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NET/SET/GATE/JAM

CHEMISTRY CLASSES

NOTES

BY

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Basics of Organic Chemistry

- → Inductive
- → Resonance
- → Steric effect
- → Hyperconjugation
- → Reactive Intermediate stability
- → Acidity & Basicity
- → Heat of combustion & Hydrogenation.

I] ⇒ Inductive effects :-

Polarisation of one bond by the influence of an adjacent polar bond or group is known as Inductive effect.

$CH_3 - CH_2 - CH_3$ (Non polar) $CH_3 \rightarrow CH_2 \rightarrow CH_2 \rightarrow Cl$ (Polar)

→ Characteristic of Inductive effect.

- Permanent effect
- Operates through sigma (σ) bond.
- Distance ↑ses, inductive effect ↓ses.

Inductive effect classified on the basis of two groups :- +I & -I

→ Negative Inductive effect (-I) group

The atom or group which withdraw electron density towards itself is called -I group.

$-\overset{\oplus}{N}F_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{S}R_2 > -\overset{\oplus}{N}H_3 > -NO_2$

$> -SO_3H > -CN > -\overset{O}{\overset{\|}{C}}-Cl > -\overset{O}{\overset{\|}{C}}-H > -\overset{O}{\overset{\|}{C}}-R$

$> -\overset{O}{\overset{\|}{C}}-OH > -F > -Cl > -Br > -I > -OR$

$> -OH > -C\equiv CH > -NH_2 > -ph > -CH=CH$

II) Positive Inductive effect. (+I group) (2)

The groups which donates electron is known as +I effect group.

$$-O^{\ominus} > -\underset{\underset{O}{\|}}{C}-O^{\ominus} > -\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 > -\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-H$$

$$> -CH_2-CH_3 > -CH_3 > -T > -D > -H$$

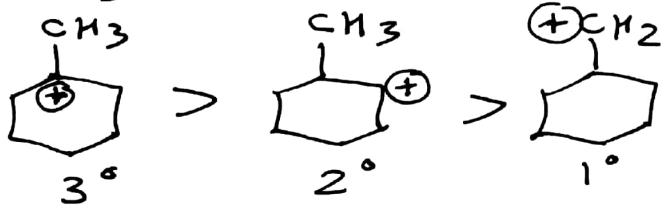
Application of Inductive effect.

a) Stability of Carbocation.

$$\overset{\oplus}{\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}}-CH_3 > \overset{\oplus}{\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}}-H > \overset{\oplus}{\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}}-CH_3 > \overset{\oplus}{C}H_3$$

Decreasing stability [3° > 2° > 1° > alkyl]

[+I group ∝ Stability of carbocation]



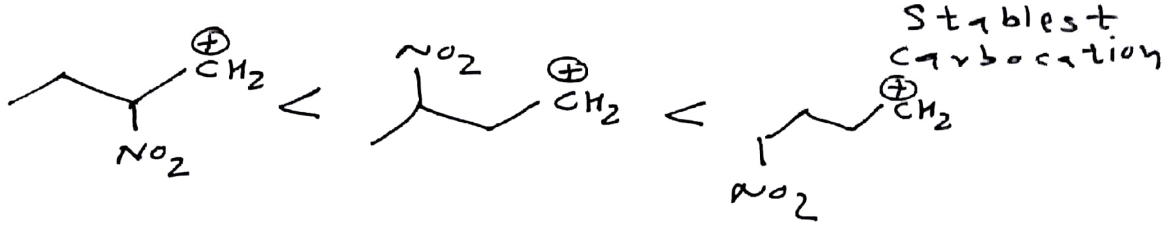
$$\overset{\oplus}{C}T_3 > \overset{\oplus}{C}D_3 > \overset{\oplus}{C}H_3$$

[−I group ∝ $\frac{1}{\text{Stability of carbocation}}$]

$$\overset{\oplus}{C}H_2-CH_3 > \overset{\oplus}{C}H_2-CH_2-Cl > \overset{\oplus}{C}H_2 > \underset{\underset{Cl}{|}}{CH}-Cl$$

$\overset{\oplus}{C}H_2-NO_2 < \overset{\oplus}{C}H_2-CN < \overset{\oplus}{C}H_2-F < \overset{\oplus}{C}H_2-Cl$

Stablest carbocation



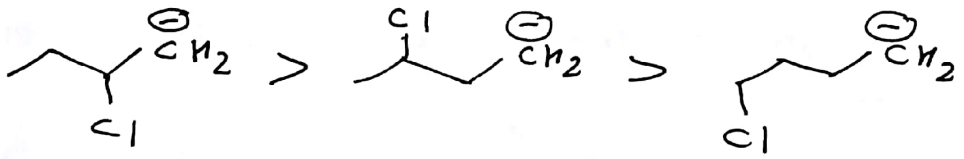
Stability of Carbanion :-

- $-I$ group $\propto$ Stability of carbanion
- $+I$ group $\propto \frac{1}{\text{Stability of Carbanion}}$

$\overset{\ominus}{C}H_3 > \overset{\ominus}{C}H_2-CH_3 > \overset{\ominus}{C}H(CH_3)_2 > \overset{\ominus}{C}(CH_3)_3$

$\overset{\ominus}{C}H_3 > \overset{\ominus}{C}D_3 > \overset{\ominus}{C}T_3$

$\overset{\ominus}{C}Cl_3 > \overset{\ominus}{C}HCl_2 > \overset{\ominus}{C}H_2Cl > \overset{\ominus}{C}H_3$



$CH_3-\overset{\ominus}{C}H_2 < CH_2=\overset{\ominus}{C}H < HC\equiv\overset{\ominus}{C}$

sp^3 sp^2 sp — most stable.

$S\% = 25\%$ $S = 33\%$ $S = 50\%$

[$S\% \propto$ Electronegativity]

Strength of aliphatic carboxylic acid.

$$A-H \rightleftharpoons A^{\ominus} + H^{\oplus}$$

$$R-\underset{\underset{O}{\|}}{C}-OH \rightleftharpoons R-\underset{\underset{O}{\|}}{C}-O^{\ominus} + H^{\oplus}$$

Ionisation of [A-H] increases, acidic strength increases & or pka decreases.

$$K_a = \frac{[A^{\ominus}]\,[H^{\oplus}]}{[A-H]}$$

$[H^+]$ or acidity $\propto K_a$, $K_a \propto [A^{\ominus}]$

[Acidity $\propto$ Conjugate base stability]

$$\left\{\begin{array}{l} -I \text{ group} \propto \text{acidity} \\ +I \text{ group} \propto \dfrac{1}{\text{acidity}} \end{array}\right\}$$

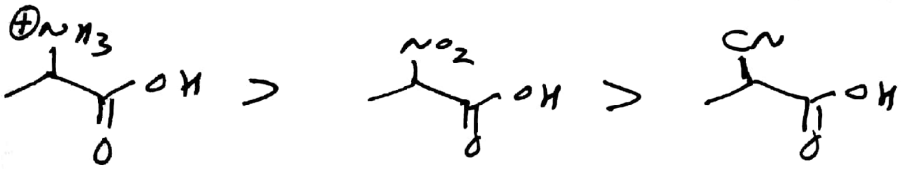
$$H-\underset{\underset{O}{\|}}{C}-OH > CH_3-\underset{\underset{O}{\|}}{C}-OH > CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OH$$

