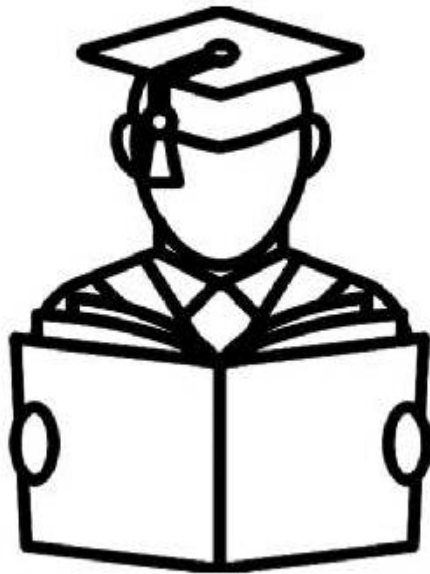


# चौधरी **PHOTOSTAT**

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*"I don't love studying. I hate studying. I like learning. Learning is beautiful."*



*"An investment in knowledge pays the best interest."*

Hi, My Name is

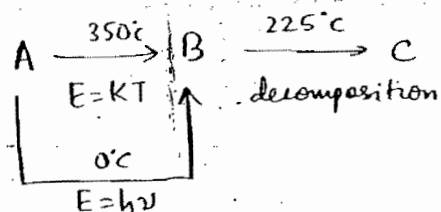
**CHEMISTRY IAS**  
**DIAS**

# PHOTOCHEMICAL REACTION

[10-20 marks]

These are those reaction in which activation energy is supplied by electromagnetic radiation.

## Isolation of cold-product -

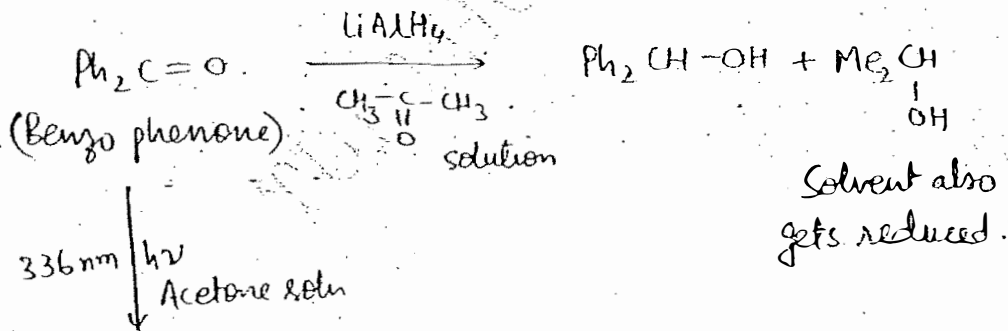


& 'B' cold product can be isolated. Energy is supplied without rise of temperature.

## High degree of selectivity -

∴ photochemical reaction takes place if & only if electromagnetic radiation is absorbed by molecule.

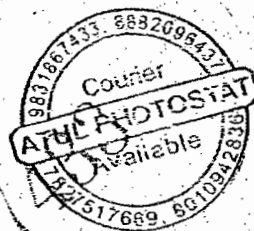
Take a case -



$336\text{nm}$   $h\nu$   
Acetone soln

$\text{Ph}_2\text{CH}-\text{OH}$  & Acetone is not reduced ∴ at  $336\text{nm}$  only benzo phenone absorb the radiation & not acetone. Hence, higher degree of selectivity is observed.

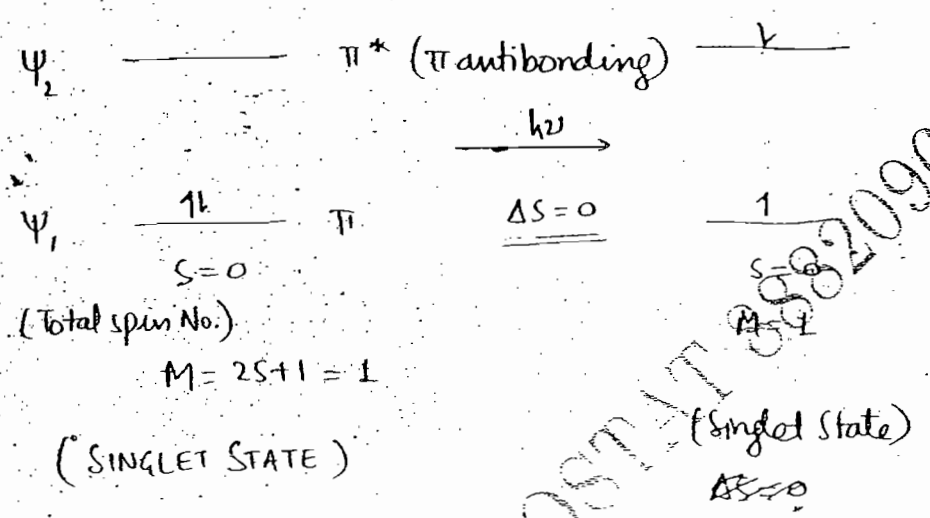
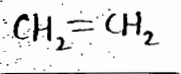
• Photochemical reaction take place in excited state.



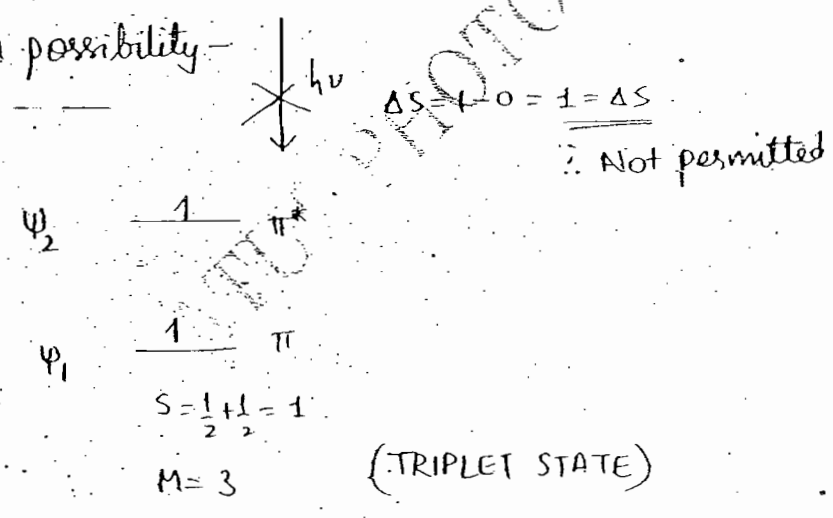
RULE OF EXCITATION:

Excitation follow spin conservation rule that during electronic excitation there is no change in spin state of electron.

$$\Delta S = 0$$



Another possibility -



- \* Singlet  $\rightarrow$  Singlet  $\checkmark$  (allowed)
- Triplet  $\rightarrow$  Triplet  $\checkmark$
- Singlet  $\rightarrow$  Triplet  $\times$  (forbidden)
- Triplet  $\rightarrow$  Singlet  $\times$

Ground state of most molecule is singlet.

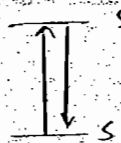
[Triplet state is more stable than singlet state]

∴ Only transition is possible i.e. singlet to singlet.

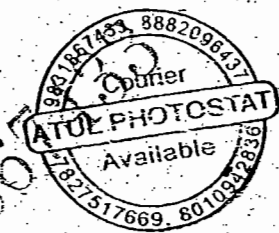
Since,  $s \rightarrow s$  transition is allowed. (excitation & de excitation)

Relaxation time of singlet state is very less ( $10^{-6} - 10^{-8}$  sec)

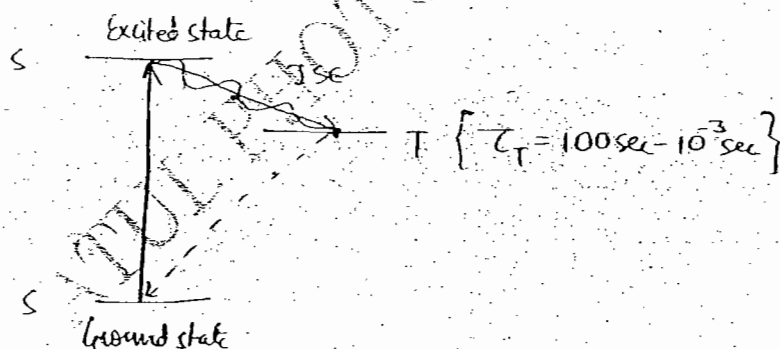
In this time, it is not sufficient for a chemical reaction.



Triplet state is most more stable due to rule of high multiplicity. & Therefore, every system tends to cross-over from singlet to triplet state in excited state. ∴ Ground state triplet is not possible.



### INTER SYSTEM CROSSING :



Write a short note on Inter system crossing (ISC)

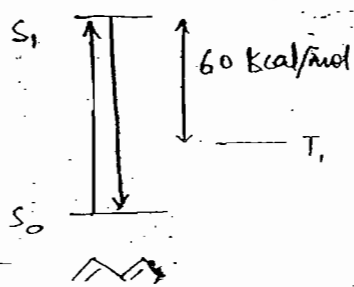
Cross-over of singlet excited state into triplet excited state is called as ISC.

