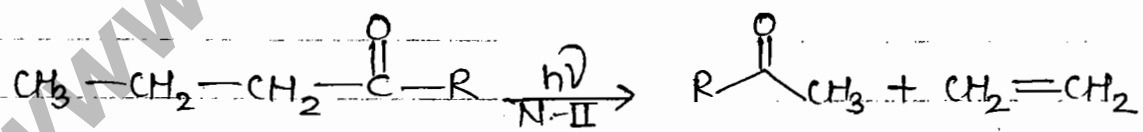



Note:- Always break κ-bond which produce more stable free radicals.

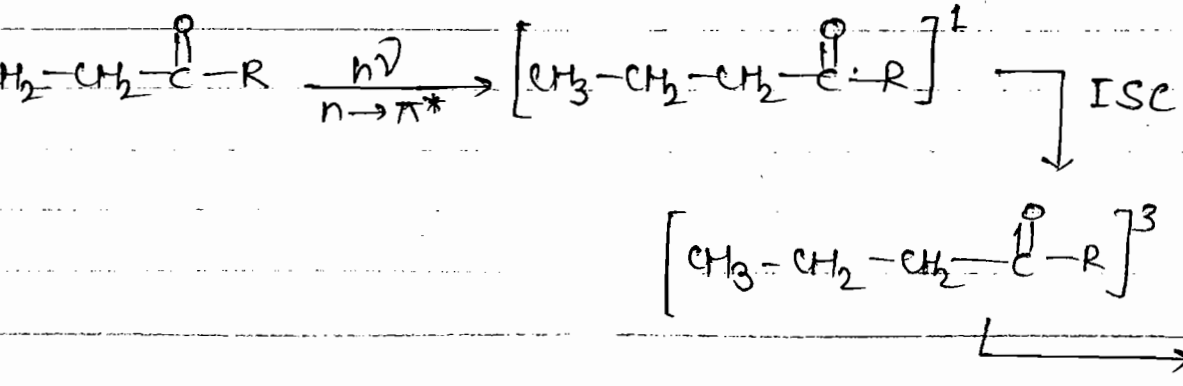
Norrish type-II :- 1) Both, singlet & triplet state takes part in the reaction.

2) γ-H transfer via 6-memb. transition state takes place & either β-bond cleavage or cyclic alcohol form.

3) Mostly Mc lafferty type rearrangement take place. in such type of carbonyl comp. which contain. γ-H.

Ex. 


Mechanism:-

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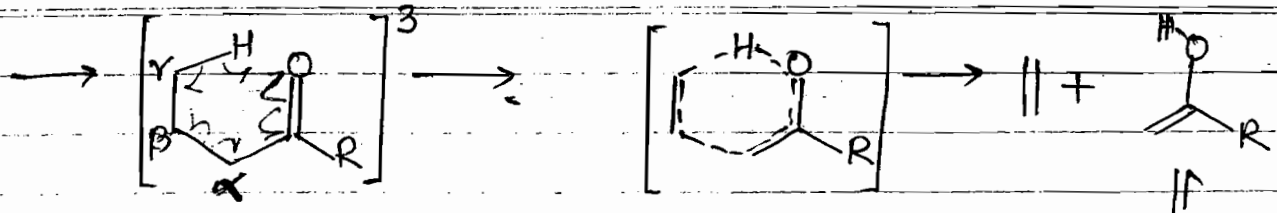
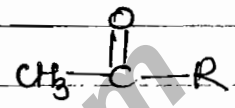


6 memb.
Cyclic T.S.



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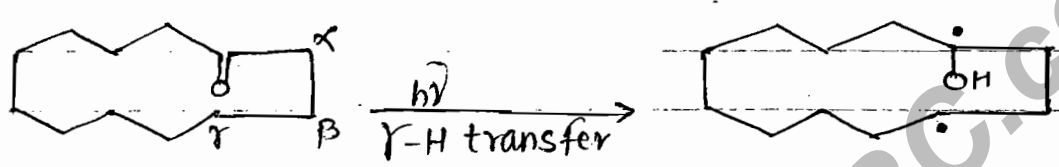
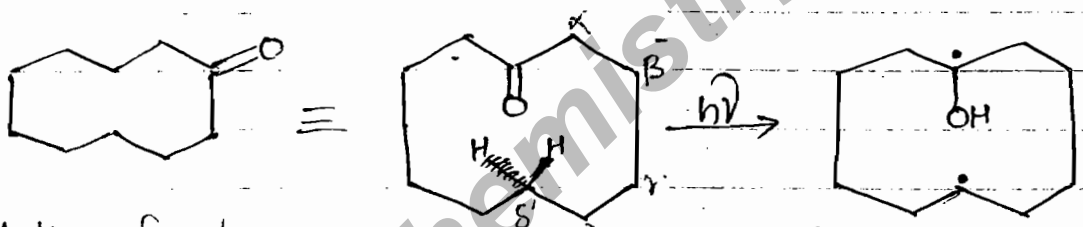


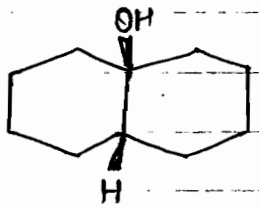
Here β-bond not breaking because both radicals are very close i.e. why forming bond.

Cyclic Alcohol →

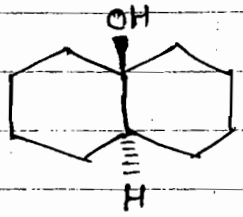
Imp.
Q



δ-H transfer because it is nearest to C=O

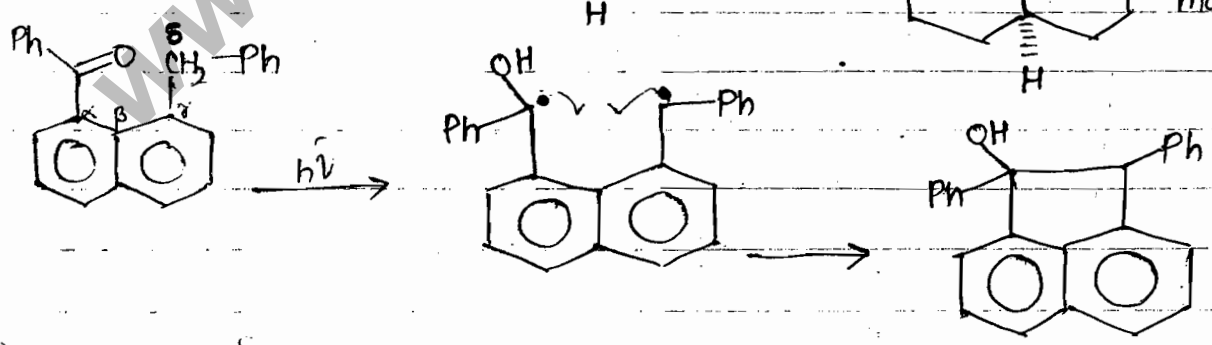


minor



major

Imp.
Q



δ-H transfer because it is nearest to >=O group.

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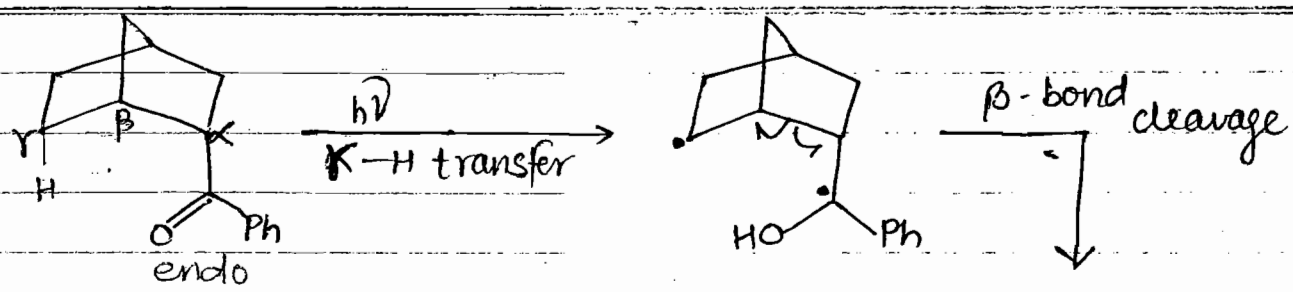
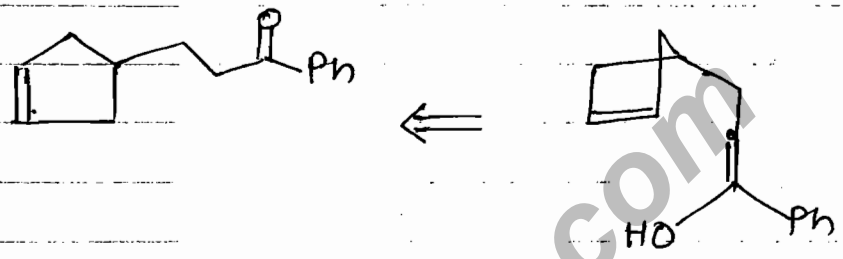
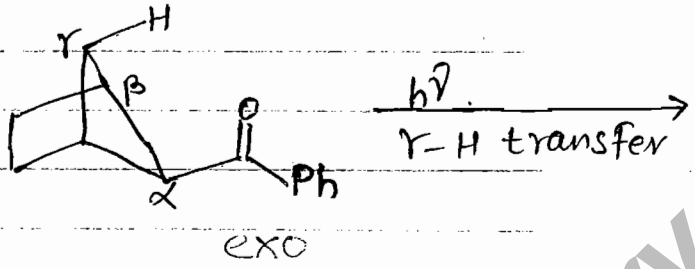
V. Imp.
Q.

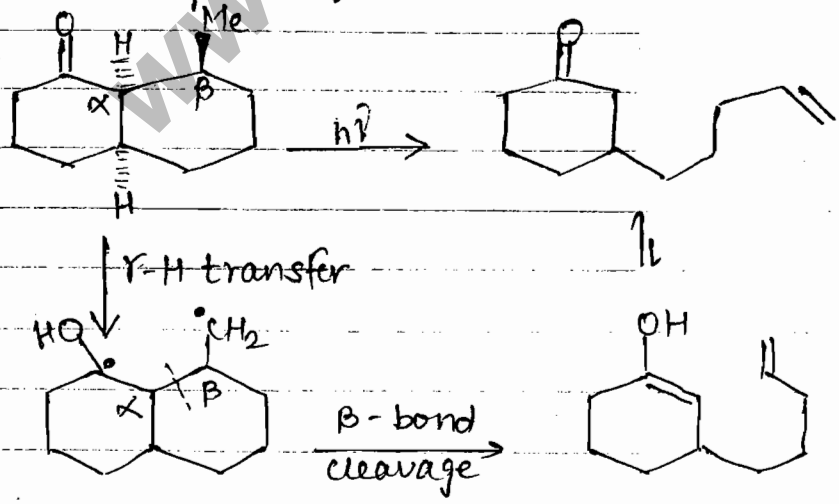



2013 D
V. Imp.
Q.




Q The following photochemical conversion proceed through

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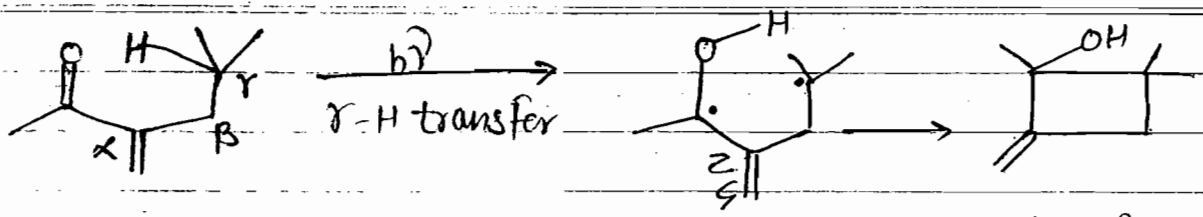
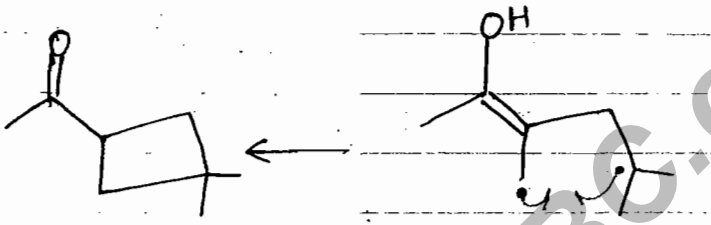
2014-J

Q.



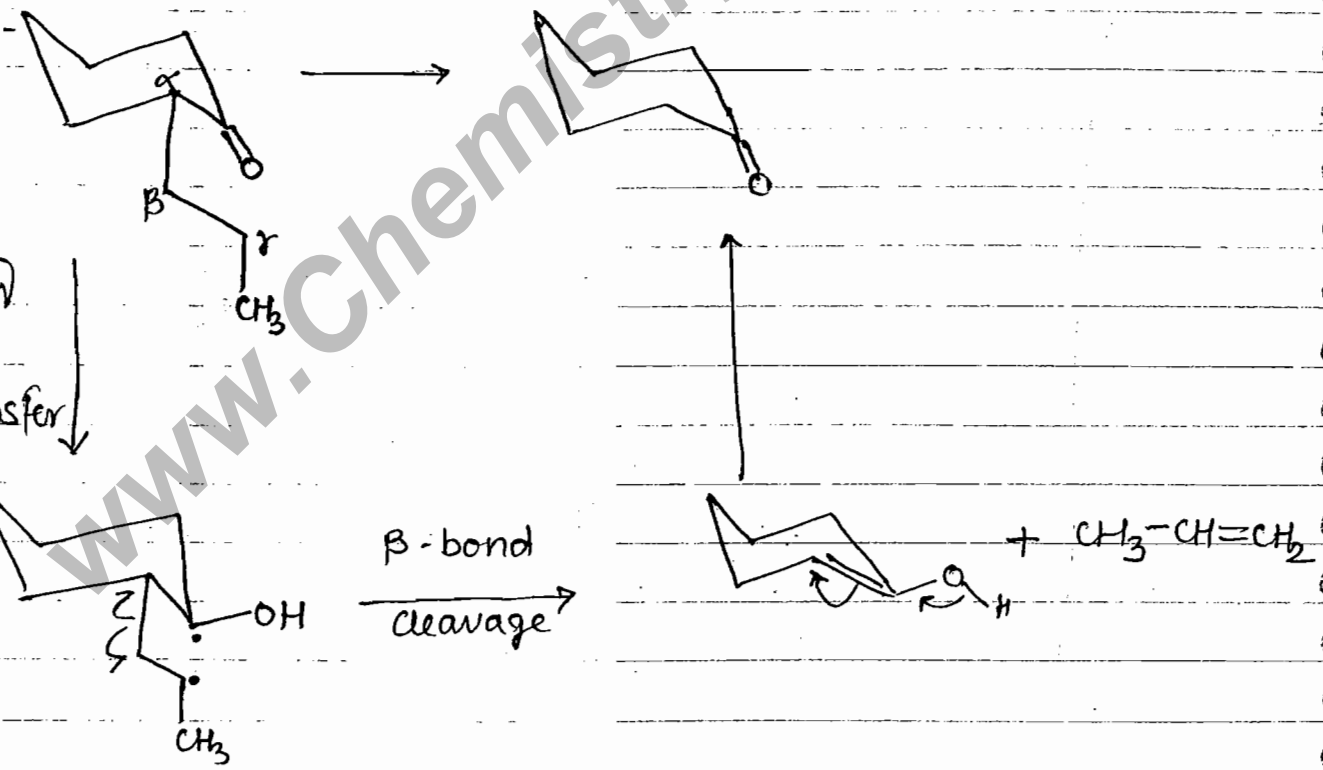

Norrish II

Pappu




* अगर Free radical के conjugation में double bond है तो Rxn. में participate कर सकता है।

