

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° & P_2° 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. 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

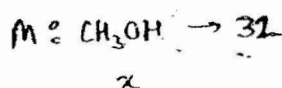
\therefore component 1 & 2 are also present in vapour phase & their vapour phase composition is given by -

$$\frac{1}{P} = \frac{y_1}{P_1^\circ} + \frac{y_2}{P_2^\circ} \quad \begin{cases} P_1^\circ x_1 = P y_1 \\ P_2^\circ x_2 = P y_2 \end{cases}$$

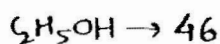
where, y_1 & y_2 are mole fraction in vapour phase

Q- Ethyl alcohol & methyl alcohol form ideal solution if 100 gm of both is mixed together & V.P. of pure methyl alcohol is 88 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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$$n_{\text{EtOH}} = \frac{100}{46} = 2.17$$

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

$$x_{\text{EtOH}} = \frac{2.17}{5.29} = \quad , \quad x_{\text{PrOH}} = \frac{3.12}{5.29} =$$

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

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

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

In vapour phase:

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

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

[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° & P_B° 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.

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

$$P = P_A^\circ x_A + P_B^\circ x_B$$

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

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

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

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

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

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

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

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

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

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

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

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

$$x = 13.69 \text{ gm in } CCl_4$$

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

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 Nearest 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 'w₁' g of solute is left in aqueous phase then weight in aqueous phase = w₁ g.

$$\text{weight in organic phase} = (w - w_1) \text{ g}$$

$$\text{Volume of aqueous phase} = V \text{ ml}$$

$$\text{Volume of organic phase} = v \text{ ml}$$

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

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

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

$$K_D W_1 V = W V - W_1 V$$

$$(K_D V + V) W_1 = W V$$

$$W_1 = \frac{W V}{K_D V + V}$$

$$\text{or } \frac{W_1}{W} = \frac{V}{K_D V + V}$$

where, W_1 = Amount left after extraction

Q- 0.5 g of DDT is present in water. If it is extracted by adding n-hexane (25 ml). Calculate the % DDT extracted from the 100 ml of water if K_D in favour of n-hexane is 12.

$$\text{sol- } 12 = \frac{x/25}{(0.5-x)/100} = \frac{4x}{0.5-x}$$

$$6 - 12x = 4x, 16x = 6, x = \frac{3}{8} \text{ gm}$$

$x = 0.374 \text{ gm}$ in n-hexane

$$\Rightarrow \frac{0.374}{0.5} \times 100 = 74.8\%$$

Q- Suppose experiment is done in 2 parts by adding V_1 & V_2 ml of equal volume of organic solvent & suppose W_2 is amount left after 2nd extraction.

Then, $K_D^* = ?$

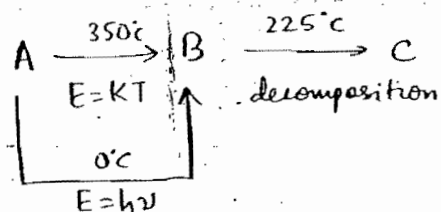
Sol- Amount in water = W_2 gm

Amount in $\text{CCl}_4 = (W_1 - W_2)$ gm

$$\therefore K_D^* = \frac{(W_1 - W_2)/V}{W_2/V} = \frac{W_1 - W_2}{W_2} \times \frac{V}{V}$$

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

• Isolation of cold product -

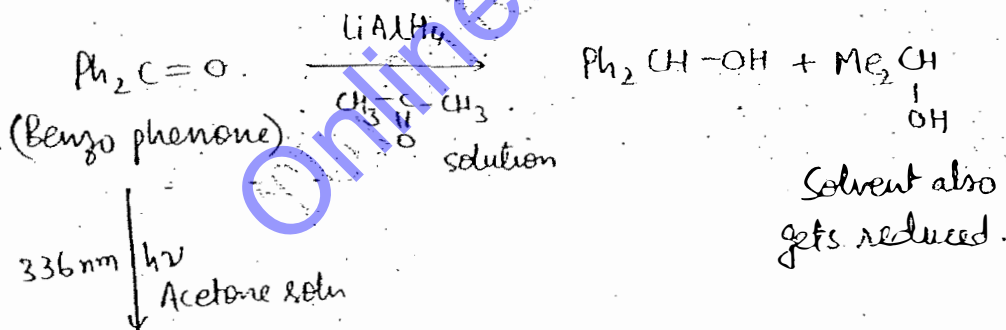


& 'B' cold product can be isolated. Energy is supplied without rise of temperature.

• High degree of selectivity -

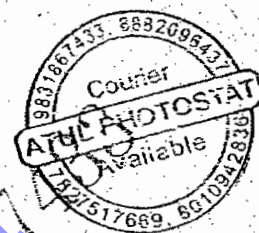
∴ photochemical reaction takes place if & only if electromagnetic radiation is absorbed by molecule.

Take a case -



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

• Photochemical reaction take place in excited

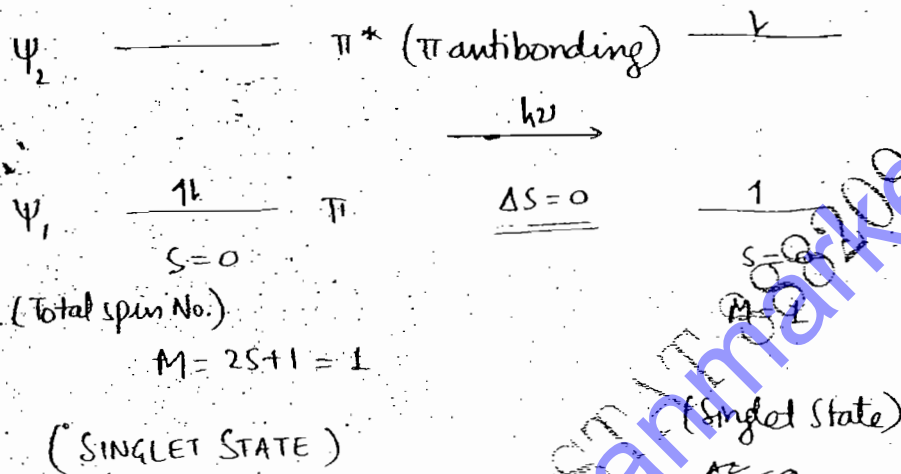
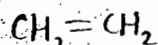


RULE OF EXCITATION :

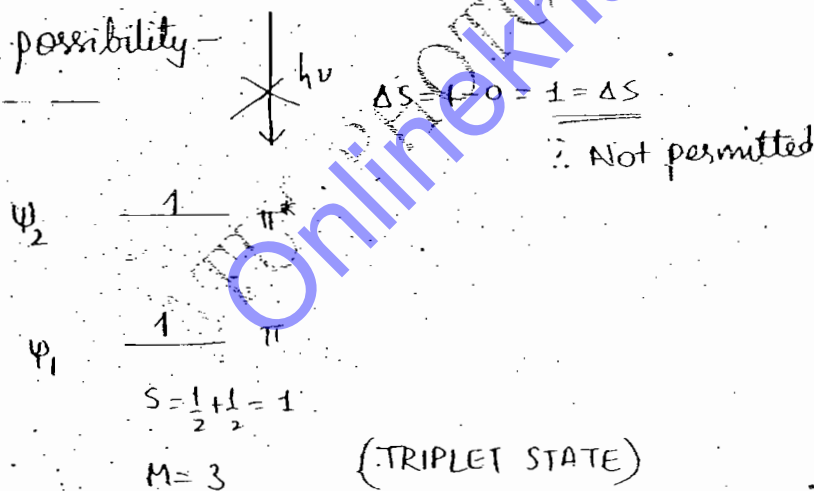
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Excitation follow spin conservation rule that during electronic excitation there is no change in spin state of electron.

$$\Delta S = 0$$



Another possibility —



- * Singlet \rightarrow Singlet ✓ (allowed)
- Triplet \rightarrow Triplet ✓
- Singlet \rightarrow Triplet ✗ (forbidden)
- Triplet \rightarrow Singlet ✗

Ground state of most molecule is singlet.

