

\* Acidic Strength:

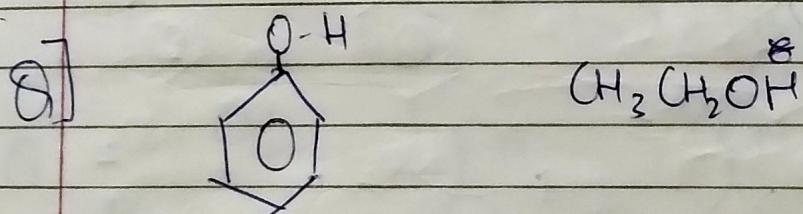
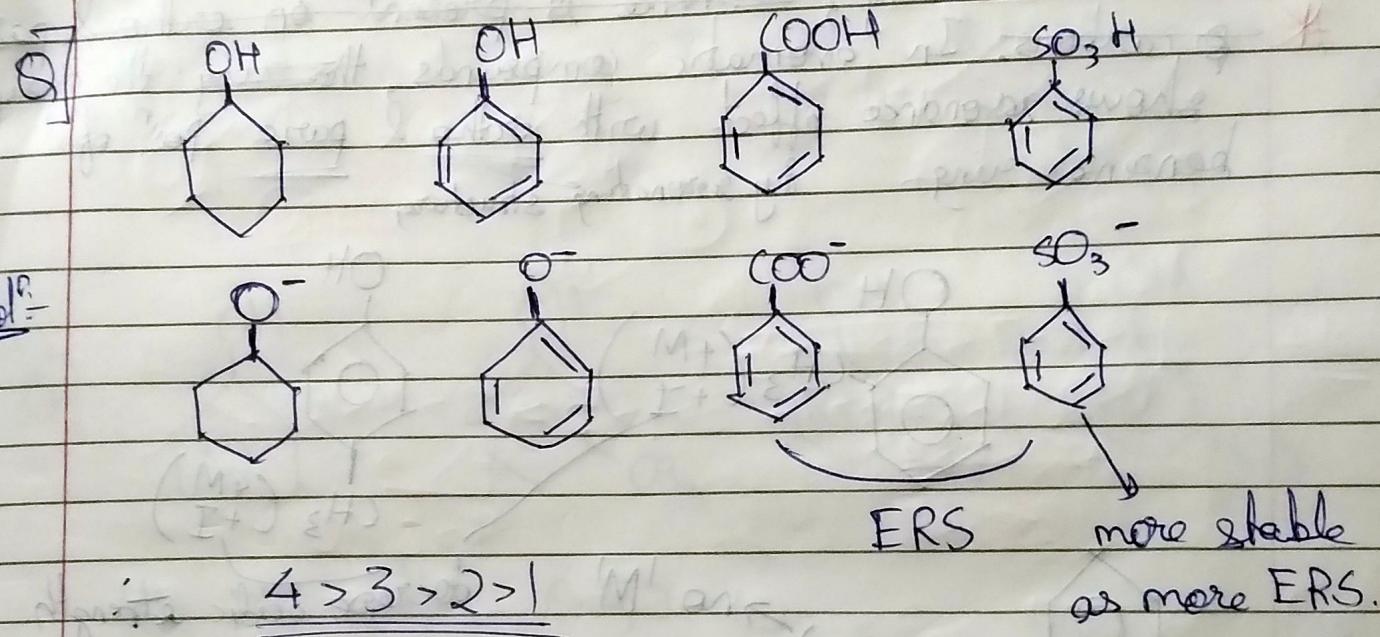
Acid →  $\text{H}^+$  ion donor

→ e<sup>-</sup> pair acceptor

Stronger Acid has weaker/stable conjugate base.

Stability of conjugate base  $\propto$  -M  
 $\propto$  Aromaticity       $\frac{1}{-H} \propto \frac{1}{+M, +H, +I}$   $\propto$  Size  
 $\propto$  E.R.S.

Aromaticity: When resonance takes place in a cyclic system and the no. of  $\pi e^-$  are  $2\pi e^-$ ,  $6\pi e^-$ ,  $10\pi e^-$ ,  $14\pi e^-$ .



Sol<sup>-</sup>: Phenoxide resonance stabilized  $\text{CH}_3\text{CH}_2\text{O}^-$  not stabilized

I > II

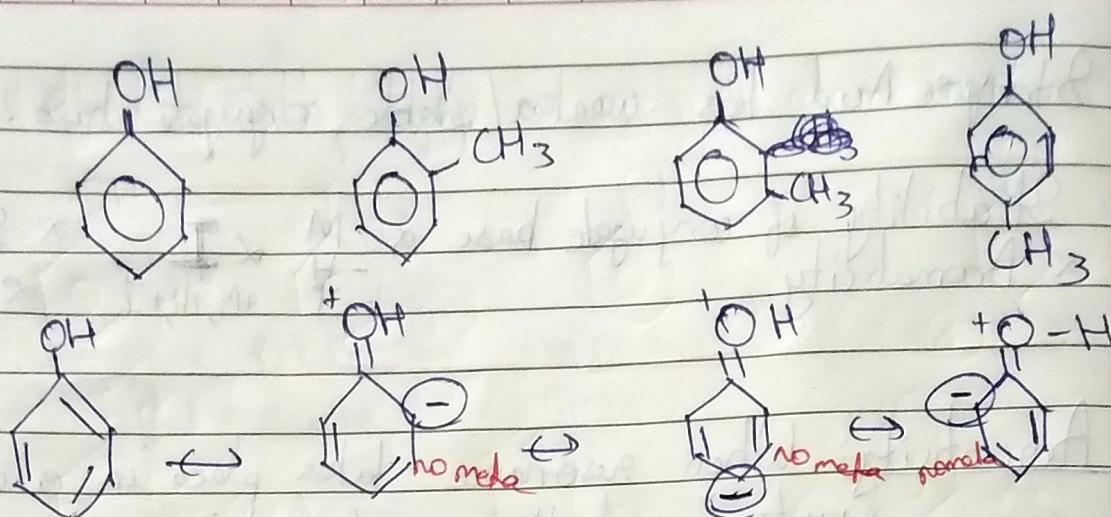
Picric Acid (2,4,6 Trinitrophenol) & 2,4 dinitrophenol

Both are more acidic than benzoic acid.

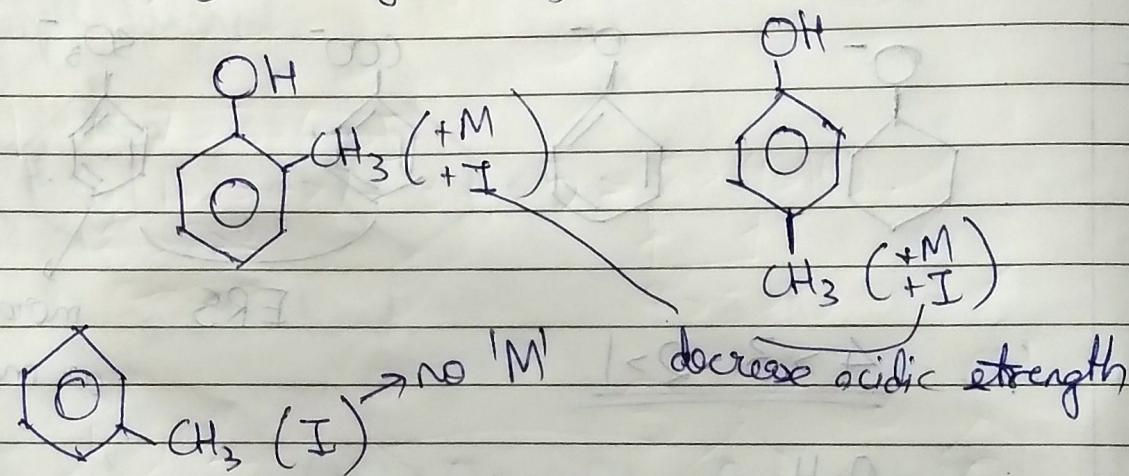
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Q)

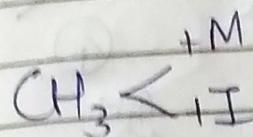
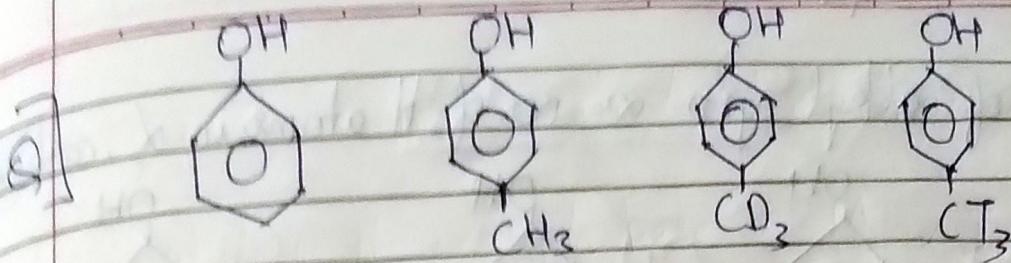


\* In Benzene Ring, resonance is present on ortho & para p carbons. In aromatic compounds, the group the group shows resonance effect with ortho & para pos' of benzene ring by resonating structure.