Q

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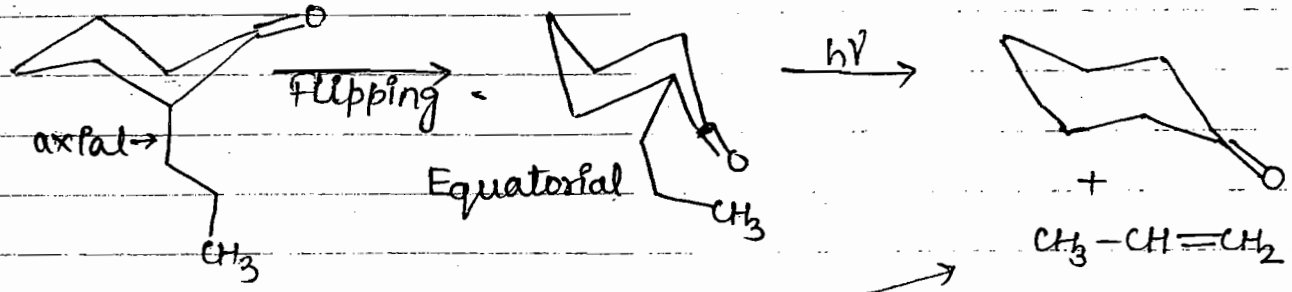
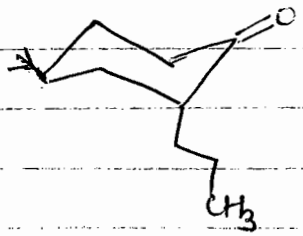
Q

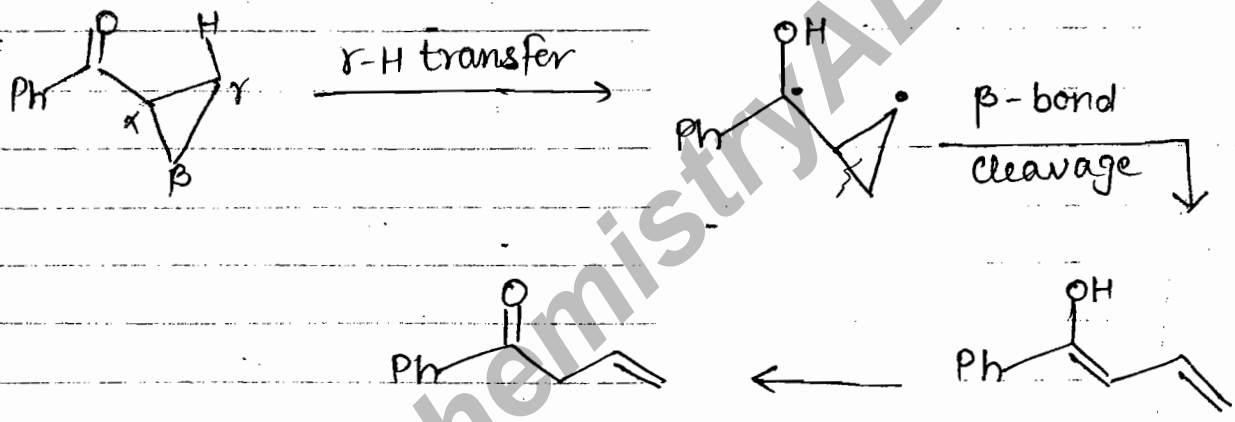



*



Can't flip due to t-Butyl (Bulky) group.
So no Norrish II rxn.

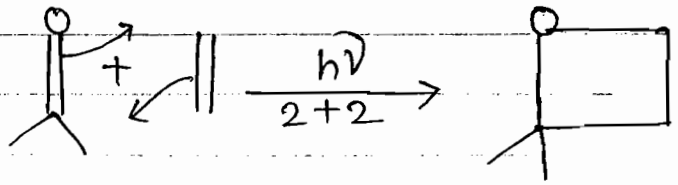
Q




## Paterno Buchi Reaction :-

1) Only triplet state participate in Rxn.
2) Case of 2+2 cycloaddn Rxn b/w Carbonyls & Alkene
3) Oxytane (4-membered ether) form.

Ex.

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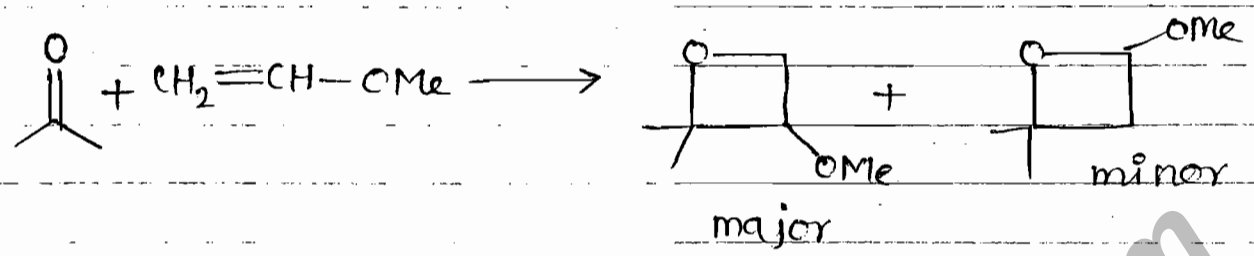
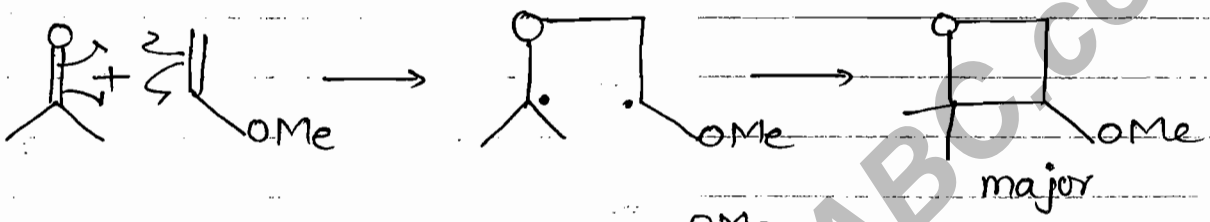
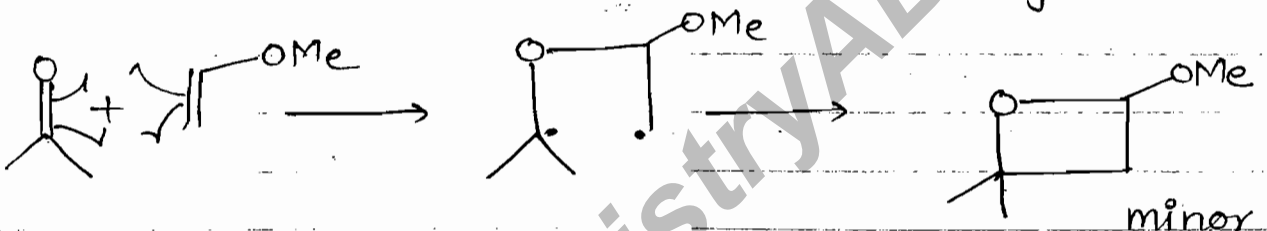
## Paternobuchi Rxn. in asymmetrical Alkene :-




### Explanation




* ← More unstable (Highly reactive)
← Less unstable
Forms bond firstly.

← More unstable (Highly reactive)
← Less unstable
OMe

⇒ In paternobuchi Rxn. more stable radical will form bond with carbonyl carbon & less stable radical (highly reactive) will form bond with carbonyl oxygen).

⇒ If in alkene, ERG +nt then mix. of two oxytane derivative form.

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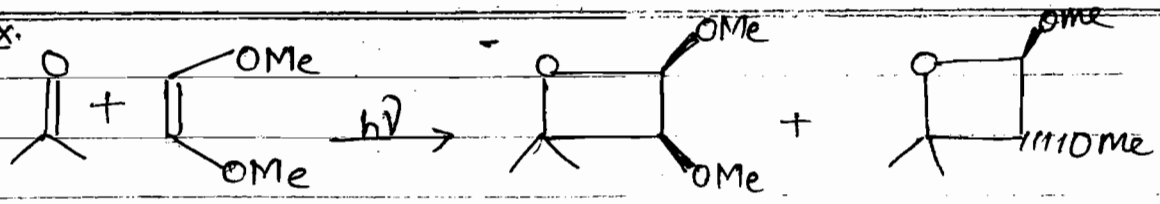
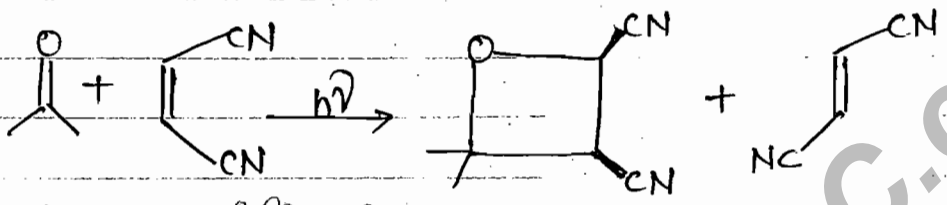
Ex.



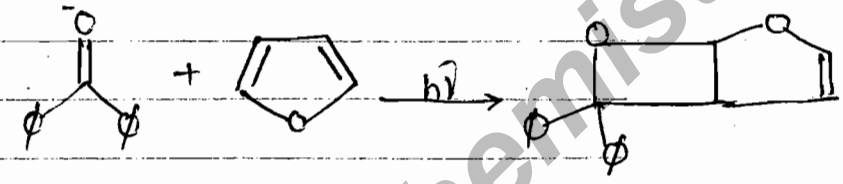

Imp. When in alkene EWG ~~tht~~ then a single oxytane derivative form with cis trans isomerism of alkene.

Ex.

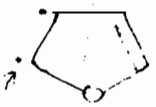



* Stetreospecific Rxn. when EWG ~~rct~~.
* EWG make alkene highly reactive i.e. why after forming O—C bond alkenic bond doesn't rotate & further react with carbonyl carbon.

Q.

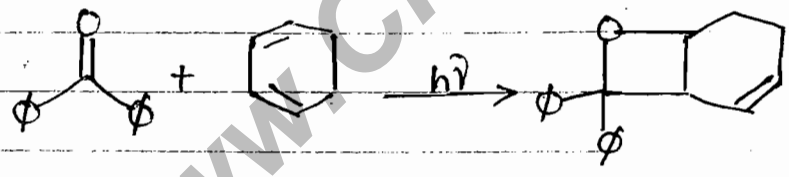



Allylic Radical More stable



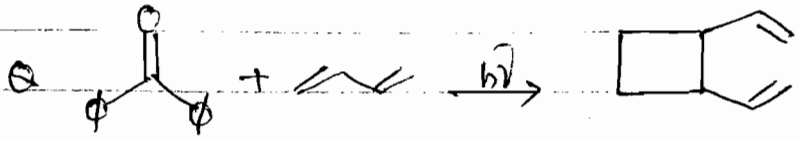
Less stable (binds with O atom)

Q.




Q.

Q.




Photosencitizer

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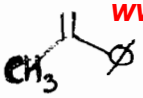
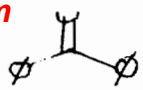
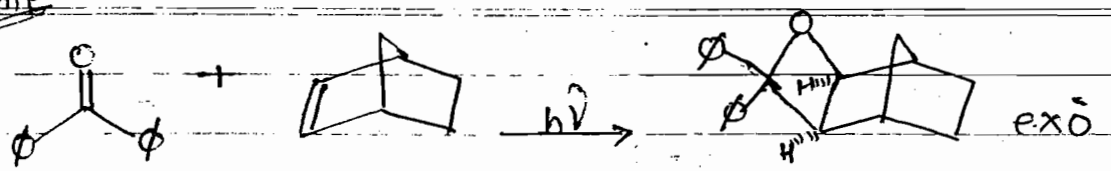
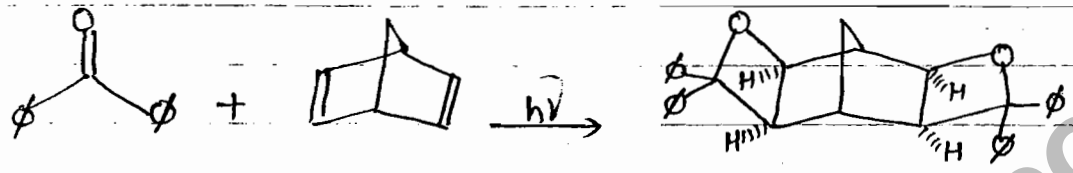
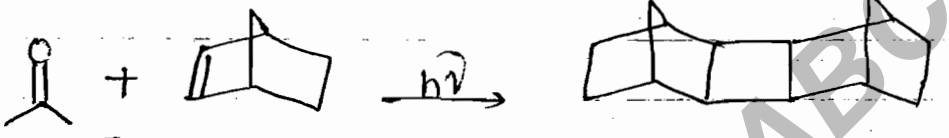
Acetophenone  Benzophenone 

M.Imp

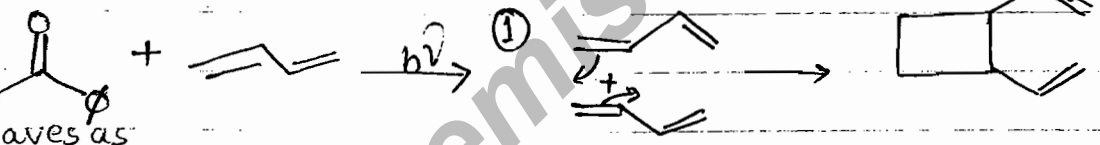
Q  exo

In norbornene type system Benzophenone gives Paternobuchi, But Acetone & Acetophenone behave as a Photosencitizer.