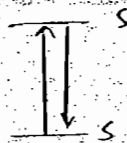
[Triplet state is more stable than singlet state]

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

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

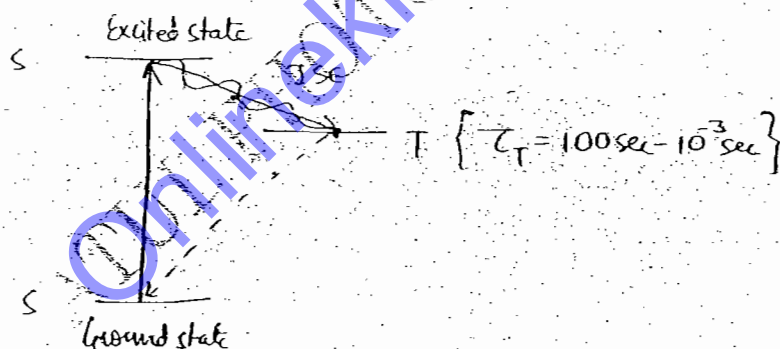
Relaxation time of singlet state is very less ($10^{-6} - 10^{-8}$ sec)

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.

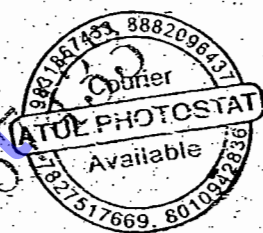
INTER SYSTEM CROSSING :



Write a short note on Inter system crossing (ISC)

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

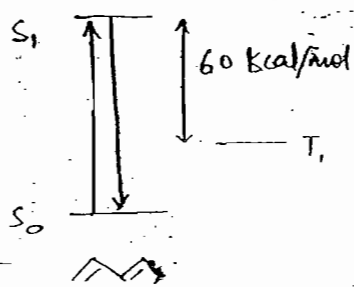
Since triplet state is more stable & also triplet to singlet relaxation is forbidden ∴ triplet state is associated with high relaxation time.



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

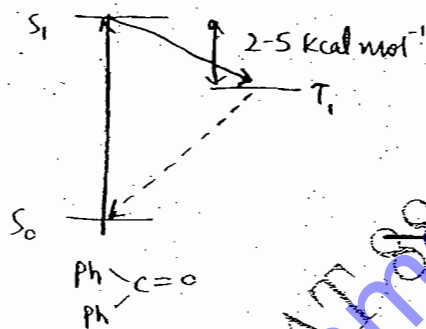
The tendency of a molecule to undergo intersystem crossing is called as Inter system crossing efficiency.

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



0%

(in conjugated alkene)

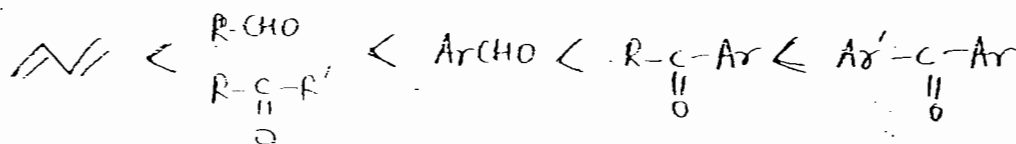


100%

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

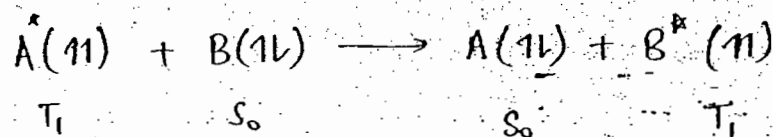
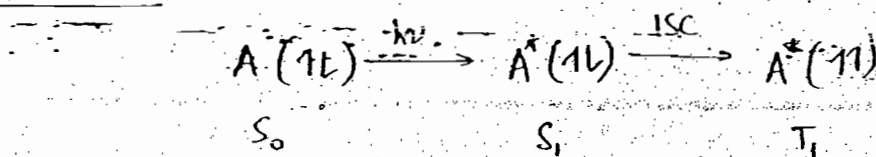
What is photosensitization. Give its mechanism. Why photosensitizer always generate triplet state.

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

must have higher ISC efficiency. That means they are highly conjugated carbonyl compound.

Eg: Benzophenone is a photosensitizer.

Mechanism -



(Always triplet)

∴ Photosensitizer always generate triplet state (as per spin selection rule). That's why, sometimes there is change in number & nature of product in the presence of photosensitizer.



Products?

(Large no. of products obtained)

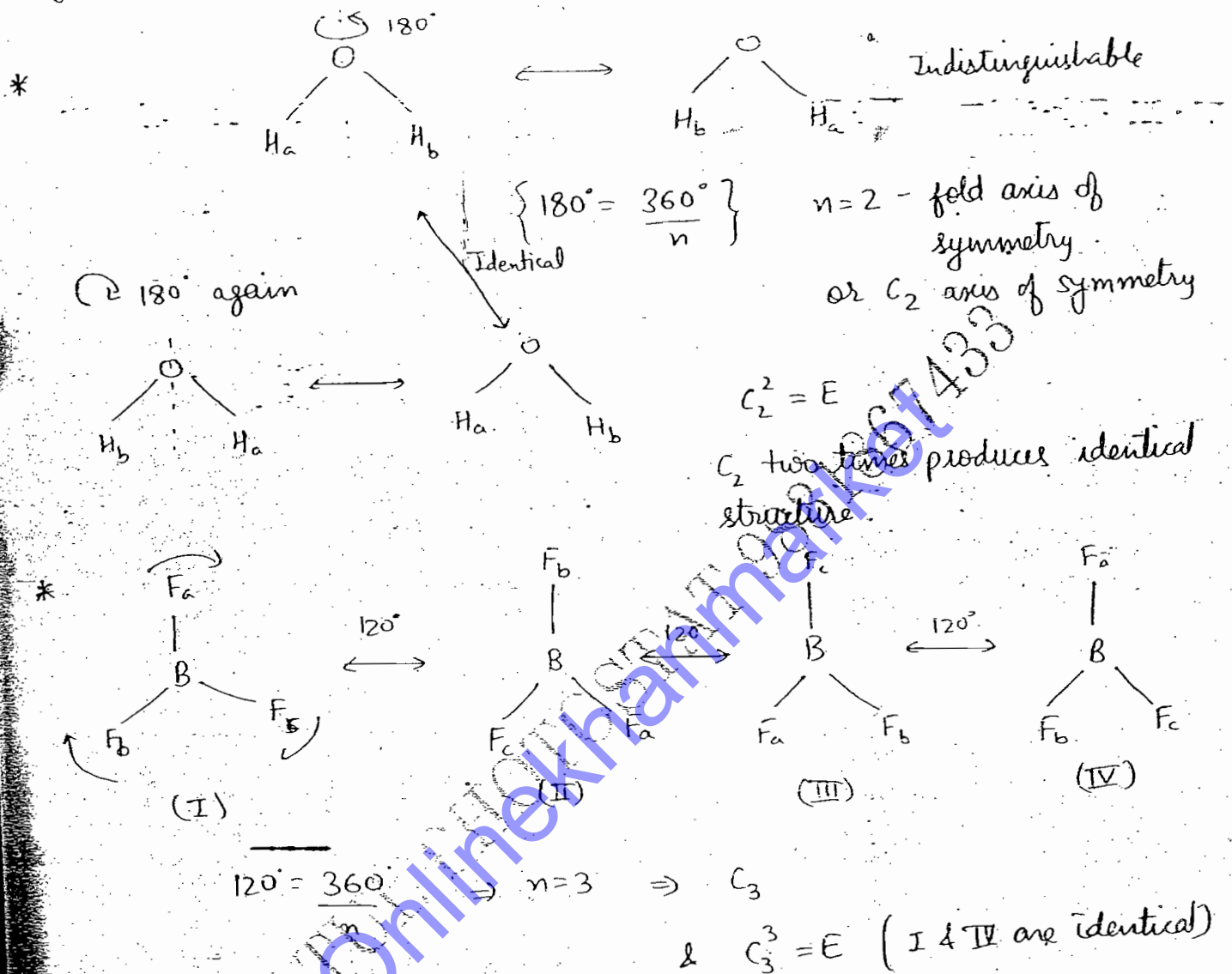
In absence of $Ph_2C=O$, only intramolecular product obtained. Only singlet state is possible. τ is very less $10^{-6} - 10^{-8}$ sec.

But photosensitizer presence provides longer reaction time ∴ large no. of products are formed.