Since triplet state is more stable & also triplet to singlet relaxation is forbidden ∴ triplet state is associated with high relaxation time.

(100 sec to 1 millise) & it is sufficient time for a variety of chemical reactions. Therefore, organic photochemistry is chemistry of triplet state.

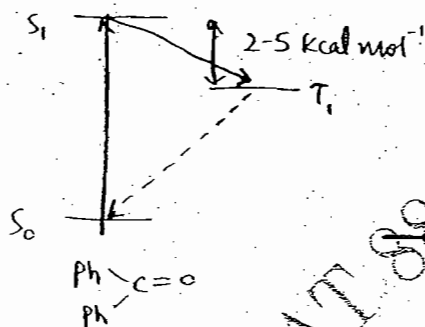
The tendency of a molecule to undergo intersystem crossing is called as Inter system crossing efficiency.

It depends upon energy gap between excited singlet & triplet state. If energy gap is very high:



0%

(In conjugated alkene)

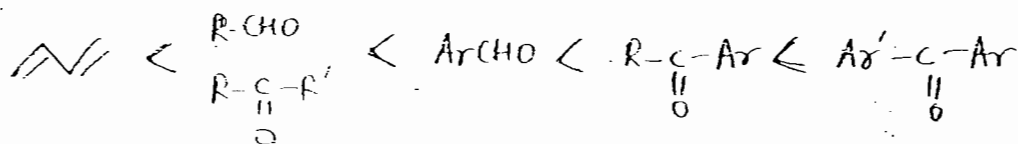


100%

ISC efficiency

ISC EFFICIENCY OF ALKENES is 0% due to very high energy gap b/w singlet & triplet excited state. On the other hand, ISC EFF. OF HIGHLY CONJUGATED KETONE i.e benzophenone is nearly 100% due to overlapping singlet & triplet excited state ( $\Delta E < 10$  kcal/mol)

All other compound have ISC efficiency between them.



(ISC efficiency)

Due to conjugation, energy gap b/w HOMO & LUMO decreases. That means, excited singlet state become lower in energy but triplet state is not affected (bond formation or conjugation is ~~in~~ singlet state)  $\therefore$  excited singlet & triplet energy gap decreases & ISC efficiency increases.

Since, carbonyl compounds have higher ISC efficiency. They can undergo a variety of organic photochemical reaction. That's why organic photochemistry is also called as chemistry of carbonyl compound.

$\Rightarrow$  Carbonyl comp easily give triplet state but alkene can't generate triplet state.

$\Downarrow$

### PHOTOSENSITIZATION

What is photosensitization. Give its mechanism. Why photosensitizer always generate triplet state.

Photosensitization is a process in which photo-active molecule absorb electromagnetic radiation & undergo excitation. Then transfer its energy to another molecule which get excited & undergo chemical reaction. Since transfer of energy require sometime  $\therefore$  photosensitization always take place in triplet state & all photosensitizer

III) TWO COMPLETELY SOLUBLE LIQ. HAVING

SIMILAR PROPERTIES: give ideal solution in which vapour pressure of is given by -

$$P_1 = P_1^{\circ} x_1 \quad ; \quad P_2 = P_2^{\circ} x_2$$

where,  $x_1$  &  $x_2$  are mole fraction while  $P_1^{\circ}$  &  $P_2^{\circ}$  is their actual V.P. (pure state) so that, total V.P. is given by -

$$P_s = P_1 + P_2 = P_1^{\circ} x_1 + P_2^{\circ} x_2$$

That means, lowering of V.P. ~~take~~ always takes place whenever a solute is added to solvent in order to form ideal solution.

Solution is always in eqm with its vapour phase

$\therefore$  component 1 & 2 are also present in vapour phase & their vapour phase composition is given by -

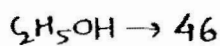
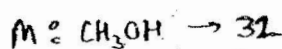
$$\frac{1}{P} = \frac{y_1}{P_1^{\circ}} + \frac{y_2}{P_2^{\circ}}$$

$$\begin{cases} P_2^{\circ} x_2 = P y_2 \\ P_1^{\circ} x_1 = P y_1 \end{cases}$$

where,  $y_1$  &  $y_2$  are mole fraction in vapour phase

Q- Ethyl alcohol & methyl alcohol form ideal solution if 100 gm of both is mixed together & V.P. of pure methyl alcohol is 89 mm Hg & of ethyl alcohol is 43 mm Hg. Calculate their mole fraction in vapour phase.

Sol [ If Raoult's law is followed in liq. phase then Dalton's law of partial pressure must be followed in vapour phase. ]



x

100-x

-

-

$\rightarrow$  Vapour phase

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$$n_{\text{EtOH}} = \frac{167}{46} = 3.63$$

$$n_{\text{PrOH}} = \frac{100}{32} = 3.12$$

$$x_{\text{EtOH}} = \frac{2.17}{5.29} =$$

$$x_{\text{PrOH}} = \frac{3.12}{5.29} =$$

$$P_s = x_{\text{EtOH}} P_{\text{EtOH}}^{\circ} + x_{\text{PrOH}} P_{\text{PrOH}}^{\circ}$$

$$P_s = \left[ \left( \frac{2.17}{5.29} \times 43 \right) + \left( \frac{3.12}{5.29} \times 88 \right) \right] \text{ mmHg}$$

$$P_s = 69.54 \text{ mmHg}$$

In vapour phase:

$$P_s y_{\text{Et}} = P_{\text{Et}}^{\circ} x_{\text{Et}}$$

$$y_{\text{Et}} = \frac{43 \times 2.17}{69.54 \times 5.29} = 0.25 = y_{\text{Et}}$$

Vapour phase is always rich in that component whose B.P. is low.

Q. Benzene & Toluene form ideal solution whose total V.P. is 170 mmHg. If mole fraction in vapour phase is 0.2 w.r.t toluene. Then calculate mole fraction of each component in liquid state.  $P_B^{\circ} : P_T^{\circ} = 1.2 : 1$

$$\text{Sol. } P_s = 170 \text{ mmHg}, \quad y_T = 0.2, \quad y_B = 0.8, \quad \frac{P_B^{\circ}}{P_T^{\circ}} = 1.2$$

$$\frac{1}{P_s} = \frac{0.2}{P_T^{\circ}} + \frac{0.8}{P_B^{\circ}}$$

$$\frac{1}{170} = \frac{0.2}{P_T^{\circ}} + \frac{0.8}{1.2 P_T^{\circ}} = \frac{1}{P_T^{\circ}} \left[ 0.2 + \frac{0.8}{1.2} \right]$$

$$P_T^{\circ} = 170 \left( 0.2 + 0.67 \right) \text{ mmHg} = 147.9 \text{ mmHg}$$

$$\text{(liq.) } \therefore P_T^{\circ} x_T = P_s y_T \quad (\text{vap})$$

$$x_T = \frac{170 \times 0.2}{147.9} = 0.23$$



Q. If 2 liq. A & B are mixed together and mixed together to form an ideal solution. If  $x_A, x_B$  are their mole fraction &  $P_A^\circ$  &  $P_B^\circ$  is their V.P. in pure state. Then, derive the relationship:

$$\frac{1}{P} = \frac{y_A}{P_A^\circ} + \frac{y_B}{P_B^\circ}$$

Assuming that Dalton's law is applicable to vapour phase &  $P$  is total V.P. of solution.

Sol  $P = P_A^\circ + (P_B^\circ - P_A^\circ) x_B$

$$P = P_A^\circ x_A + P_B^\circ (1 - x_A)$$

$$P = P_B^\circ + (P_A^\circ - P_B^\circ) x_A$$

$$\Rightarrow P_B^\circ x_B = P y_B$$

$$\therefore P = \frac{P_B^\circ x_B}{y_B} = P_A^\circ \frac{P_B^\circ}{y_B} \left[ \frac{P - P_A^\circ}{P_B^\circ - P_A^\circ} \right]$$

$$\frac{1}{P} = \frac{y_B}{P_B^\circ} \left[ \frac{P_B^\circ - P_A^\circ}{P - P_A^\circ} \right]$$

$$\Rightarrow P_A^\circ x_A = P y_A \quad P = \frac{P_A^\circ x_A}{y_A}$$

$$P \frac{y}{P} = \frac{P_A^\circ}{y_A} (1 - x_A) = \frac{P_A^\circ}{y_A} \left( 1 - \frac{P - P_A^\circ}{P_B^\circ - P_A^\circ} \right)$$

$$\frac{1}{P} = \frac{y_A}{P_A^\circ} \left( \frac{P_B^\circ - P_A^\circ}{P_B^\circ - P_A^\circ - P + P_A^\circ} \right) = \frac{y_A}{P_A^\circ} \left( \frac{P_B^\circ - P_A^\circ}{P_B^\circ - P} \right)$$

$$2P = \left[ \frac{P_B^\circ}{y_B} (P - P_A^\circ) + \frac{P_A^\circ}{y_A} (P_B^\circ - P) \right] \frac{1}{(P_B^\circ - P_A^\circ)} = \frac{P_B^\circ}{y_B} x_B + \frac{P_A^\circ}{y_A} x_A$$

$$= \frac{P_B^\circ}{y_B} x_B + \frac{P_A^\circ}{y_A} (1 - x_B) = \frac{P_A^\circ}{y_A} + \left( \frac{P_B^\circ}{y_B} - \frac{P_A^\circ}{y_A} \right) x_B =$$

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Another aspect of solution is DISTRIBUTION

Whenever a solute is added in 2 insoluble liquids it distributes itself in such a way that -

Ratio of its concentration in 2 solvent phase remain constant. This constant is called as Nernst Distribution law which holds good whenever -

- (i) Temp. & Pressure remain constt throughout the experiment.
- (ii) Solute doesn't undergo association, dissociation or any kind of reaction in the either solvent.