Q 

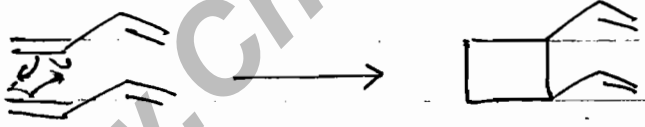
Q 

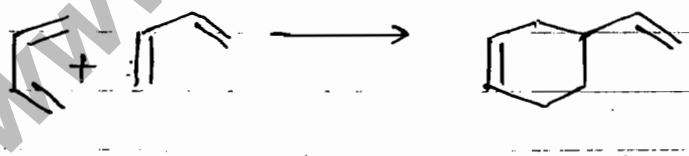
(n) $CH_3CO\phi$ Photosencitizer

Q 

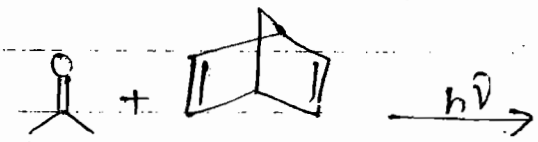
Behaves as a photosencitizer

① 

② 

③ 

(4+2) Don't confuse it's free radical Rxn. not DA.R.

Q 

(n) $CH_3CO\phi$ Photosensitizer

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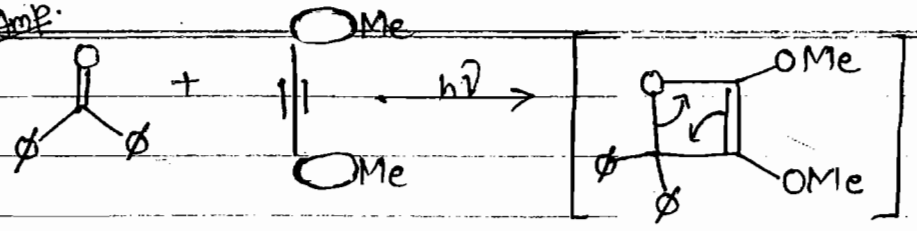
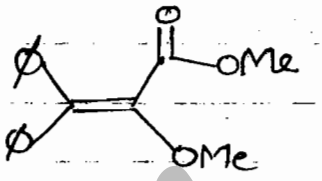
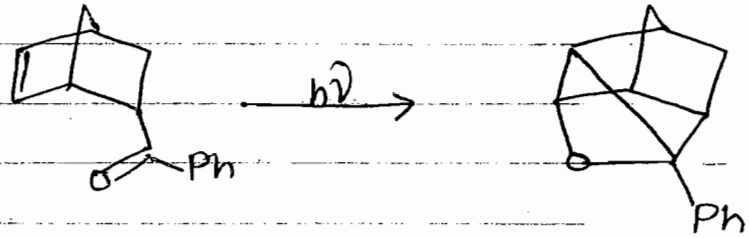
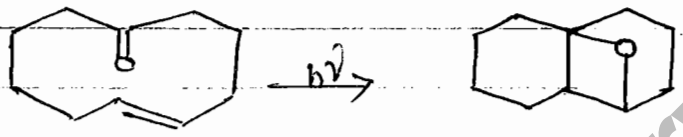
M.Imp.

Q 

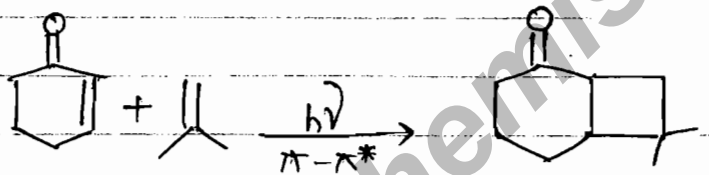

Unstable




Q 


Q 


but in enone system $\pi - \pi^*$ transition take place

* 


enone

ENONE ⇒ $\pi - \pi^*$ Transition.

⇒ Benzophenone with norbornene ⇒ Paternobuchi

⇒ Acetophenone / Acetone with " ⇒ No "

↳ Paternobuchi ✗ sensitizer

Dimerisation of Norborane.

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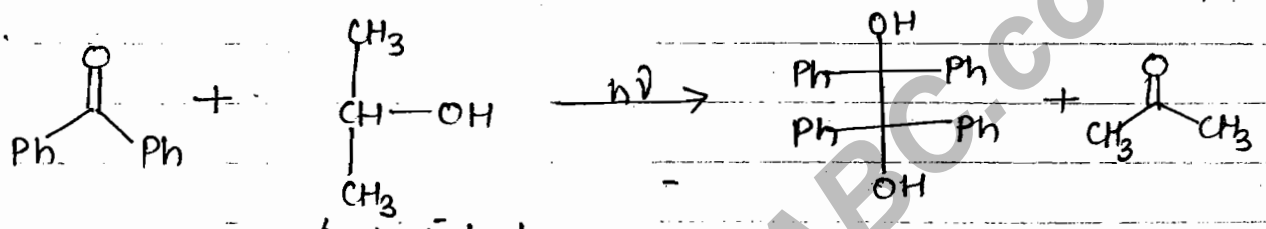
# PHOTOREDUCTION OF CARBONYL COMPOUNDS

* Only triplet state takes part in the reaction.
* In photoreduction of carbonyl compound, carbonyl convert into pinacol like product in the presence of iso-propyl alcohol (some times methanol or toluene)

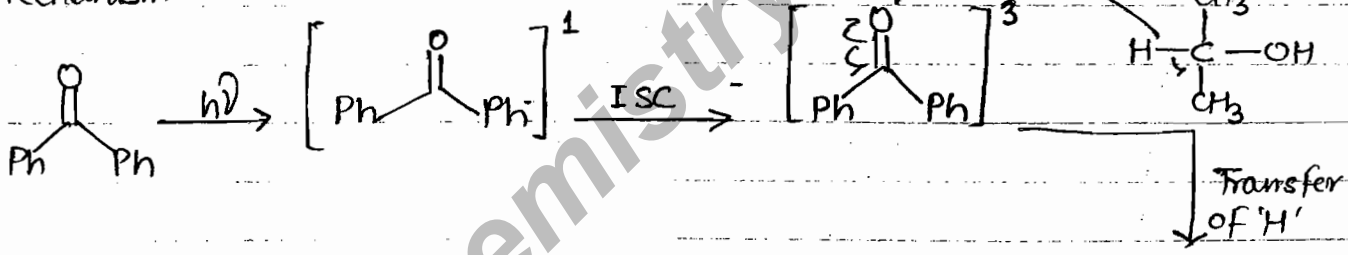
Ex.

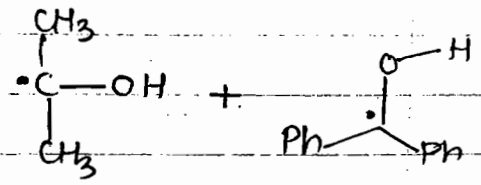



Isopropyl alco.

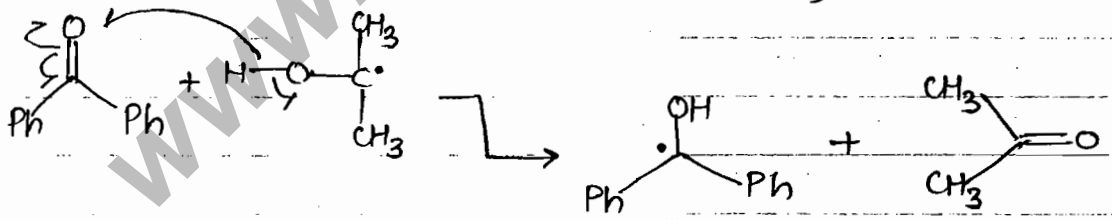
Mechanism

(I)

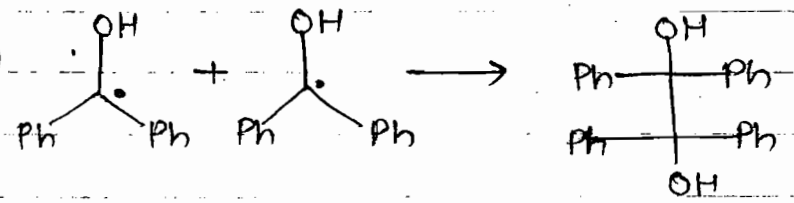



(II)




(III)

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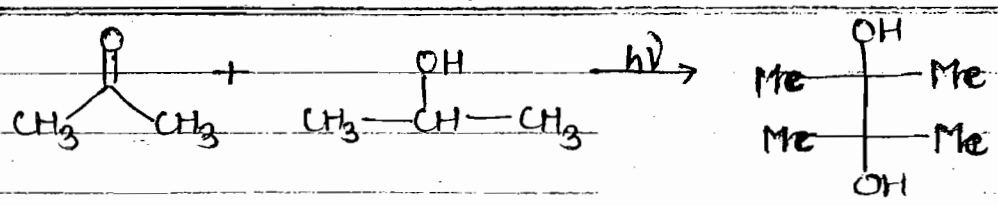
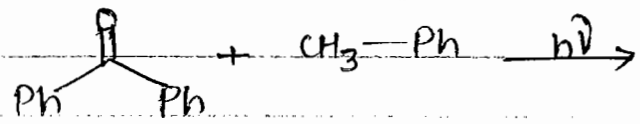
* 

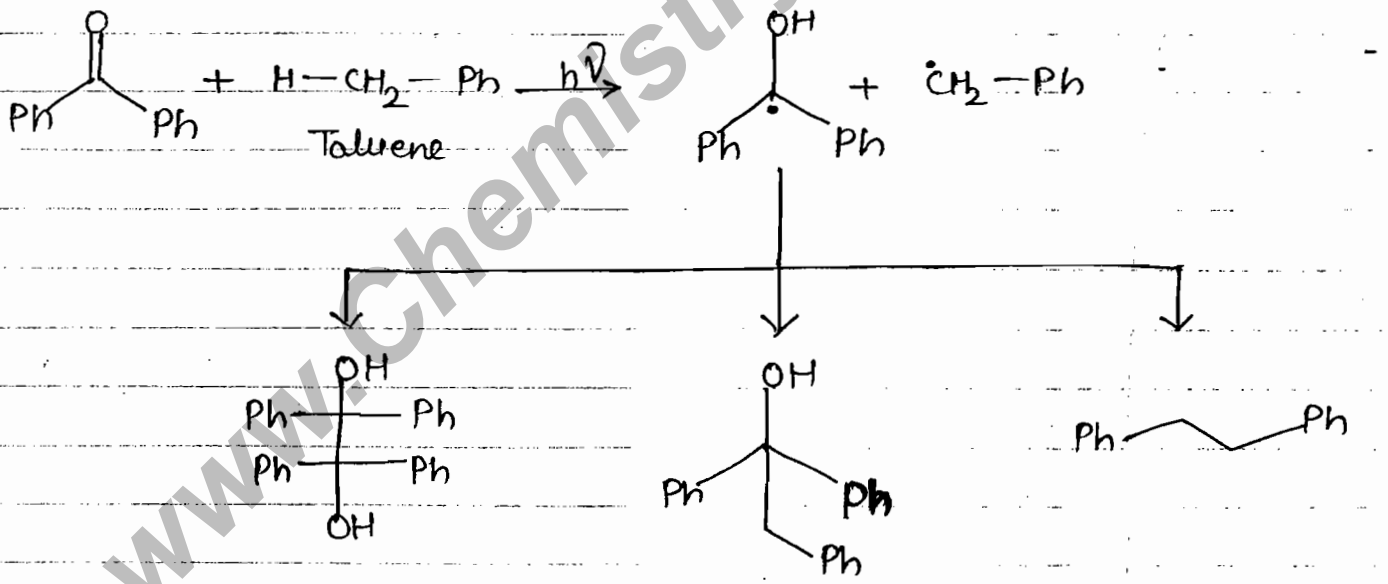

Carbonyl के साथ

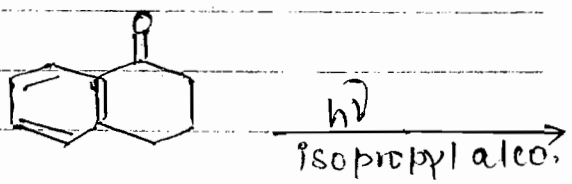
⇒ Photoreduction carbonyl हो रहा है तो, isopropyl alco. or methanol, or toluene ; जरूर दिया होगा।

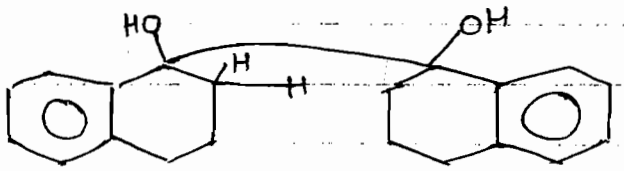
⇒ Patemobuchi ⇒ carbonyl with alkene

⇒ Norrish I or II only one comp. पर hν condition.

Q. 


Q. 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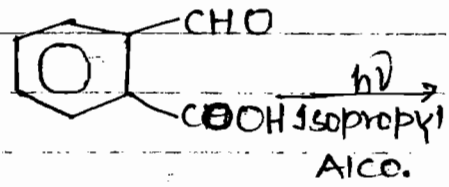
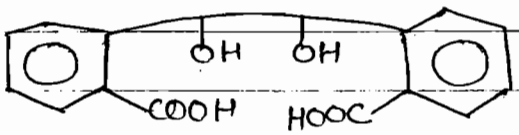
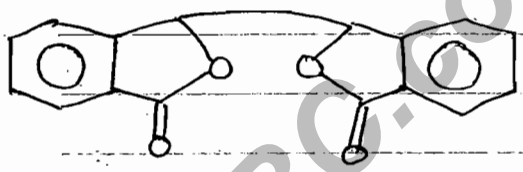
V. imp.