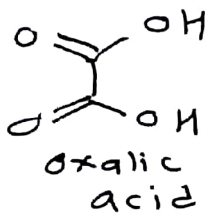
$$H_3C-\underset{\underset{O}{\|}}{C}-OH < Cl-CH_2-\underset{\underset{O}{\|}}{C}-OH < Cl_2CH-\underset{\underset{O}{\|}}{C}-OH < Cl_3C-\underset{\underset{O}{\|}}{C}-OH$$

pka = 4.8 pka = 2.8 pka = 1.3 pka = 0.9

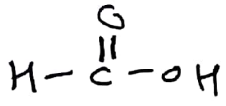
[Acidity ↑ses pka ↓ses]

$$F-CH_2-\underset{\underset{O}{\|}}{C}-OH > Cl-CH_2-\underset{\underset{O}{\|}}{C}-OH > Br-CH_2-\underset{\underset{O}{\|}}{C}-OH$$



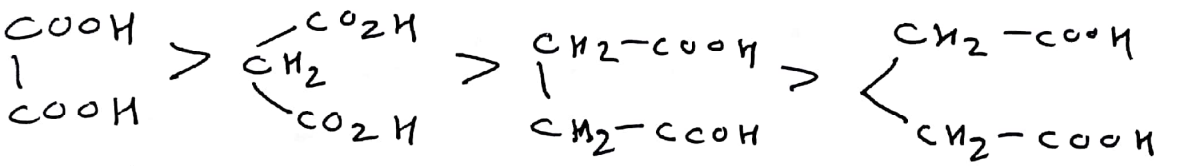


oxalic acid

> 

formic acid

Dibasic acid



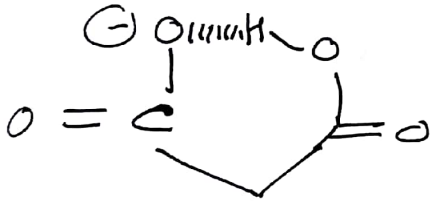
~~$pKa_1 = 1.27$~~ ~~3.86~~

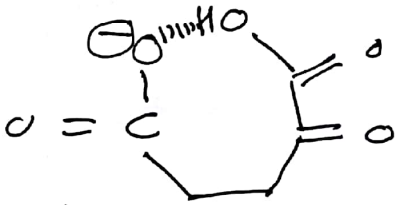
~~$pKa_2 = 4.27$~~

oxalic acid — malonic acid — Succinic acid — Glutaric acid

$pKa_1 = 1.27$ $pKa_1 = 2.86$ 4.21 4.34

$pKa_2 = 4.27$ $pKa_2 = 5.7$ 5.61 5.27

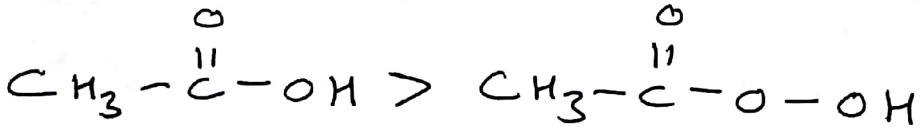




Stabilized by Intramolecular H-bonding

So $pKa_2 > pKa_1$ as well as

$[-COO^{\ominus}]$ group is +I & it uses acidity.



More acidic

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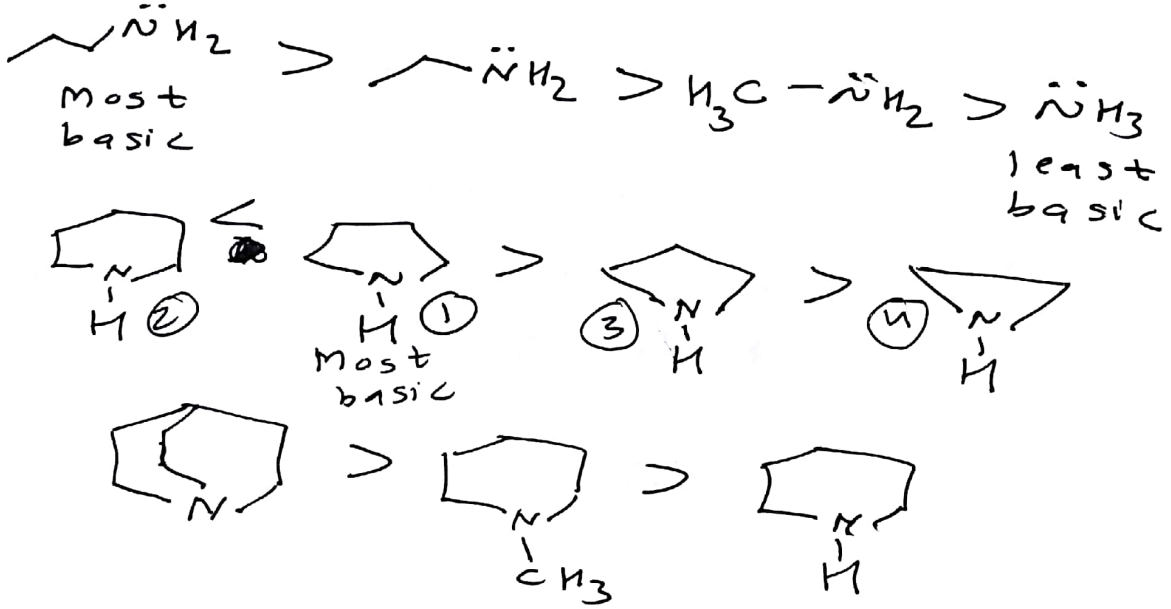
Basicity of alkyl amine.

$$R-\ddot{N}H_2 + H^+ \rightleftharpoons R-\overset{\oplus}{\ddot{N}}H_3$$

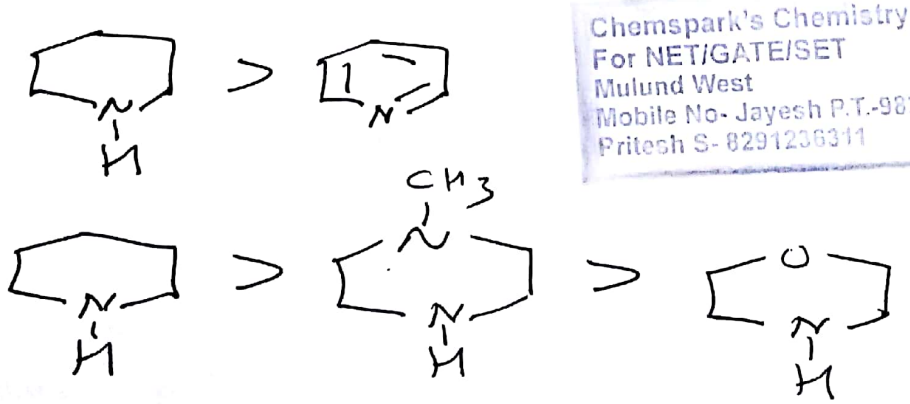
- +I group $\propto$ Stability of ammonium $\propto$ basicity
- −I group $\propto \frac{1}{\text{basicity}}$



$$CH_3-\ddot{N}H_2 > ClCH_2-\ddot{N}H_2 > Cl_2CH-\ddot{N}H_2 > Cl_3C-\ddot{N}H_2$$

$$H_3C-\ddot{N}H_2 > H_2C=\ddot{N}H > HC\equiv\ddot{N}$$

(sp^3 > sp^2 > sp)



Alkyl amine basicity in gas phase

$3^\circ > 2^\circ > 1^\circ$ alkyl amine $> NH_3$

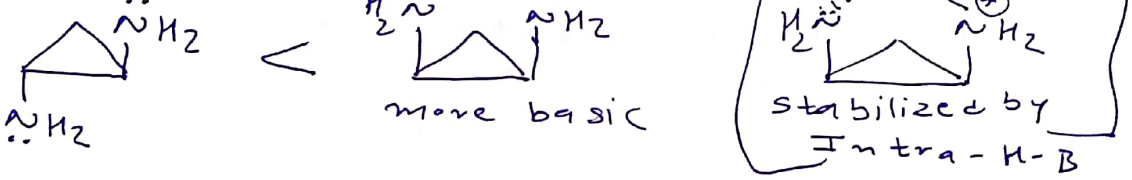
Alkyl amine basicity in Aqueous / solution phase

$CH_3 \longrightarrow HN(CH_3)_2 > CH_3-NH_2 > (CH_3)_3N > NH_3$

$C_2H_5 \longrightarrow HN(Et)_2 > (Et)_3N > Et-NH_2 > NH_3$

$ipr \longrightarrow ipr-NH_2 > NH_3 > (ipr)_2NH > (ipr)_3N$

$t\text{-}Bu \longrightarrow NH_3 > 1^\circ > 2^\circ > 3^\circ$

→ 

→  Basicity order

Hydrophobicity
Solvation
+I

Resonance Effect:

It is a phenomenon in which a particular compound can be written in two or more structures with identical position of atoms. These lewis structures are called resonating / canonical / contributing structures.