This distribution coefficient is always expressed in favour of denominator numerator.

$$K_D = \frac{C_{org}}{C_{aq}}$$

$$K_D C_{aq} = C_{org}$$

$C_{org}$  → organic phase

$C_{aq}$  → aqueous phase

Q. 15 gm of  $I_2$  is added to a solution containing 30 ml water & 50 ml  $CCl_4$  solution is thoroughly shaken at  $25^\circ C$  & 1 atm pressure. If Distribution coefficient of  $I_2$  in favour of  $CCl_4$  is 6.25. Calculate the weight of  $I_2$  in aqueous phase &  $CCl_4$ .

Sol.  $6.25 = K_D = \frac{C_{org}}{C_{aq}}$

Let  $x$  is wt. of  $I_2$  in  $CCl_4$  phase

$$\therefore K_D = \frac{x/50}{15-x/30} = 6.25$$

$$\frac{x}{15-x} = \frac{6.25 \times 5}{3}$$

$$\frac{15}{x} = \frac{11 \times 3}{6.25 \times 5} \quad x = 15 \left( \frac{6.25 \times 5}{3 + 6.25 \times 5} \right)$$

$x = 13.69 \text{ gm in } \text{CCl}_4$

$\& 1.31 \text{ gm in aqueous phase}$

### SOLVENT EXTRACTION:

It is a separation technique which is based on distribution law.

Suppose a component is more soluble in organic phase compared to aqueous phase then it can be transferred from aqueous phase to organic phase by addition of organic solvent in mother solution in which compound is present. The overall principle can be understood by taking Nernst distribution law.

Assume 'w' gm of solute is present in 'V' ml of water & it is extracted by adding small 'v' ml of organic solvent for which its distribution coeff. is  $K_D$ . Suppose after extraction 'w<sub>1</sub>' g of solute is left in aqueous phase then weight in aqueous phase = w<sub>1</sub> g.

Weight in organic phase = (w - w<sub>1</sub>) g

Volume of aqueous phase = V ml

Volume of organic phase = v ml

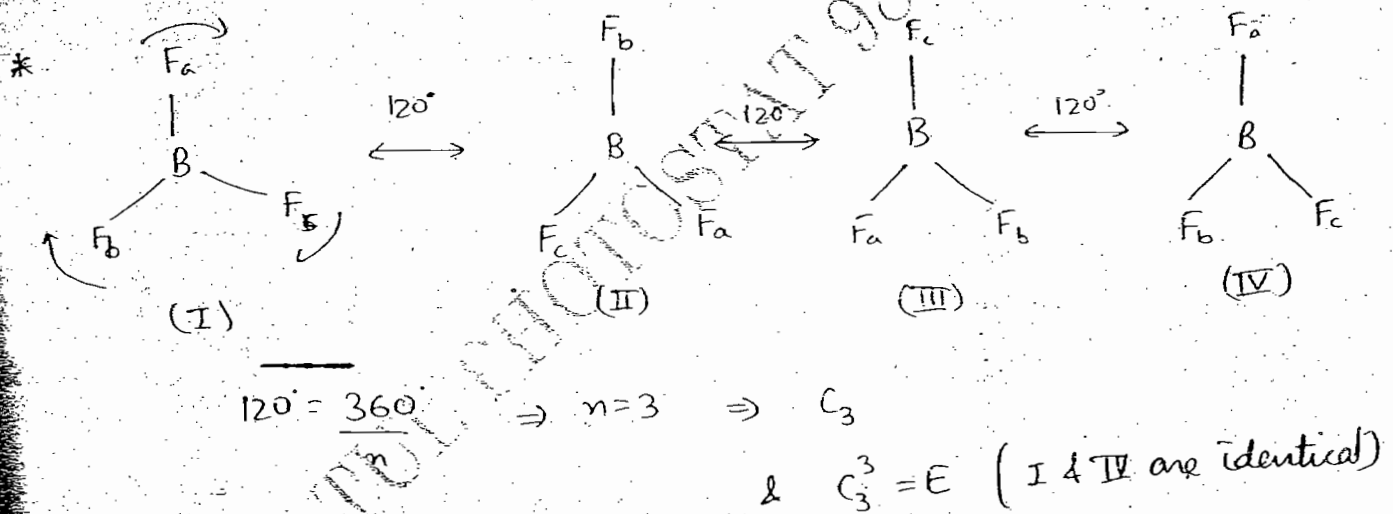
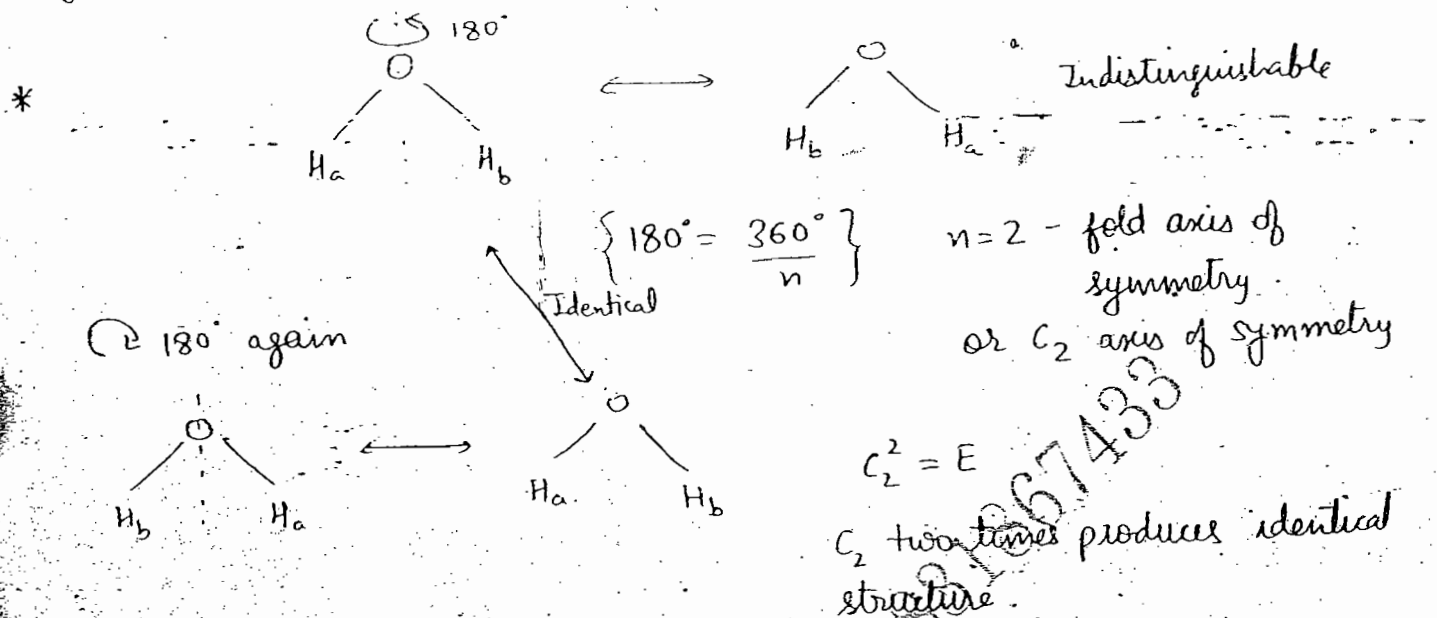
$\Rightarrow K_D$  in favour of organic phase =  $\frac{C_{org}}{C_{aq}}$

$$K_D = \frac{(w - w_1)/v}{w_1/V}$$

$$K_D = \frac{w - w_1}{w_1} \times \frac{V}{v}$$

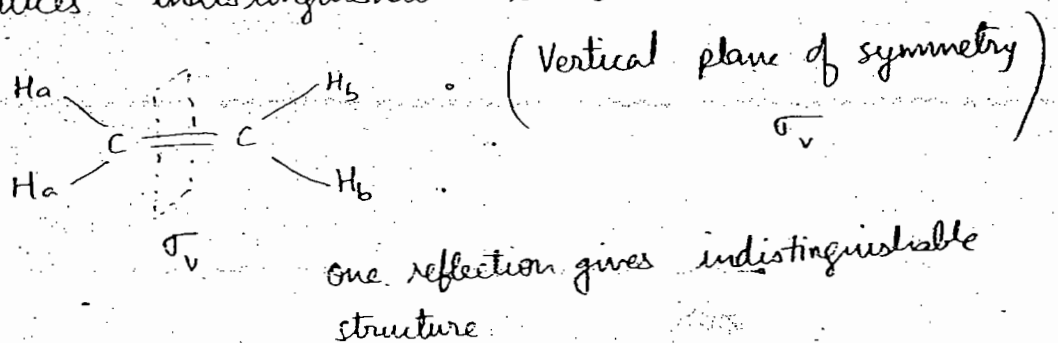
## AXIS OF SYMMETRY:

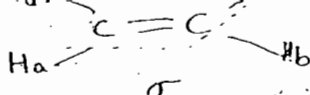
It is imaginary or real axis through which a rotation of  $360/n$  degree produces indistinguishable structure.