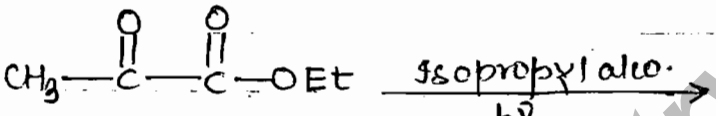
Q

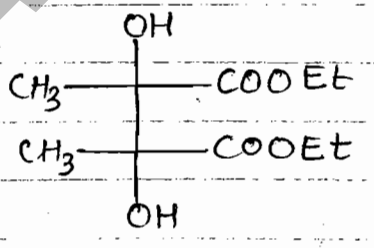



Esterification

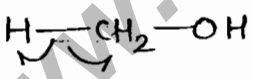


* 

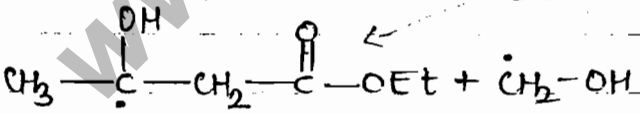




VV. imp

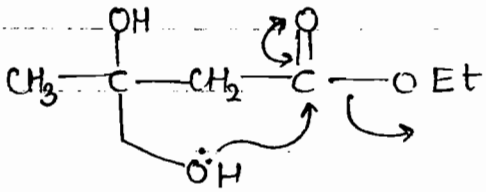
Q.



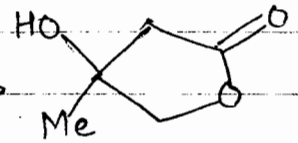

Due to steric crowding this radical doesn't dimerise.




Very reactive




N.S.R.

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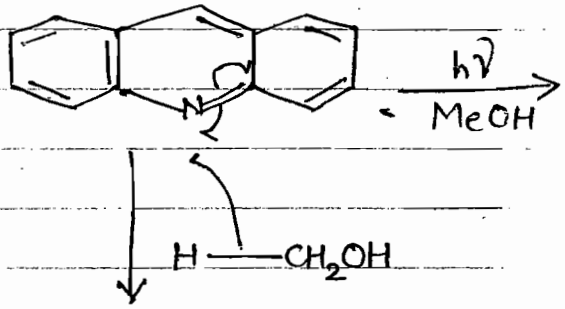
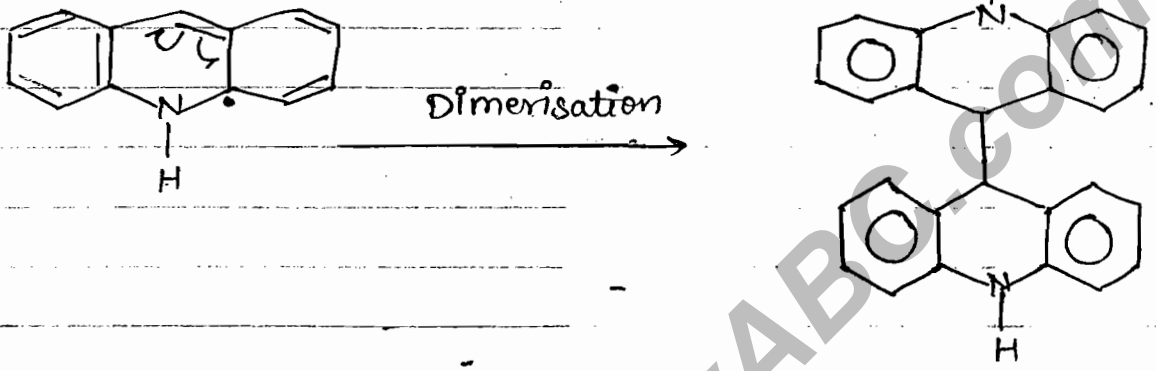
V. Imp.

Q

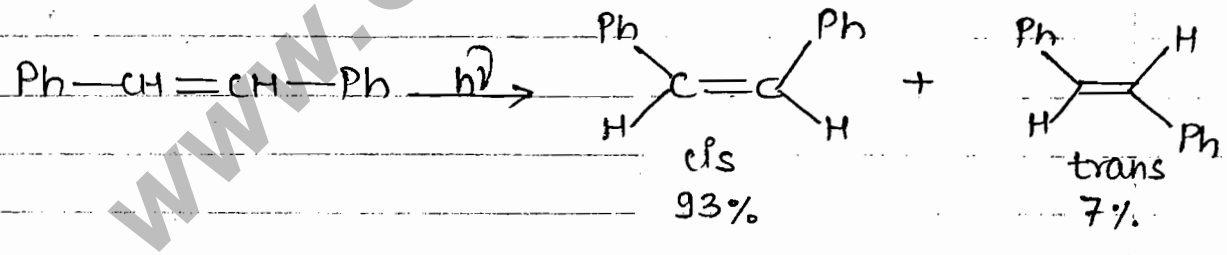


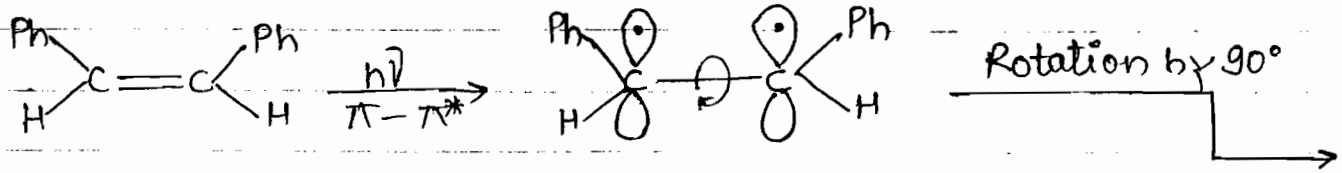

# PHOTOCHEMISTRY OF OLEFIN

## Cis- Trans Isomerism :-

In cis - trans isomerism of stilbene, the cis prod is major and trans prod. is minor.




## Mechanism

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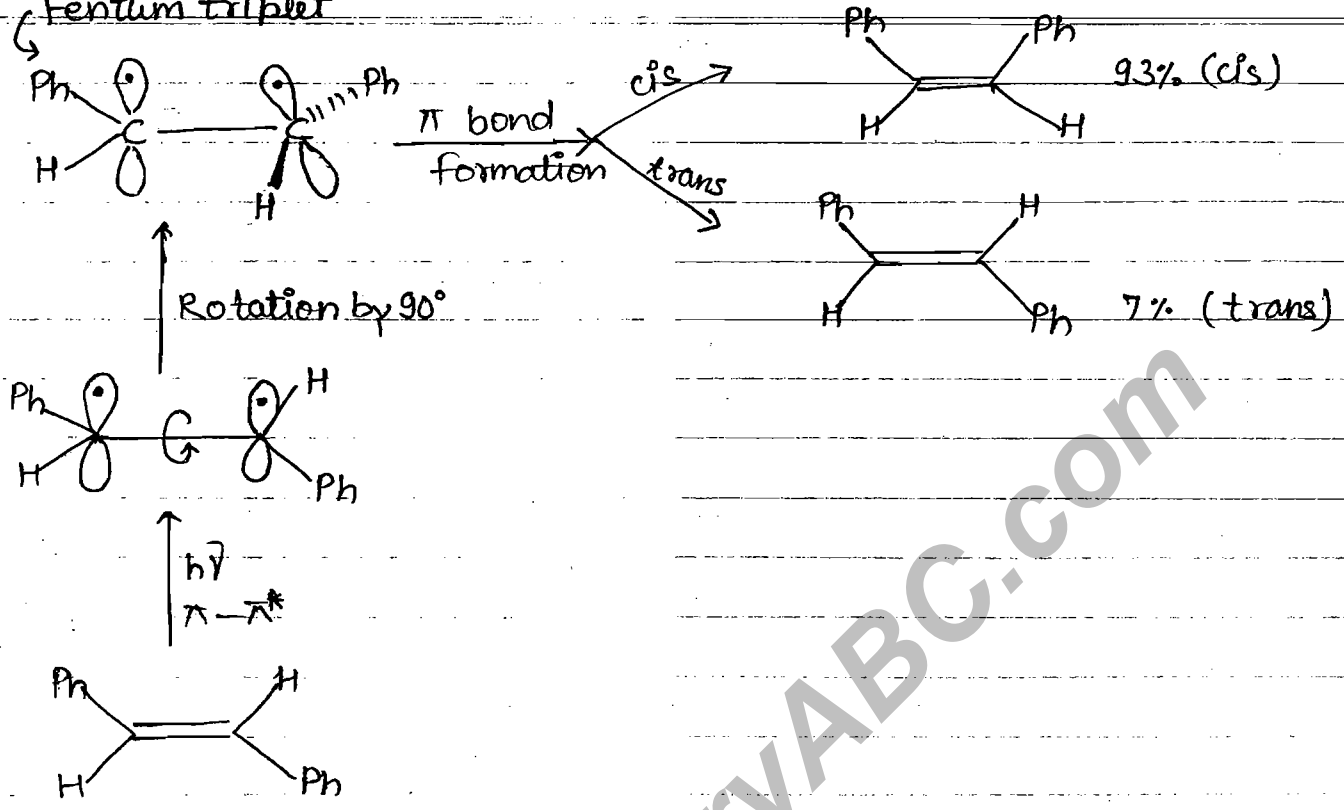
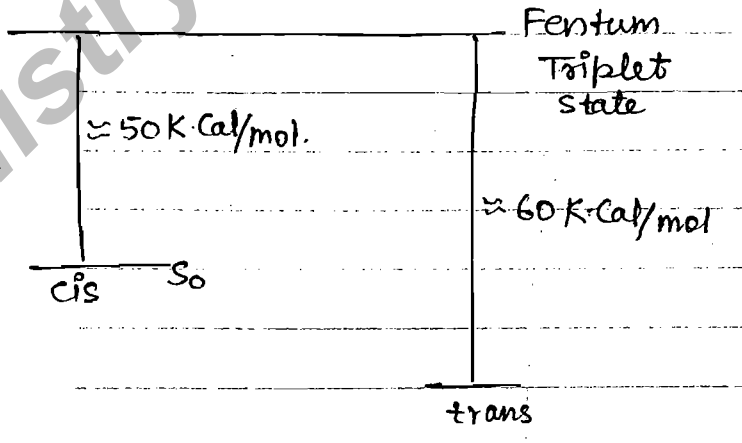
Twisted triplet
(or)
Pseudo triplet
(or)
Fentum triplet




In cis-trans isomerism of stilbene the cis prod. is major because, both cis- and trans stilbene forms same excited triplet state called Fentum triplet or twos' twisted triplet. The rate of conversion of cis stilbene of fentum triplet is greater than trans: and the because the energy gap b/w fentum triplet state of ground state of cis stilbene is lower (≃50 K·cal/mole) than trans stilbene (60 K·cal·/mole).

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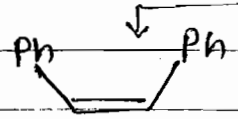
Q. Types.

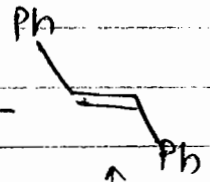
① Ph—CH=CH—Ph $\xrightarrow{h\nu}$ 7% Trans + 93% Cis

Identical (Reactant)

②  $\xrightarrow{h\nu}$ 7% Trans + 93% Cis

This is prod.

This is not prod. It further react and form Trans.

③  $\xrightarrow{h\nu}$ 93% cis + 7% Trans.

Product.

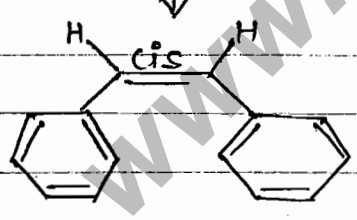
Same mol. (Reactant)

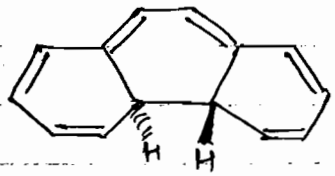
⇒ Cis से trans prod. बनेगा

⇒ Trans " cis " "

Q. Ph—CH=CH—Ph $\xrightarrow{h\nu}$ A $\xrightarrow{h\nu}$ B $\xrightarrow{I_2/\text{Benzene}}$ C

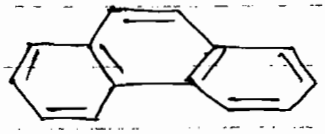
$\downarrow h\nu$



$\xrightarrow[h\nu \text{ con}]{(4n+2)}$ 

⇓ Change

$\xrightarrow[\text{or Air}]{I_2/\text{Benzene}}$ [O]



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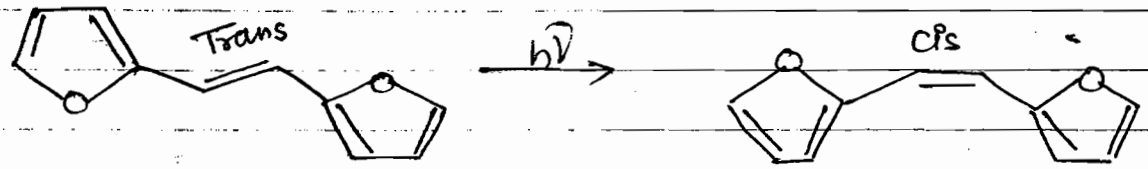
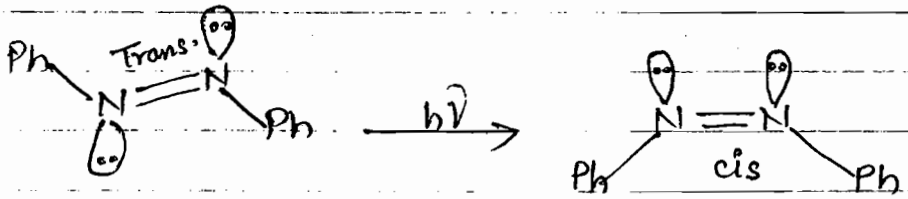
Imp.

Q



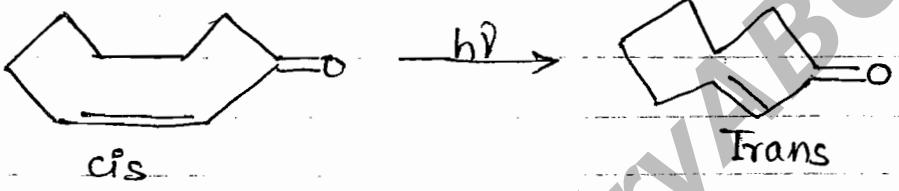

Imp.

Q




V.V. Imp

Q




M. Imp.

GATE's fav.

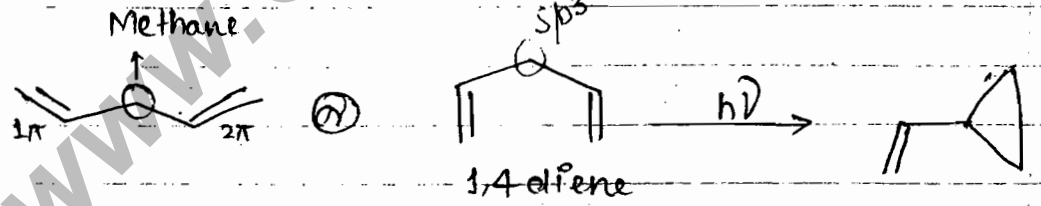
## Di-π Methane Rearrangement :- Topic.