Meta pos'  $\rightarrow$  I effect only ; no M effect -  
 $\therefore 3 > 4 \&$

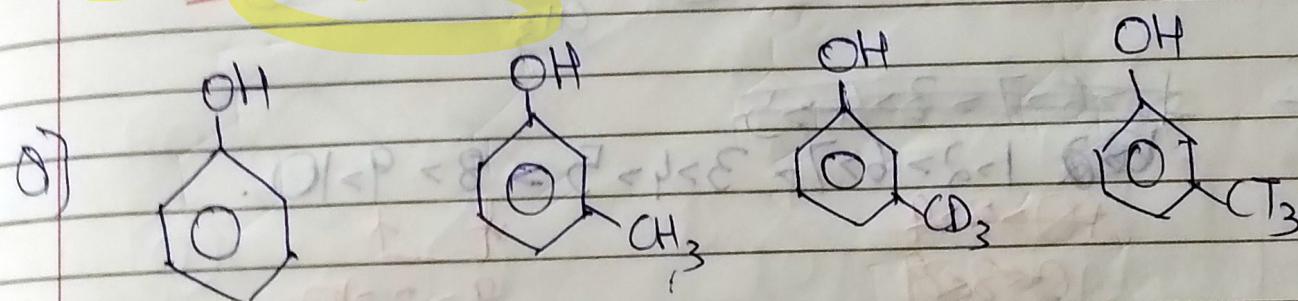
I effect is dist. dependent.  $\therefore$  In 2, I<sup>+</sup> is nearer. less acidic strength in 2.



$\text{For} + \text{M} ; \text{CH}_3 > \text{CD}_3 > \text{CT}_3 \text{ & For} + \text{H}$

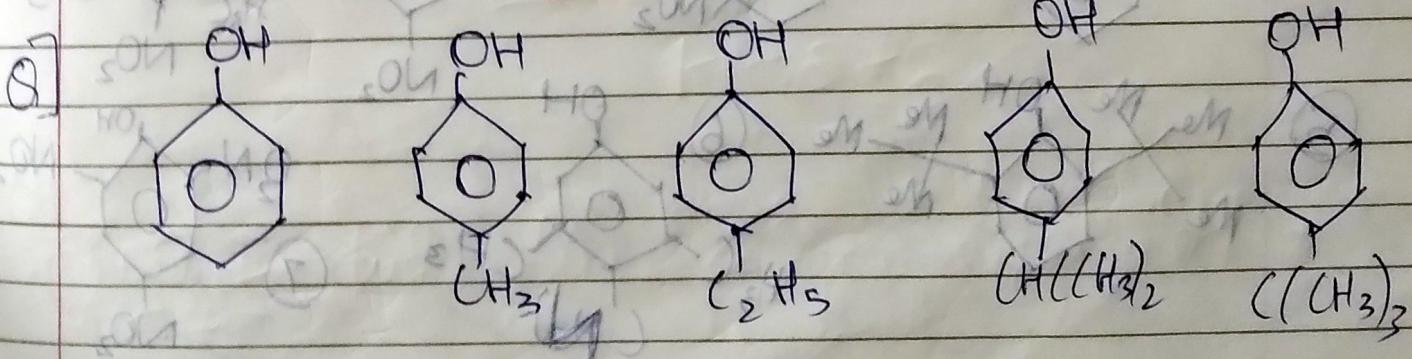
$\text{Dec. order of } +\text{I}, -\text{CT}_3 > -\text{CD}_3 > -\text{CH}_3$

$1 > 4 > 3 > 2$



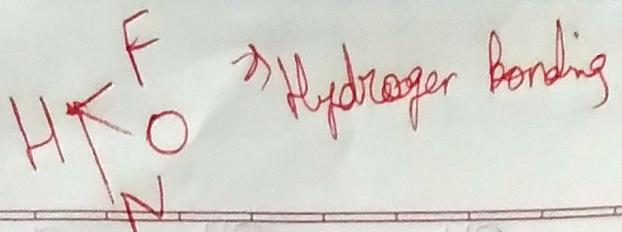
No M-effect. Only J

$1 > 2 > 3 > 4$



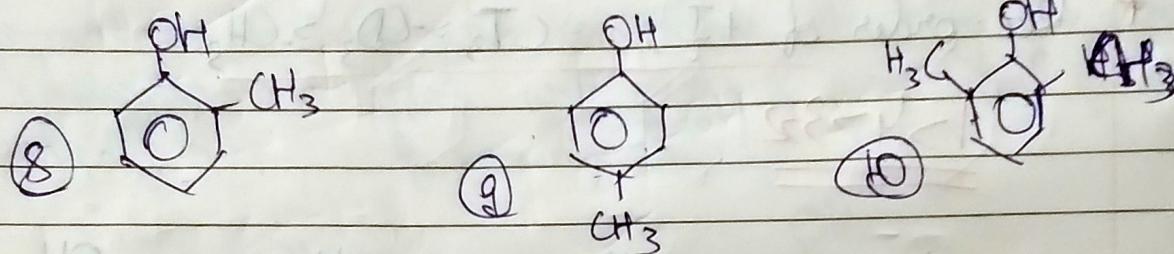
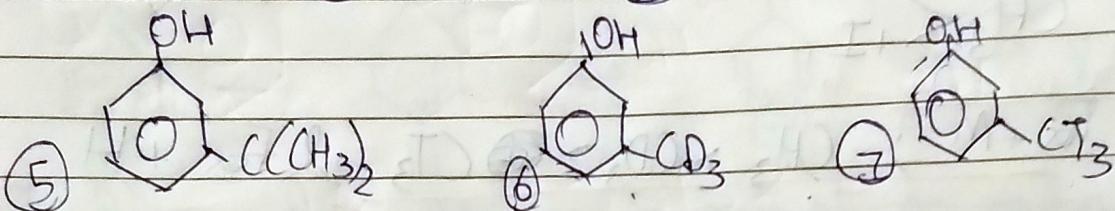
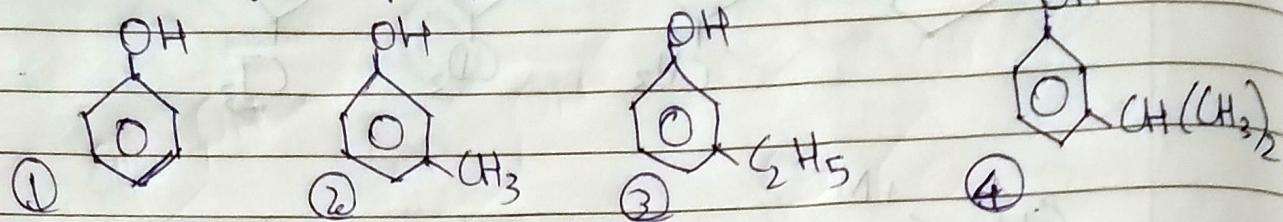
$1 > 5 > 4 > 3 > 2$  And: I- & M- effect OH affects J

• Strength: isobutyl

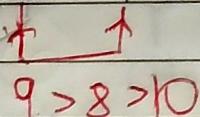
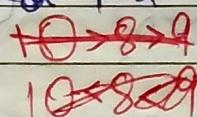
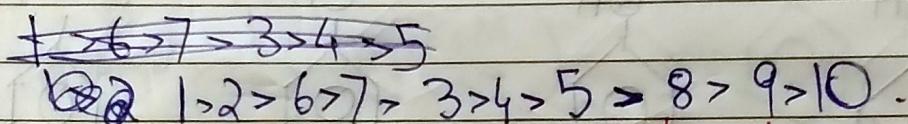


\* M- effect of alkyl grp  $\propto$  no. of H atoms in X. carbon

Q]

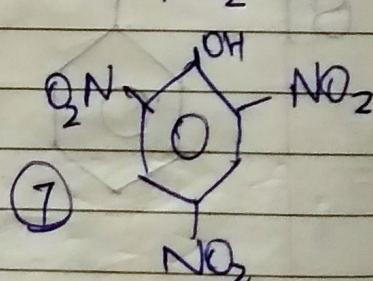
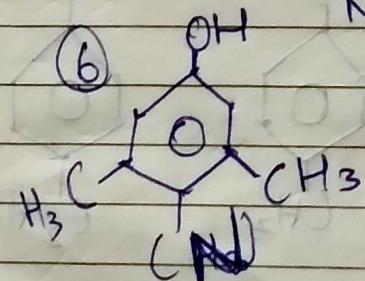
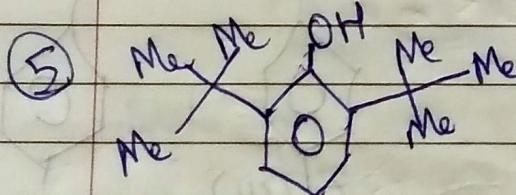
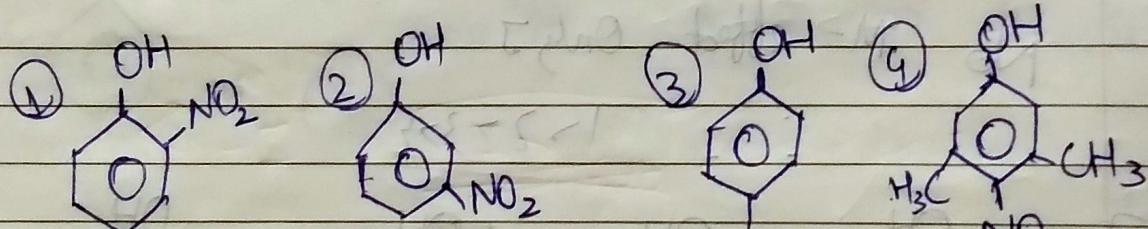


Sol:



Acidic Strength ↗

Q]



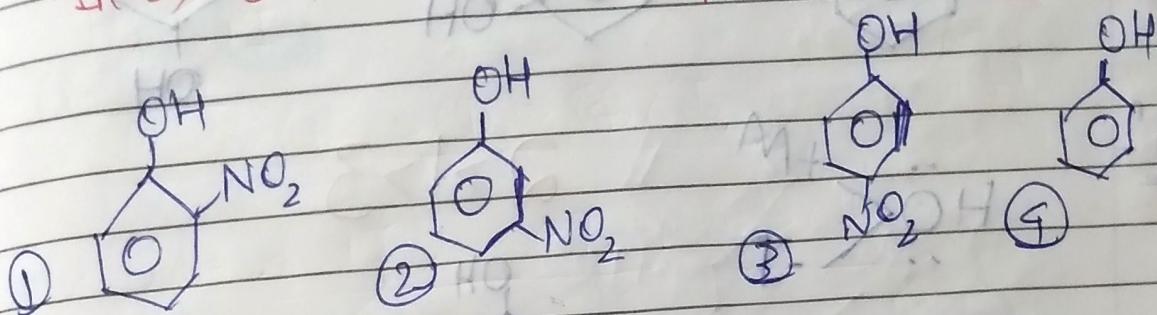
$\text{NO}_2$  has -M & -I; both are favourable for acidic strength.