AXIS OF SYMMETRY:

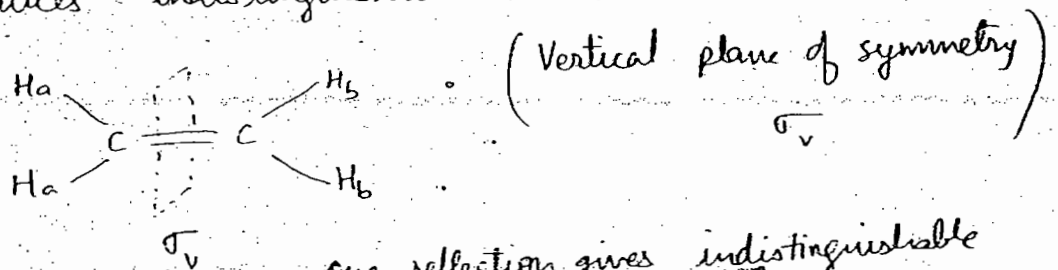
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It is imaginary or real axis through which a rotation of $360^\circ/n$ degree produces indistinguishable structure.



PLANE OF SYMMETRY:

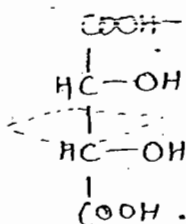
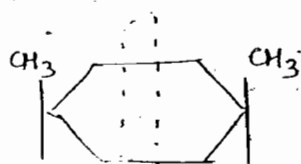
It is imaginary or real plane through which reflection of molecule produces indistinguishable structure.



σ_h \rightarrow horizontal axis plane of symmetry

Two plane of symmetry gives identical structure

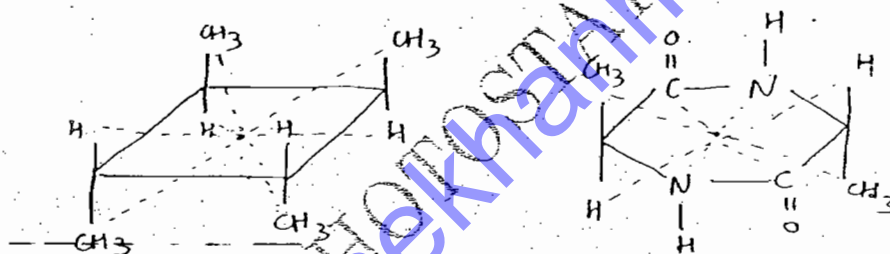
$$\sigma_v^2 = \sigma_h^2 = E$$



CENTRE OF SYMMETRY:

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

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

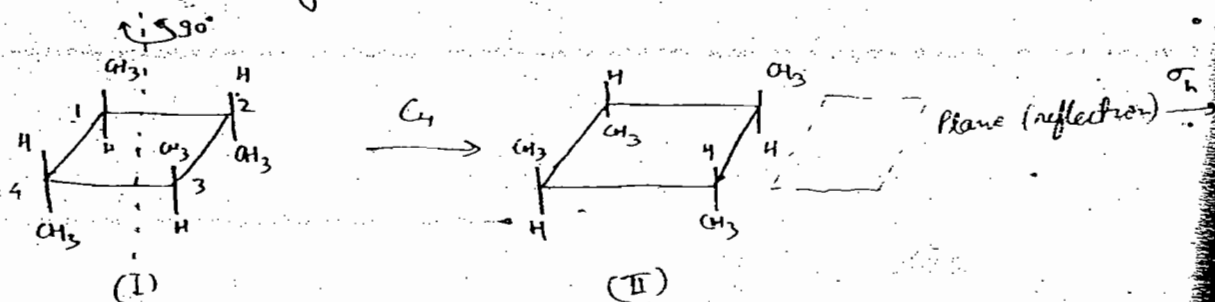


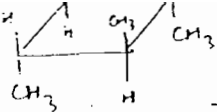
Above all are regarded as PROPER SYMMETRY ELEMENTS.

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 called as alternating axis of symmetry.





(III)

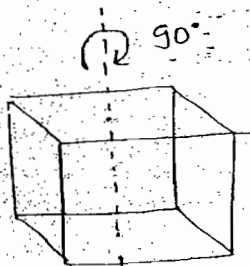
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(Super Impossible includes both Identical as well as Interchangeable)

ELEMENTS OF A SYMMETRY OF A CUBE

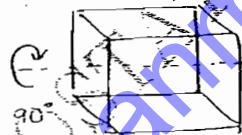
A cube with 23 elements of symmetry is highly symmetrical. It contains all the elements of symmetry.

(1) AXIS OF SYMMETRY -



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

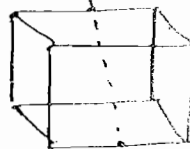
There are 3 such axes.



(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° through an axis passing through the opposite diagonal corners. There are 4 such axis. It is known as Triad axis of symmetry.

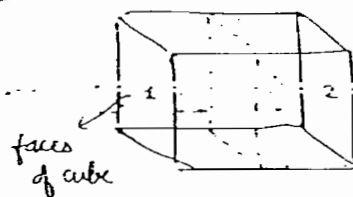
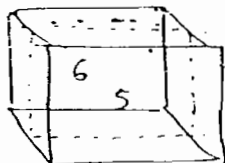
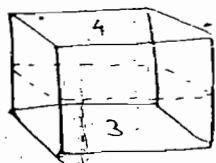


4 Triad possible

PLANE OF SYMMETRY - (POS)

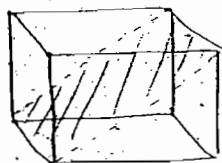
A cube also contains plane of symmetry - (i) Rectangular POS

1a) Rectangular Plane of Symmetry -



So, there are 3 rectangular plane of symmetry.

4b) 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.

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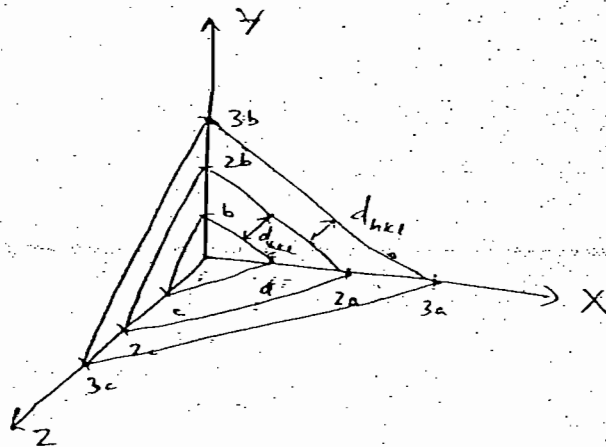
CRYSTAL	Length	Angle	Min. Symm.	Bravais Lattice
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	$4C_3 + 3C_4 + 6C_2$	P, F, I
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	$4C_2$	P, I, F, C
Tetragonal	$a = b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$ $\alpha = \beta = \gamma = 90^\circ$	$1C_4$	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	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ; \beta \neq 90^\circ$	$1C_3$	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 :



the multiple of some minimum unit vector a, b, c in coordinate direction such that intercept by unit vector ratio is known as Weiss Indices $= \frac{h'}{a}$

Intercept	Weiss Indices
(a, b, c)	$(1, 1, 1)$
$(2a, 2b, 2c)$	$(2, 2, 2)$
$(3a, 3b, 3c)$	$(3, 3, 3)$
$(\infty a, 2b, 2c)$	$(\infty, 2, 2)$

→ major drawback of Weiss

Indices is that it gives ∞ value to a plane parallel about any axis. That's why, another quantity is defined known as

MILLER INDICES → Reciprocal of Weiss indices multiplied by minimum quantity to make clear fraction of number.

Intercept	Weiss I.	$1/WI$	MI
$(3a, 2b, c)$	$(3, 2, 1)$	$(\frac{1}{3}, \frac{1}{2}, 1)$	$(2, 3, 6)$
$(4a, 3b, 2c)$	$(4, 3, 2)$	$(\frac{1}{4}, \frac{1}{3}, \frac{1}{2})$	$(3, 4, 6)$
$(2a, 2b, 2c)$	$(2, 2, 2)$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(1, 1, 1)$
$(3a, 2b, \infty c)$	$(3, 2, \infty)$	$(\frac{1}{3}, \frac{1}{2}, 0)$	$(2, 3, 0)$
$(2a, b, 5c)$	$(2, 1, 5)$	$(\frac{1}{2}, 1, \frac{1}{5})$	$(5, 10, 2)$

↪ Represent -ve by bar

Q- What are Miller Indices. Give characteristics of MI.

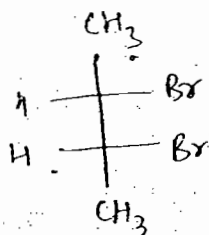
Ans Miller Indices are reciprocal of Weiss Indices multiplied by lowest no. to make clear fraction.