Di-π methane rearrangement ↵

Exist in 1,4 diene under photochemical condition.

Cyclopropyl derivative formed.

Ex.




Remember :- Wherever you see 1,4-diene in hν condition think about di-π rearrangement.

Short trick :- In prod. make cyclopropyl ring and add a venyl group.

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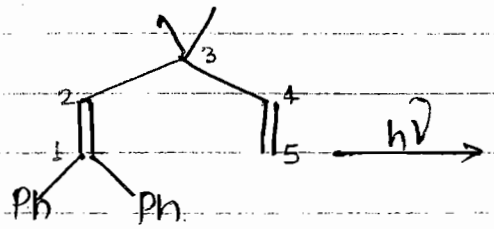
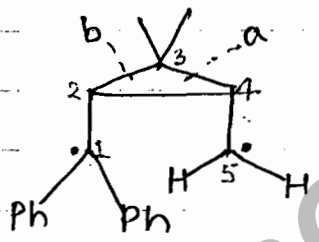
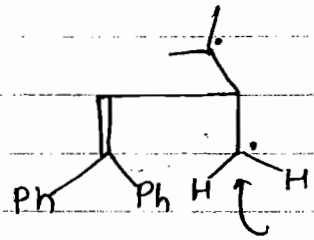
Mechanism :-

first of all bond form b/w 4 & 2

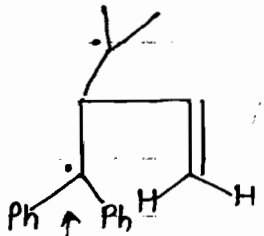
Q



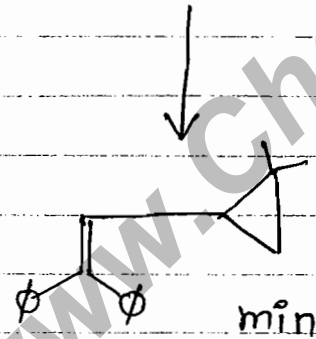




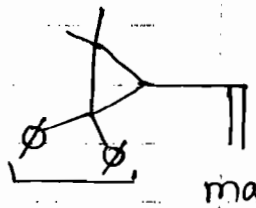
Less stable free radical.



more stable free radical.



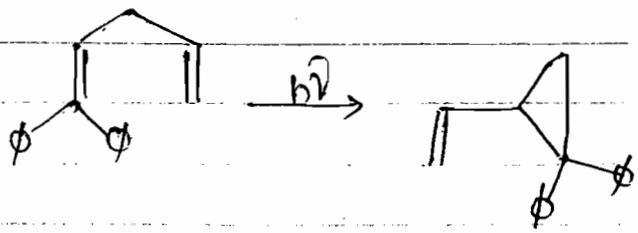
minor



major

Free radical stabilizing gp always on the ring (in major product).

Q



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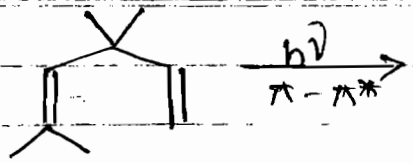
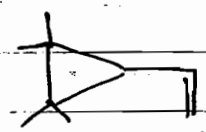
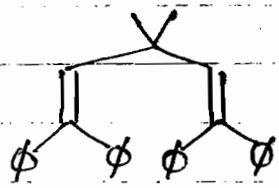
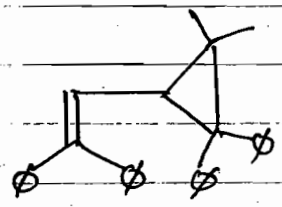
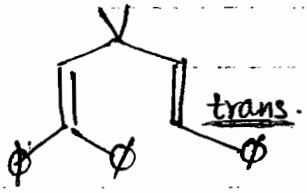
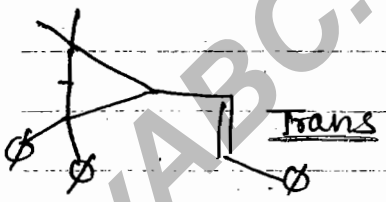
Q 

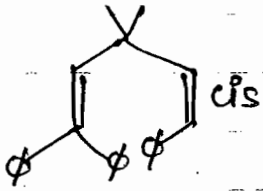


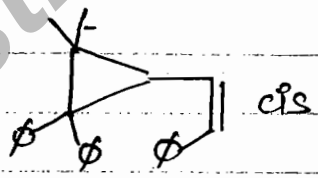
Q 

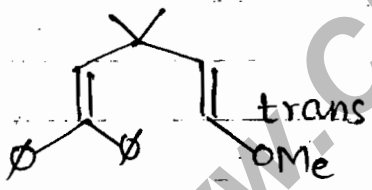


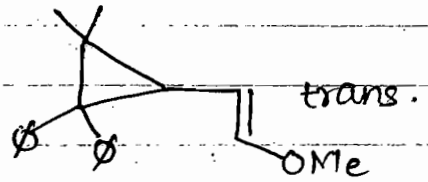
Imp. Q 

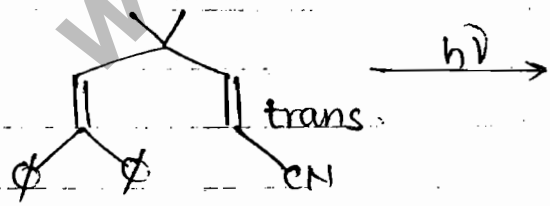


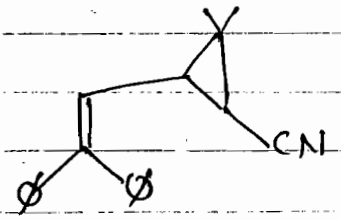

Q 

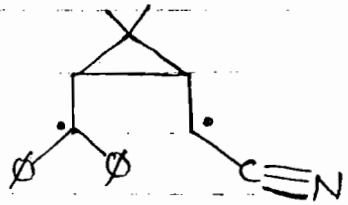



Q 




Imp. Q 




-CN more stabilizing to radical i.e. why added with Δ ring

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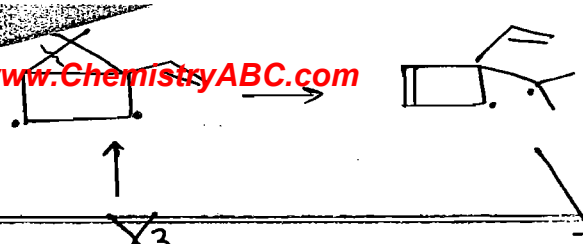
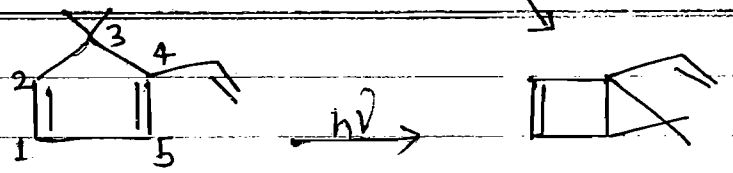
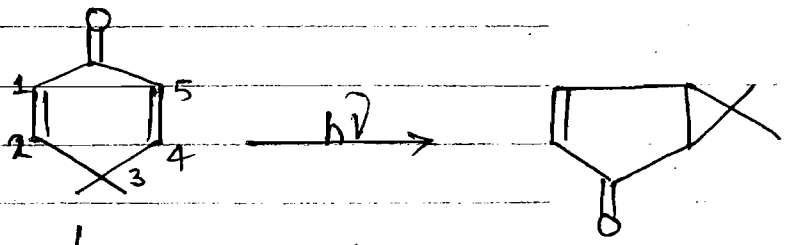
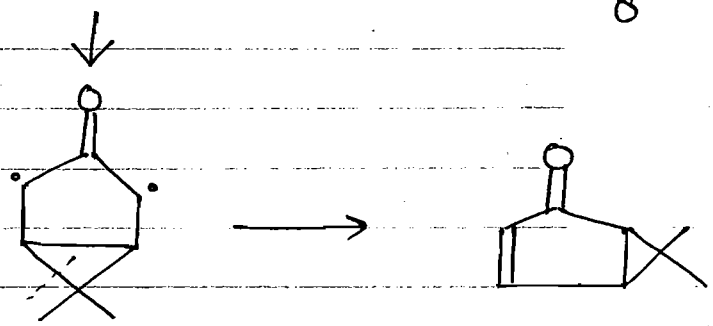


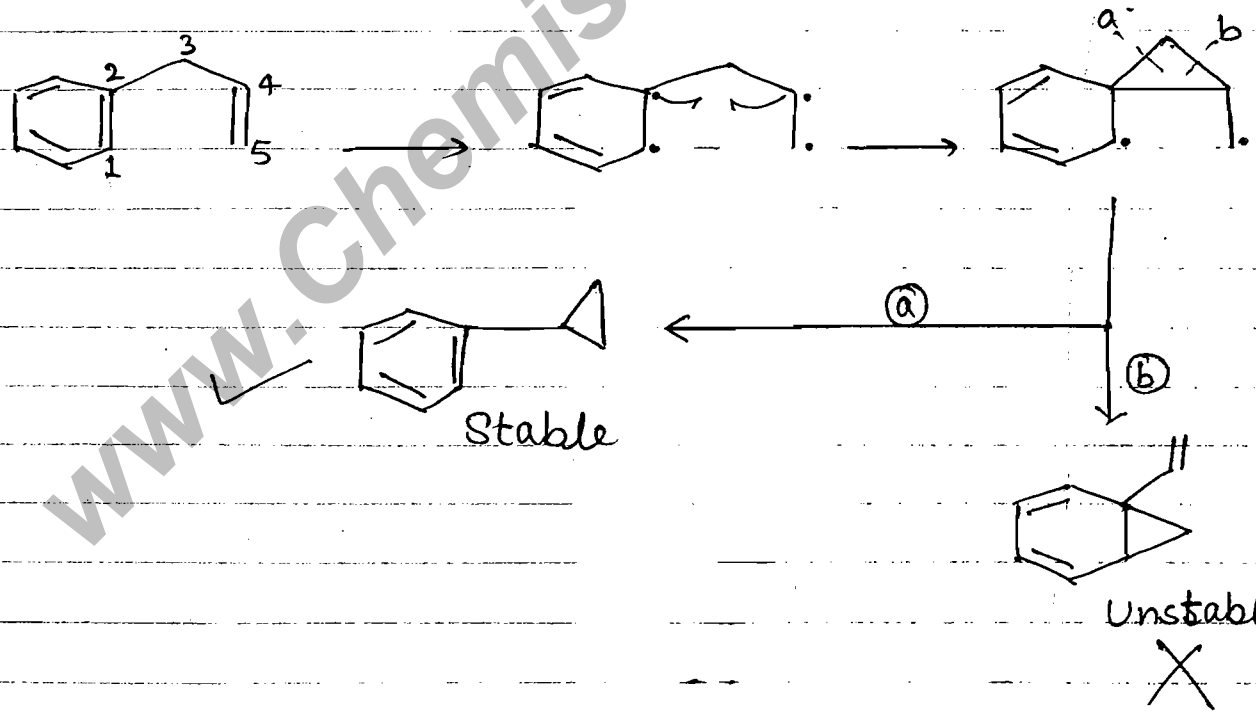
Q 


Q 

M. Imp

Q $Ph-CH_2-CH=CH_2 \xrightarrow{h\nu} (P)$

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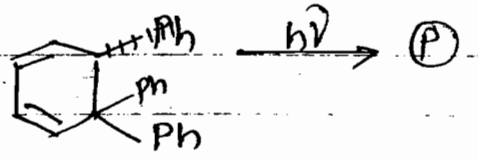
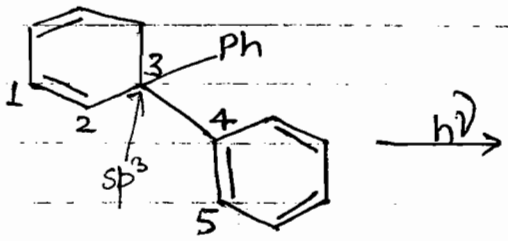
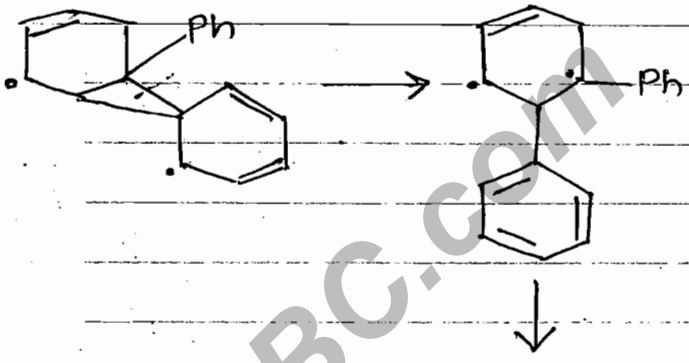
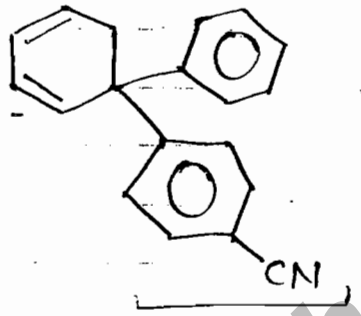
V. imp Q

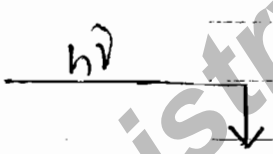


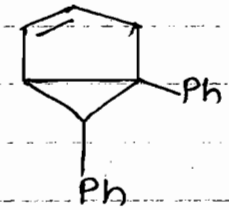




imp. Q

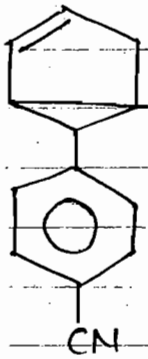



This ring will stabilise more to free radical i.e. why added with cyclo-propane ring in prod.

Phenyl which does not take part in react$^{n}$ tht at the junction of 3 & 5 memb. ring.




← Free radical stabilise, gp always with △ ring.

