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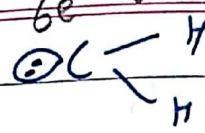
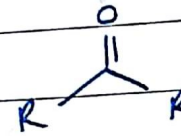
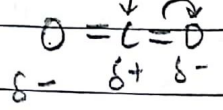
- **Neutral** : BF_3 / $AlCl_3$ / $FeBr_3$ / 

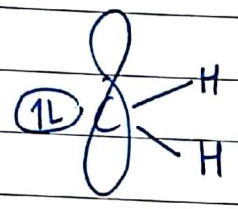
CO_2 / SO_3 /  / PCl_5 / $SbCl_5$



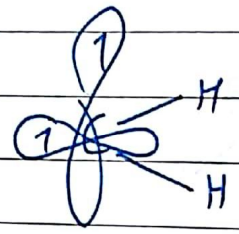
Lewis acid → adduct.

* **Carbenes** :
are of two types,

(multiplicity) M = 2S+1

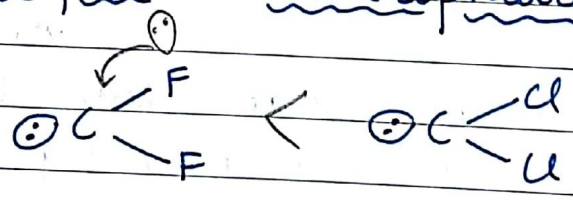


Singlet



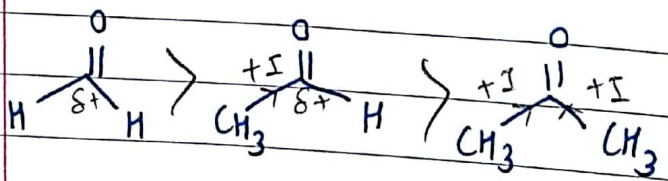
Triplet

Q. **Compare Electrophilicity** :

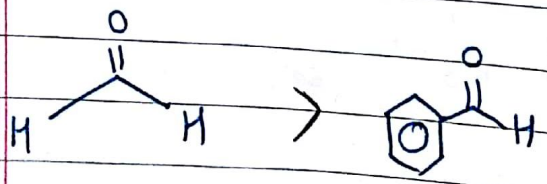
* 1. 

(Backbonding 2p–2p better than 2p–3p)

* 2. $BF_3 < BCl_3 < BBr_3 < BI_3$

3. 

{Check δ+ on 'C' containing 'O'}

4. 

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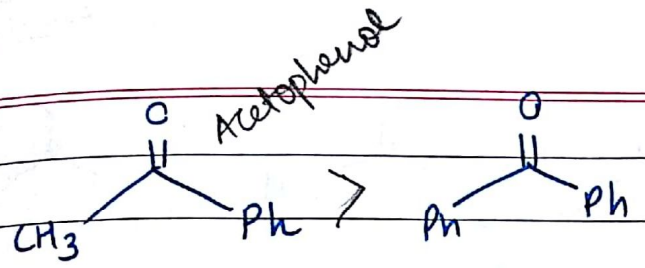
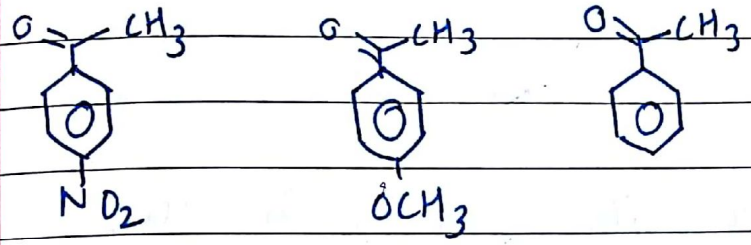
5. 

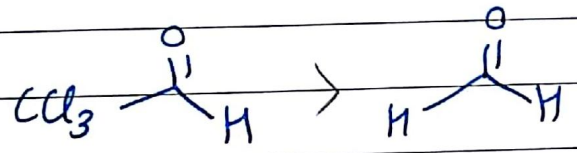
6. 

(+m)

a > c > b

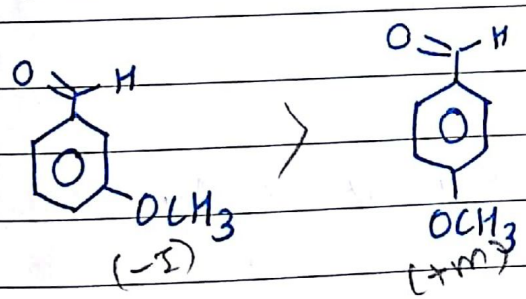
7.

c > a > b

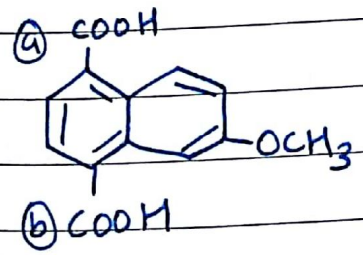
8. 

(−I)

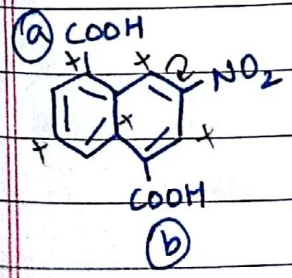
Chloral

9. 