## PLANE OF SYMMETRY:

It is imaginary or real plane through which reflection of molecule produces indistinguishable structure.

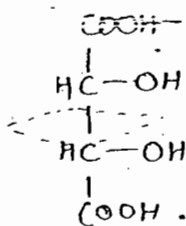
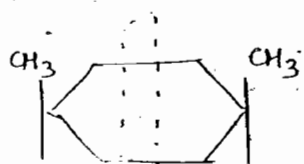




$\sigma_h \rightarrow$  horizontal axis plane of symmetry.

Two plane of symmetry gives identical structure

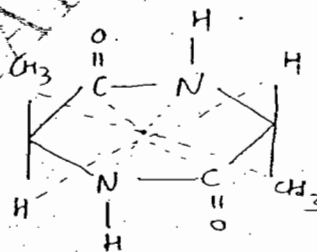
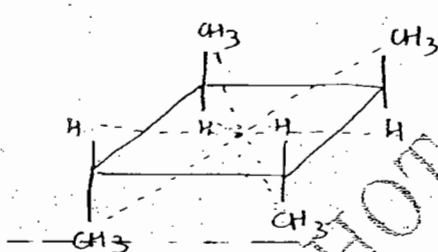
$$\sigma_v^2 = \sigma_h^2 = E$$



CENTRE OF SYMMETRY:

Imaginary or real centre along which all coordinates position changes its side sign.

$$(x \ y \ z) \xrightarrow{s} (-x \ -y \ -z)$$

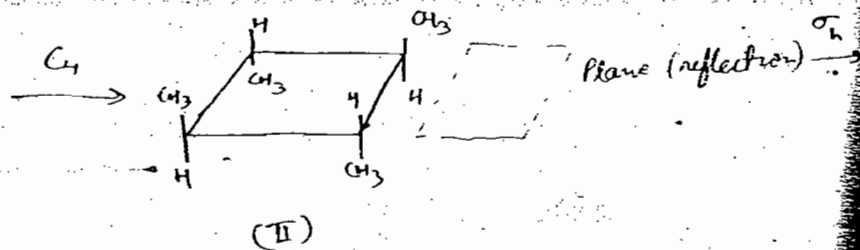
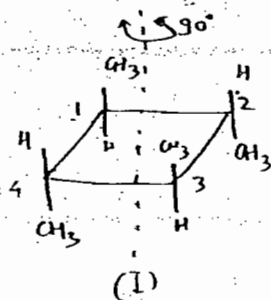


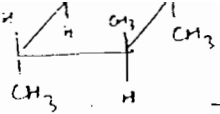
Above all are regarded as PROPER SYMMETRY ELEMENTS:

There are some improper symmetry elements as follows-

ALTERNATING AXIS OF SYMMETRY:

Rotation through an axis by  $360/n^\circ$  followed by reflection through a plane perpendicular to rotation axis is  $S_n$  called as alternating axis of symmetry.





(III)

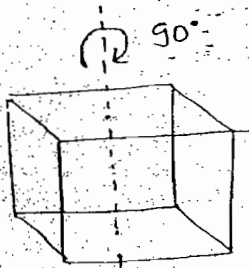
$S_4 \rightarrow$  4 fold improper axis of symmetry

(Super Imposable includes both Identical as well as non-superimposable)

ELEMENTS OF A SYMMETRY OF A CUBE:

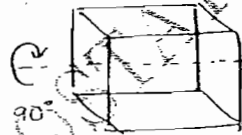
A cube with 23 elements of symmetry is highly symmetrical. It contains all the elements of symmetry.

(1) AXIS OF SYMMETRY -



$\rightarrow C_4$ , 4 fold axis of symmetry passing through the centre of opposite face. It is also known as TETRAD AXIS.

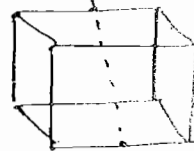
There are 3 such axes.



$(3 C_2)$

(2) 2 fold axis of symmetry passing through the opposite centre of opposite edge. It is also known as DYAD axis or BIAD AXIS.

$6 \times C_2 \rightarrow 6$  are possible



(3) TRIAD AXIS -

Rotation at  $120^\circ$  through an axis passing through the opposite diagonal corners. There are 4 such axis & is known as Triad axis of symmetry.

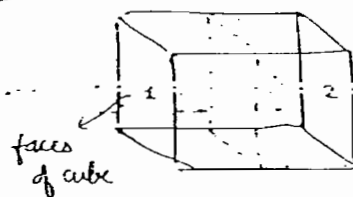
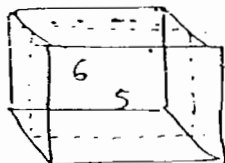
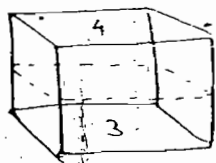


4 Triad possible

## PLANE OF SYMMETRY - (POS)

A cube also contains plane of symmetry - (i) Rectangular POS

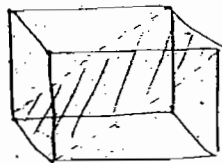
### 1a) Rectangular Plane of Symmetry -



faces  
of cube

So, there are 3 rectangular plane of symmetry.

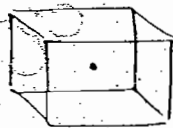
### 1b) Diagonal Plane of Symmetry - Joining the opposite diagonals



Total of 6 diagonal plane of symmetry

(3+6 POS)

### 5) CENTRE OF SYMMETRY -



A cube is also associated with centre of symmetry.

A cube with 23 symmetry elements is highly symmetrical. Since nature always follow symmetry  $\therefore$  most of crystals are in the form of cubic structure.

## 7 CRYSTAL SYSTEM :

6 parameter of unit cell i.e. 3 length parameter  
3 angle parameter

are not combined randomly but they can be combined in such a way that law of translational symmetry must be followed. Whenever symmetry element is combined with length & angle parameter - 240 space group is possible.

These 240 space group, whenever projected 3 dimensionally -

classified into only 7 type of different geometry which is known as 7 crystal system.

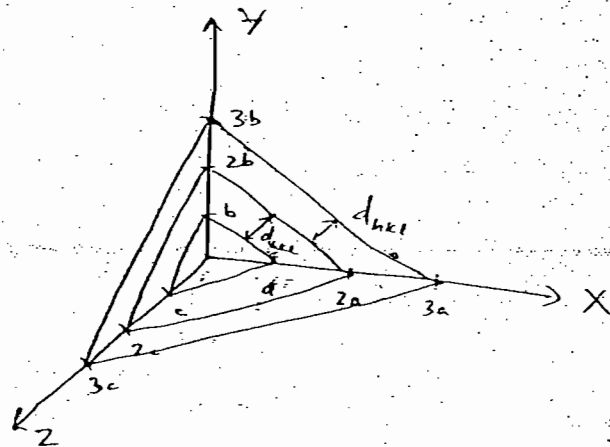
CRYSTAL	Length	Angle	Min. Symm.	Bravais Lattice
Cubic	$a=b=c$	$\alpha=\beta=\gamma=90^\circ$	$4C_3+3C_4+6C_2$	P, F, I
Orthorhombic	$a \neq b \neq c$	$\alpha=\beta=\gamma=90^\circ$	$4C_2$	P, I, F, C
Tetragonal	$a=b \neq c$	$\alpha=\beta=90^\circ \neq \gamma$ $\alpha=\beta=\gamma=90^\circ$	$1C_4$	P, I
Monoclinic	$a \neq b \neq c$	$\alpha=\gamma=90^\circ \neq \beta$	$1C_2$	P, C
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$1C_1$	P
Hexagonal	$a=b \neq c$	$\alpha=\beta=90^\circ, \gamma=120^\circ$	$1C_6$	P
Rhombohedral or Trigonal	$a=b=c$	$\alpha=\beta=\gamma \neq 90^\circ$	$1C_3$	P

All kinds of unit cells can be distributed to particular crystal system on the basis of minimum symmetry elements.

Auguste Bravais by studying the symmetric properties of crystal in combination of unit cell suggested that only 14 combinations are possible to distribute among the 7 crystal system. These 14 combinations are known as BRAVIS LATTICE.

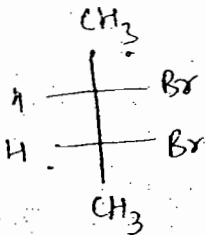
### DEVELOPMENT OF CRYSTAL STRUCTURE :

Law of Rational Indices :

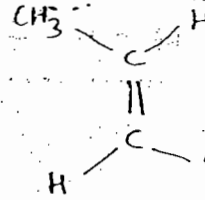
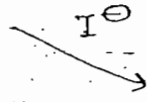




Q- What will be product with stereochemistry?