↑ cyclopropane ring

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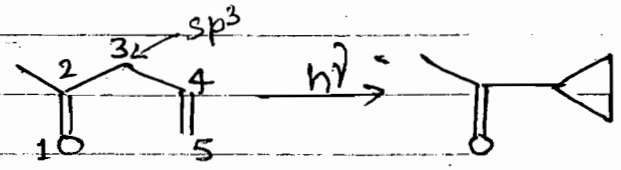
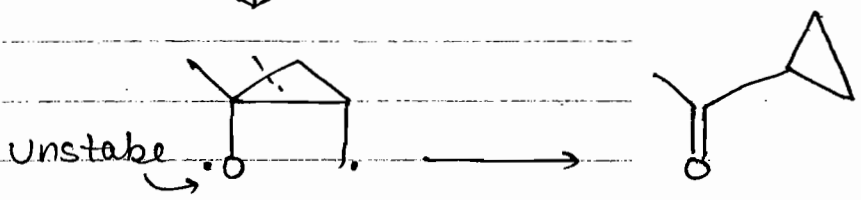
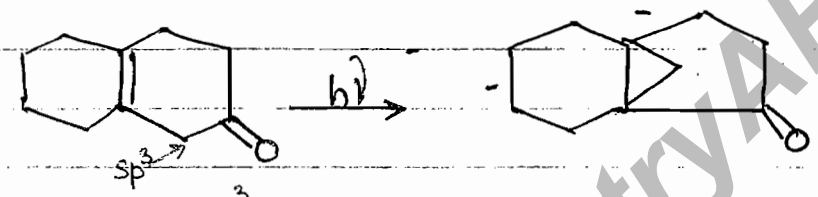
# Oxo- di-π Methane Rearrangement:

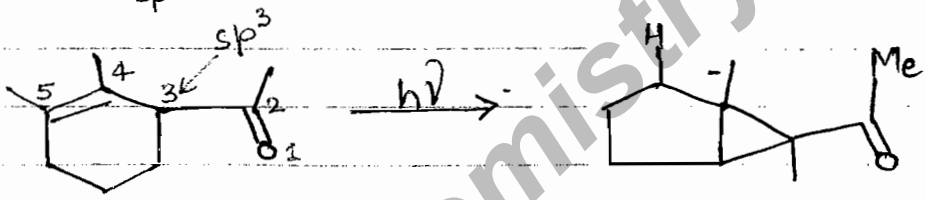
Ex. 


Mech. hν

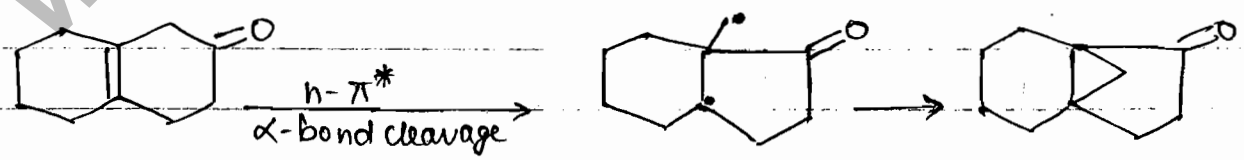



Q1 


N-I as well as Oxo di-pi methane Rearrangement. both can produce this product.

Q2 


If carbonyl and double bond of Alkene is seperated by one $sp^3$ hyb. 'C' then Oxo di-pi methane rearrangement take place. Never think about Paterobuchi for such comp.

Ans① 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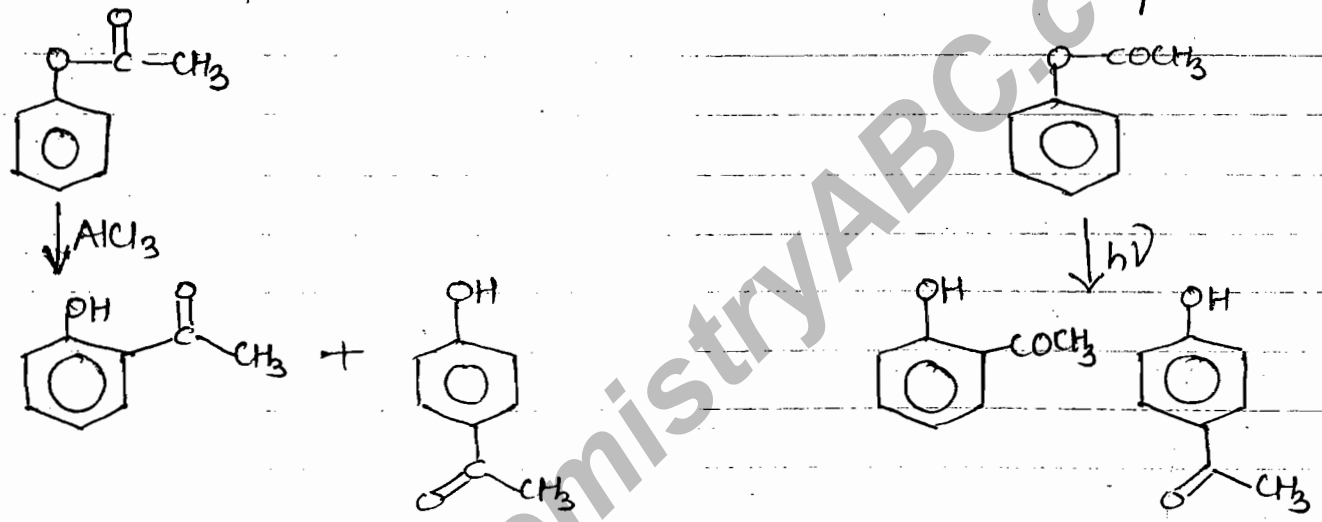
# PHOTOCHEMISTRY OF AROMATIC COMP.

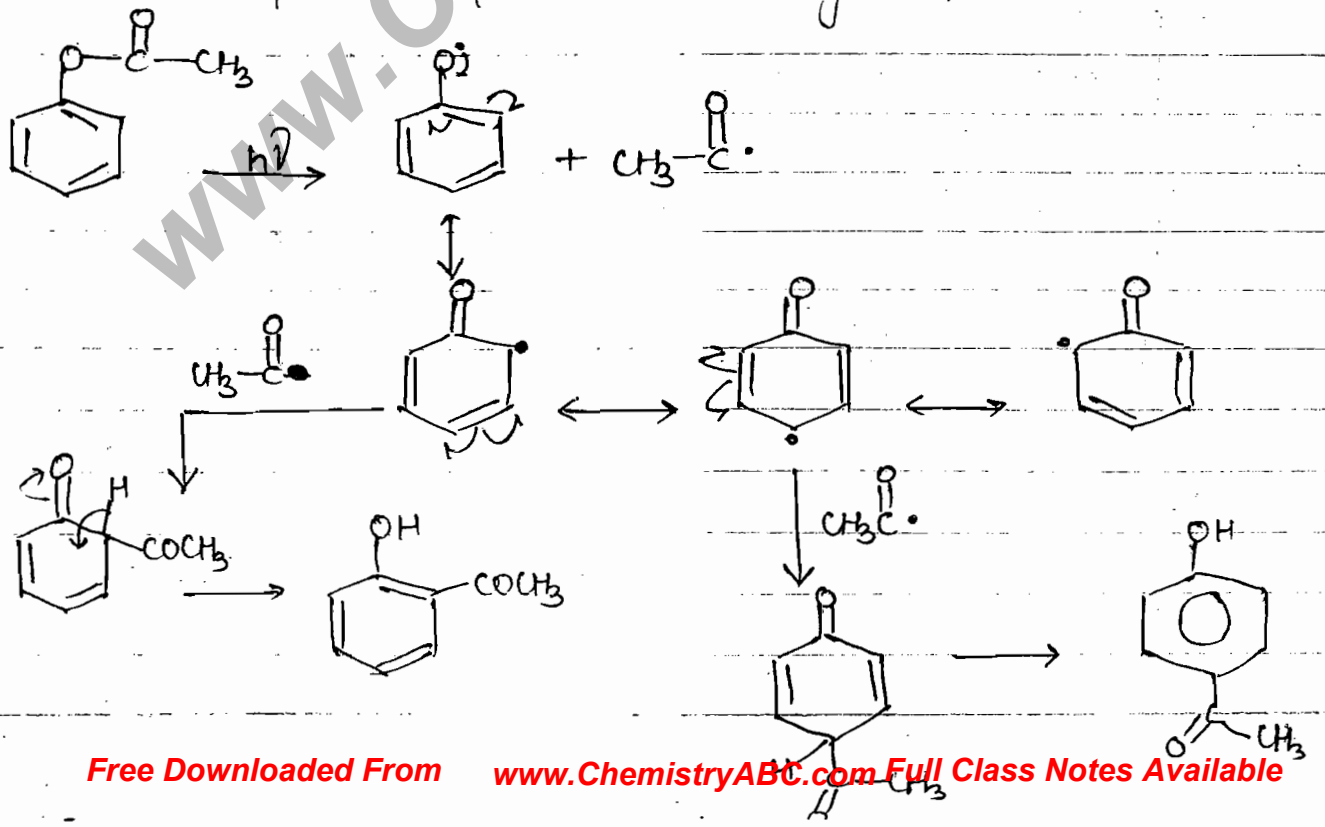
## Photo Fries Rearrangement:-

Fries Rearrangement

- Thermal fries
- Photo fries




## Mechanism of Photo Fries Rearrangement:-

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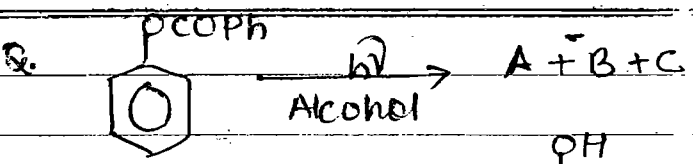
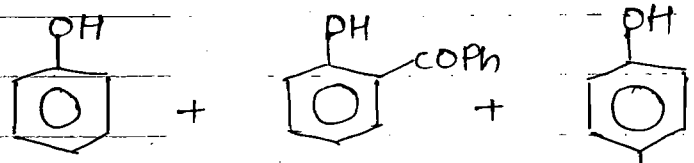
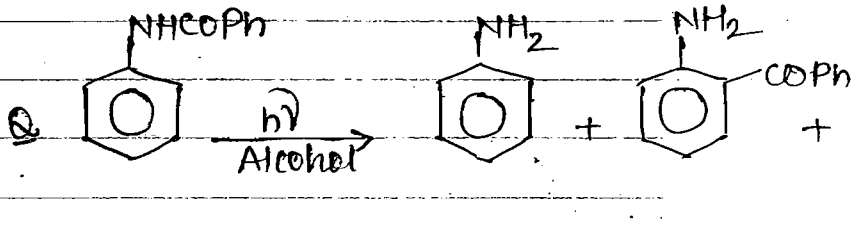
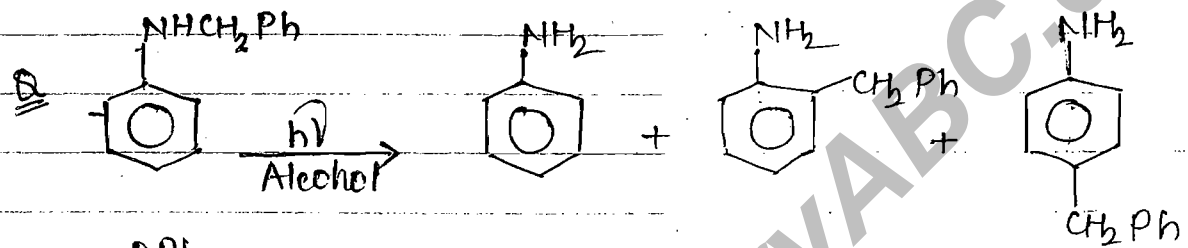
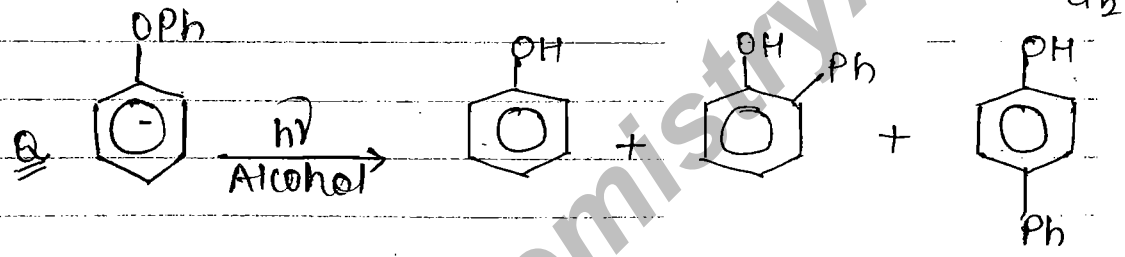
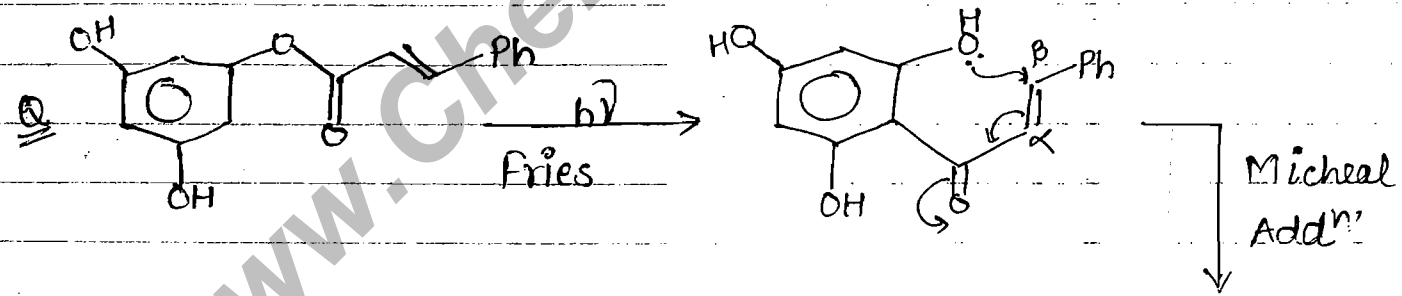
Q. 