{better donation due to presence on para.}

10. 

a > b

11. 

a > b

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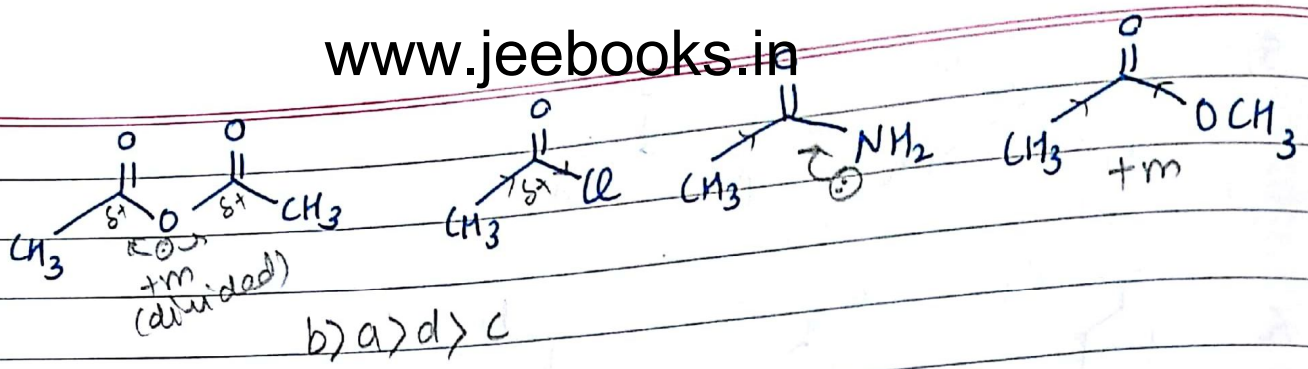
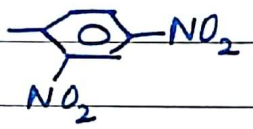
12. 

b > a > d > c

Q. Identify the donor site (major) in the following reagents.

1. $\overset{*}{N}H_2OH$ } hydroxy amine

2. $NH_2NHCONH_2 \rightarrow H_2\overset{*}{N}-NH-\overset{O}{\overset{\|}{C}}-NH_2$ } semicarbazide

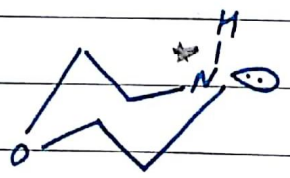
3. $\overset{*}{N}H_2-NH$  } Brady's Reagent

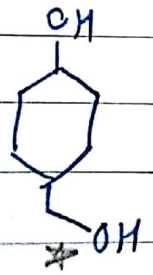
(2,4-DNPhydrazine)

4. $\overset{*}{C}N^-$

5. $Ag\ \overset{*}{N}O_2$ $\quad Ag-O-\overset{*}{N}=O$

6. $\overset{*}{N}H_2-NH-Ph$ } Phenyl hydrazine

7. 

8. 

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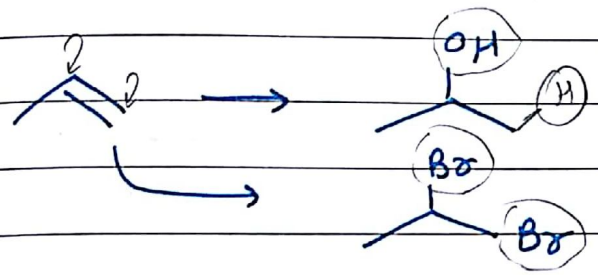
* Types of Reaction :

1] Addition Reaction :

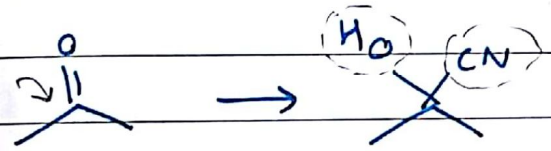
Reagent is added on the substrate containing π-bond

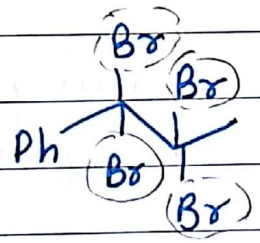
$$\underset{\text{Substrate}}{A = B} \xrightarrow[\text{Reagent}]{X-Y} A(X)-B(Y)$$

- 

} Hydroxination
} Bromination

☆ Only incoming no outgoing

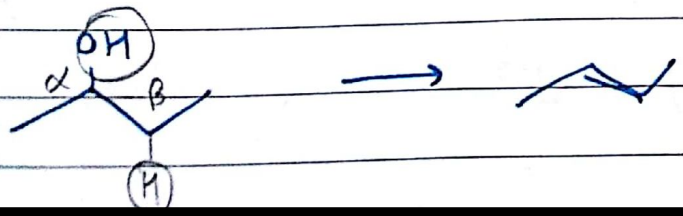
- 

- $Ph-C\equiv C-CH_3 \longrightarrow$ 

2] Elimination Reaction :

- It is reverse of addⁿ rxn.
- In most of elimination rxns, π bond is formed.

- $A(X)-B(Y) \xrightarrow{-XY} A \overset{\pi}{=} B$

- 

) β/(1,2) elimination

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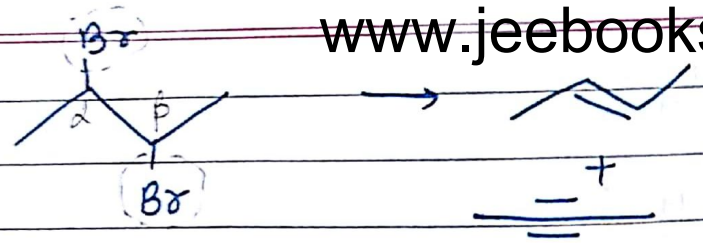
- 

-

- $CHCl_3 \xrightarrow[\Delta]{KOH} :CCl_2 + HCl + H_2O$

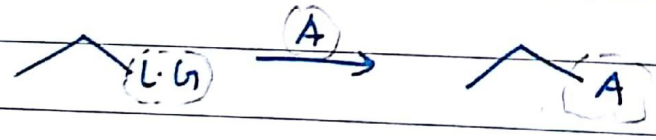
- $CHFClBr \xrightarrow[\Delta]{KOH} :CFCl$