Properties -

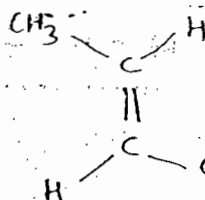
- (1) Miller Indices represents a set of parallel planes.
- (2) Higher the intercept, lower will be miller indices.
- (3) A bar over miller indices represents intercept in opposite direction.
- (4) A zero miller indices represent plane parallel to that axis i.e. $(0, k, l)$ is parallel to x-axis.

Q- What will be product with stereochemistry?

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Sol-



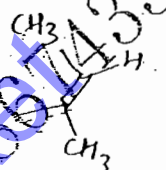
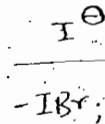
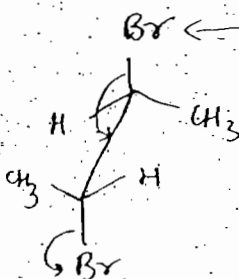
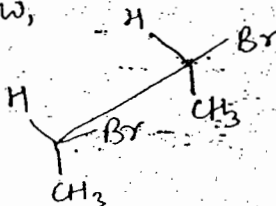
ATUL PHOTOSTAT

57/16 & 56/5, Old Rajendra Nagar,
Sada Bazar Road, New Delhi-60

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Now,

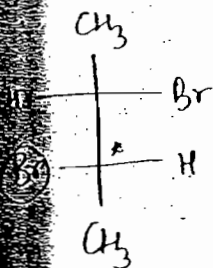


(trans alkene)

(Meso 2,3-dibromo butane)

Meso 2,3-

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

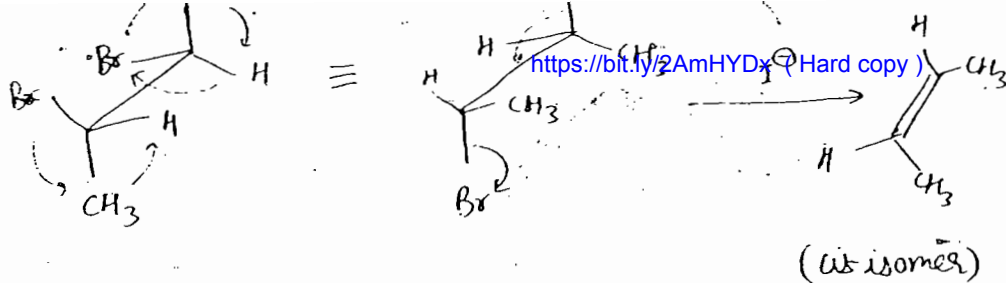


(l)

Thereo

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

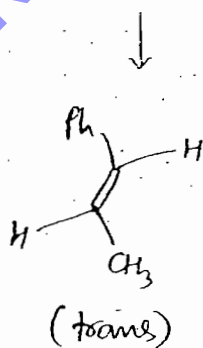
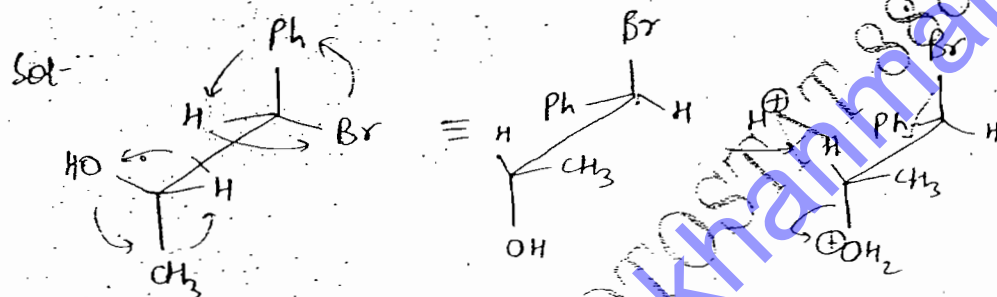
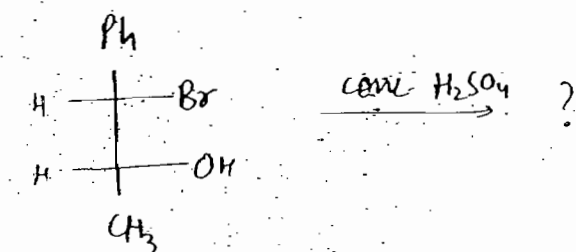
{ Erythreo = 2,3 dibromobutane
→ Br, Br same side in fisher }



Threo will give cis-isomer.

(T \Rightarrow trans)

Q. Discuss product with stereochemistry?

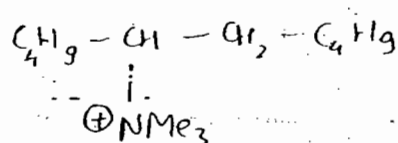


(self bleaching property of Br)

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

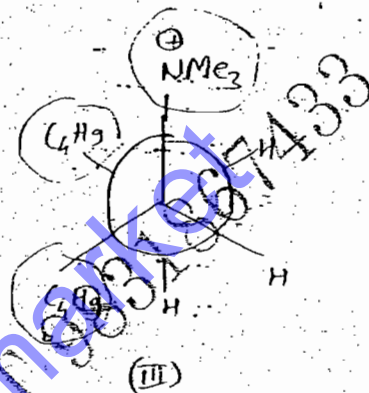
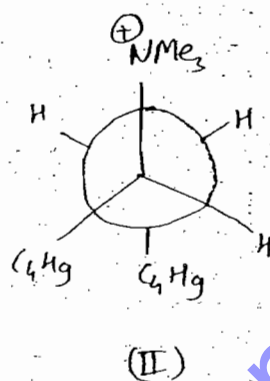
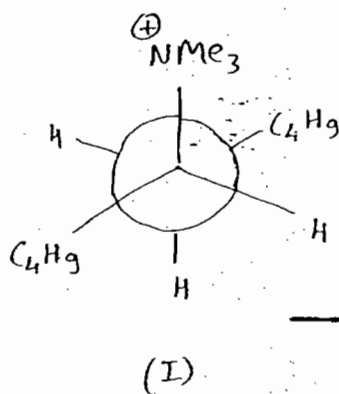
Sometimes due to conformational instability, E_2 elimination takes place in syn manner.

SYN-MANNER (E_2 elimination)



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 NMe_3^+ in (II). Therefore (I) will react undergo anti elimination & (II) will undergo syn elimination.

(I)
35% anti

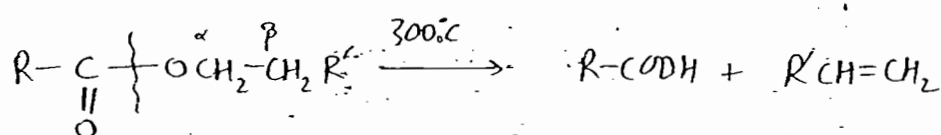
(II)
65% syn

(III)
No elimination

Stability check \rightarrow Newmann projection
Reaction \rightarrow Saw horse projection

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 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:



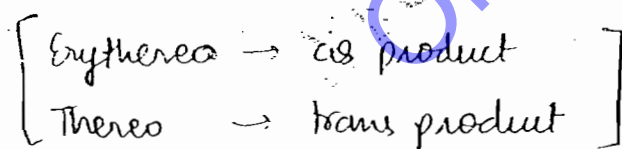
acidic
part

alcoholic
part

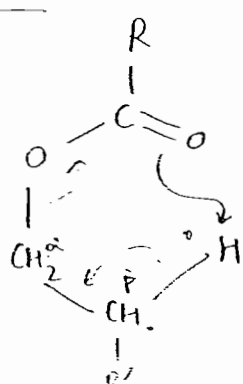
Whenever carboxy-ester having atleast one β hydrogen on alcoholic part is heated at about 300°C , it undergo elimination to give alkene as product.

A unimolecular kinetics is observed & elimination is highly stereospecific.

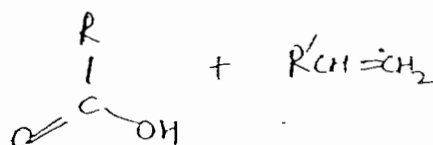
Stereochemistry is syn elimination.

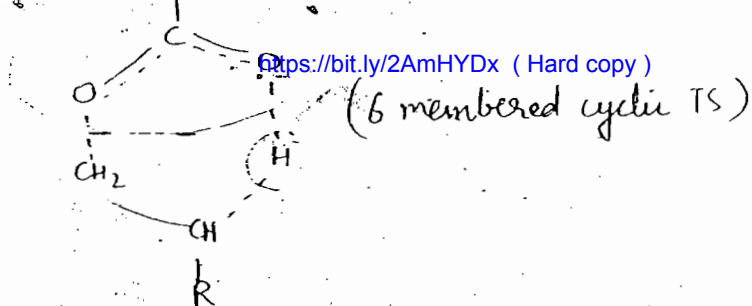


Mechanism -



A pericyclic mechanism is observed through the 6 member transition state





(In fact π e⁻ act as internal-base) & that's why.