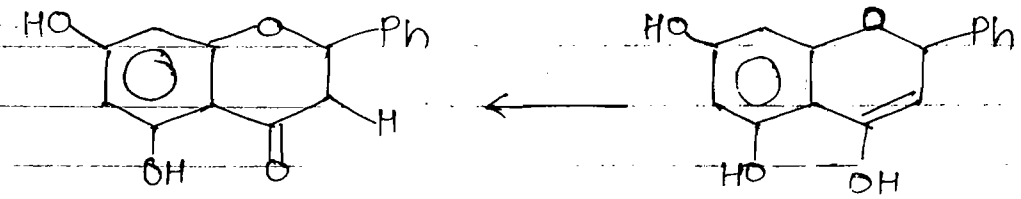




Q 


Q 


Q 


Q 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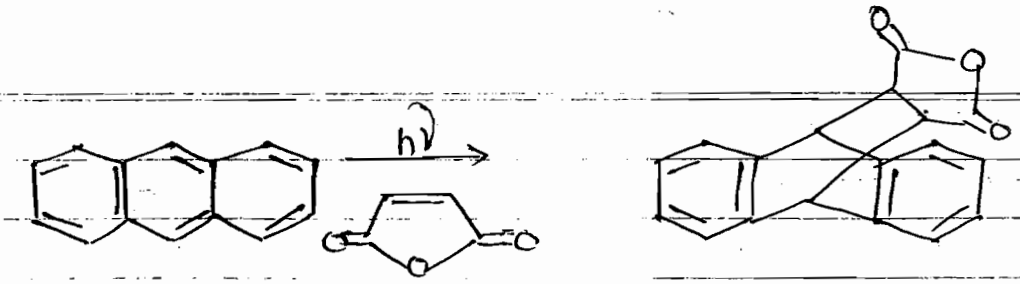
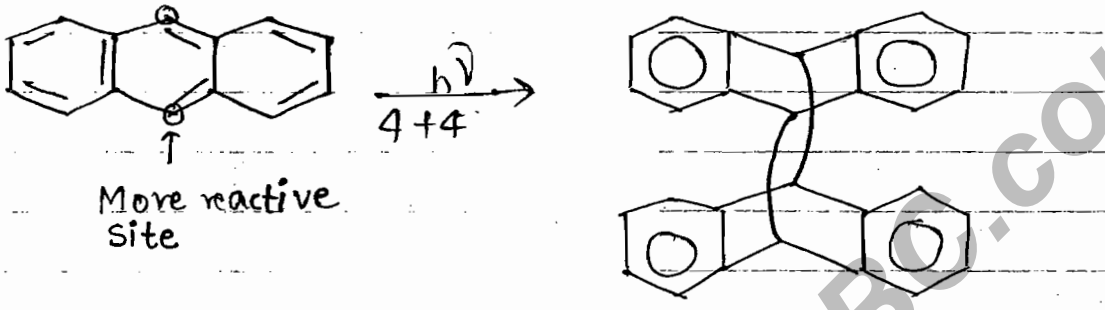
Imp.
Q



4+2 Free radical Mechanism.

Q

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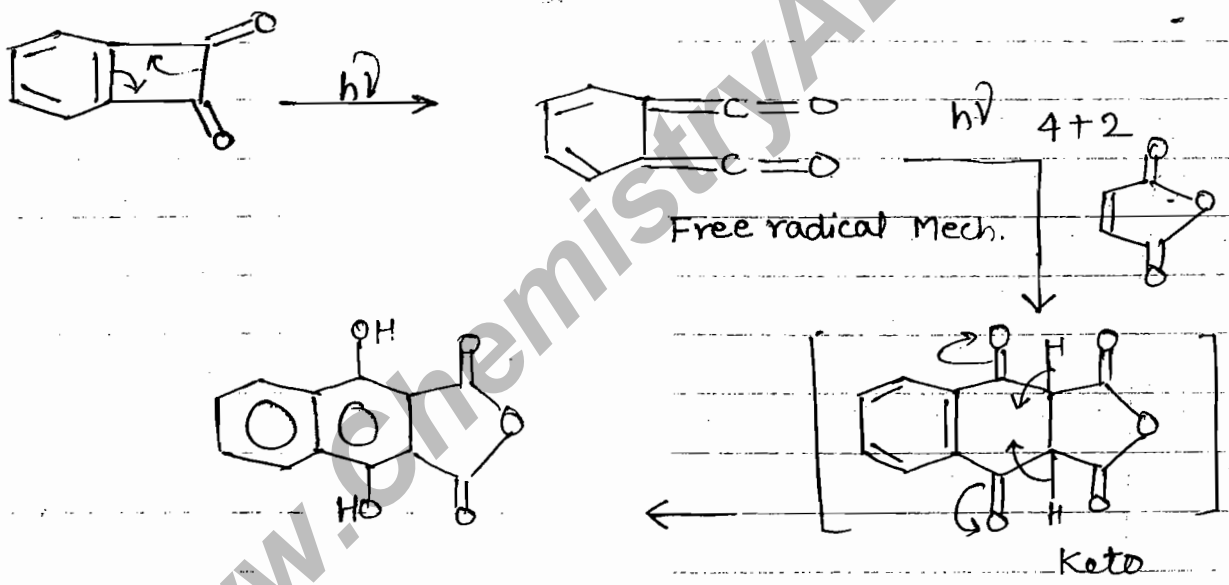


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## PHOTOCHEMISTRY OF SINGLET OXYGEN:-

In normal conditions oxygen exist in triplet form, two unpaired e⁻ present in mol. orb. but in the +nce of light triplet oxygen convert into singlet via spin rotion of one e⁻ and this singlet $O_2$ gives photochemical reac$^n$ with alkene in the +nce of ① Naphthalene, ② methylene blue, ③ Rose bengal ⇒ ①, ② ③ are photosensitizer.

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$O_2$ के साथ कोई भी comp. दिया हो, वो Sensitizer की तरह work करता है।

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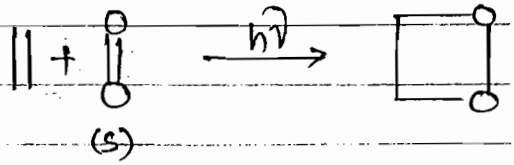
Ex.



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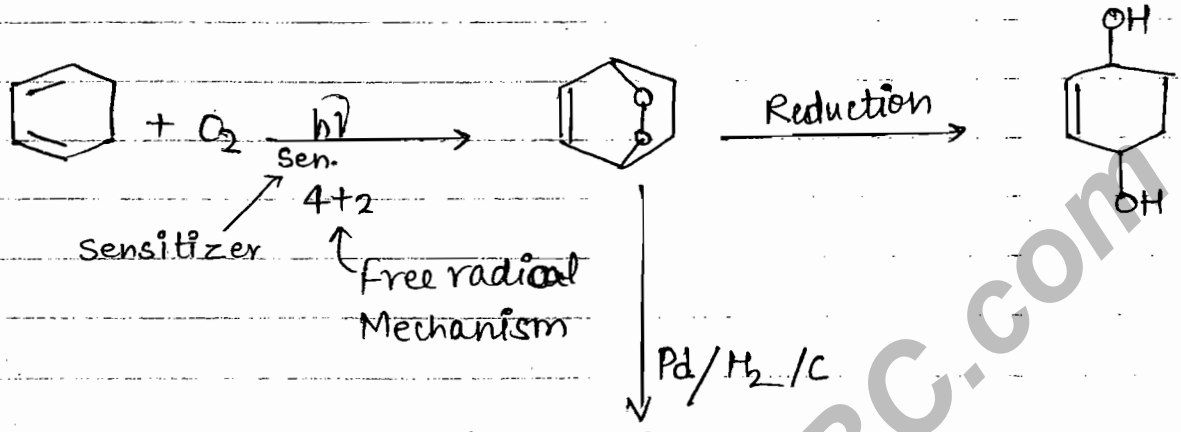


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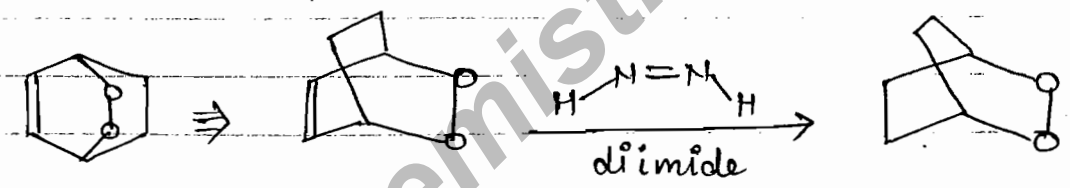
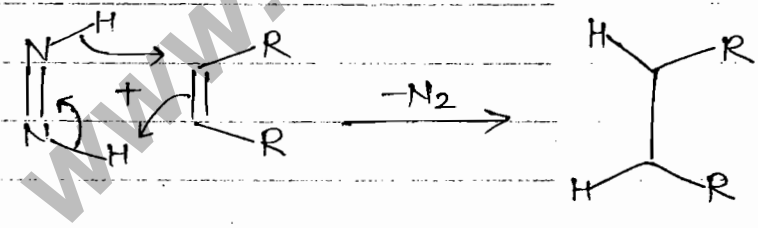



⇒ Reduction of C=C or C≡C

*

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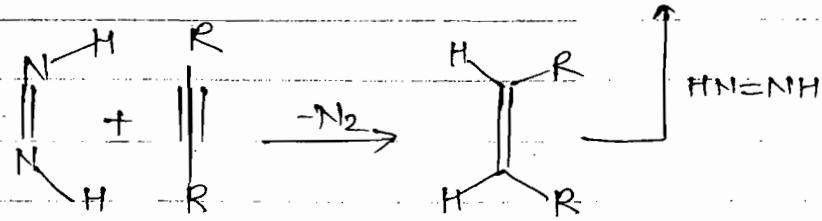
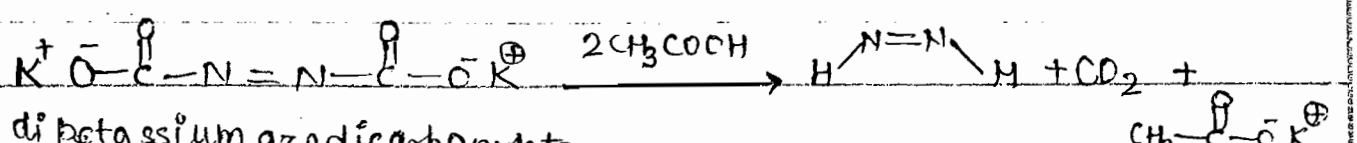



⇒




dipotassium azodicarbonylate

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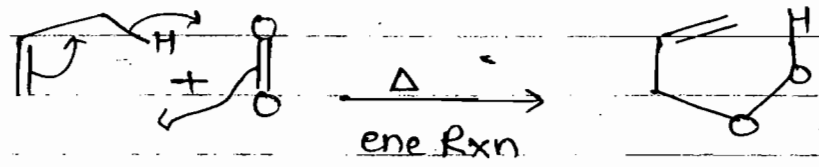
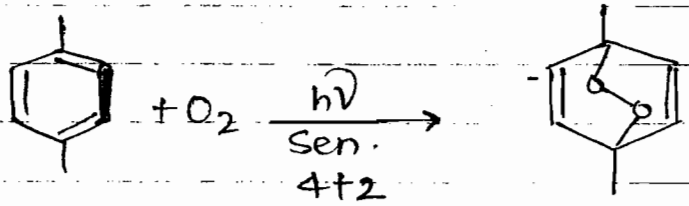
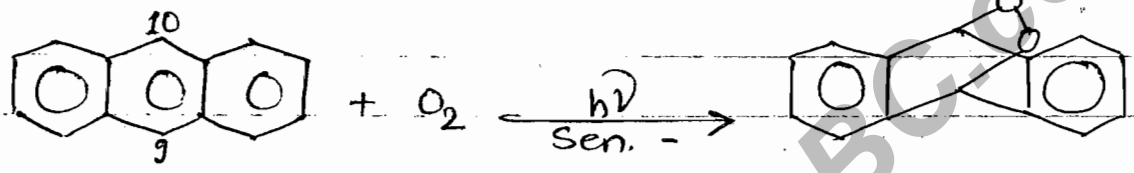
Q. 

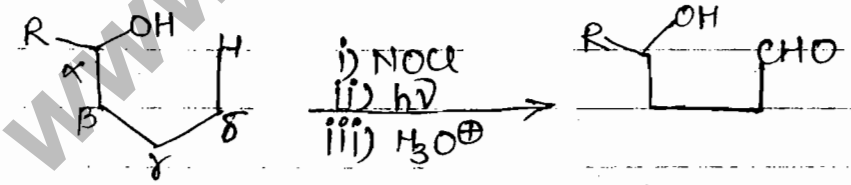

Q. 


Q. 


M. Imp.

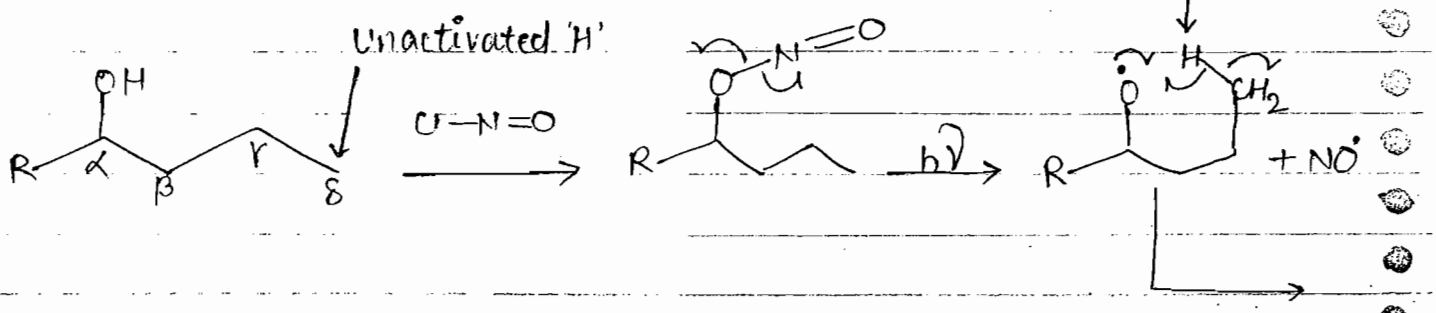
# BORTON Rxn.

In Borton Rxn. $-CH_3$ or $-CH_2-$ group lies at δ-position w.r.t. Hydroxy group, can be oxidised into carbonyl in the presence of NOCl (Tilden reagent) and photochemical condition followed by acidic hydrolysis.

Ex. 


Mechanism:-

If deuterium (D) then deuterinated alco. will form

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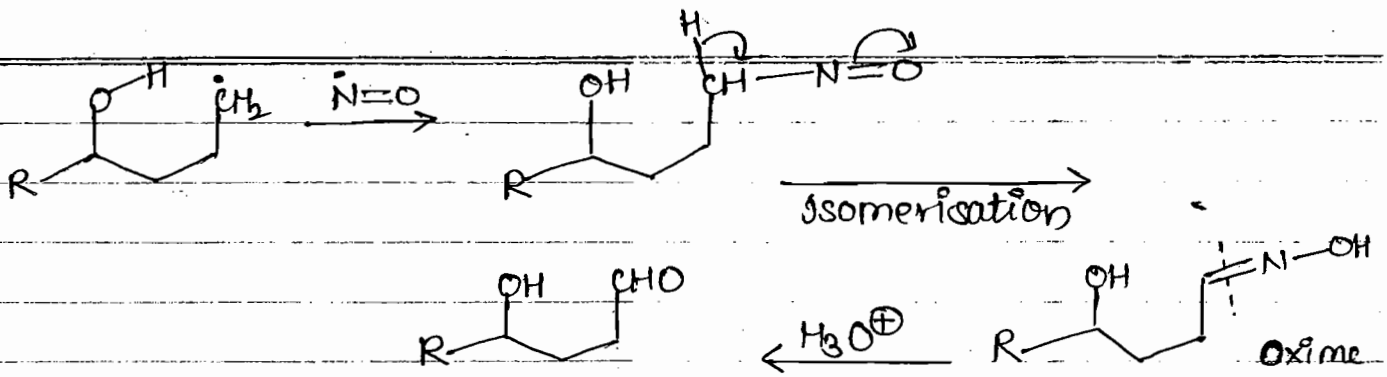
If $-CH_2-$ & $-CH_3$ both +nt in δ position then $-CH_3$ will oxidise in Barton Rxn.