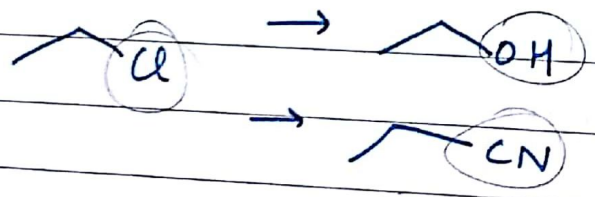
- $CH_2ClBr \xrightarrow[\Delta]{t\text{-}BuOK} :CCl_2$

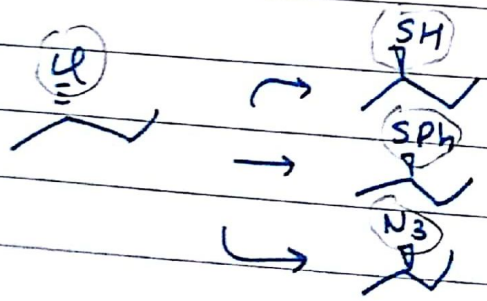
α (1,1) elimination (carbenes are formed)

3] Substitution (Replacement) Reactions :→

- In these rxns, leaving grp is replaced by another atom or group of atoms.



- 

- 

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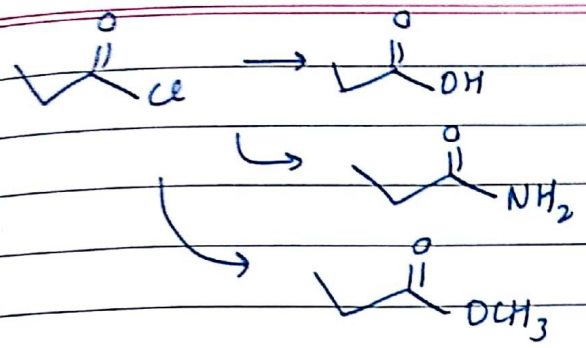
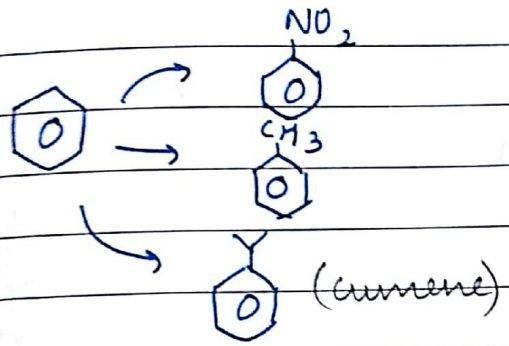
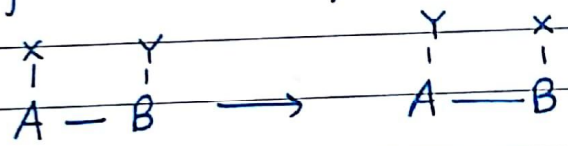
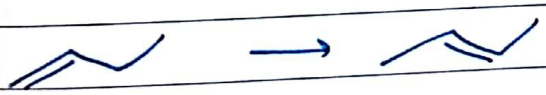
- 

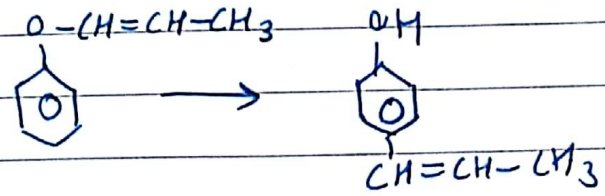
- 

4] Rearrangement Reactions :→

- One isomer converts to other and thermodynamically more favourable form is formed.



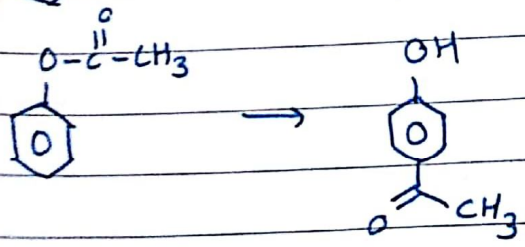
- 

- 

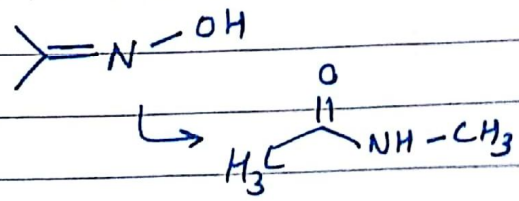
-

-

* MF must be same i.e. should be structural isomers.

- 

[oxime]