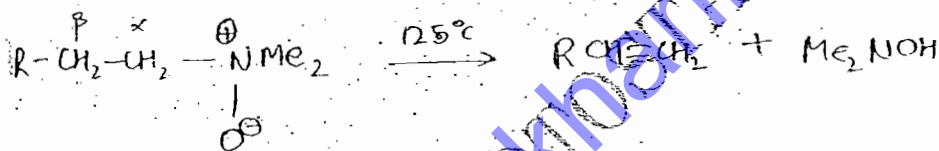
Eliminating group act as internal base. ($R-COO^-$)

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

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

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

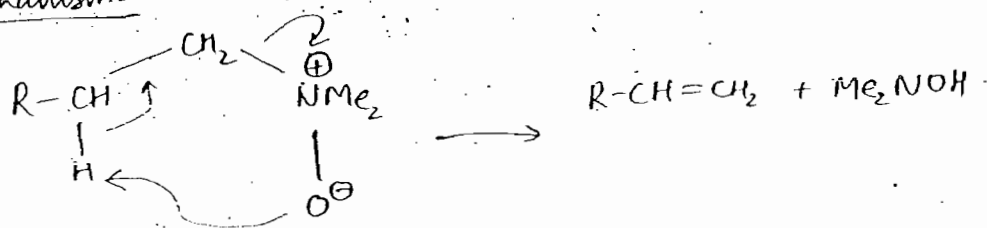
COPE - ELIMINATION :



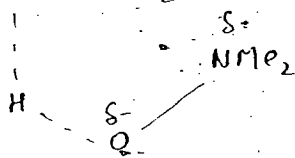
(N-amine oxide)

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

Mechanism-



Reaction takes place through 5 membered cyclic TS.



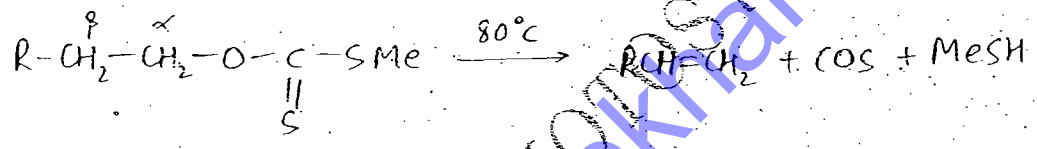
Temp. is low because internal base is very strong
 5 member cyclic TS is stabilised by ionic interaction also.

[If group attached to "N" is other than methyl then
 → Hoffman elimination or other reaction will take place]

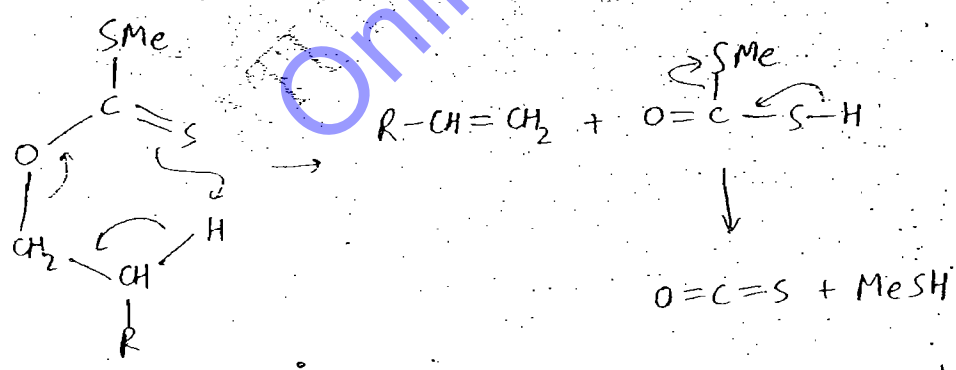
Another example in this series is-

CHAUGAV REACTION:

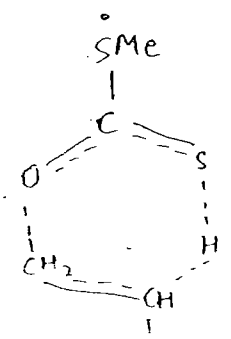
Xanthate ester undergo pyrolysis at 80°C to give alkene. Xanthate ester at least having one β hydrogen give alkene in stereospecifically syn manner.



Mechanism-



TS:



AROMATICITY

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

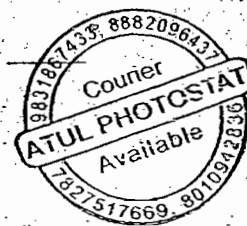
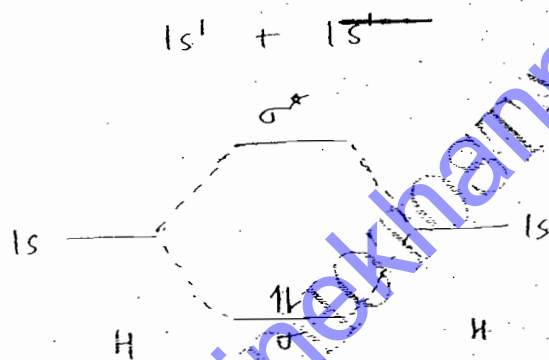
This overlap can be in the phase overlap i.e.

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

Anti Bonding MO (ABMO).

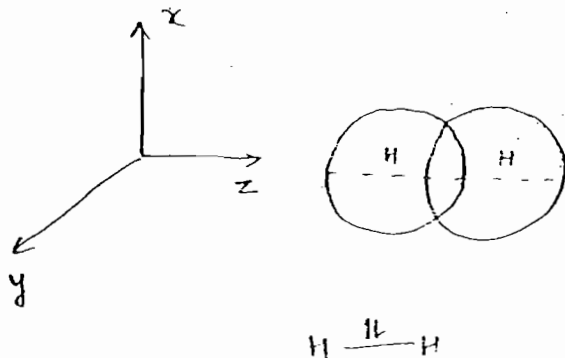
If 'N' atomic orbital combine together, it produces N MO out of which $N/2$ are bonding & rest $N/2$ anti bonding.

Consider the formation of H_2 molecule -



This type of MO is called as σ -MO.

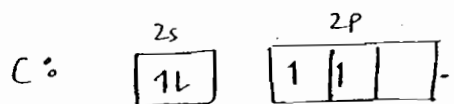
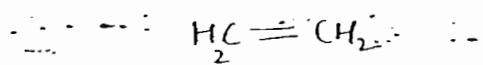
σ -MO is formed due to overlap of atomic orbitals along the internuclear axis.



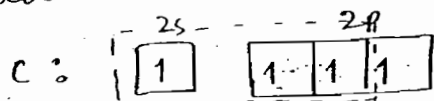
∴ σ-e is under the influence of two nucleus.
And they are localised - (can't be displaced)

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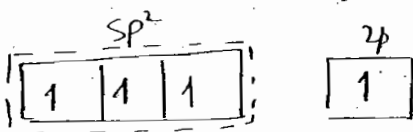
Consider the case of ethane molecule. In which each 'C' is sp^2 hybridised



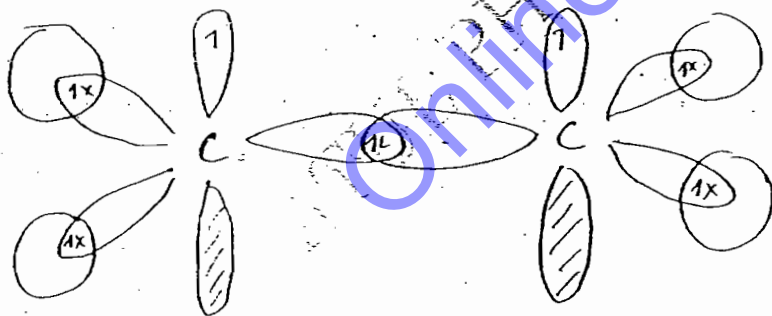
In excited state -



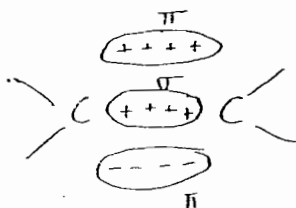
& Hybridisation takes place to give 'p' orbital & sp^2 orbital.