Resonating Structure
Imaginary structure.

Resonance hybrid
Real Structure

→ Resonance hybrid is more stable than resonating structure.

→ Most stable resonating structure contribute maximum to resonance hybrid & least stable resonating structure contribute minimum to resonance hybrid.

Resonance energy:-

→ The Potential energy difference between the most stable resonating structure & resonance hybrid is called resonance energy.

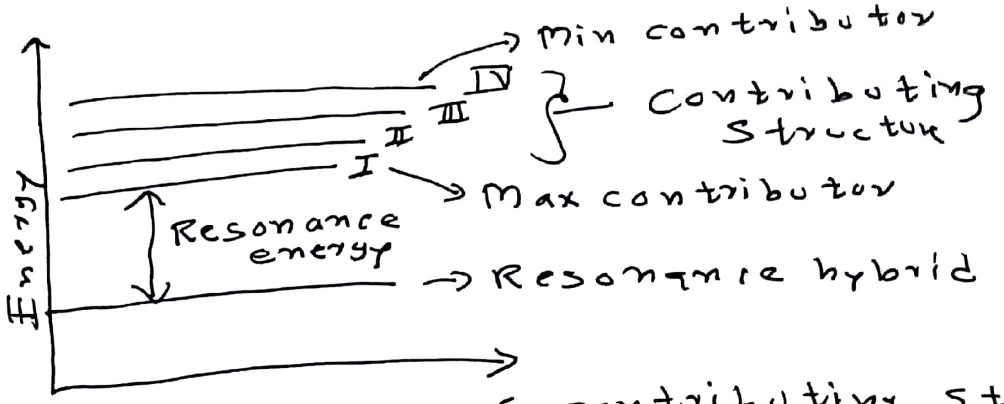
→ Stability of molecule is directly proportional to resonance energy.

Condition for Resonance

→ All atoms participating in resonance must be sp or sp^2 hybridized.

→ Parallel p-orbitals overlap to each other.

→ Molecule should have conjugated system.



Resonance energy of contributing structure.

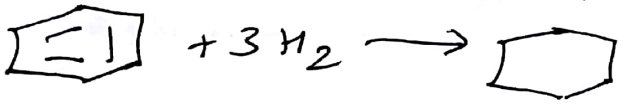
Hydrogenation of Benzene

→ Hydrogenation of cyclohexene is exothermic by 120 kJ/mol (28.6 kcal/mol)

→ Hydrogenation of 1,4-cyclohexadiene is exothermic by 240 kJ/mol (57.4 kcal/mol) The resonance energy is zero for isolated double bond.

→ Hydrogenation of 1,3-cyclohexadiene is exothermic by 232 kJ/mol (55.4 kcal/mol) about 8 kJ (1.8 kcal) less than twice the value of cyclohexene.
Resonance energy = 8 kJ (1.8 kcal)

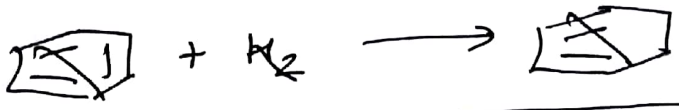
→ Hydrogenation of benzene requires higher pressure of H_2 & active catalyst. Hydrogenation is exothermic by 208 kJ/mol (49.8 kcal/mol), about 151 kJ (36 kcal/mol) less than 3 times the value of cyclohexene.