- 

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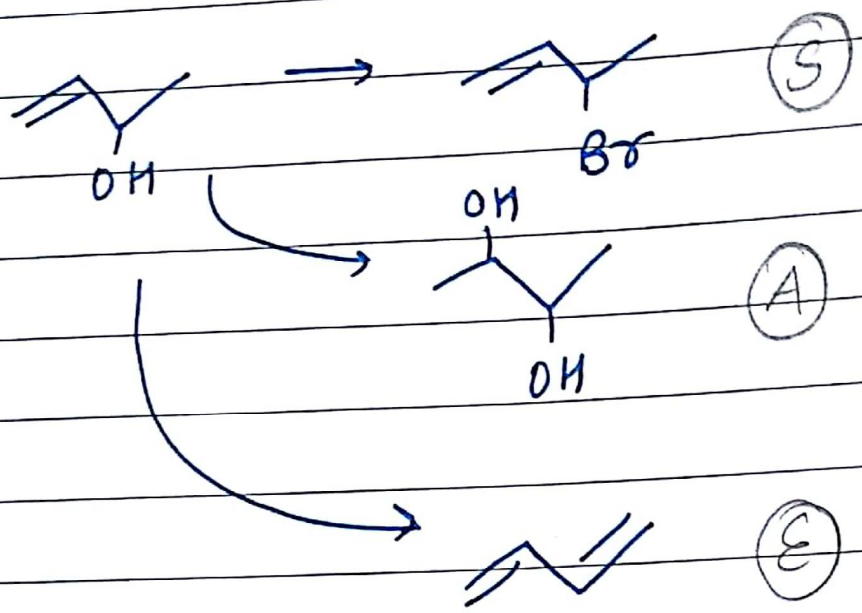
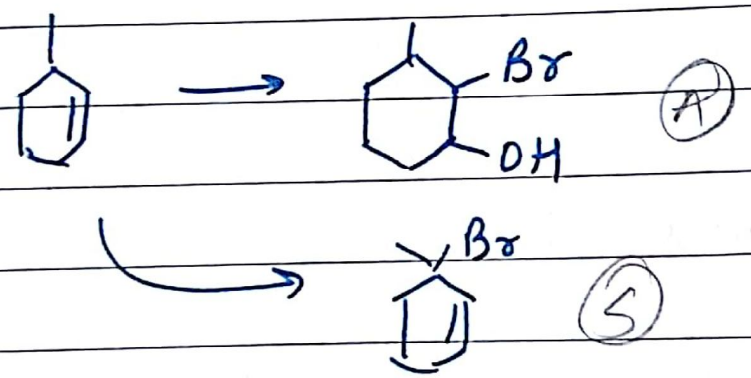
S → substitution
A → Addition
E → Elimination
R → Rearrang

Identify T.O.R.





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* FREE RADICALS & REACTIONS :

Eg, $\dot{Cl}$, $R\dot{O}$, $\dot{Br}$, $\dot{I}$, $\dot{O}H$, $\dot{H}$, $\dot{N}O$

- species containing one unpaired e^-.

• Generation :→

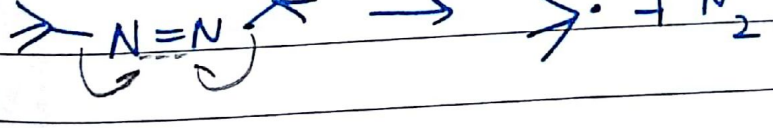
- It takes place in presence of heat / light
- It is favourable in presence of gas phase / non polar solvent
- By homolysis of weak bonds.

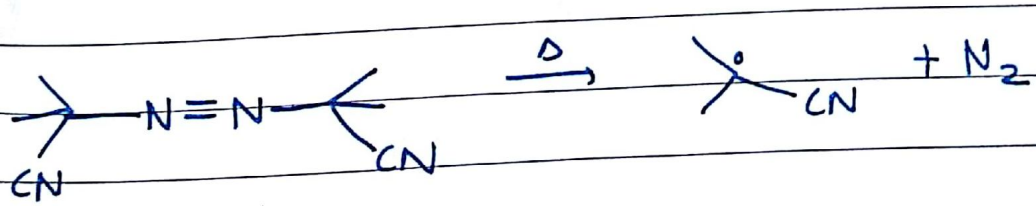
• $Br-Br \xrightarrow[\Delta]{h\nu} 2\dot{Br}$

• $Cl-Cl \xrightarrow[\Delta]{h\nu} 2\dot{Cl}$

• $R-\ddot{O}-\ddot{O}-R \longrightarrow 2R\dot{O}$

• $O=N-\ddot{Cl} \longrightarrow \dot{N}O + \dot{Cl}$

• 

• 

AIBN

Azo bis Isobutyl nitrile

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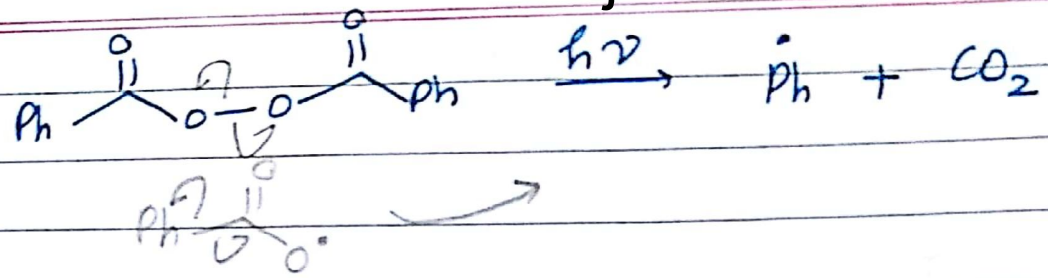
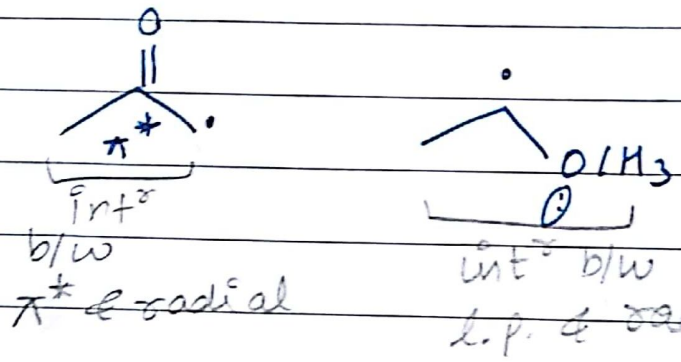
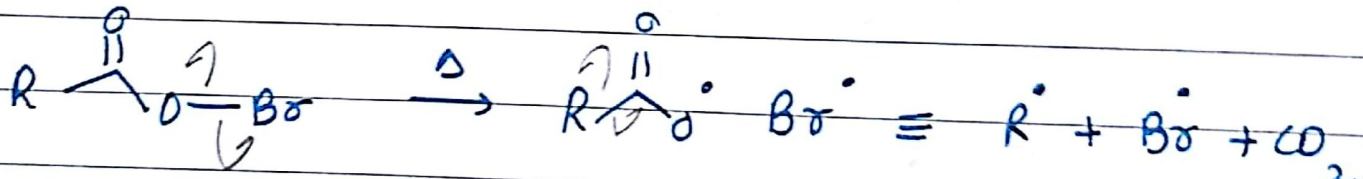
- 