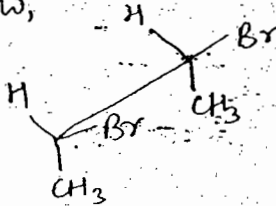


Sol-

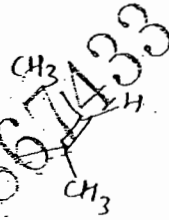
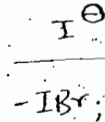
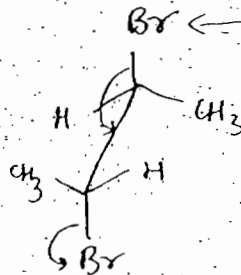


ATUL PHOTOSTAT  
 57/16 & 56/5, Old Rajendra Nagar,  
 Sada Bazar Road, New Delhi-60  
 8831567433, 8882096437  
 8827517888, 8010942836

Now,



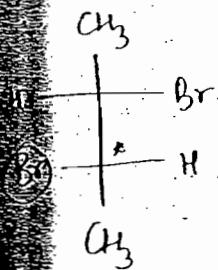
≡



(trans alkene)

(Meso 2,3-dibromo butane) Meso 2,3-butane

Meso 2,3-dibromo butane undergo Iodide ion induced elimination to give exclusively trans-2-butene while d,l racemic always give cis-2-butene under same condition. Explain

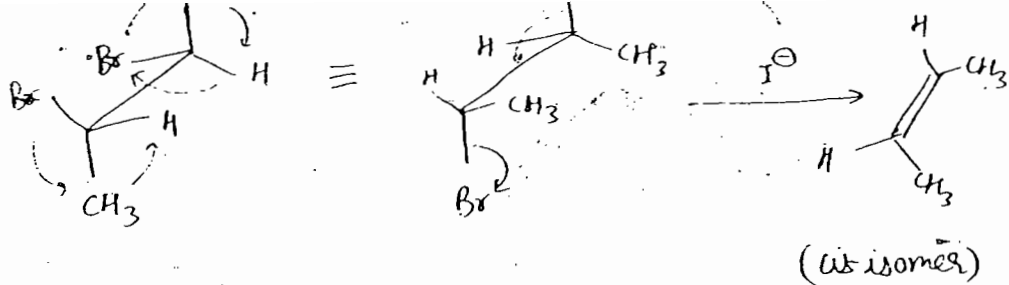


(l)

Thereo

Atomic mass of Br at last chiral carbon is max & it is at left ∴ l

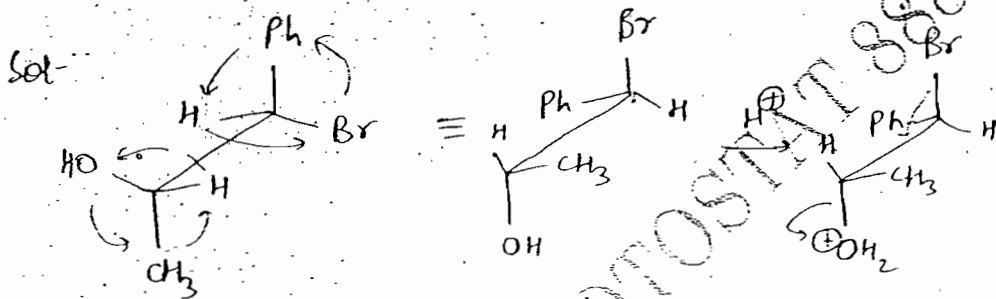
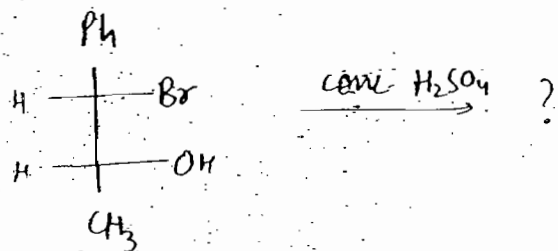
{ Erythreo = 2,3 dibromobutane }  
 → Br, Br same side in fisher.



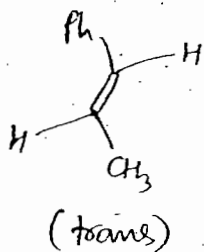
Thereo will give cis-isomer.

(T  $\Rightarrow$  trans)

Q. Discuss product with stereochemistry?



(Erythro)



(self bleaching property of Br)

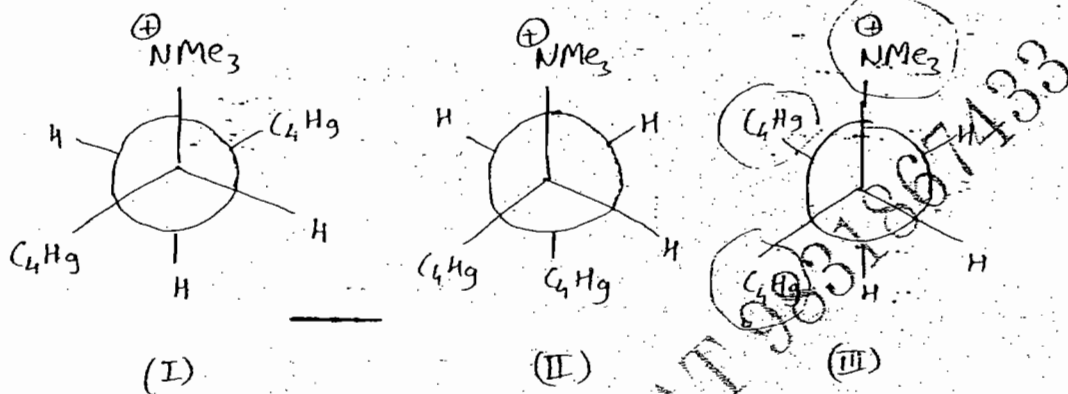
$E_2$  elimination is highly stereospecific. Erythro give trans isomer. Thereo give cis isomer exclusively & it is due to anti-elimination.

Sometimes due to conformational instability,  $E_2$  elimination takes place in syn manner.

SYN-MANNER ( $E_2$  elimination)

$\text{C}_4\text{H}_9 - \text{CH} - \text{NMe}_3^+ - \text{C}_4\text{H}_9$  undergo non stereospecific  $E_2$  elimination. Explain. [10 marks]

Sol- Conformation -



Most stable      Most unstable

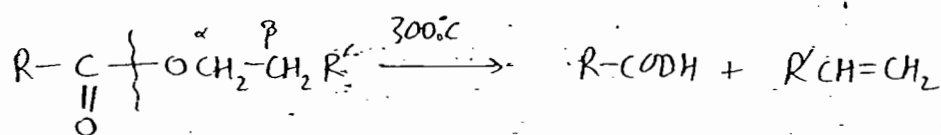
but a drawback is that there is no proton anti to  $\text{NMe}_3^+$  in (II). Therefore (I) will react undergo anti elimination & (II) will undergo syn elimination.

(I)      (II)      (III)  
35% anti      65% syn      No elimination

Stability check → Newmann projection  
Reaction → Saw horse projection

$E_1$  elimination takes place through carbocation intermediate in which free rotation is present. That's why  $E_1$  elimination is non stereospecific. Either erythro or Threo, both give a mixture of cis & trans isomer.

### PYROLYTIC ELIMINATION or $E_i$ ELIMINATION:

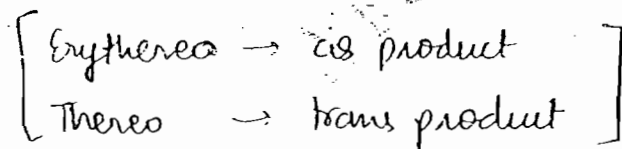


acidic part      alcoholic part

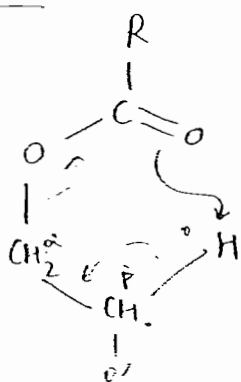
Whenever carboxy-ester having atleast one  $\beta$  hydrogen on alcoholic part is heated at about  $300^\circ\text{C}$ , it undergo elimination to give alkene as product.

A unimolecular kinetics is observed & elimination is highly stereospecific.