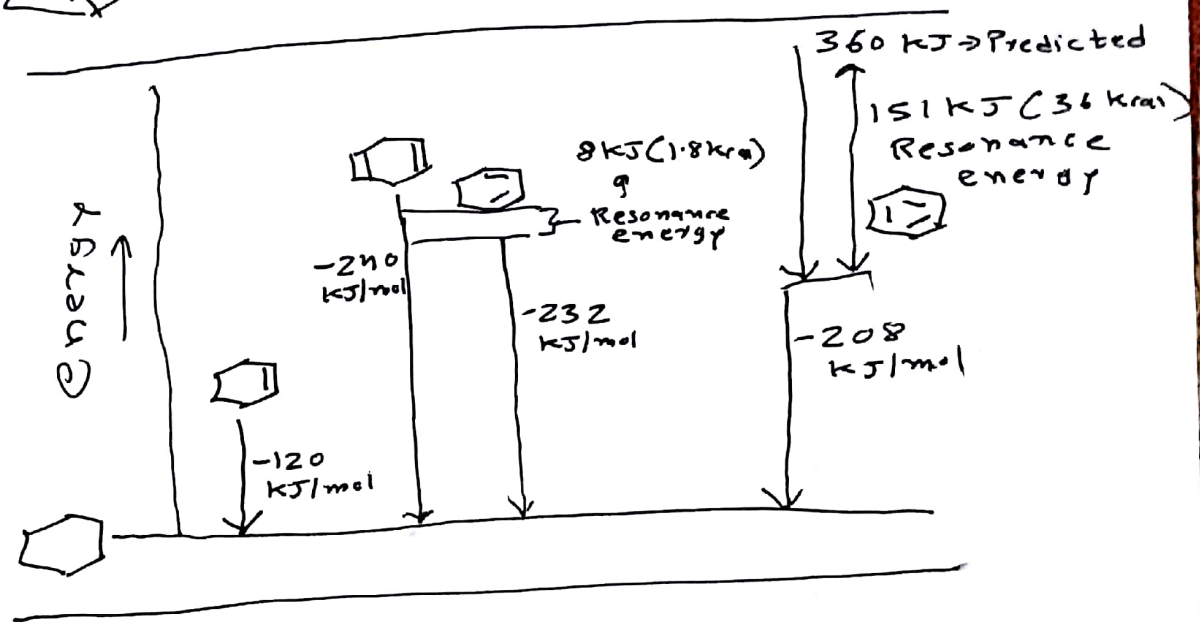


ΔH° = 208 kJ/mol

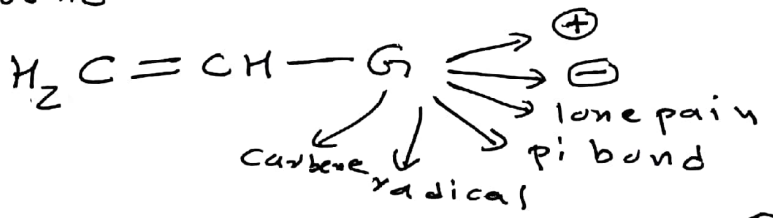
3 × cyclohexene = 359 kJ/mol

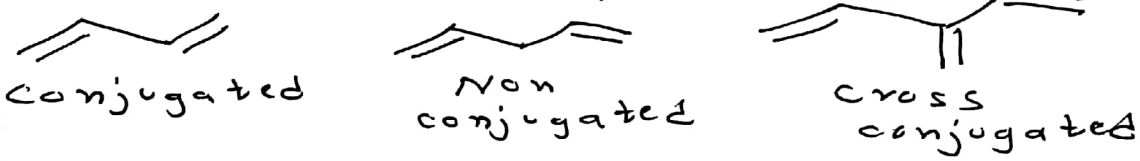
Resonance energy — 151 kJ/mol

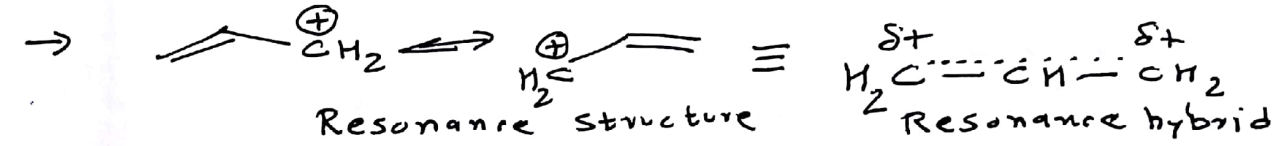


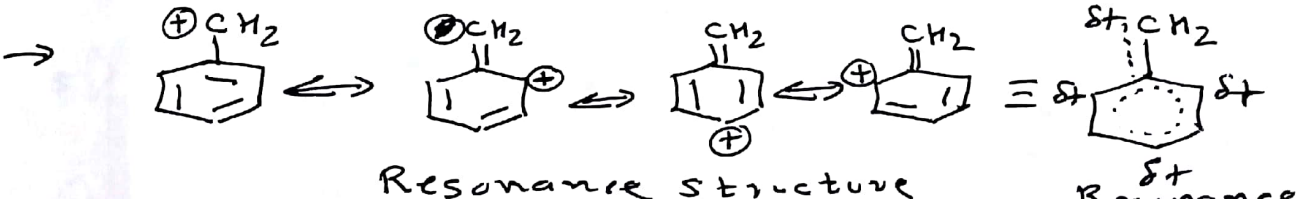


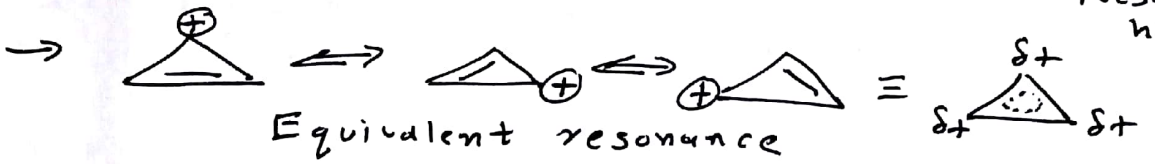
"For a compound to show resonance, compound should be conjugated"

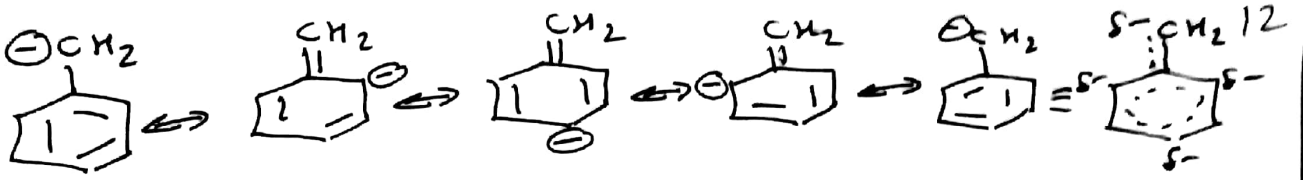


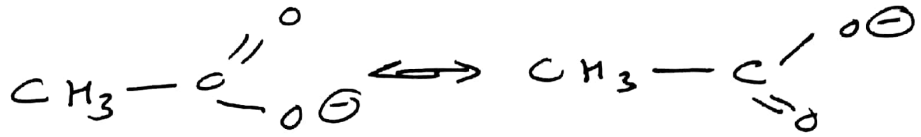


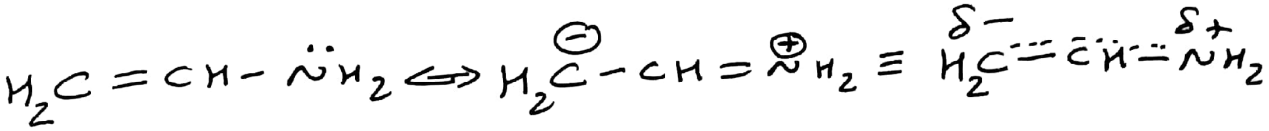


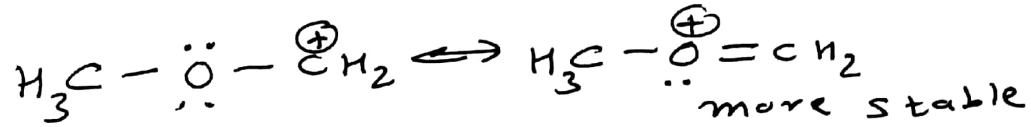




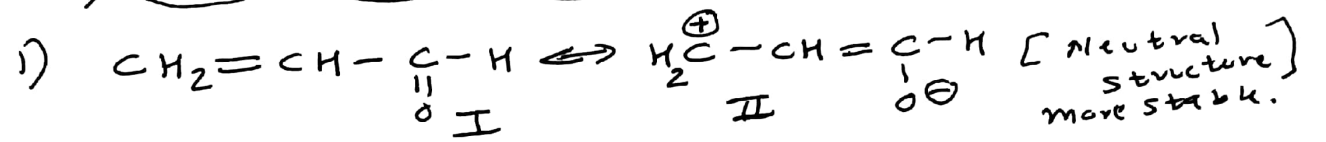






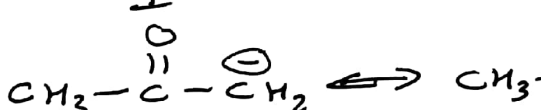


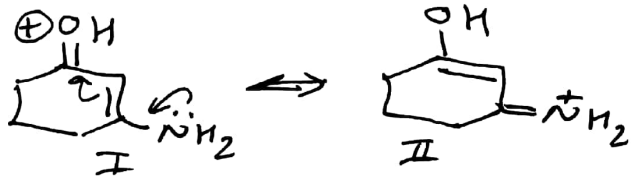
Relative stability of Resonance Structure

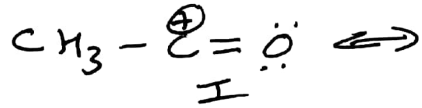
1) 
[Neutral structure more stable.]

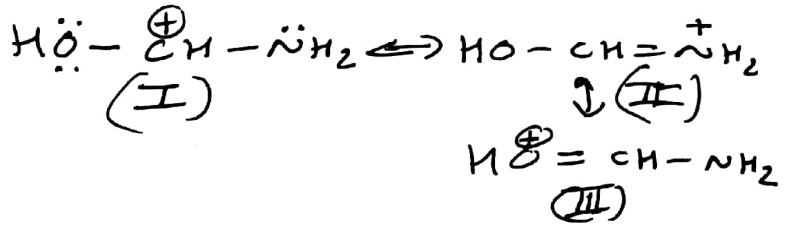
Stability I > II

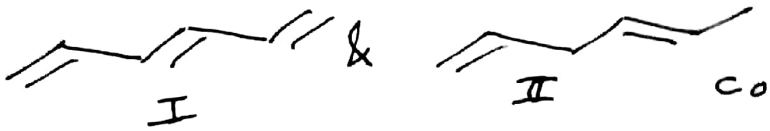
2) 
Stability order
II > I
[octet rule]

3) 
Stability order
II > I
[-ve charge on O]