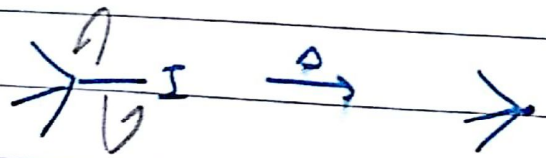
Dibenzoyl peroxide

- Any group which is e^- withdrawing or donor will stabalize free radical.





$NOBr \xrightarrow{\Delta} \dot{N}O \quad \dot{B}r$



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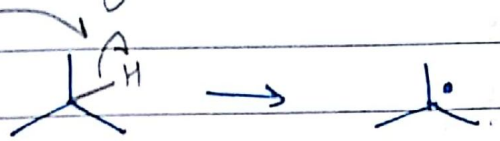
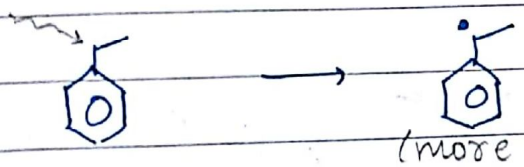
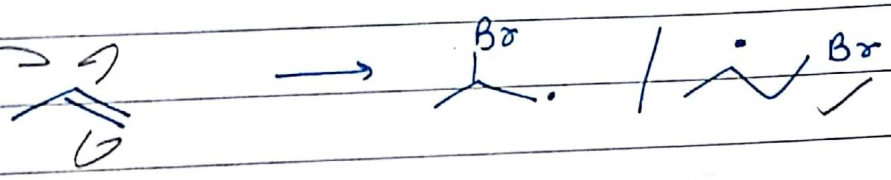
30/5/18

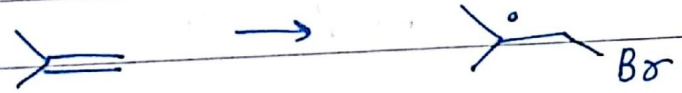
- In presence of radicals, new radicals can be generated.
  It can be due to H- abstraction or addition on π bonds.

- $RO^{\bullet} \cdots H-Br \longrightarrow ROH + Br^{\bullet}$

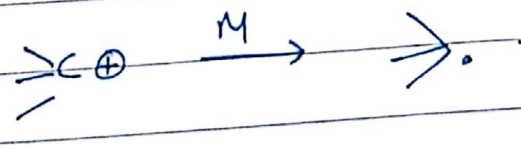
- $Cl^{\bullet}$  + HCl

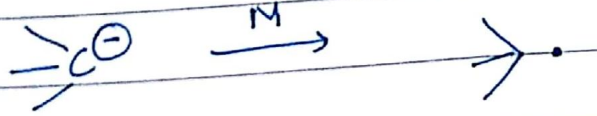
- $Br^{\bullet}$  + HBr
  (more stable)

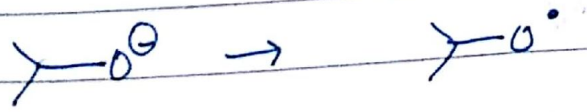
- $Br^{\bullet}$ 

- $Br^{\bullet}$ 

- From Metals,
  It can take place in presence of metals. Redox rans take place.

- 

- 

- 

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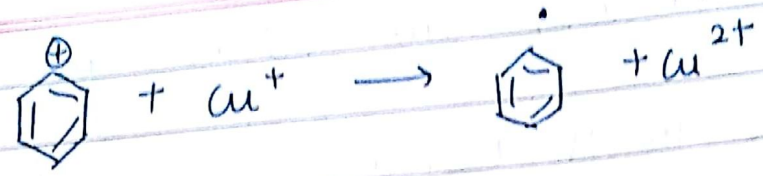
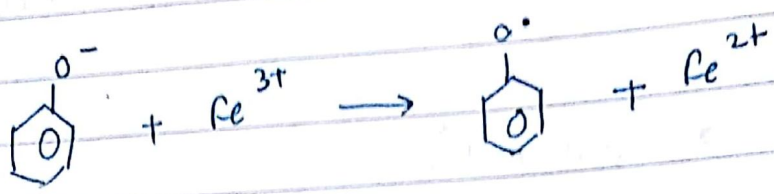
- 