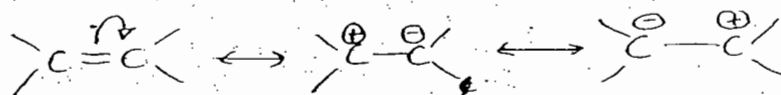
Each sp^2 orbital forms σ bond. And we are left with 2 p-orbital ⊥ to each other



Unpaired e^- form bond -

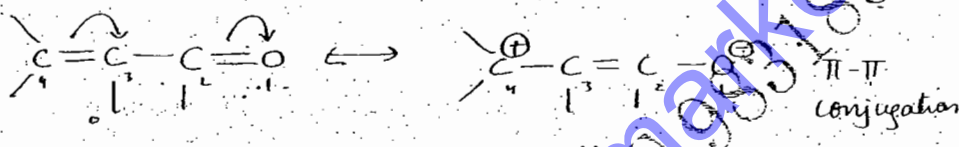
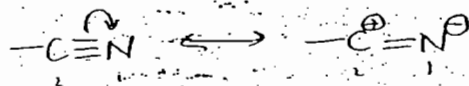
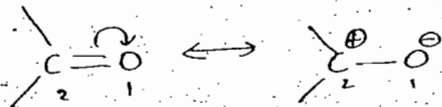


π -e are not under direct influence of nucleus
 & \therefore they are not localised. They always have
 tendency to oscillate b/w two atoms -



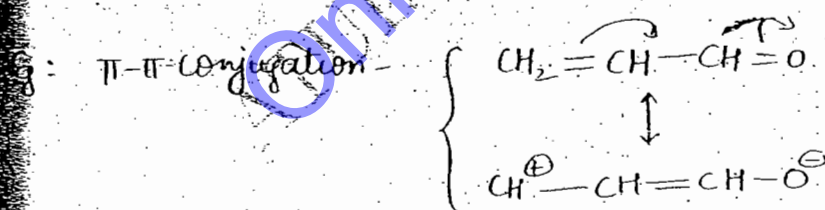
& this delocalisation of π -e⁻ is known as MESOMERISM.
 (oscillation)

Eg:

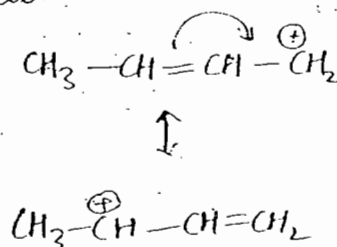


(In above case \oplus charge is on 4 instead of 2)

Extension of Mesomerism due to adjacent π bond,
 positive charge, negative charge, lone pair of e⁻ or
 odd e⁻ is called as CONJUGATION (property of sp^2 hybrid)

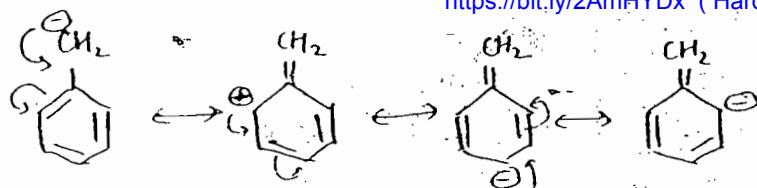


π \oplus ve charge conjugation -

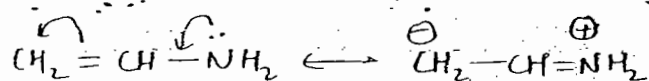


H - Negative charge conjugation

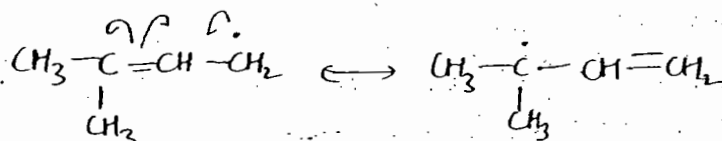
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π - lone pair -

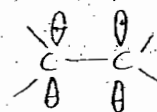


π - odd e^- -



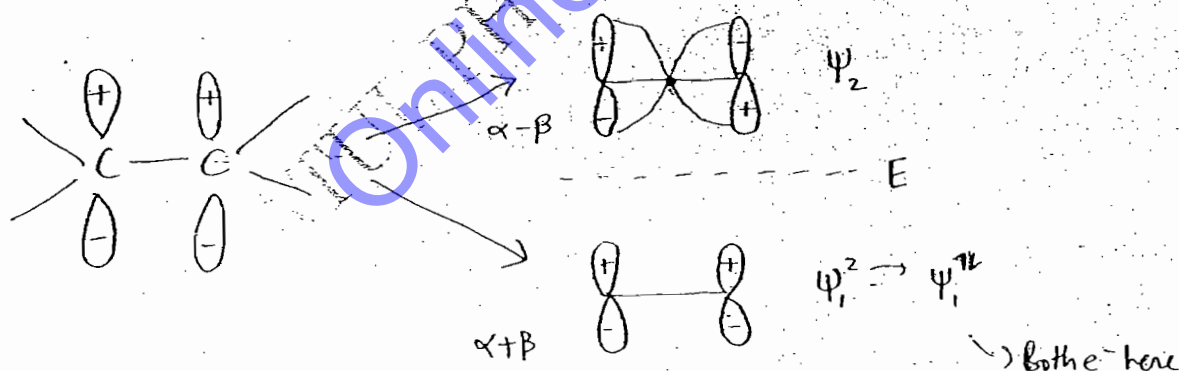
Conjugation can be explained on the basis of MO theory through the formation of π -MO.

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



The MO formed by overlap of atomic orbital

\perp to internuclear axis is called as π -MO



~~E_{linear} = α~~

In the linear system - ACYCLIC CONJUGATION

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

α = Coulomb parameter

α measures the energy of e present at a particular carbon

<https://bit.ly/2AmHYDx> (Hard copy)

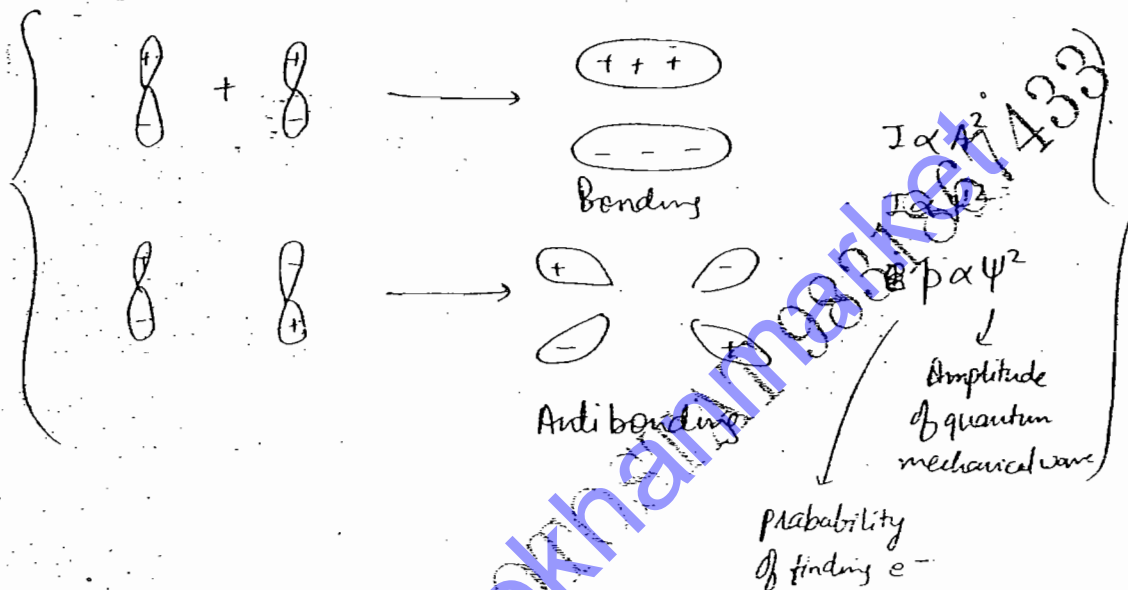
β = Overlap parameter

' β ' measures the energy due to overlap of orbitals

Both α & β are negative

$$j = 1, 2, 3, 4, \dots, n$$

→ 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 π system = $E_{\text{conjugated}}$

Total energy of conjugated system = <https://bit.ly/2AmHYDx> (Hard copy)

= total no. of e^- \times energy of MO

$$E_{conj} = 2(\alpha + \beta) + 0(\alpha - \beta)$$

$$= 2\alpha + 2\beta$$

$E_{unconjugated}$ is always = No. of $e^- \times (\alpha + \beta)$

$$E_{uc} = 2(\alpha + \beta)$$

$$= 2\alpha + 2\beta$$

Defining a quantity = Resonance Stabilisation Energy

$$RSE = E_{conj} - E_{uc}$$

$$RSE = 0$$

\therefore Ethene molecule doesn't show any resonance.