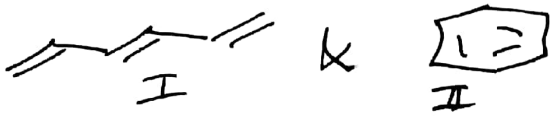
4) 
Stability order
II > I
[+ve charge on N]

5) 
II > I
octet rule

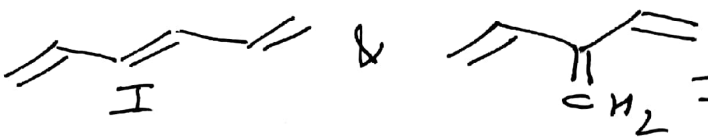
6) 
Stability
II > III > I



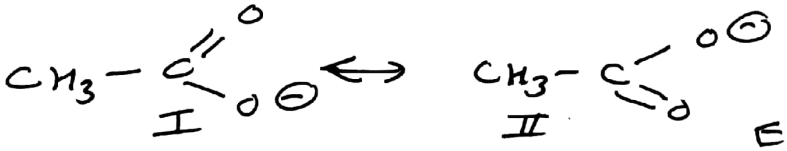
I > II
conjugated



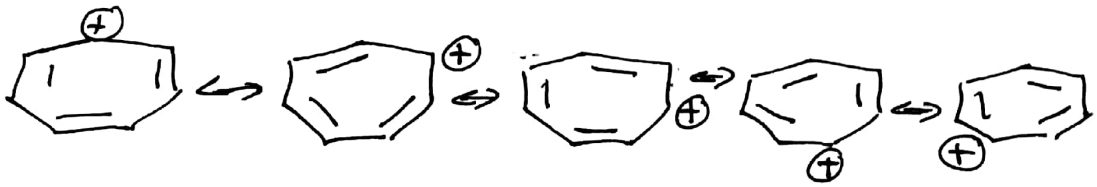
II > I
cyclic aromatic



I > II
linear conjugation



I = II
Equally stable.



7 → Equivalent resonance.

Mesomeric / Resonance Effect

→ +m / +R group [Electron donating]

$-\overset{\ominus}{O} > -\ddot{N}H_2 > -\ddot{N}HR > -\ddot{N}R_2$

$> -\ddot{O}H > -\ddot{O}R > -\ddot{N}HCOR$

$> \ddot{O}COR > -ph > F > Cl > Br > I > -\ddot{N}O$

→ −m / −R group [Electron withdrawing]

$-NO_2 > -CN > SO_3H > -CHO > -\overset{O}{\overset{\|}{C}}-R$

$> -\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}- > -\overset{O}{\overset{\|}{C}}-OR > -\overset{O}{\overset{\|}{C}}-OH$

$> -\overset{O}{\overset{\|}{C}}-NH_2$

→ Permanent effect.

→ Distance ↑ses, resonance effect ↑ses.

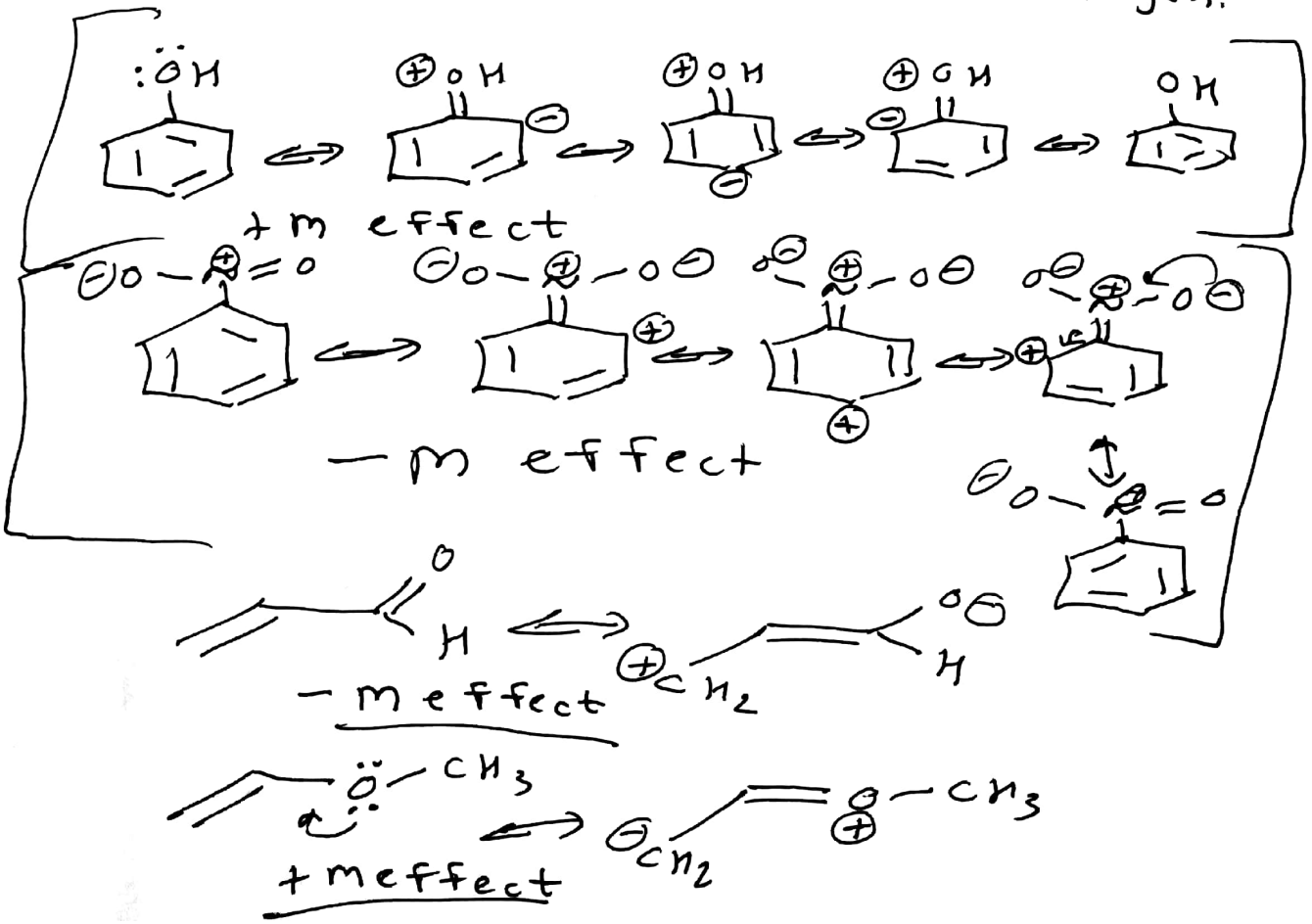
↔ mesomeric effect is dominant over Inductive & Hyperconjugation

→ +m & -m groups are always in conjugation with benzene ring at ortho & para positions.

+m group :- donate e⊖ at ortho & para

-m group :- withdraw e⊖ at ortho & para.

↔ In case of Halogen, orientation of Electrophile depends on +m effect of halogen & acidic, basic properties decided by -I effect of halogen.



Hyperconjugation / Sigma bond resonance / no-bond resonance / Baker-Nathan effect

When a sigma C-H bond of sp^3 hybridised carbon is in conjugation with π-bond / p-orbital, then the bond pair $e^\ominus$ of sigma C-H bond overlap with adjacent p-orbital. This phenomena is called Hyperconjugation.

→ It takes place in alkene, carbocation, carbon free radicals, Toluene derivative.

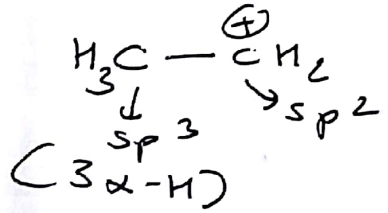
→ Hyperconjugation is less dominating than resonance effect.