$H, F, OH, NH_2, OR \rightarrow$  no steric repulsion  
due to small size

$7 > 3 > 1 > 6 > 2 > 4 > 5$

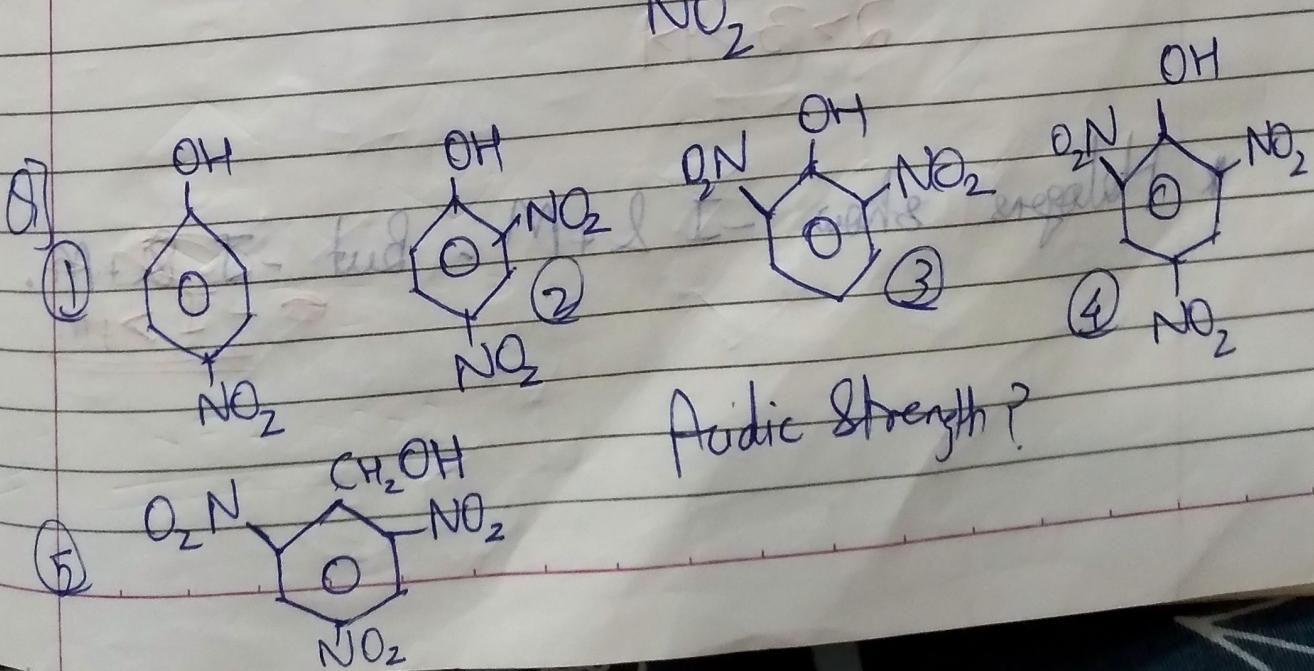
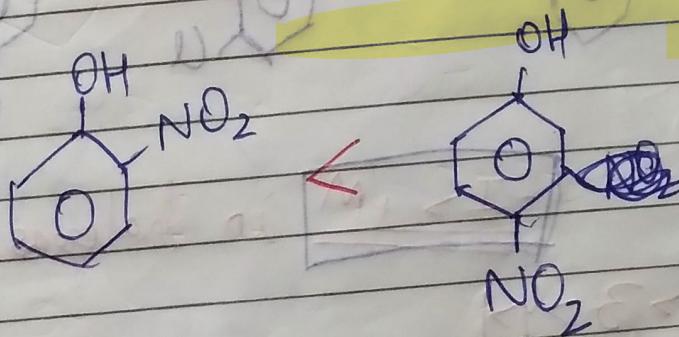
In 4;  $NO_2$  will face  $\text{H}$  repulsion [No - MX] only - I

In 5;  $OH$  will become non planar due to  $\text{H}$



$3 > 1 > 2 > 4 \rightarrow$  Intramolecular Hydrogen Bonding

Orthonitrophenol is less acidic than paracetamol due to intramolecular H bonding

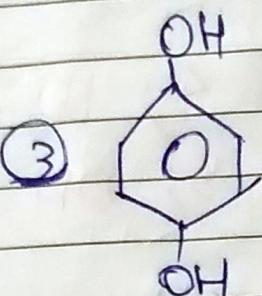
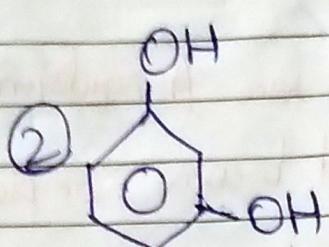
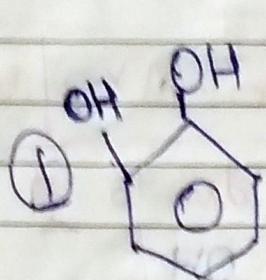


Acidic Strength?

Sol:

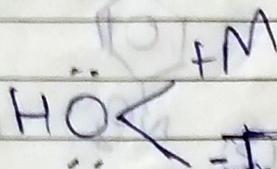
$\text{F} > \text{I} > \text{Br} > \text{Cl} > \text{O} = \text{S} > \text{N} > \text{C} > \text{H}$

Q)

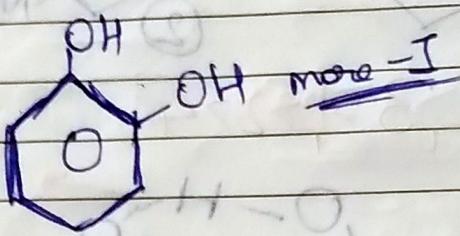


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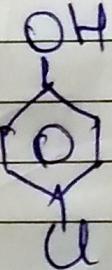
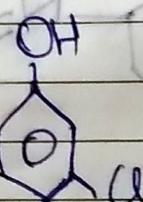
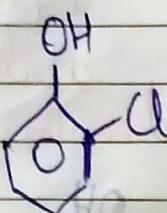
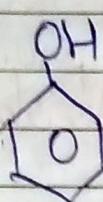
Sol:



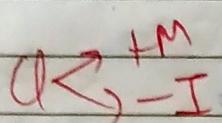
$2 > 1 > 3$



Q)



Sol:



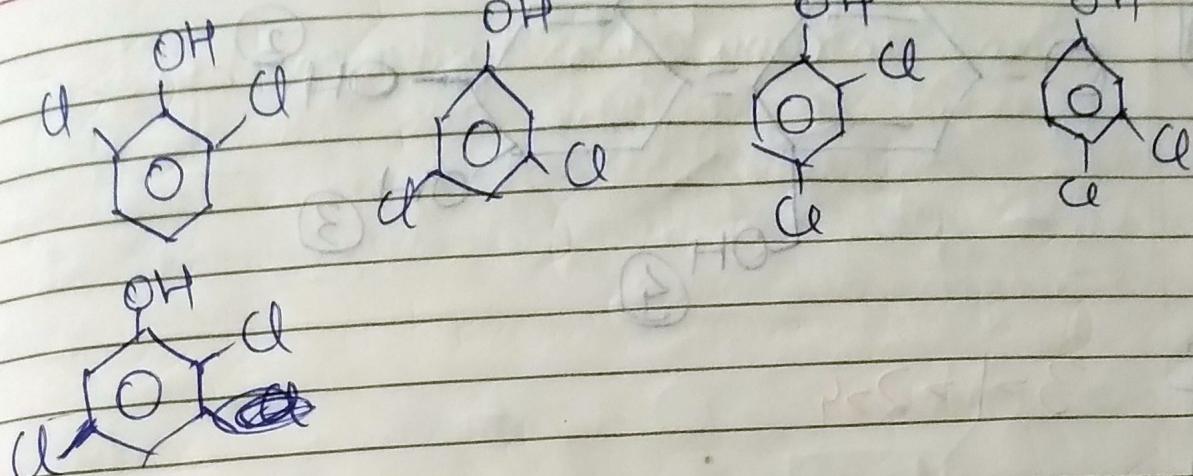
$-I > +\text{M}$

in halogens.

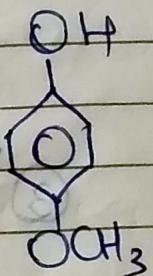
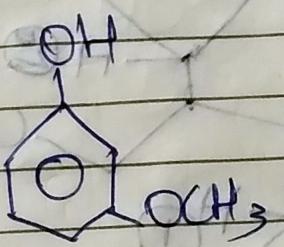
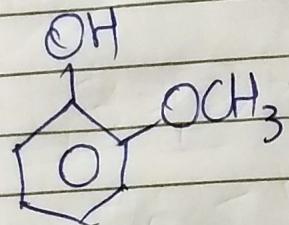
$2 > 3 > 4 > 1$

\* Halogens show  $-I & +\text{M}$ . But  $-I > +\text{M}$ .