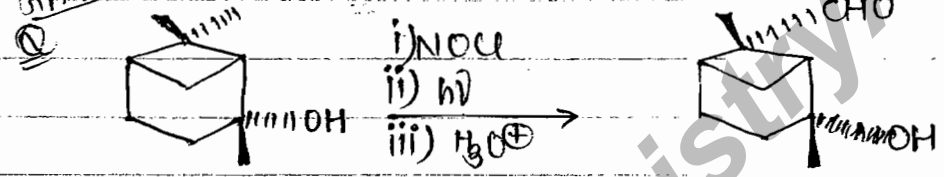

Barton Rxn. is a method an oxidⁿ. of an unactivated carbon

Condⁿ. for Barton Rxn.

$-CH_3$ or $-CH_2-$ group should be +nt in favourable steric hindrance position.

GATE

Q

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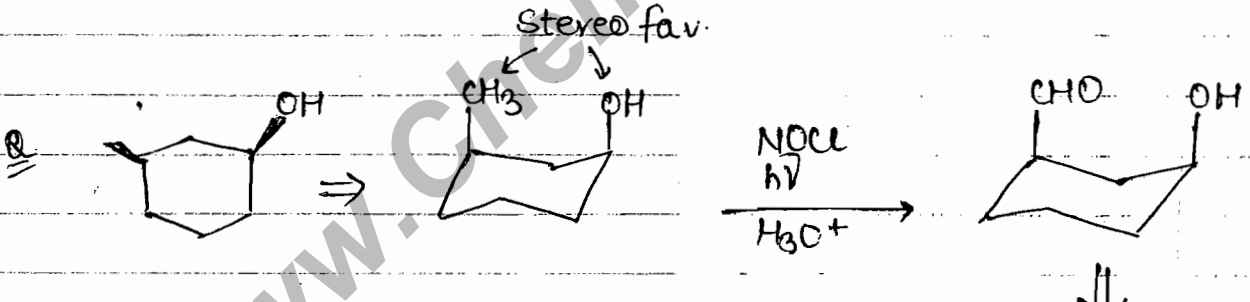
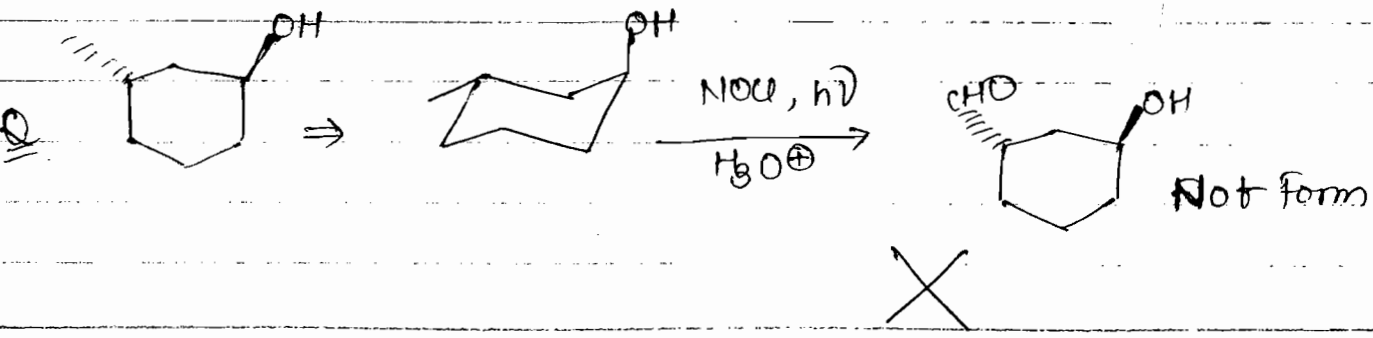



Stereo unfavourable

Q

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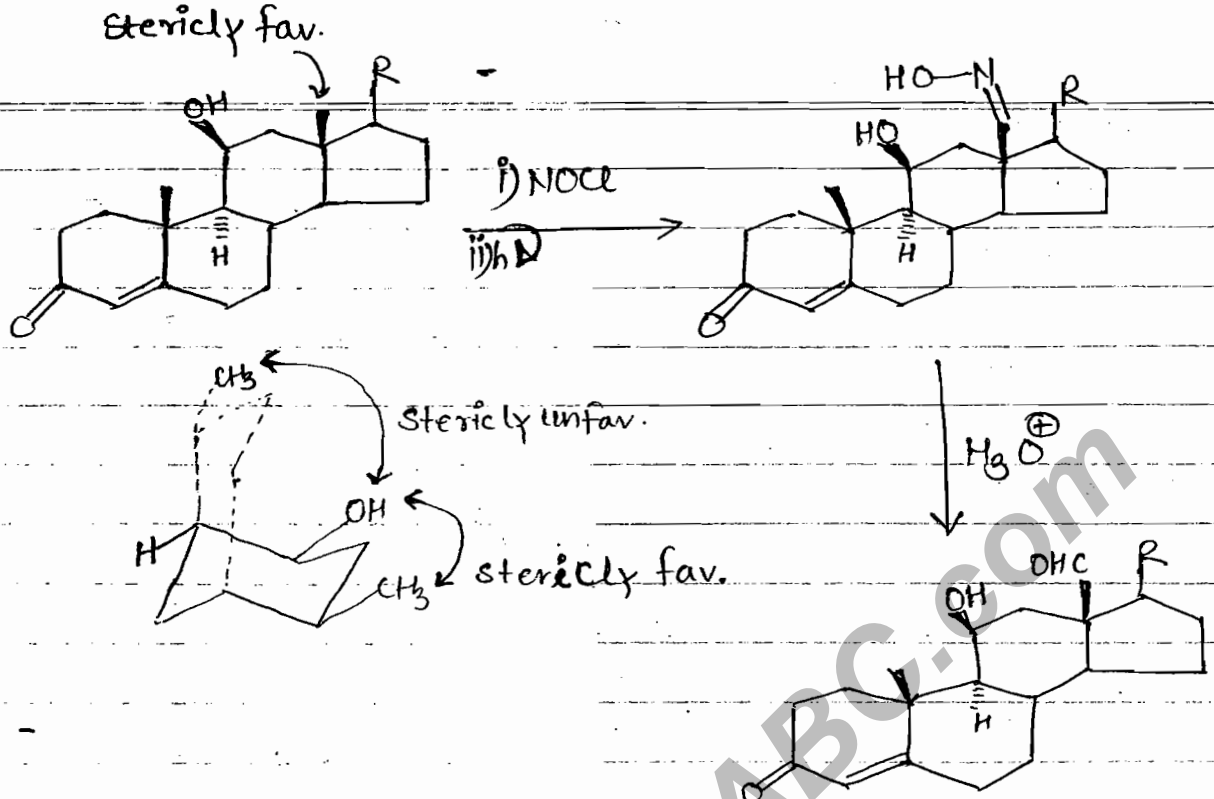
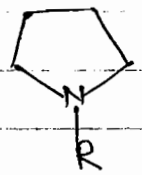
Imp. GATE Q




## HOFMANN LOFLER Freytag rearrangement:-

When N-haloginated amine containing 'H' atom at fourth or fifth position are radiated in the ince of acid followed by basic workup the five memb. or 6-membered heterocyclic comp. form. Generally 5-memb. ring form.

Ex. $R-\underset{\underset{Cl}{|}}{N}-CH_2-CH_2-CH_2-CH_3$ $\xrightarrow[\text{iii) } \bar{O}H]{\text{i) } H^{\oplus}\ \text{ii) } h\nu}$ 


Mechanism:-

$R-\ddot{\underset{\underset{Cl}{|}}{N}}-\overset{1}{CH_2}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_3}$ $\xrightarrow{H^{\oplus}}$ $R-\overset{\oplus}{\underset{\underset{Cl}{|}}{NH}}-CH_2-CH_2-CH_2-CH_3$

$\xrightarrow{h\nu}$ $\cdot Cl$

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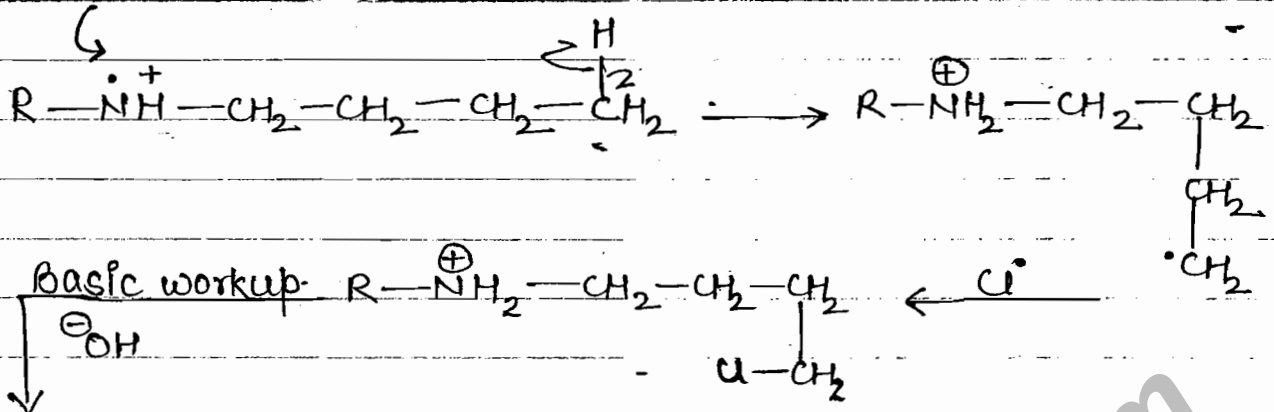
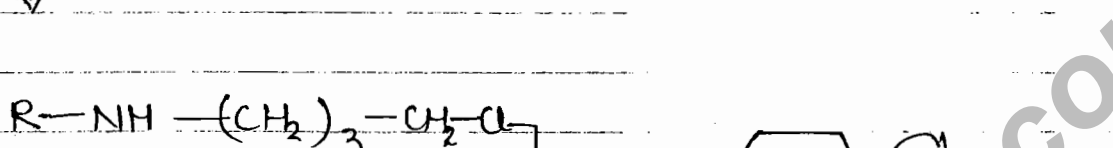
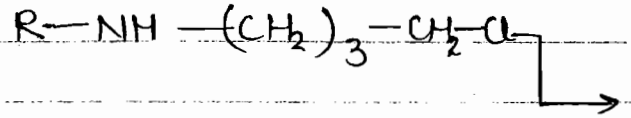
## Free radical cyclization as an intermediate:



Basic workup





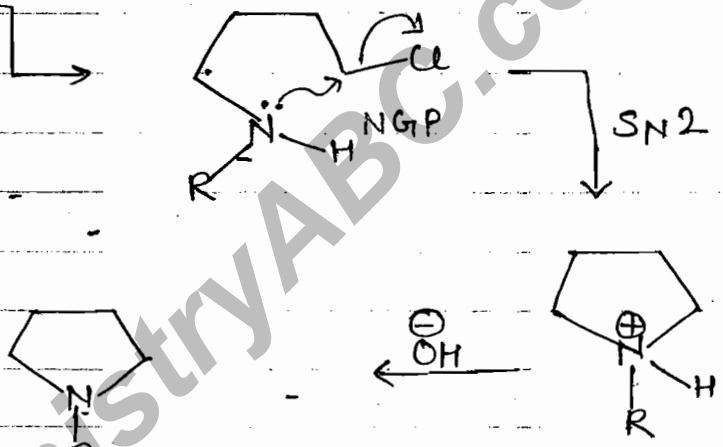
Shortcut

Halogen हटाओ

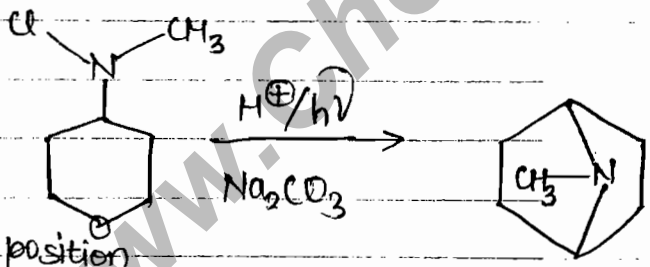
4th position के 'C' पर

लगाओ then Basic

work up कराओ.

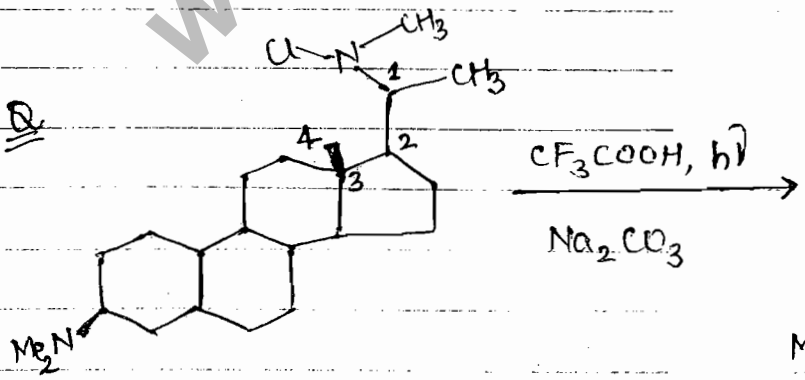


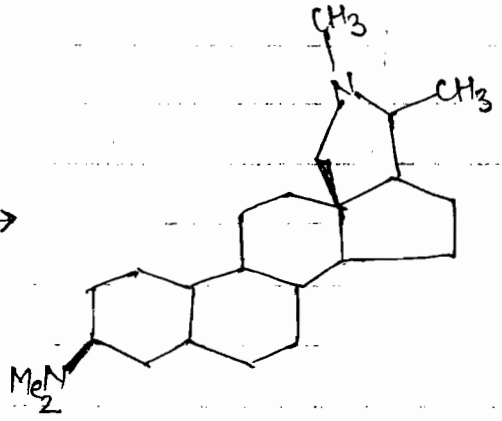
Q.



forth position

Q





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