- 

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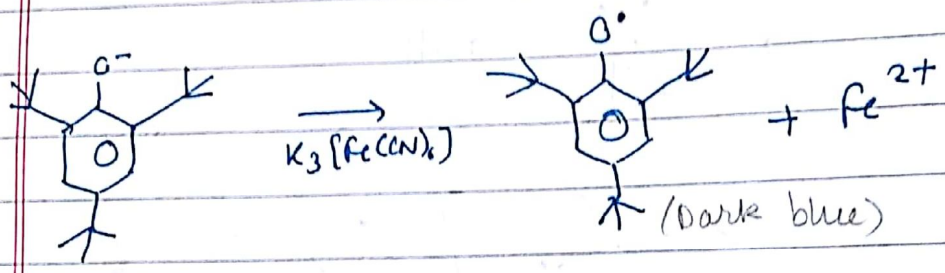
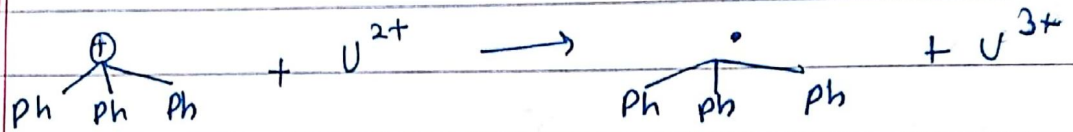
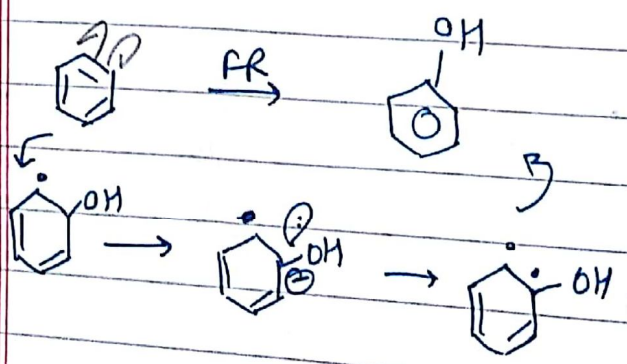
- 

- 

(N.I.S) - Fenton's Reagent → It will act as an oxidising agent

$$Fe^{2+} + \underbrace{H-O-O-H}_{F.R.} \longrightarrow Fe^{3+} + \dot{O}H + \bar{O}H$$

- 

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* General rxns of Radical :→

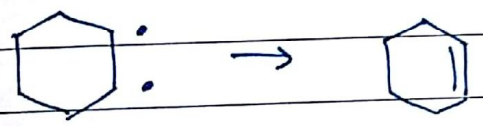
1] Combination :

- $\dot{Cl} + \dot{Cl} \longrightarrow Cl-Cl$

- $\dot{R} + \dot{R} \longrightarrow R-R$

- $\dot{R} + \dot{I} \longrightarrow R-I + R-R + I-I$ (2)

- $\dot{Me} + \dot{Et} + \dot{Pr} \longrightarrow Me-Me + Me-Et + Me-Pr + Et-Pr + Pr-Pr + Et-Et$ (5)

- 

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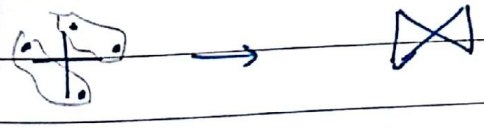
} In diradical intramolecular is better

Q.

1) 

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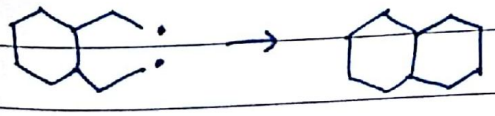
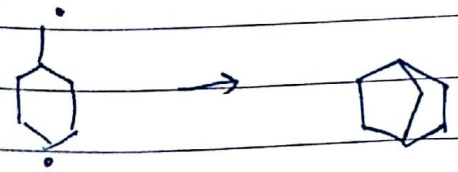
3)  decalin

4) 

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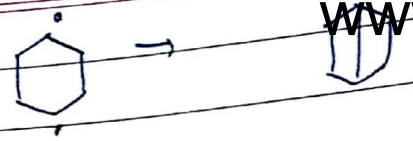
6) 

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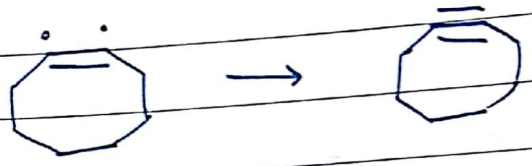
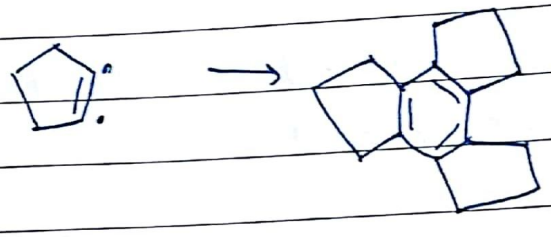
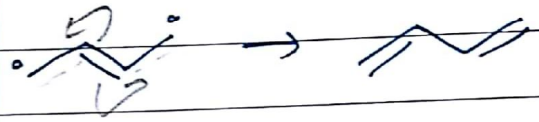
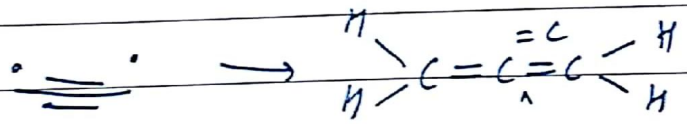
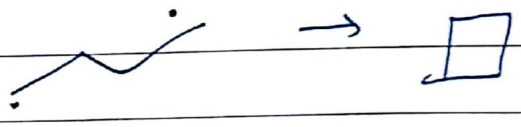
8) 

Dimerisation

9) 

10) 

11) 

12) 

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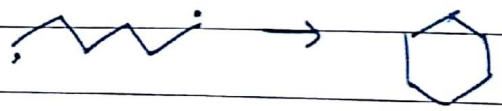
14) 

Polymerisation

15) $\rightarrow -(CH_2)_n-$

$-(CH_2)_n-$

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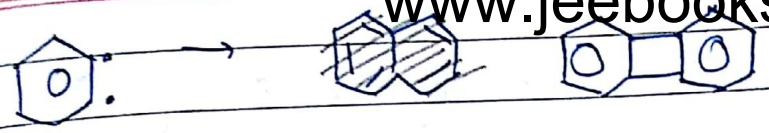
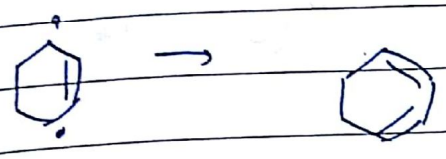
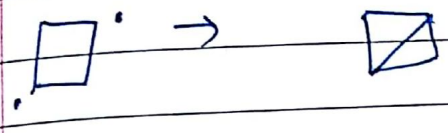
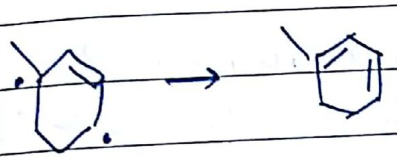
16) 