$\text{---} -I > +\text{M}$

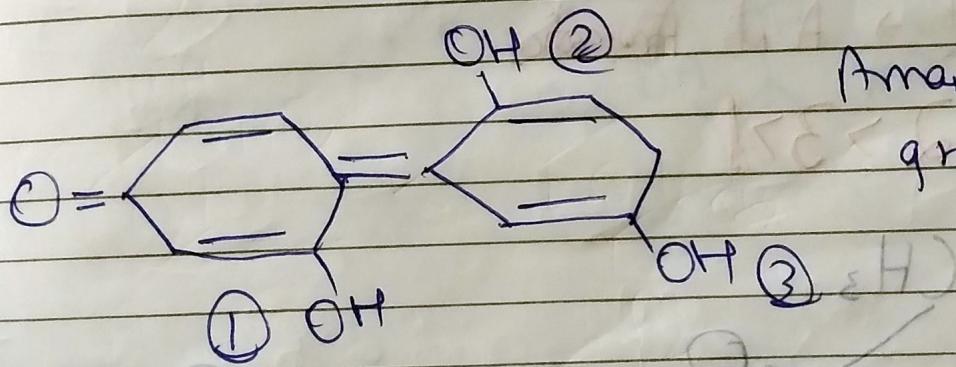


$1 > 5 > 3 > 2 > 4$



$\text{OCH}_3 < \text{-I}$

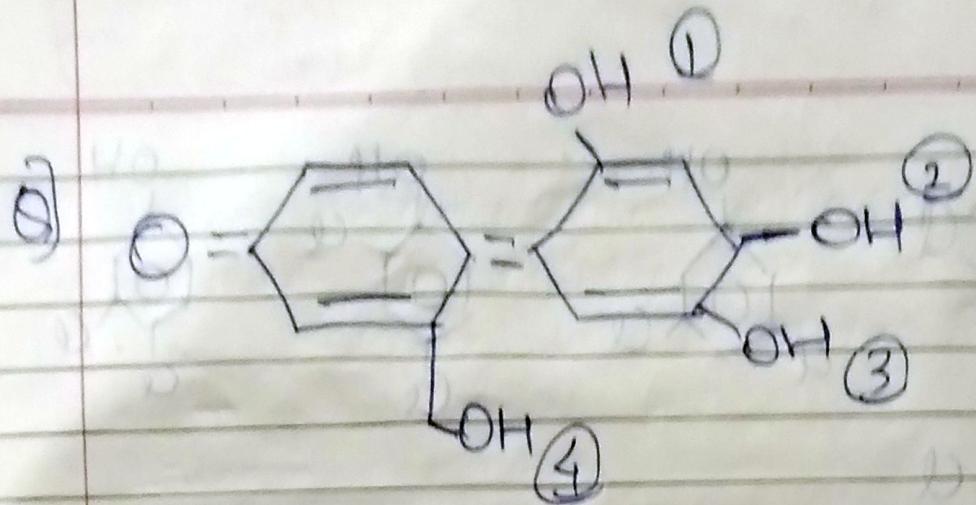
$2 > 1 > 3$



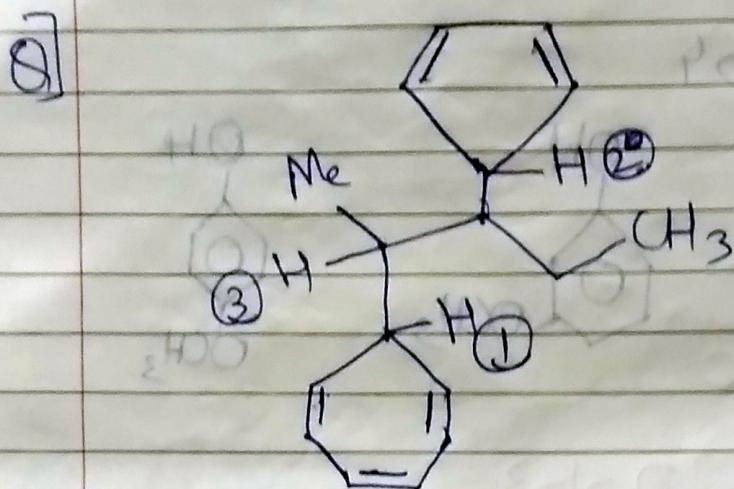
Arrange OH  
grps in acidic  
strength.

$3 > 1 > 2$

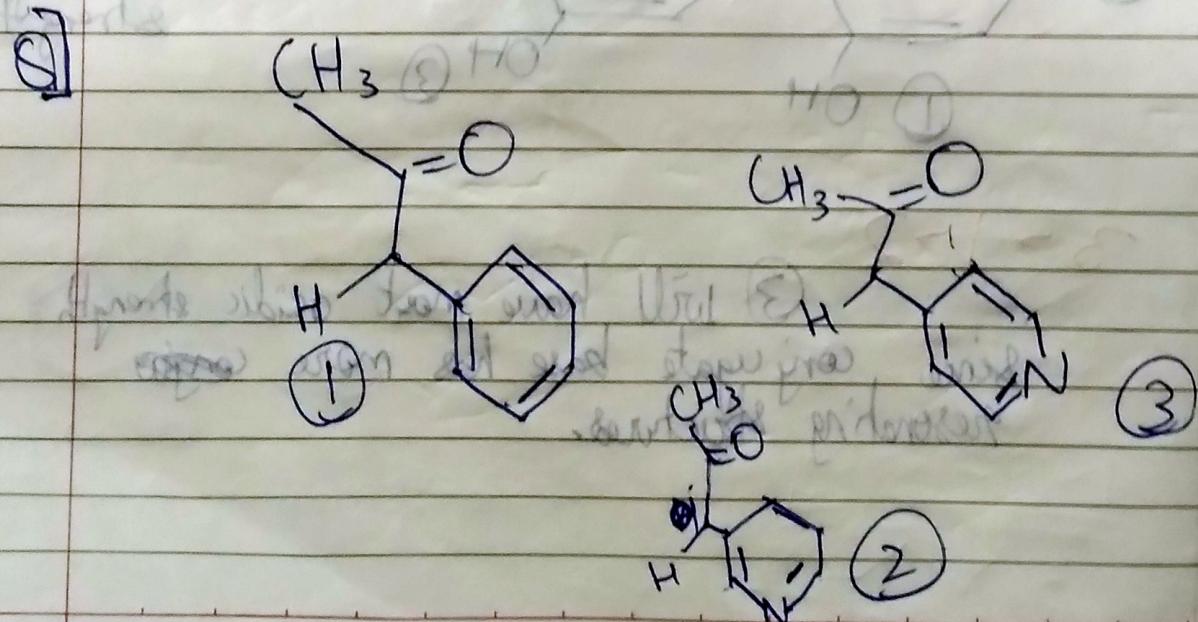
③ will have most acidic strength  
since conjugate base has more ~~cong~~  
resonating structures.



Sol:  $3 > 1 > 2 > 4$



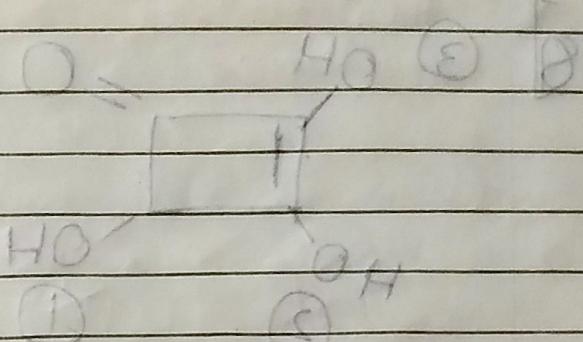
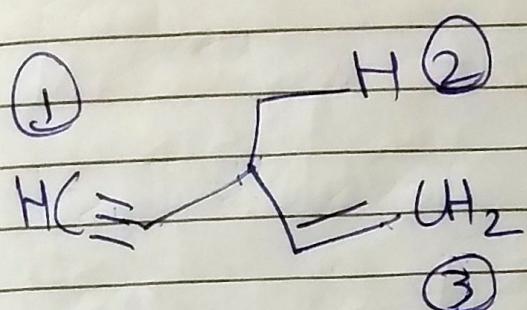
Sol:  
Cyclopent  $\rightarrow$  Aromatic  
Cyclohept  $\rightarrow$  Anti-Aromatic



Sol: $3 > 2 > 1$ 

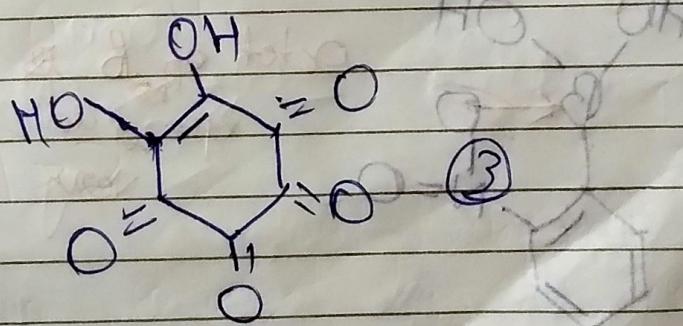
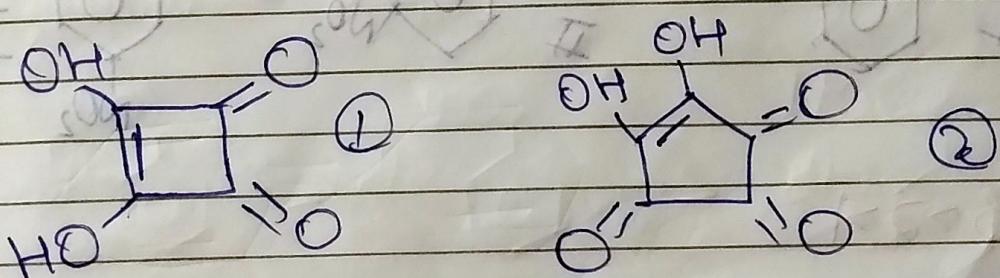
In 3<sup>rd</sup>; N will have both -M & -I as in resonating structure N gets -ve charge & it is more EN.