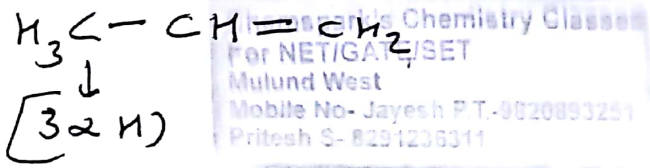
Condition for Hyperconjugation

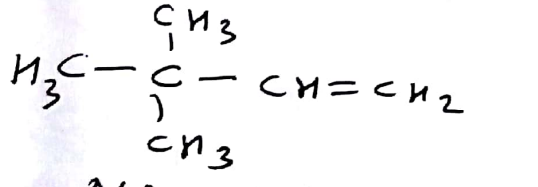
→ Compound should have atleast one sp^2 carbon

→ α-carbon w.r.t sp^2 hybrid carbon should be sp^3.

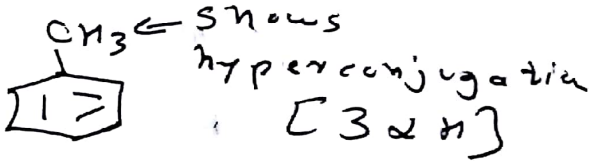
→ α-carbon should have atleast one hydrogen



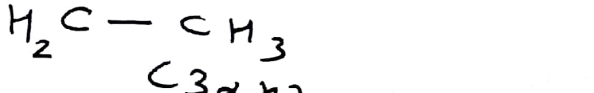


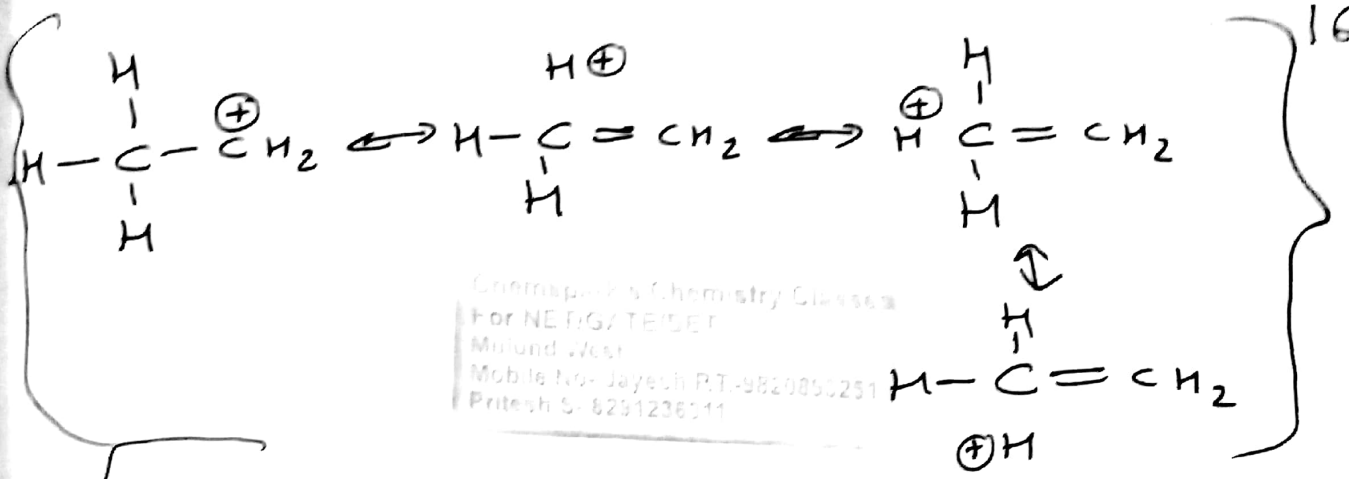


No α-hydrogen
No Hyperconjugation

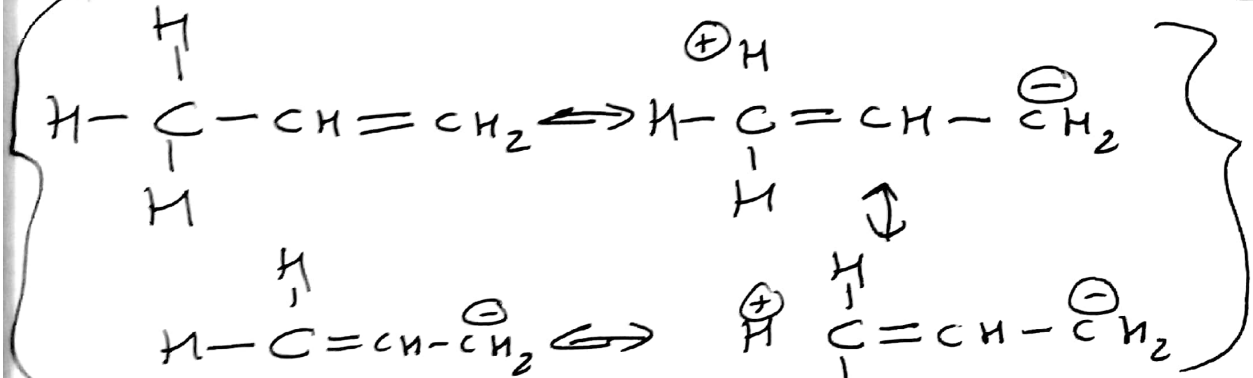


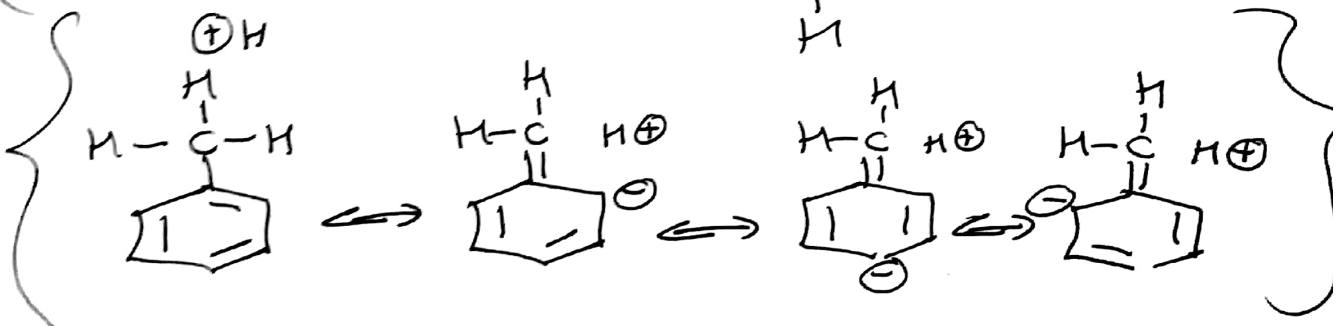
shows hyperconjugation [3α H]





Number of Hyperconjugation Structure = Number of alpha hydrogen + 1





Stability of Carbocation & alkene $\propto$ No. of alpha hydrogens

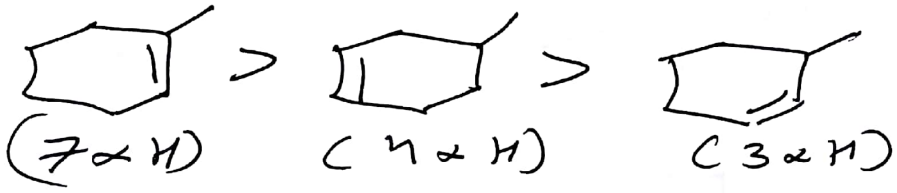
$(CH_3)_3\overset{\oplus}{C}$ > $(H_3C)_2\overset{\oplus}{C}H$ > $CH_3-\overset{\oplus}{C}H_2$ > $\overset{\oplus}{C}H_3$