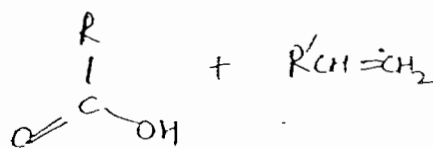
Stereochemistry is syn elimination

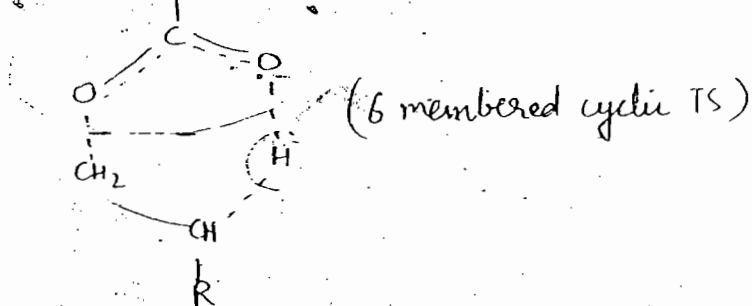


Mechanism -



A pericyclic mechanism is observed through the 6 member transition state





(In fact  $\pi$  e<sup>-</sup> act as internal-base) & that's why

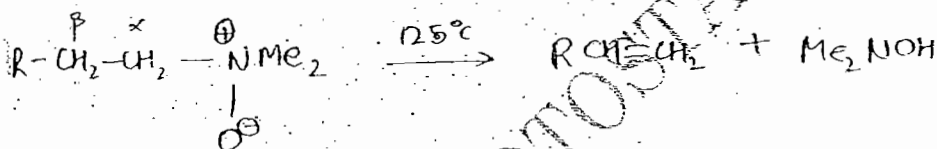
Eliminating group act as internal base. ( $R-COO^{\ominus}$ )

& that's why this mechanism is called  $E_i$ . For the

purpose of cyclic TS, eliminating group &  $\beta$ -Hydrogen must be on same side of plane i.e. syn elimination

(since temp is very high  $\therefore$  not useful method)

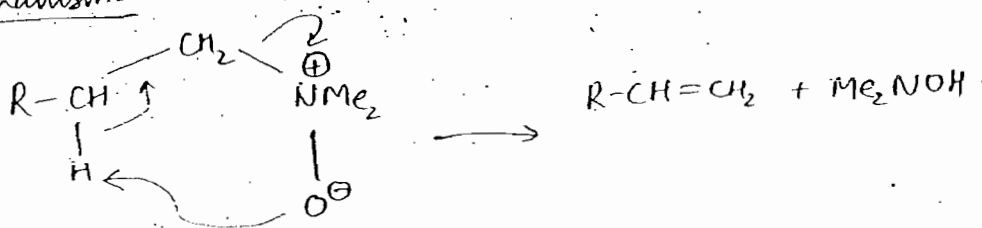
### # COPE - ELIMINATION :



(N-amine oxide)

N-amine oxide having at least one  $\beta$ -hydrogen undergoes pyrolytic elimination at  $125^\circ C$  to give alkene in stereospecifically syn manner.

Mechanism-



(internal attack of base)

Reaction takes place through 5 membered cyclic TS.

# AROMATICITY

Aromaticity utilises the concept of delocalised molecular orbital (M.O.). MO is formed by overlap of two individual atomic orbitals.

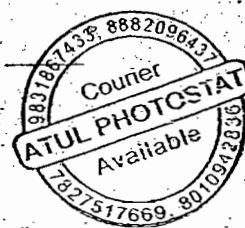
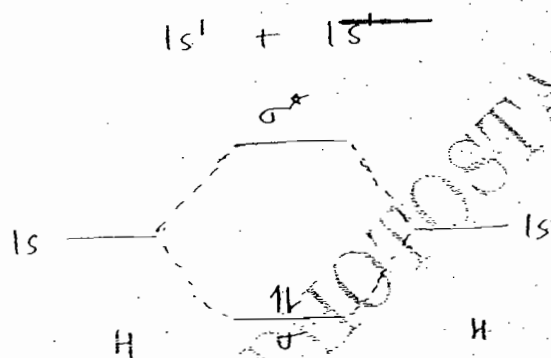
This overlap can be in the phase overlap i.e.

Bonding MO (BMO) & out of phase i.e.

Anti Bonding MO (ABMO).

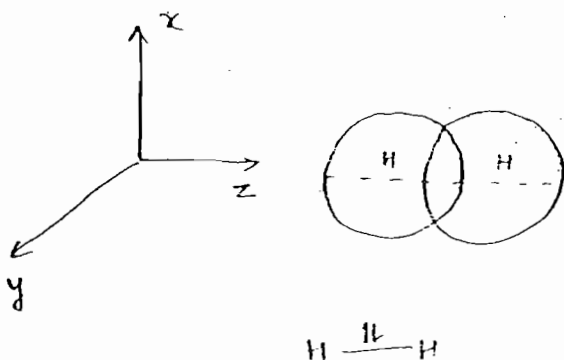
If 'N' atomic orbital combine together, it produces  $N \rightarrow$  MO out of which  $N/2$  are bonding & rest  $N/2$  anti bonding.

Consider the formation of  $H_2$  molecule -



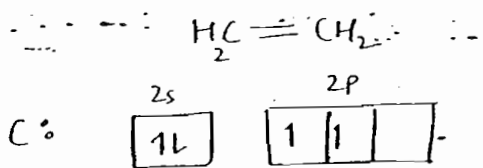
This type of MO is called as  $\sigma$ -MO.

$\sigma$ -MO is formed due to overlap <sup>of atomic orbitals</sup> along the internuclear axis.

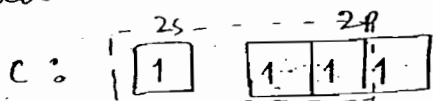


$\therefore \sigma$ -e is under the influence of two nucleus.  
And they are localised - (can't be displaced)

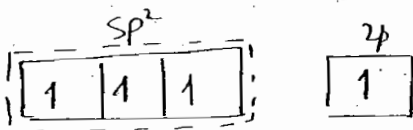
Consider the case of ethane molecule. In which each 'C' is  $sp^2$  hybridised



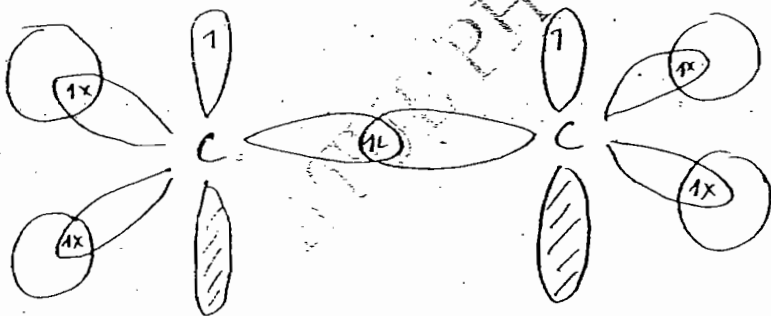
In excited state -



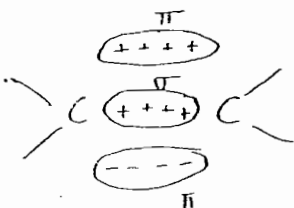
& Hybridisation takes place to give 'p' orbital &  $sp^2$  orbital.



Each  $sp^2$  orbital forms  $\sigma$  bond. And we are left with 2 p-orbitals  $\perp$  to each other.

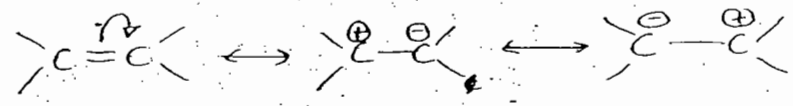


Unpaired  $e^-$  form bond -



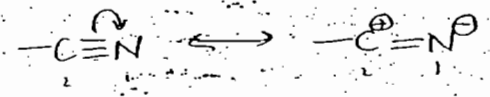
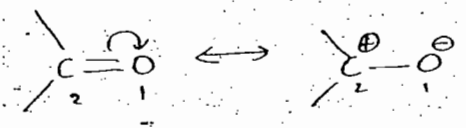
$\pi$ -e are not under direct influence of nucleus

&  $\therefore$  they are not localised. They always have tendency to oscillate b/w two atoms -



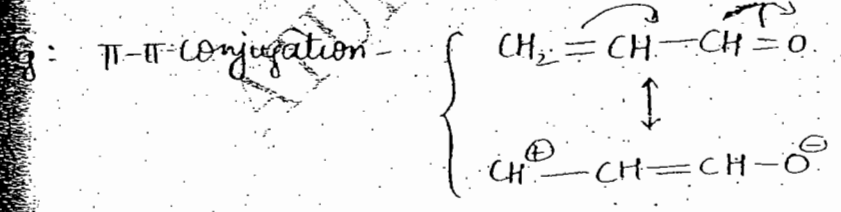
& this delocalisation of  $\pi$ -e<sup>-</sup> is known as MESOMERISM.  
(oscillation)

Eg:

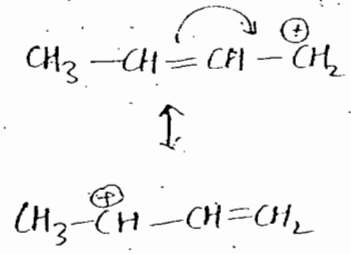


(In above case  $\oplus$  charge is on 4 instead of 2)

Extension of Mesomerism due to adjacent  $\pi$  bond, positive charge, negative charge, lone pair of e<sup>-</sup> or odd e<sup>-</sup> is called as CONJUGATION  $\rightarrow$  (property of  $sp^2$  hybrid)