Q)

Sol: $1 > 3 > 2$ 

In 1<sup>st</sup>; C  $\rightarrow$  50% S; sp  
 2<sup>nd</sup>; C  $\rightarrow$  25% S;  $sp^3$   
 3<sup>rd</sup>; C  $\rightarrow$  33% S;  $sp^2$

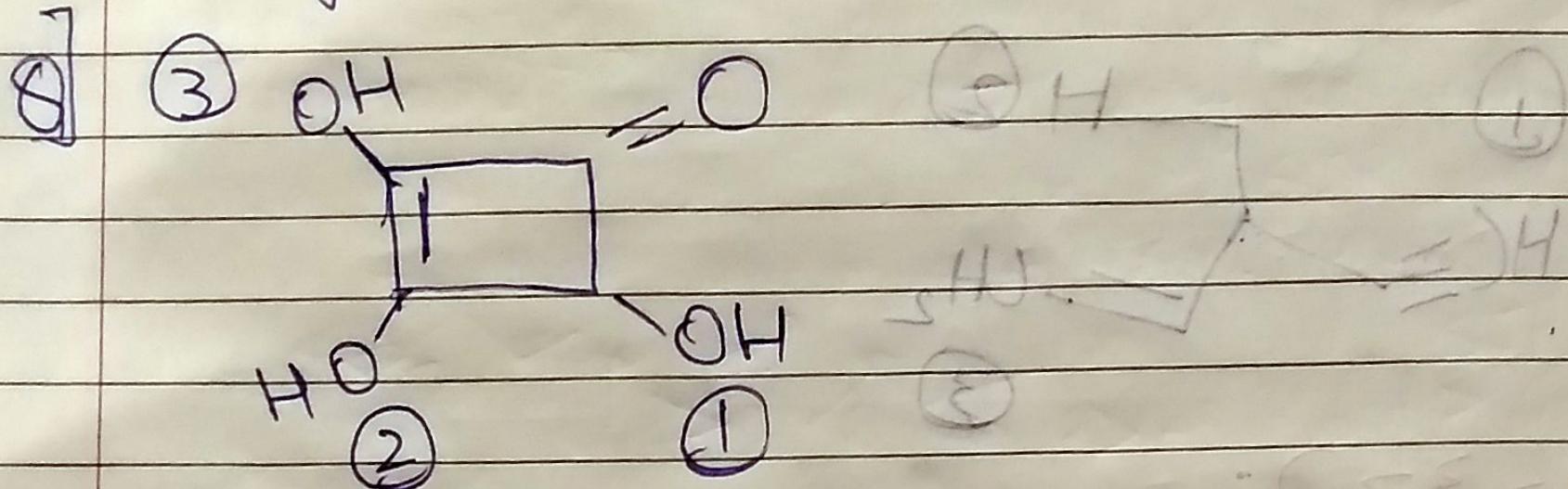
Q)

Sol: $3 > 2 > 1$ 

O grp is -I.

Q) When

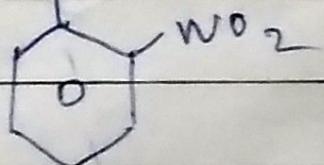
\* When intramolecular hydrogen bonding is present in conjugate base then the stability of conjugate base or acidic strength increases but when it is present in compound, acidic strength decreases.



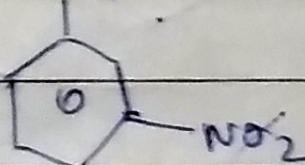
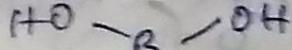
Sol:

$2 > 3 >$

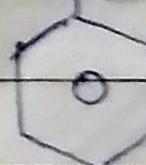
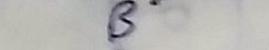
a) which is most acidic order. (+O<sub>2</sub>) / OH



I



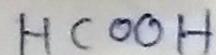
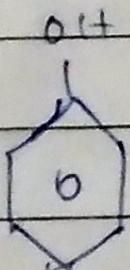
II



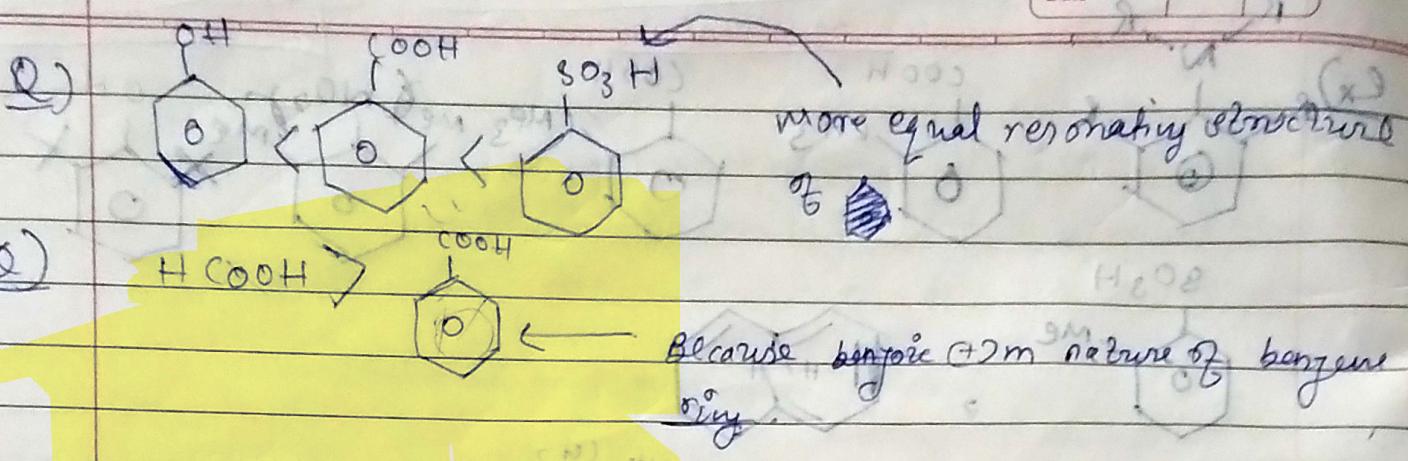
III

~~Ex~~  $\boxed{III > II > I}$

Q)



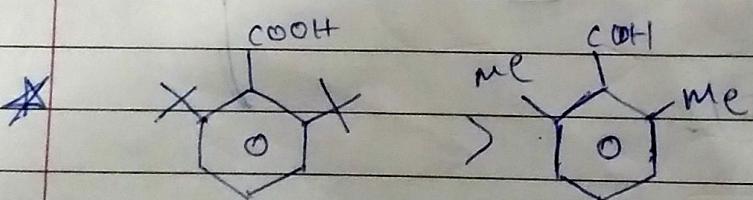
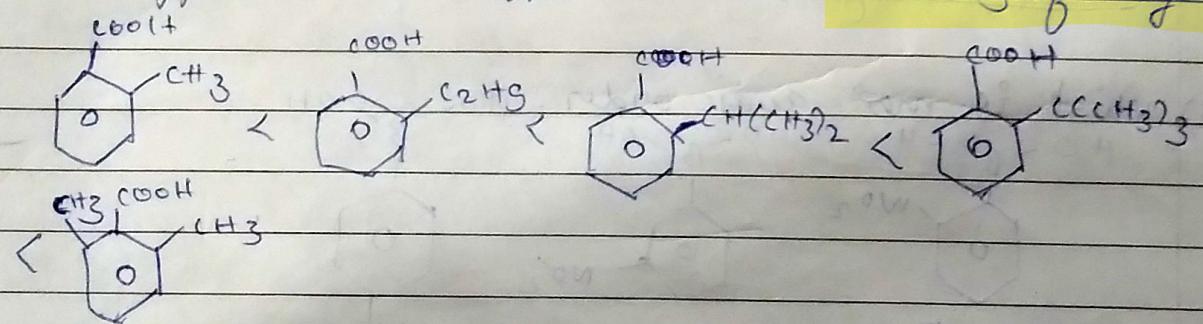
Because of equal resonance structures  
in conjugate base.