Only electronic effect.

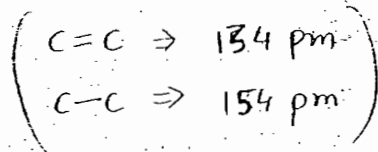
Only Br_2 polarises ethene.

\rightarrow Consider another molecule \rightarrow 1,3-Butadiene.

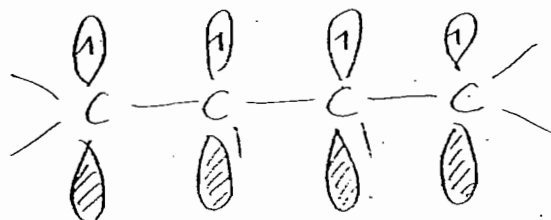


\rightarrow less double bond character

\rightarrow Bond order > 1



(possible when delocalisation happens)



$$\psi_4^0 \quad \alpha - 1.614\beta$$

$$\psi_3^0 \quad \alpha - 0.812\beta$$

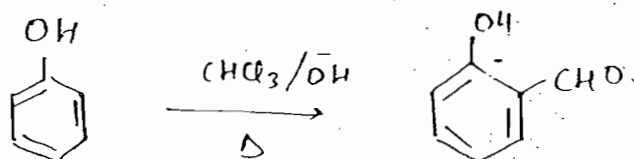
$$\psi_2^0 \quad \alpha + 0.812\beta$$

$$\psi_1^0 \quad \alpha + 1.614\beta$$

4 MO \rightarrow 2 bonding \rightarrow 2 antibonding

2 bonding MOs

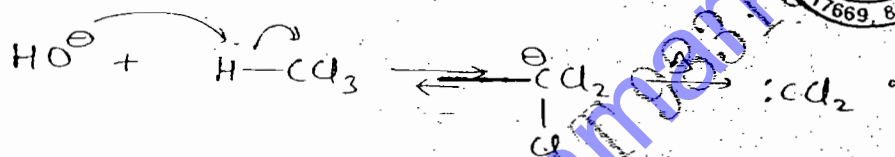
carbene addition doesn't take place in aromatic DB.



But highly activated benzene ring undergo electrophilic substitution in a process called as REIMER-TIEMANN REAC^N (RTR)

Mechanism -

Step 1: Generation of carbene -

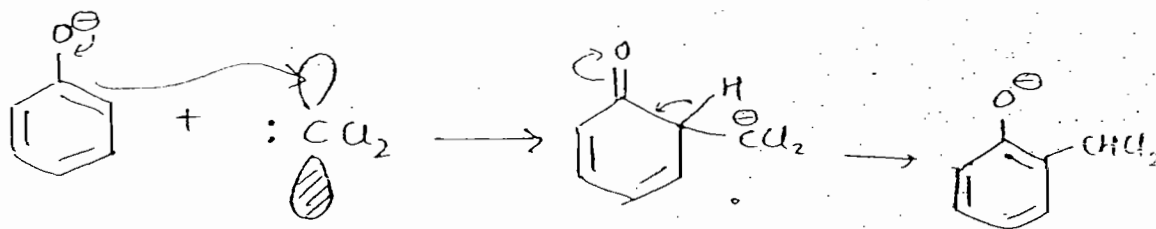


Dichlorocarbene is very poor electrophile but in the basic medium phenol is fully ionised as phenoxide ion, which is highly activated benzene ring.

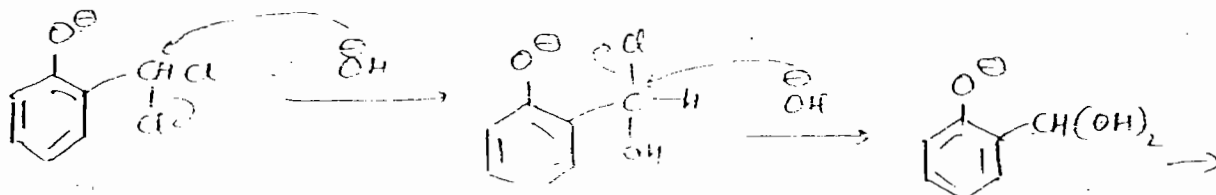


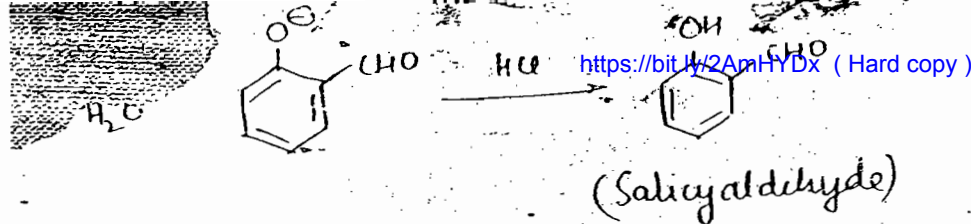
Step 2: Activated E^\ominus substitution -

Thermodynamically controlled.



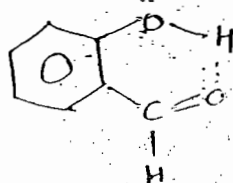
Step 3: Nucleophilic substitution -



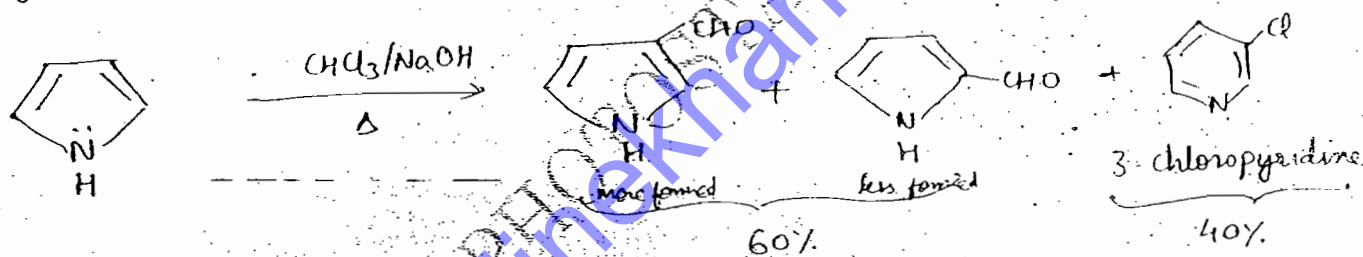


In this case, addition doesn't take place
 otherwise aromaticity will be lost & hence
 alternative route is chosen $\Rightarrow E^+$ rules.

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

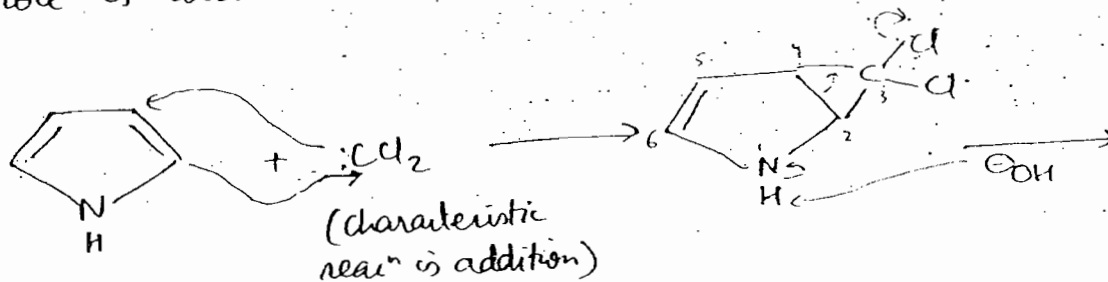


Pyrole also act as activated benzene ring



\Rightarrow How & why 3-chloropyridine is formed?

Pyrole is aromatic but aromaticity is less.