(9 α-H) (6 α H) (3 α H) (0 α

most least

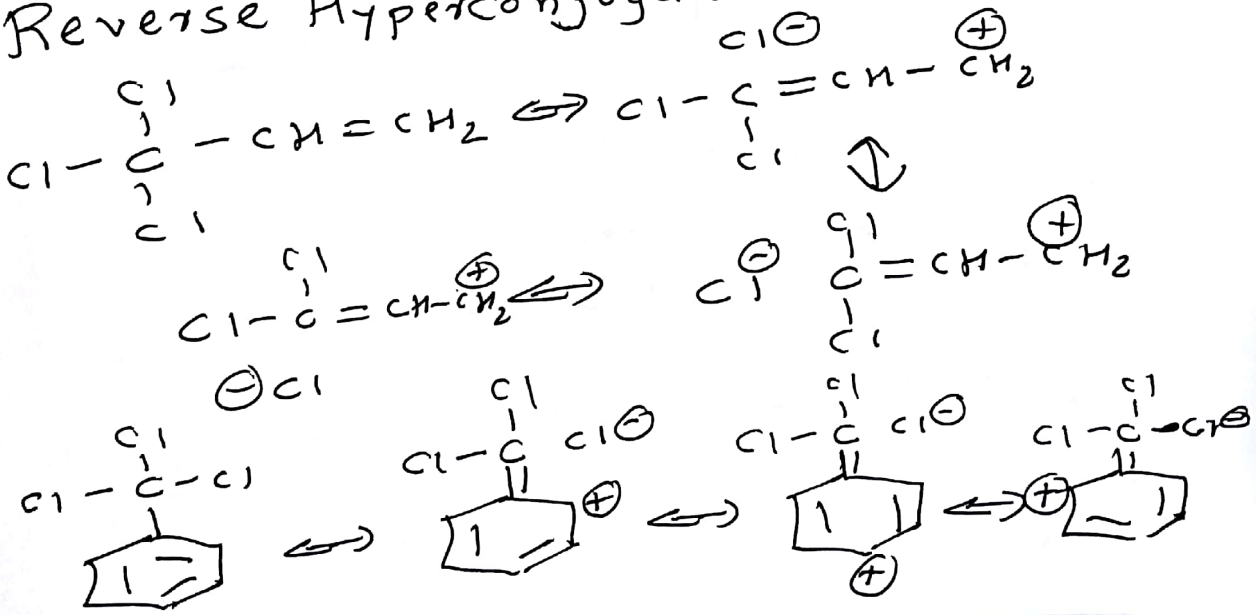
Alkene	No. of α-H
$H_2C=CH_2$	0
$H_3C-CH=CH_2$	3
$H_3C-CH=CH-CH_3$	6
$H_3C-C(CH_3)=C(CH_3)_2$	9
$(H_3C)_2C=C(CH_3)_2$	12

α-H ↑ ⇒ Stability ↑



Stability.

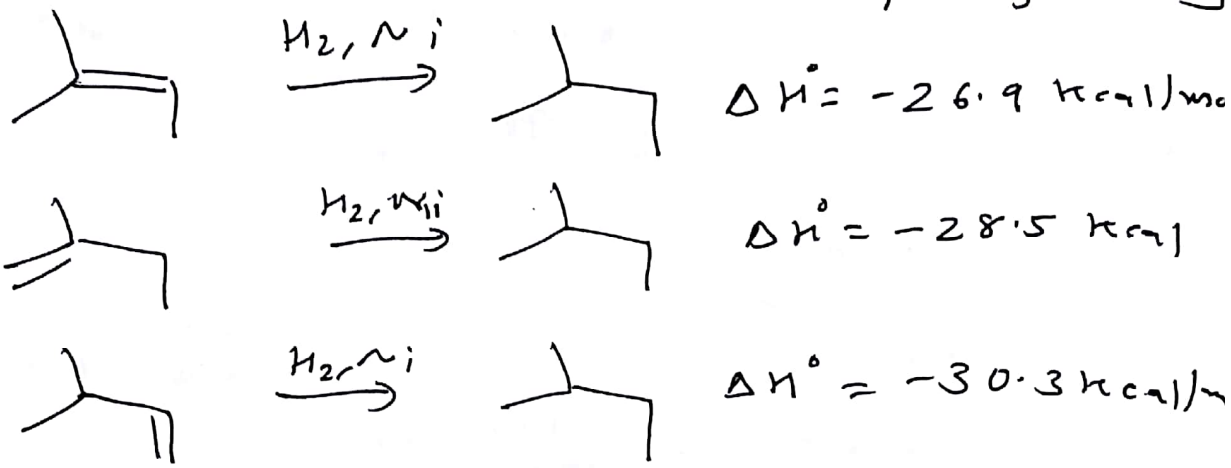
Reverse Hyperconjugation :-

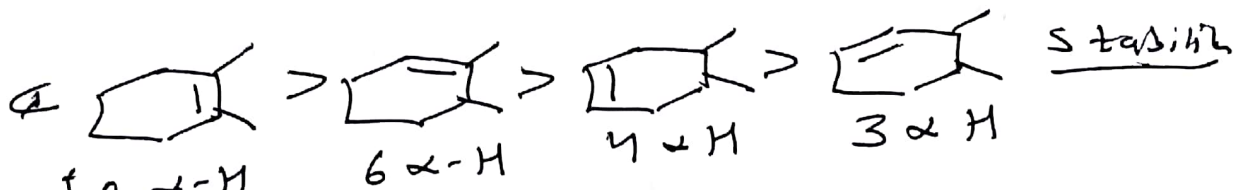


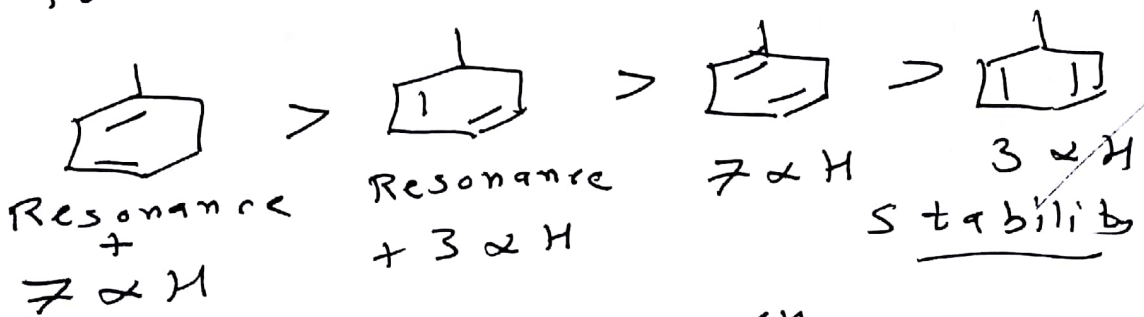
Heat of Hydrogenation

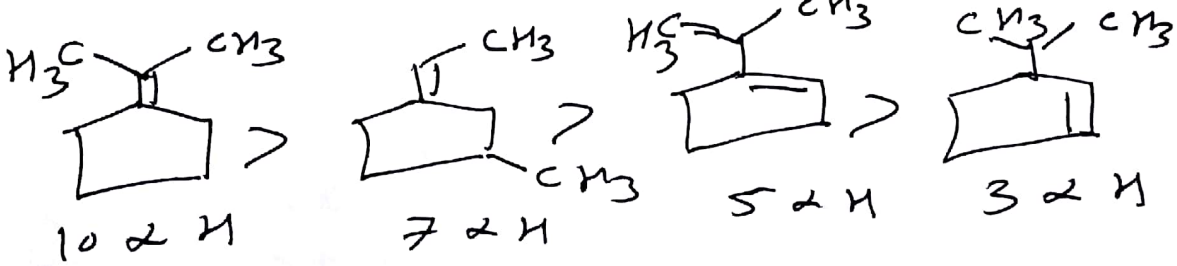
Heat released in hydrogenation reaction is called Heat of hydrogenata