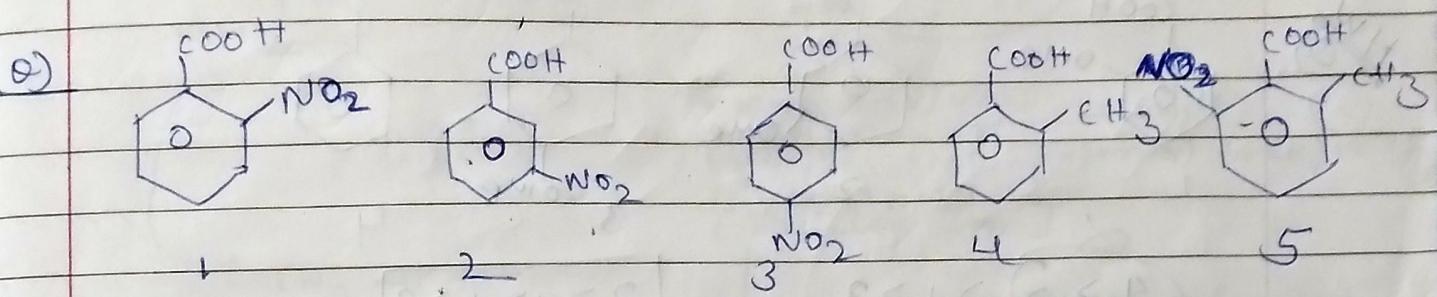
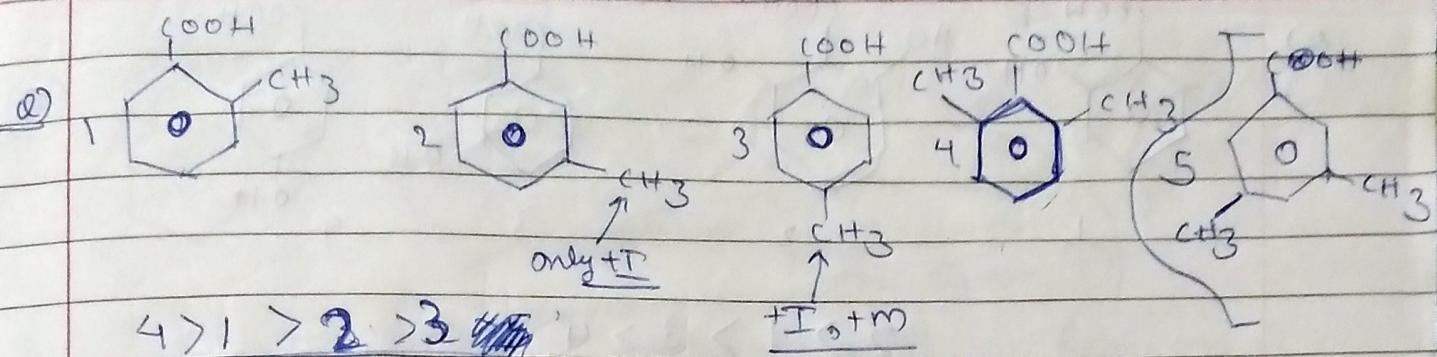
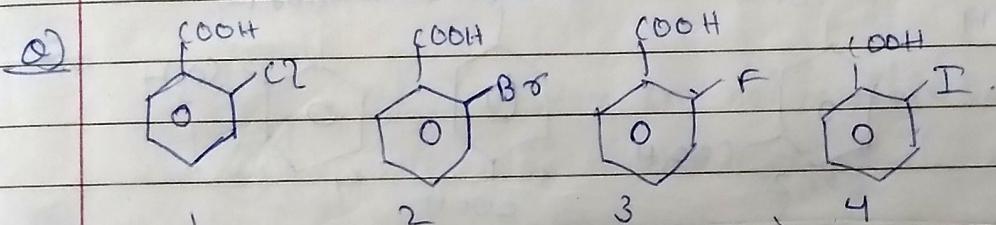
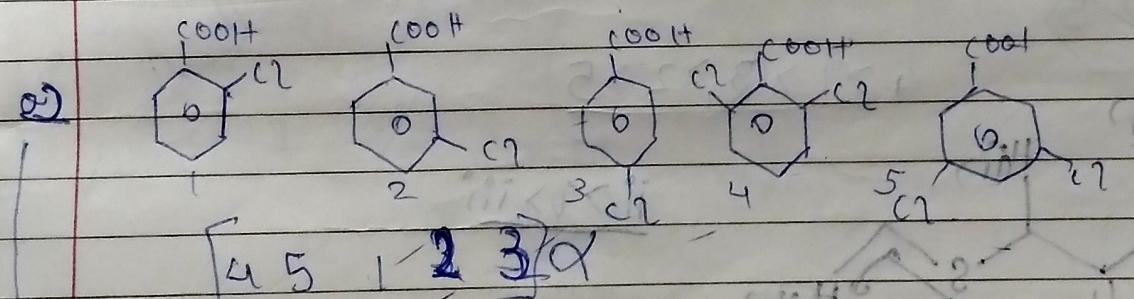
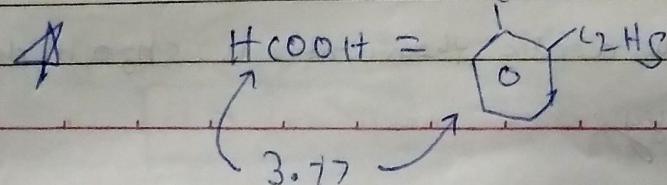
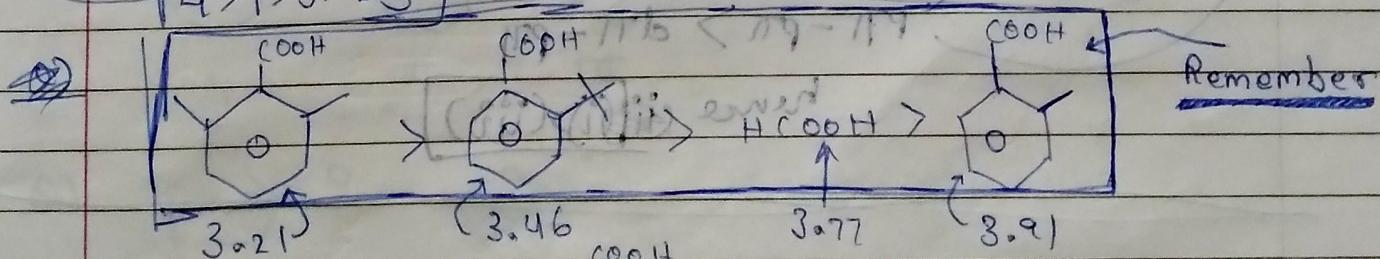


\* Ortho substituted benzoic acid is most acidic than benzoic acid. Due to very less (+m) effect of benzene on -COOH group due to SIR effect or ortho effect.

When we place bulkier groups like  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{CH}_3\text{CH}_2\text{CH}_3$  at ortho position of benzoic acid, steric repulsion takes place between  $-\text{COOH}$  and ortho substituent which forces  $-\text{COOH}$  out of plane or due to this  $-\text{COOH}$  loses planarity and decreases (+m) effect of benzene ring on  $-\text{COOH}$ .  $\text{CH}_3$ ,  $\text{CH}_2\text{F}$ ,  $\text{CH}_2\text{Cl}$ ,  $\text{NH}_2$ ,  $\text{OR}$  don't show ortho effect.

Ortho effect or SIR effect is  $\propto$  Bulkiness of the group.



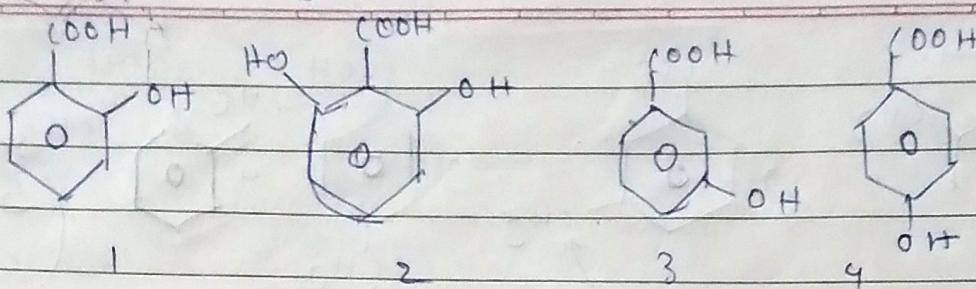
~~5 > 2 > 1~~ $5 > 1 > 4 > 3 > 2$  $4 > 2 > 1 > 3$  $+4 > 1 > 5 > 2 > 3$ 

# Intra-molecular H bonding

Page No.