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

Riv
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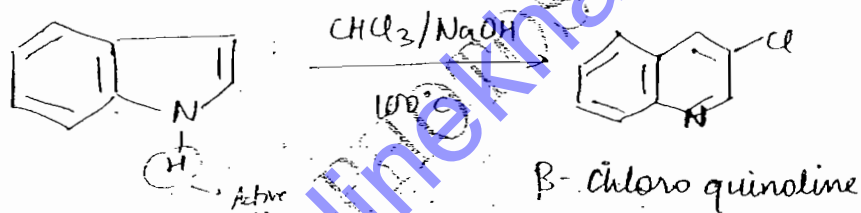
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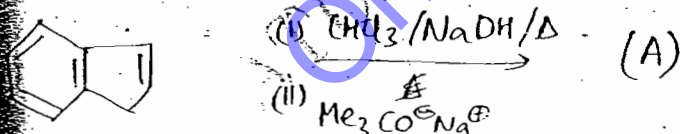
Ring expansion takes place conveniently
Sometimes this reacⁿ is called as ABNORMAL RTR.
∴ it is completely new reaction.

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,

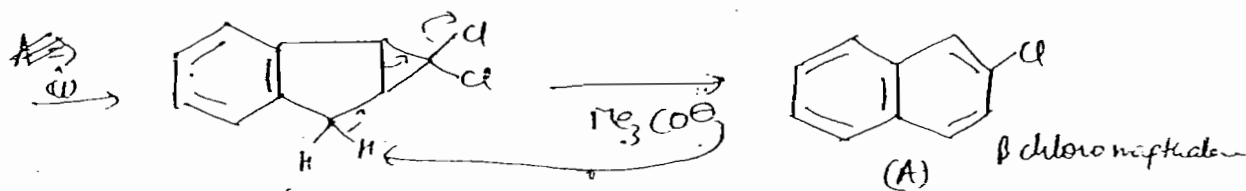
This Abnormal RTR opens another route
for the reaction.



{ 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?



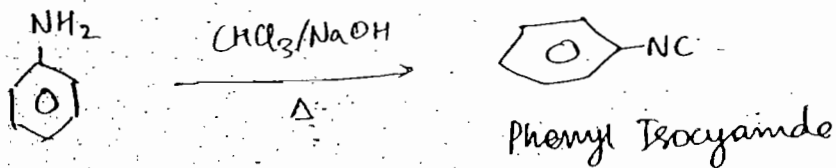
These are not active H. So, tertiary butoxide ion is required

i.e. a more stronger base.

<https://bit.ly/2AmHYDx> (Hard copy)

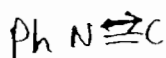
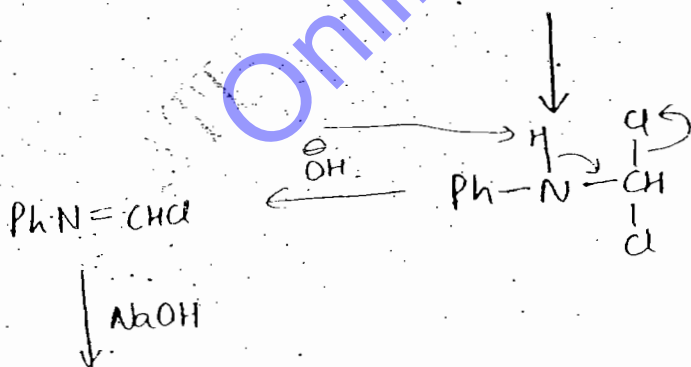
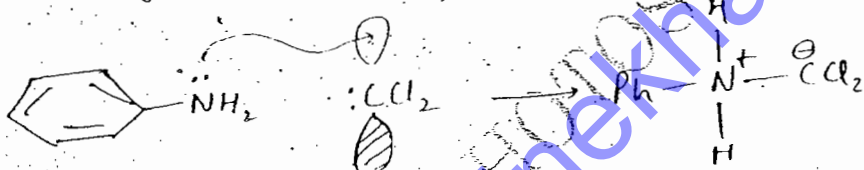
[In not activated benzene ring, addition] -
will take place.

* Another activated benzene ring is ANILINE.

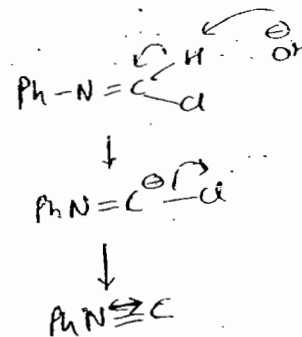


CARBYLAMINE REAC^N

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



{ offensive repelling
 smell → confirmatory
 test of 1° Amine }



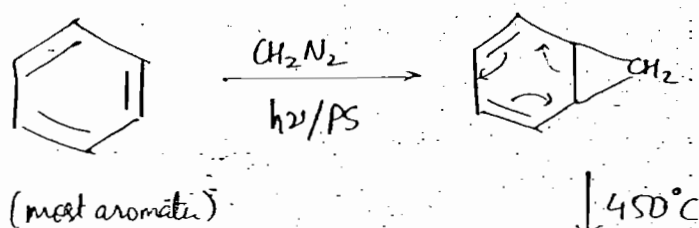
No
RTI
the
phc
TRI
ade

TV

A

RTR reaction due to <https://bit.ly/2AmHYDx> (Hard copy)
That's why RTR is specific reaction of phenyl.

TRIPLET CARBENE always undergo addition reaction \therefore of high reactivity



$\downarrow 450^\circ C$



$\downarrow MnO_2$



(Tropone)



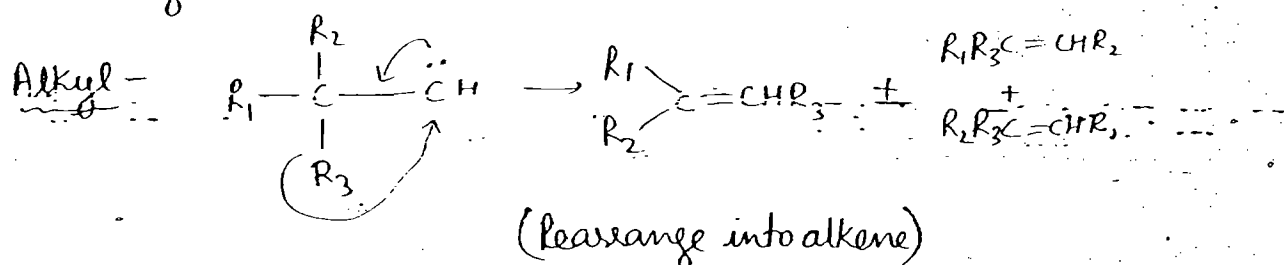
These are imp. addition reaction of carbene.

Another imp. carbene reaction are Rearrangement.

2/ REARRANGEMENT:

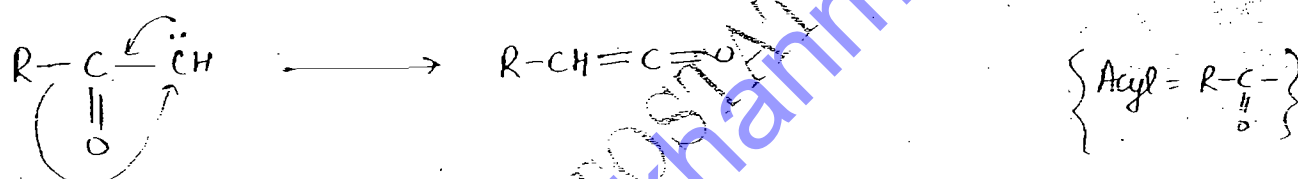
<https://bit.ly/2AmHYDx> (Hard copy)

Both alkyl & acyl carbene undergo rearrangement:



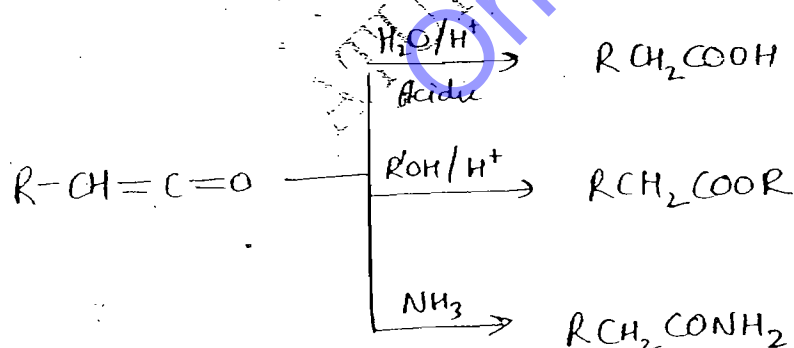
{ Very fast rearrangement }
 & Any alkyl group can migrate
 \therefore Not important.

Acyl Carbene - Relatively more stable & undergoes



rearrangement to give Ketene & is called

as WOLFF REARRANGEMENT.



\therefore Very important reaction, but why?