17) 

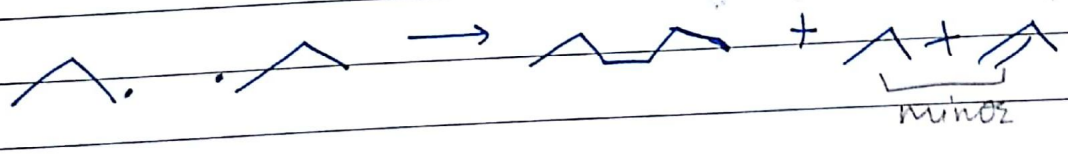
18) 

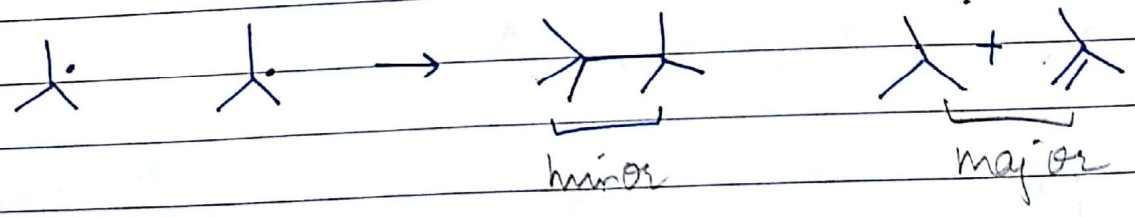
19) 

2] <u>Disproportionation</u> :→

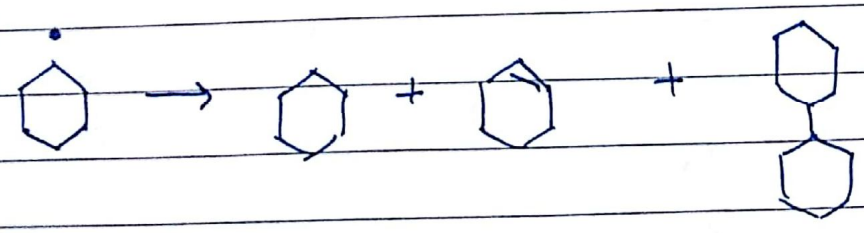
-

i/2° → Dimer
3° → Dis p.

- 

- 

Q.

1) 

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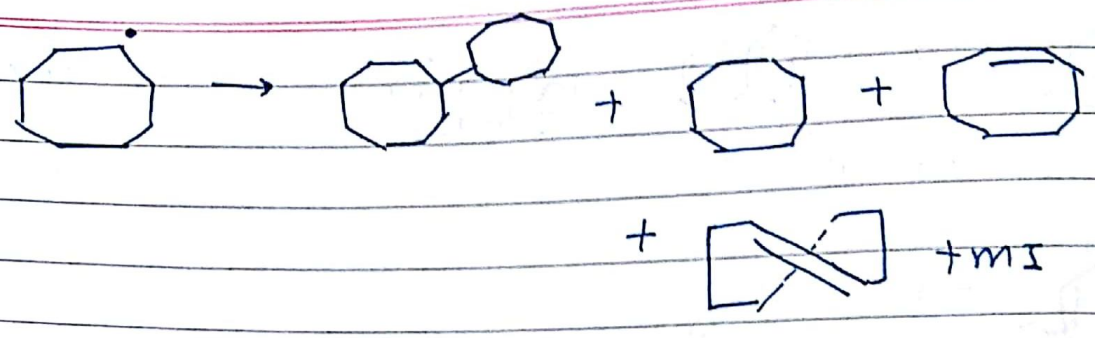
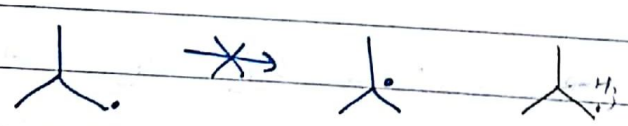
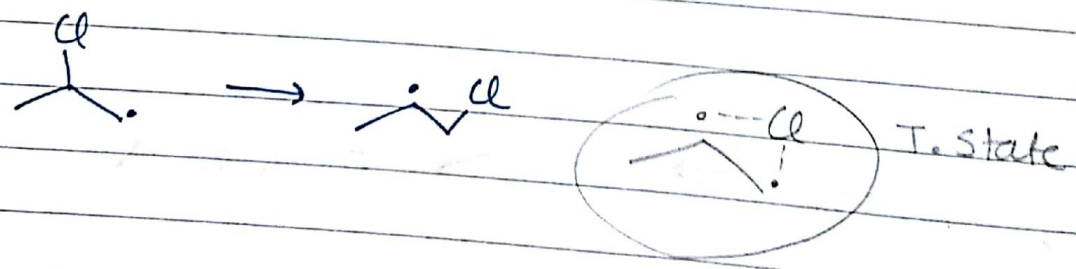
2) 

3] <u>Rearrangement</u> :→

- Radicals fail to undergo rearrangement coz of high energy requirements but it is possible when transition state is stabalised.