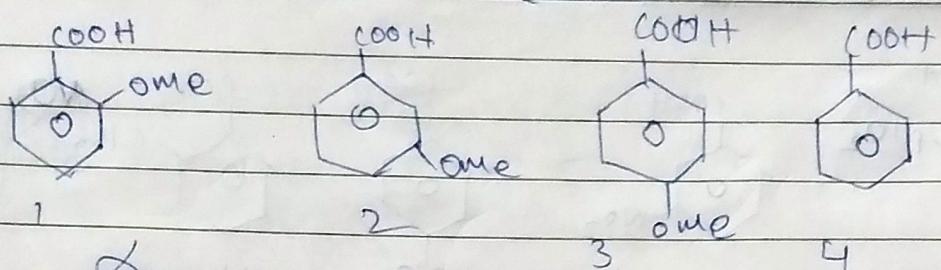
Date

Q2



$$2 > 1 > 3 > 4$$

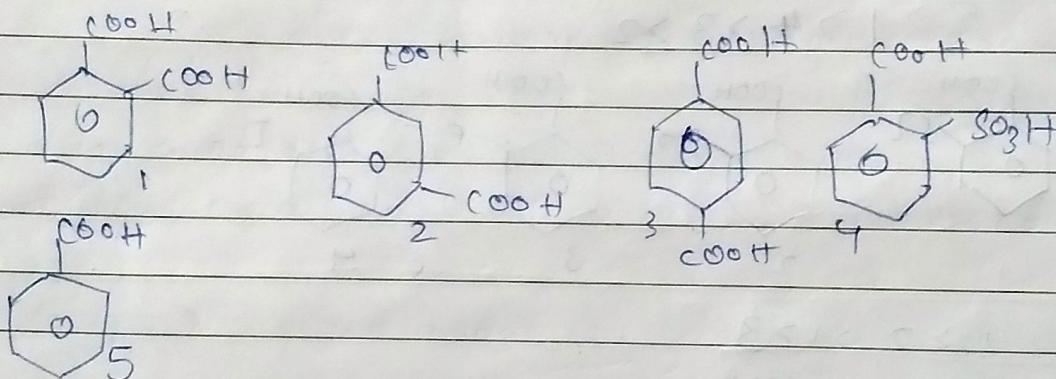
~~H.W.~~



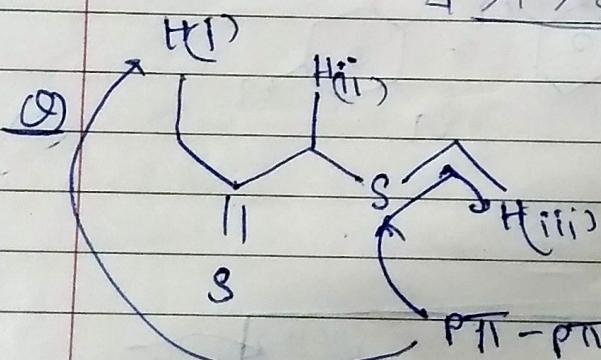
$$4 > 2 > 1 > 3$$

$$2 > 4 > 1 > 3$$

Q3



$$4 > 1 > 3 > 2 > 5$$



$$i > ii > iii$$

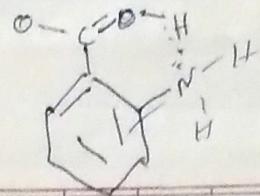
$$\text{PII} - \text{PI} > \text{dPII} - \text{dPI}$$

hence  $(i) > (ii)$



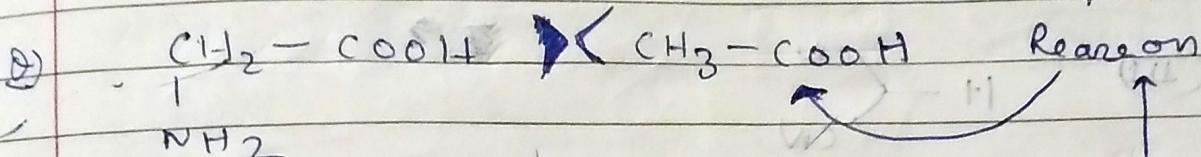
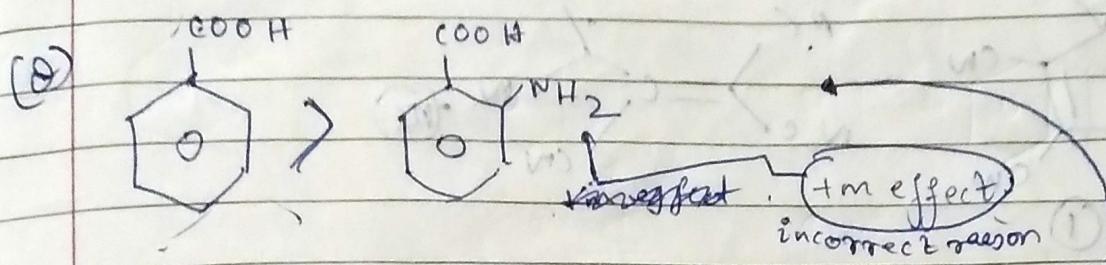
Only alcohol more acidic than water is  $\text{CH}_3\text{OH}$  due to more solvation energy.

9<sup>th</sup> May

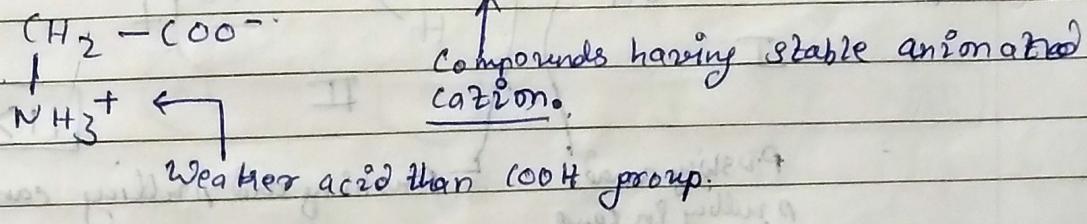


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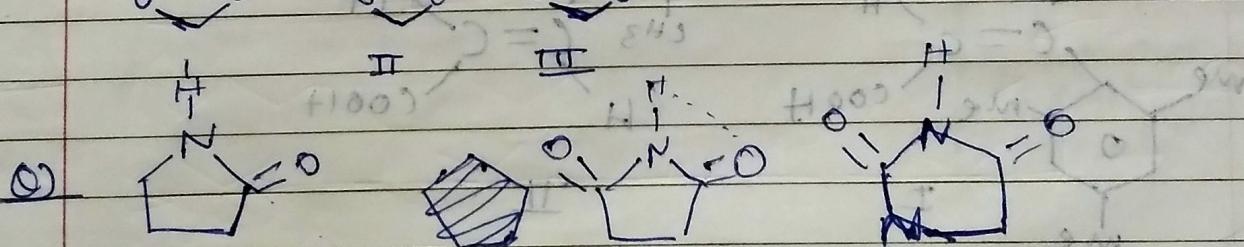
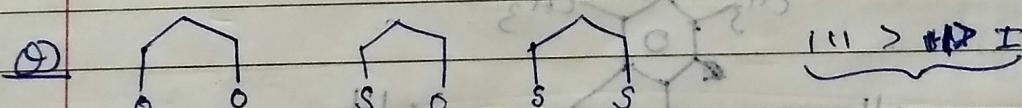
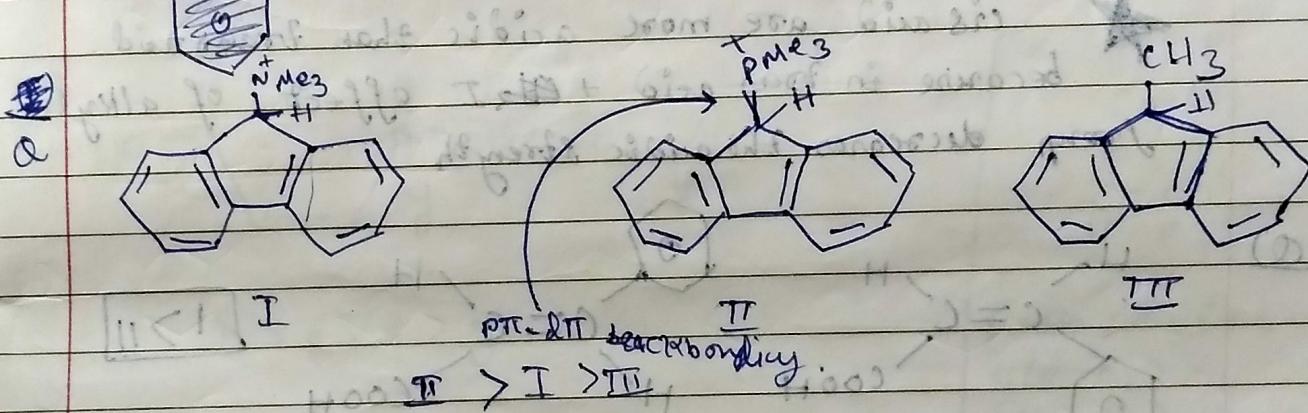
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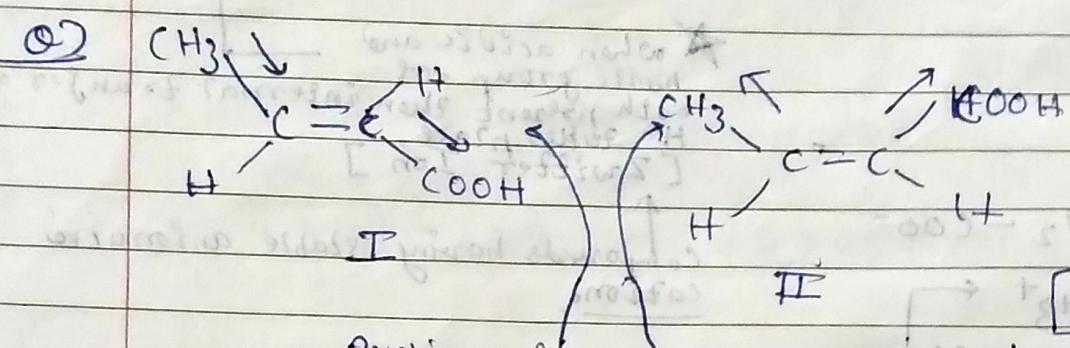
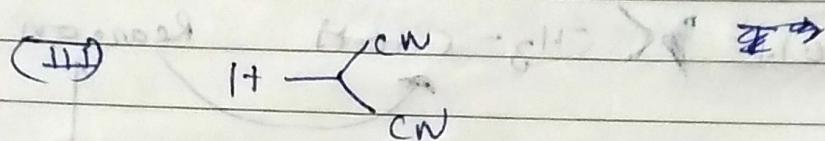
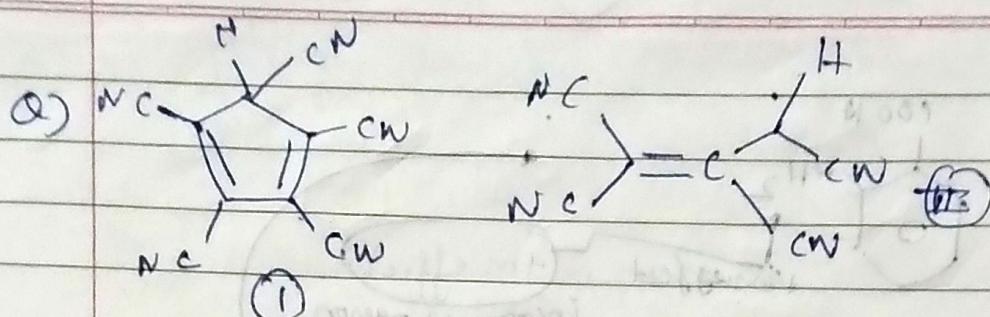
\* When acidic and basic group are both present then internal transfer of  $\text{H}^+$  takes place [Zwitter Ion]