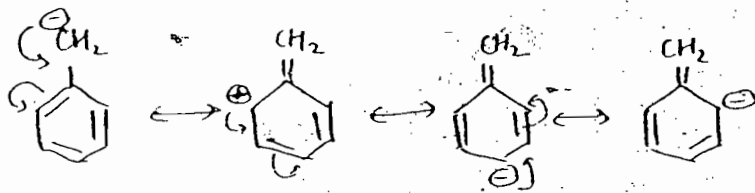


$\pi$   $\oplus$ ve charge conjugation -

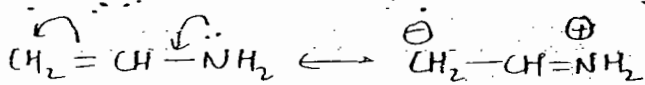




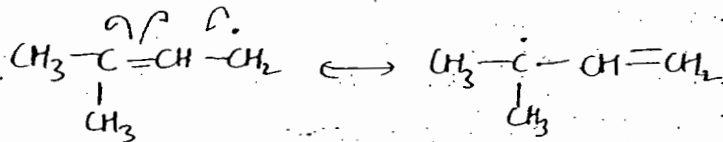
π-negative charge conjugation



π-lone pair -

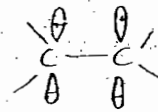


π-odd e<sup>-</sup> -



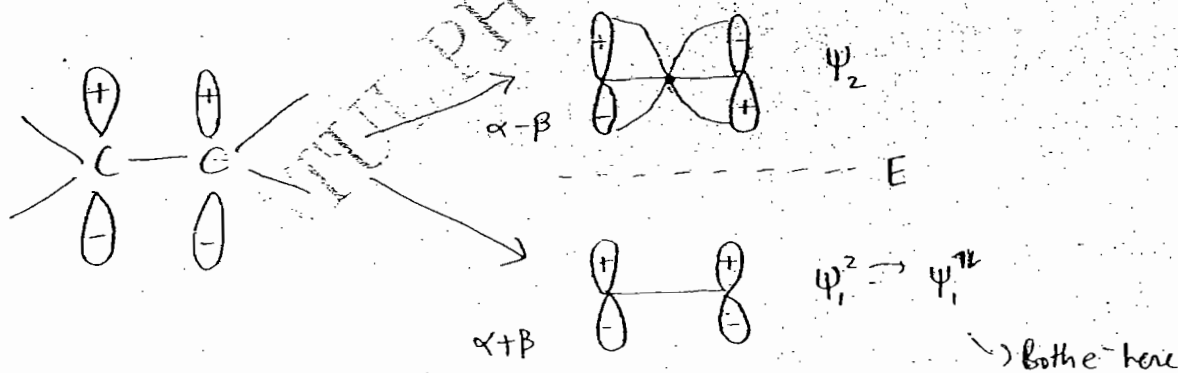
Conjugation can be explained on the basis of MO theory through the formation of π-MO.

(Q) What orbital left in ethene after formation of σ bond? (Two p orbital left)



The MO formed by overlap of atomic orbital

⊥ to internuclear axis is called as π-MO



~~E<sub>linear</sub> = α~~

In the linear system - ACYCLIC CONJUGATION

$$E_j = \alpha + 2\beta \cos\left(\frac{j\pi}{n+1}\right)$$

α = Coulomb parameter

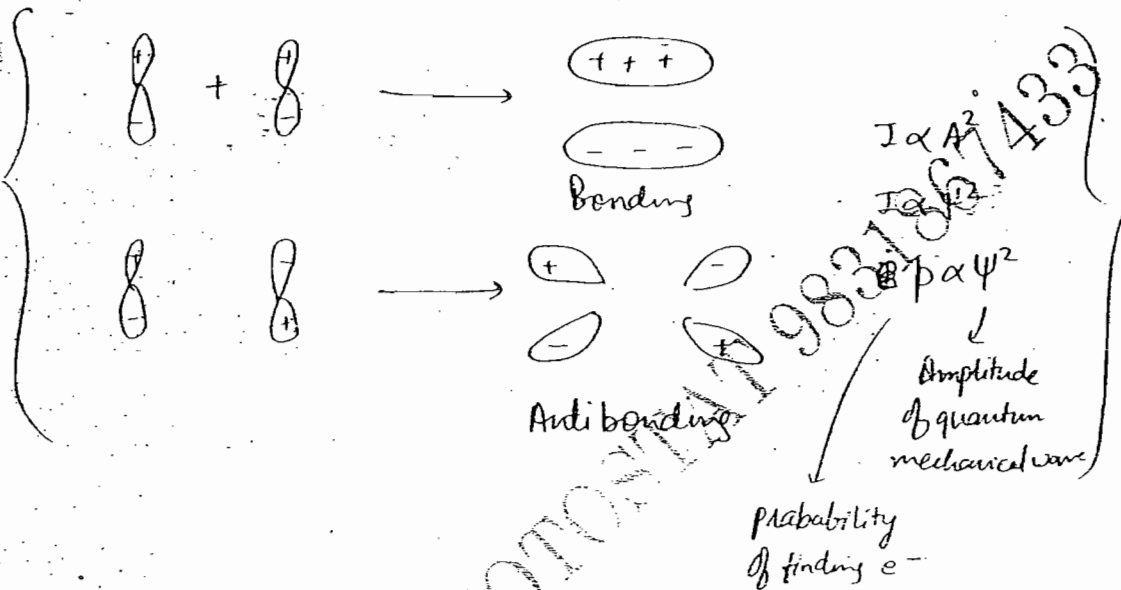
$\alpha$  measures the energy of e present at a particular carbon

$\beta$  = Overlap parameter

' $\beta$ ' measures the energy due to overlap of orbitals

Both  $\alpha$  &  $\beta$  are negative

$j = 1, 2, 3, 4, \dots, n$   
 $\rightarrow$  no. of carbon atoms  
 or no. of p orbitals



Linear system  $\Rightarrow$  C=C (acyclic system & not cyclic system)

for ethene,  $n=2$

$$E_j = \alpha + 2\beta \cos\left(\frac{j\pi}{3}\right)$$

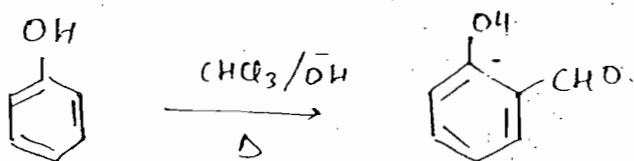
$$j = 1, 2$$

$$E_1 = \alpha + 2\beta \cos\frac{\pi}{3} = \alpha + \beta \rightarrow \text{More negative}$$

$$E_2 = \alpha + 2\beta \cos\frac{2\pi}{3} = \alpha - \beta \rightarrow \text{higher energy}$$

Total energy of  $\pi$  system =  $E_{\text{conjugated}}$

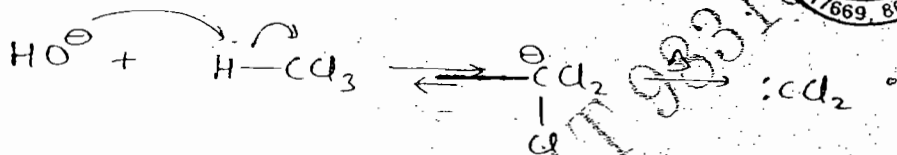
Carbene addition doesn't take place in aromatic DB.



But highly activated benzene ring undergoes electrophilic substitution in a process called as REIMER-TIEMANN REAC<sup>N</sup> (RTR)

Mechanism -

Step 1: Generation of carbene -

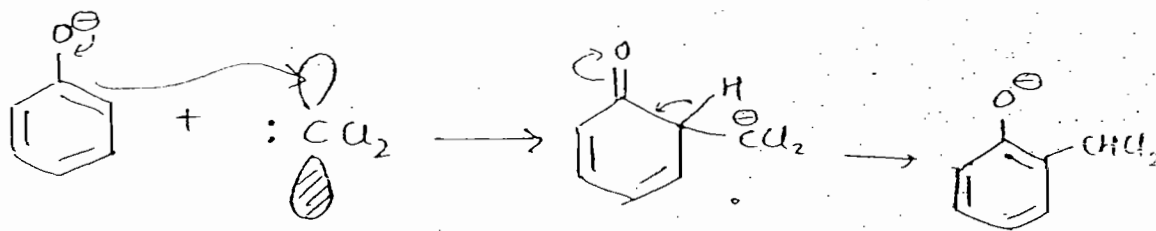


Dichlorocarbene is very poor electrophile but in the basic medium phenol is fully ionised as phenoxide ion, which is highly activated benzene ring.

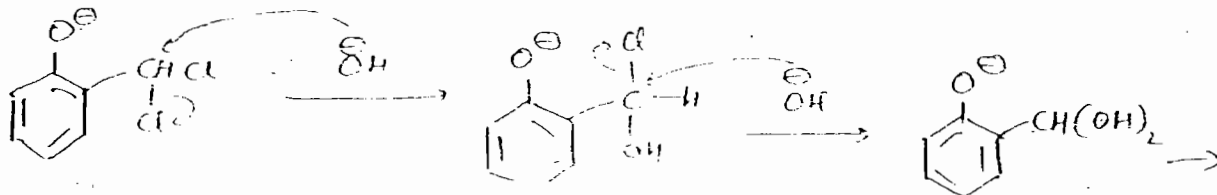


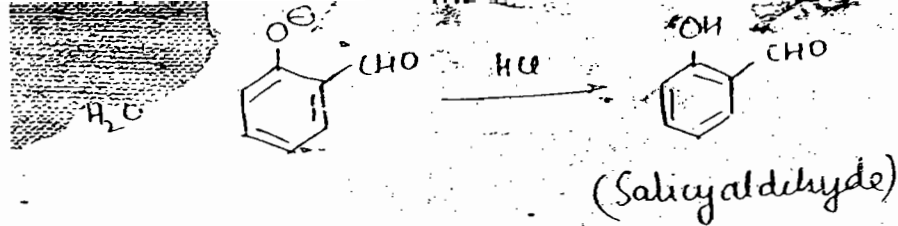
Step 2: Activated  $\text{E}^\ominus$  substitution -

Thermodynamically controlled.