eg,

- 

- 

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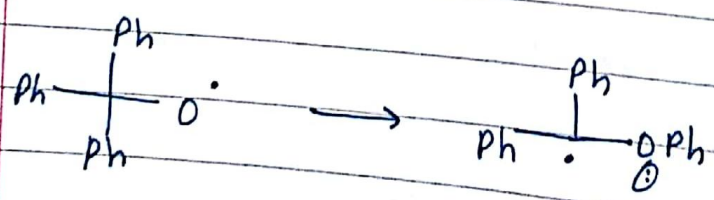
- 

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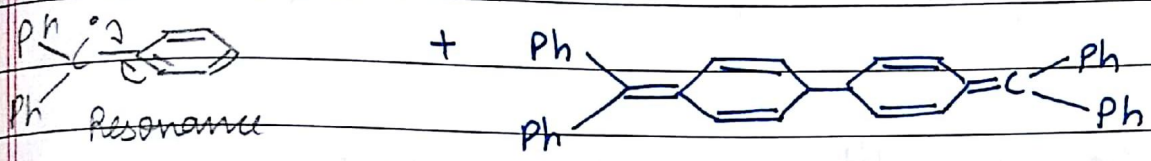
4/6/18

Q. Observe the rxn & write down the mechanism.

1] $Ph_3\dot{C} \longrightarrow Ph_3C-CPh_3$ (negligible (steric)) + Ph_3C–⟨benzene⟩=C(Ph)(Ph) } Major



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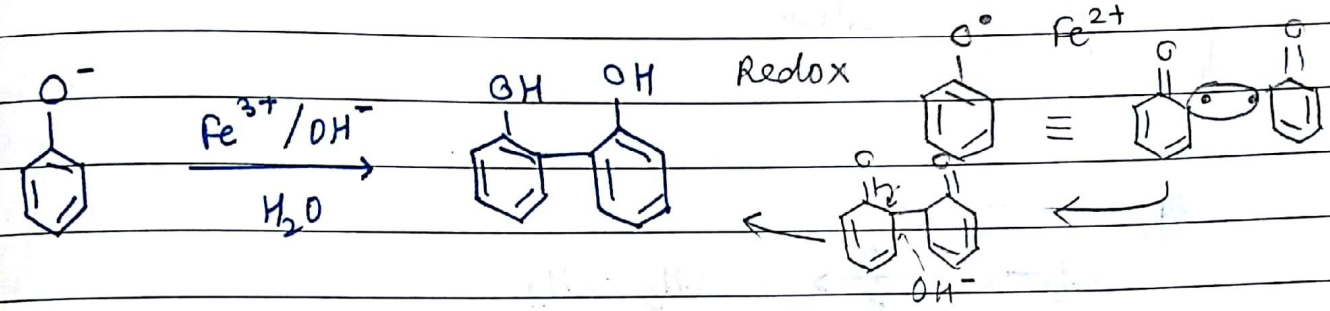

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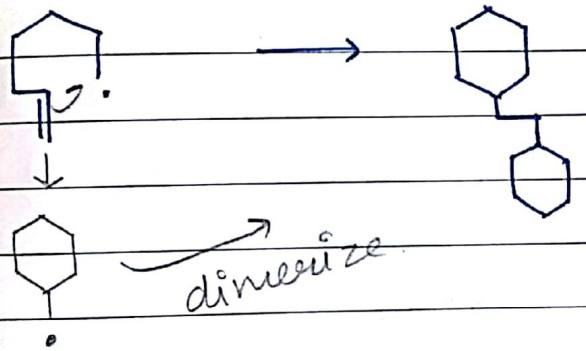

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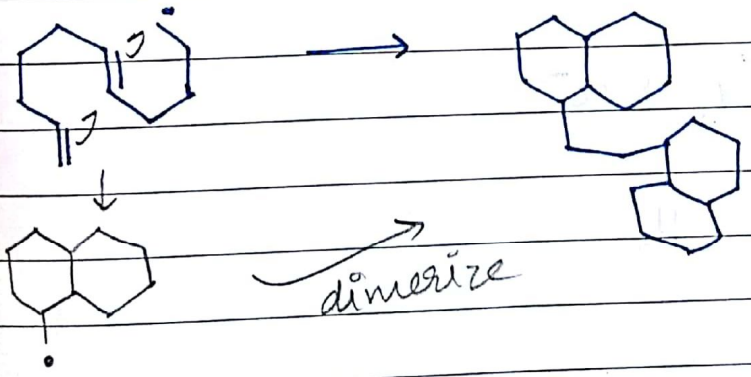
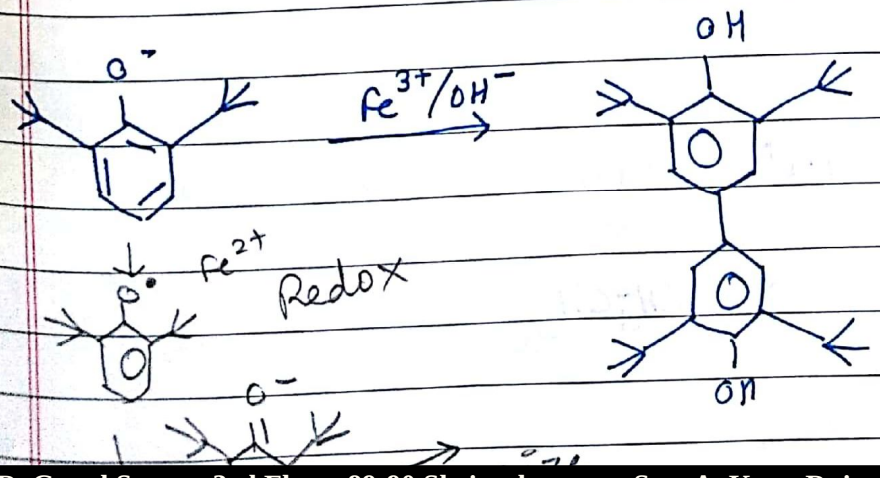
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