(Q) \* Zwitter ion not possible on para



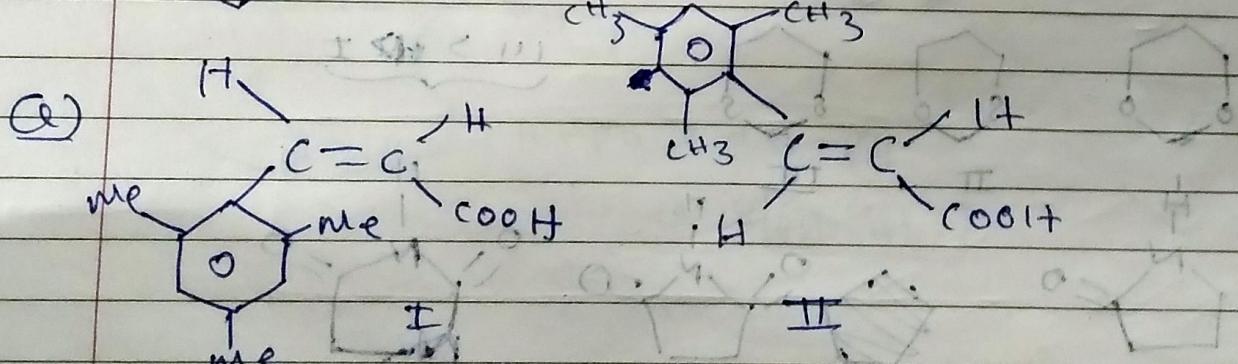
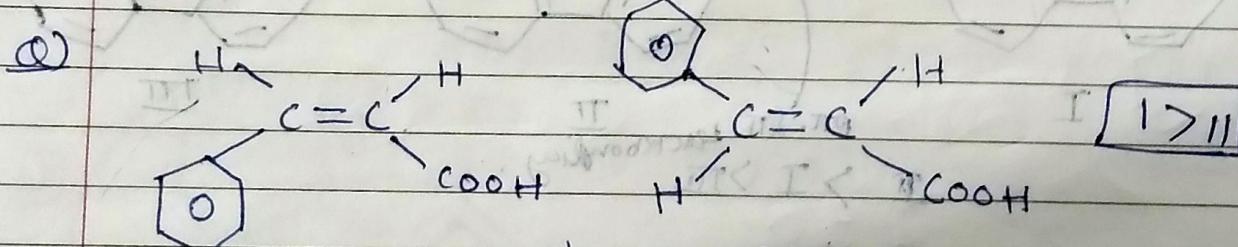
$\text{II} > \text{III} > \text{I}$  because  $\text{I}$  of  $\text{NHO}_2 > \text{I}$  of  $\text{amide}$



Pushing and pulling cancel.

Dipole addition

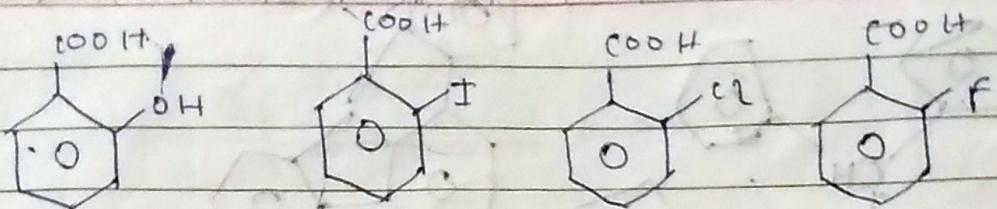
\* cis acid are more acidic than trans acid.  
because in ~~trans~~ acid + ~~H~~, I effect of alkyl group decreases the acidic strength.



This time  $|II| > |I|$  because of steric hindrance in case I.

\* Sterically hindered cis acid is more acidic than trans acid.

(1)



$$2 > 3 > 1 > 4$$

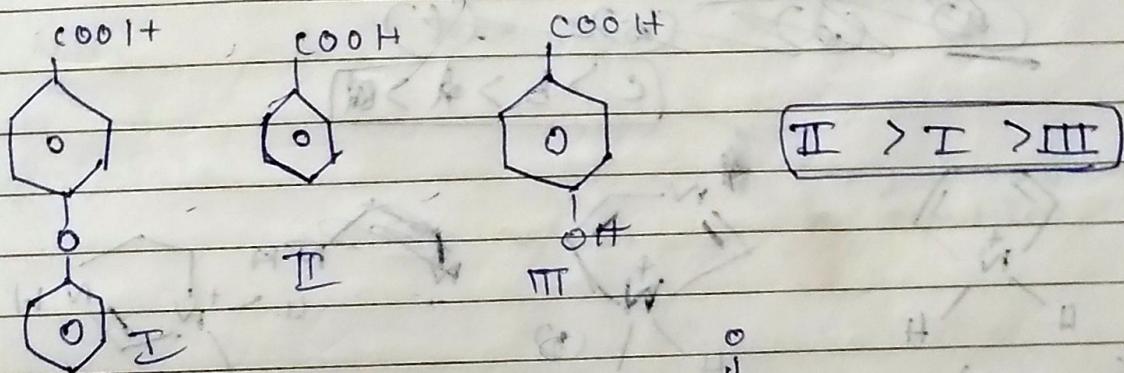
Ortho effect. H-bonding so  $\text{II} > \text{I} > \text{III} > \text{IV}$

present priority

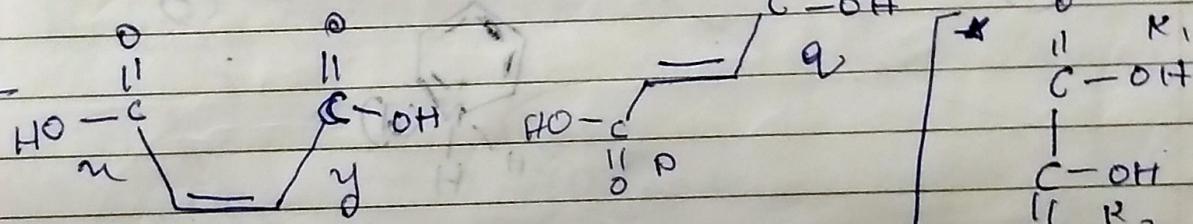
Priority

Ortho effect > H-bonding.

(2)



(3)



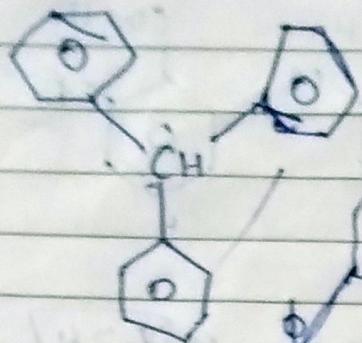
$x > y > z$

(4)

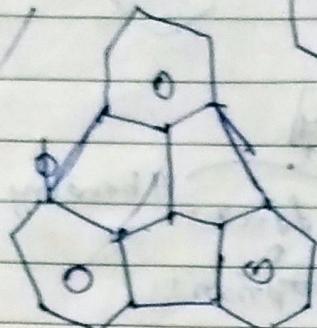
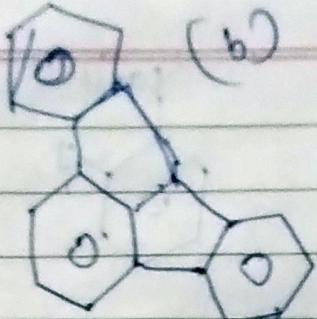
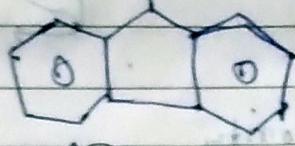
[In diacarboxylic acid  $K_1 > K_2$  faster first H loss is greater than N<sub>2</sub>] because after the loss of 1 H<sup>+</sup> ion H atom of another COO+ group is stabilized intramolecular H-bonding.

(a)

3)



(b)

CH<sub>3</sub>

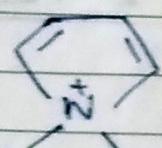
(d)

(c)

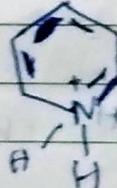
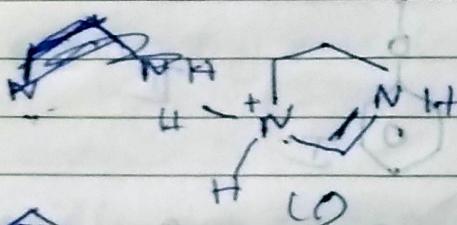
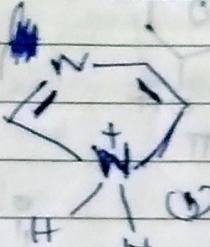
(b) &lt; (d) &lt; (c) &lt; (a)

 $c > b > d > a$ 

(e)



(a)



(b)

 $a > d > b > c$