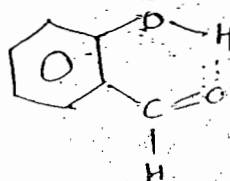
Step 3: Nucleophilic substitution -



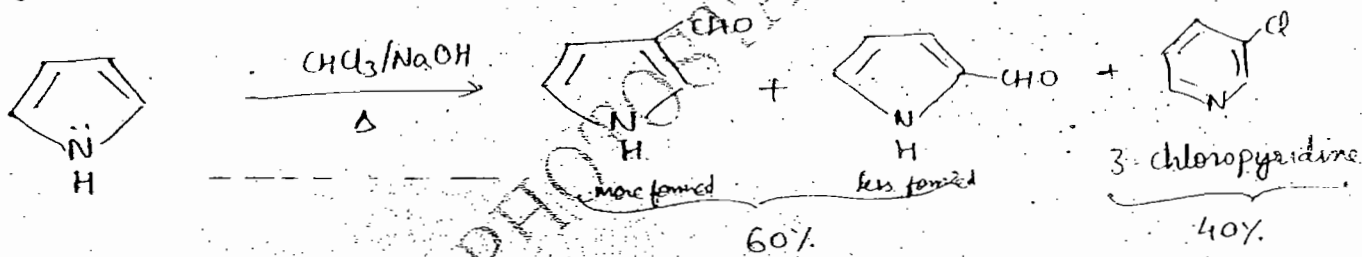


In this case, addition doesn't take place  $\therefore$  otherwise aromaticity will be lost & hence alternative route is chosen  $\Rightarrow E^+$  subs.

It is expected to attack at para position but product is stabilised at ortho position. (not kinetically controlled) weak  $\ominus$  is here

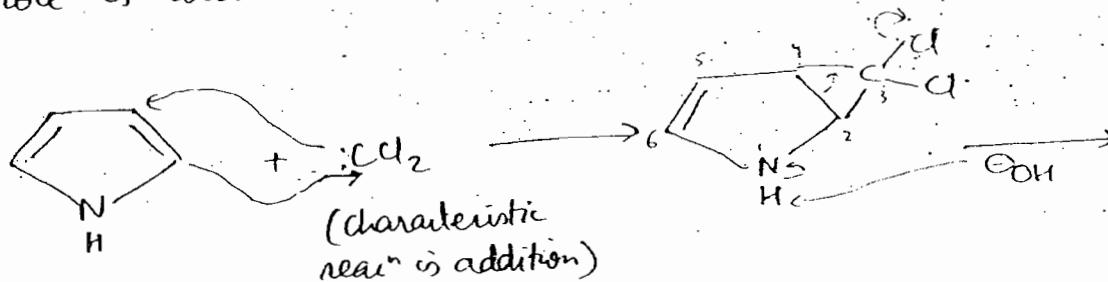


Pyrole also act as activated benzene ring



$\Rightarrow$  How & why 3-chloropyridine is formed?

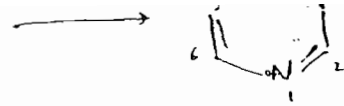
• Pyrole is aromatic but aromaticity is less.



Since aromaticity loss is less  $\therefore$  addition will take place.

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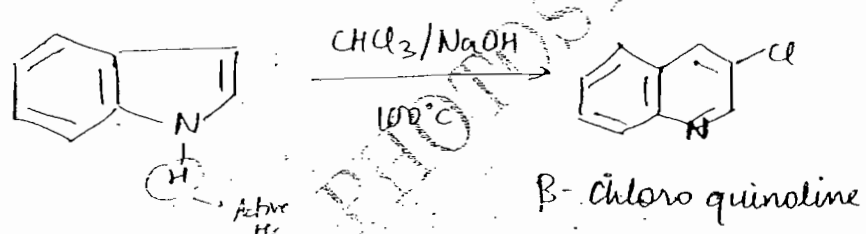
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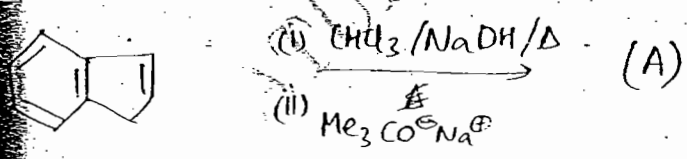
Ring expansion takes place conveniently  
 Sometimes this reac<sup>n</sup> is called as ABNORMAL RTR.  
 ∴ it is completely new reaction.

As temp. increases, proportion of  
 Abnormal RTR increases. Because at high  
 temperature singlet carbene has tendency  
 to change into triplet carbene which  
 is highly reactive with no electrophilic  
 property. That's why,

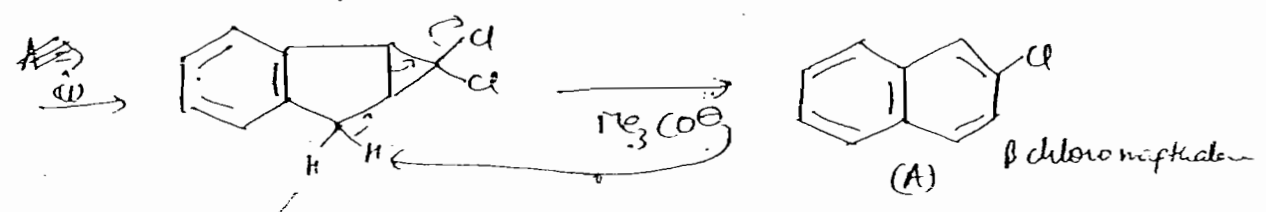
This Abnormal RTR opens another route  
 for the reaction.



{ OH can attack but  
 H is more acidic  
 as attached to N }



What is role of the tertiary butoxide ion  
 in this reaction & what is A?

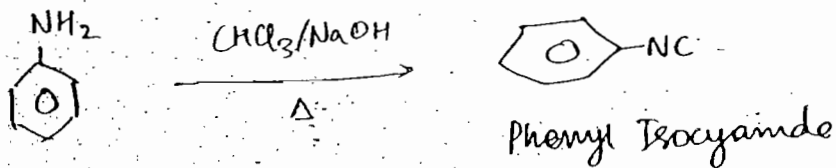


These are not active H. So, tertiary butoxide ion is required

i.e. a more stronger base.

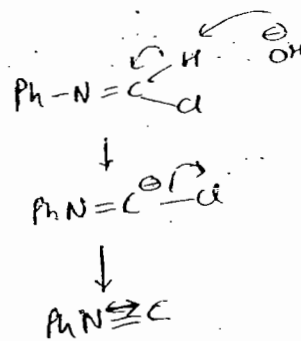
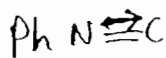
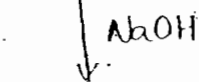
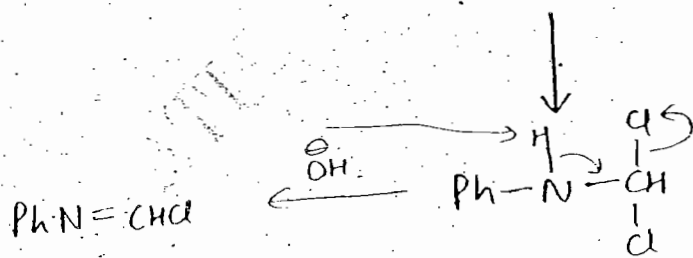
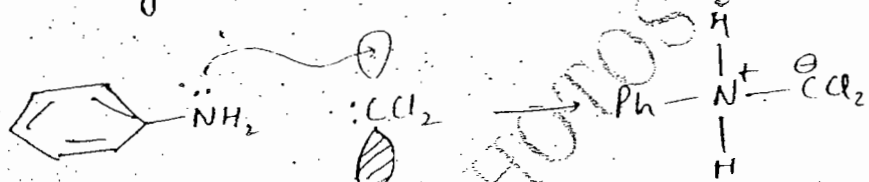
[In not activated benzene ring, addition will take place.]

\* Another activated benzene ring is ANILINE.



### CARBYLAMINE REAC<sup>N</sup>

Even it is activated benzene ring but it doesn't give RTR reaction. Instead



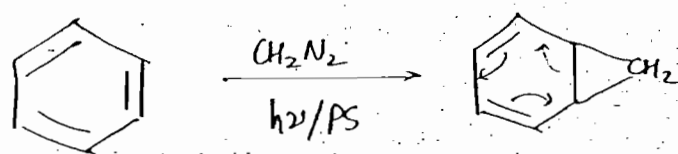
{ offensive repelling smell  $\rightarrow$  confirmatory test of 1<sup>o</sup> Amine }

No  
RTR  
the  
phc  
TRI  
ade

TV  
A

RTR reaction due to one or other reason  
that's why RTR is specific reaction of  
phenyl.

TRIPLET CARBENE always undergo  
addition reaction  $\therefore$  of high reactivity



(most aromatic)

$\downarrow 450^\circ\text{C}$



$\downarrow \text{MnO}_2$



(tropone)



These are imp. addition reaction of carbene.

Another imp. carbene reaction are Rearrangement.