[Stability of alkene $\propto$ No. of α-H $\propto \frac{1}{\text{Heat of hydrogenation}}$]





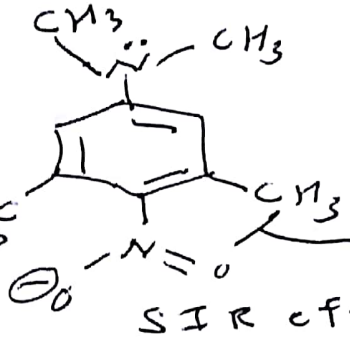




Steric Inhibition of Resonance (SIR effect)

became nonplanar

SIR effect

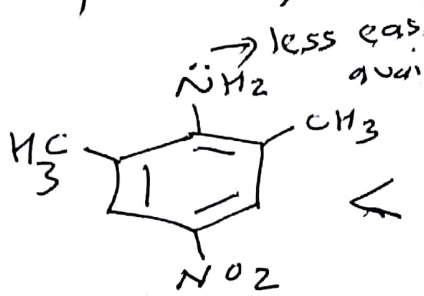


became non planar

SIR effect

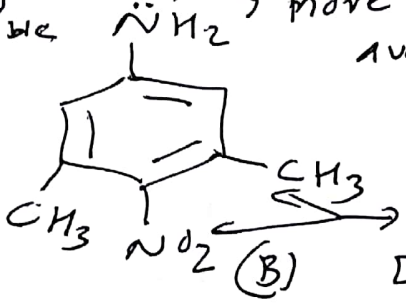
more stable due to planarity

goes out of the plane so cannot enjoy resonance of benzene.



less easily available

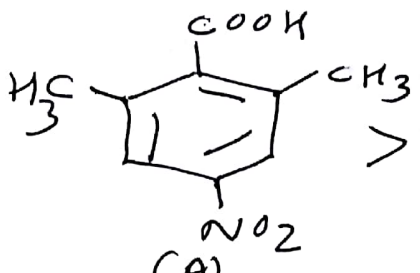
(A) less basic



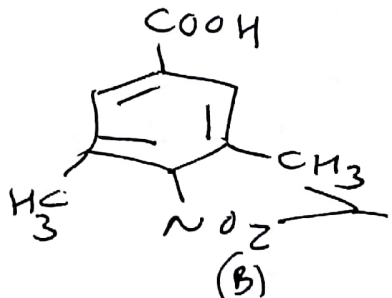
more easily available

(B) more basic

Steric crowding ($-NO_2$ group out of plane & ↓se resonance)



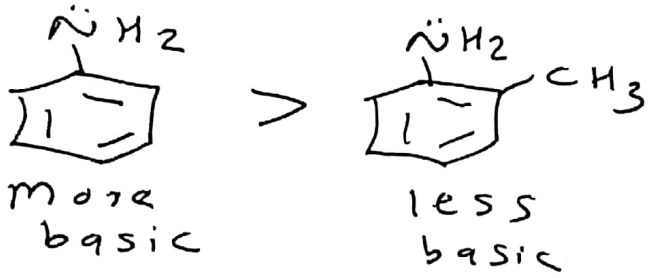
(A) strong acid



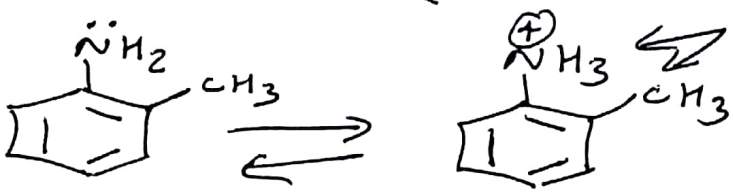
Steric crowding

(B) weak acid

Steric Inhibition of Protonation (SIP)

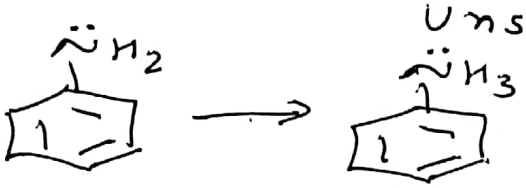


more basic — less basic



Steric crowding → Both group repel each other

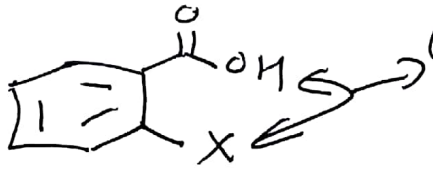
Unstable conjugate acid



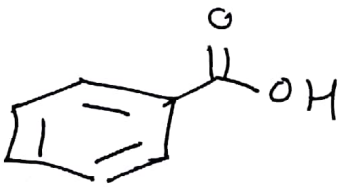
More stable conjugate acid

Ortho effect

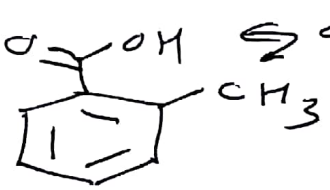
Any group present at ortho position of benzoic acid increases the acidity of benzoic acid.



(Due to repulsion between acid & X group, acid group get deviated from planarity & get devoid of resonance effect of benzene)

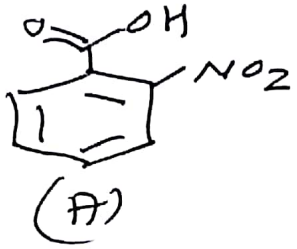


pKa = 4.17



ortho effect

pKa = 3.91

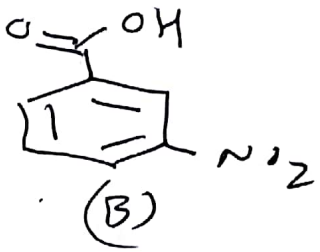


(A)

pka = 2.17

↓

due to ortho effect.



(B)

pka = 3.44

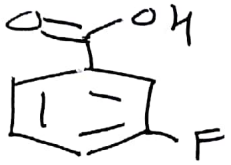
(C)

pka = 3.43

pka = 3.27

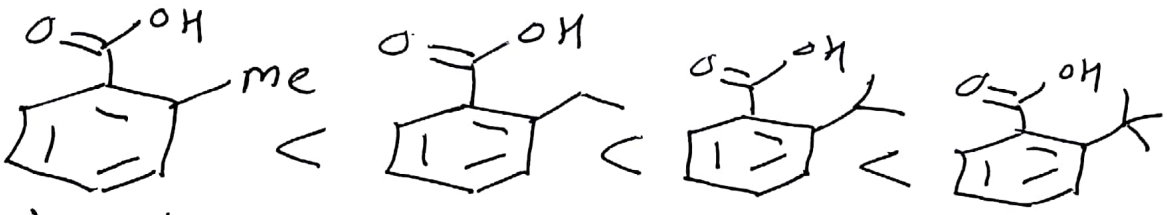
↓

due to ortho effect



pka = 3.87

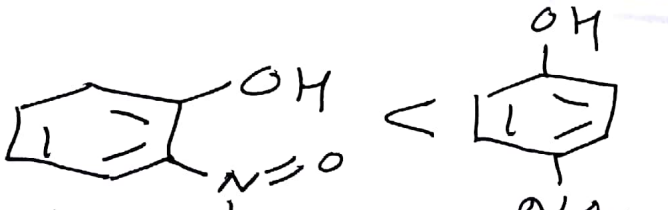
pka = 4.14



least acidic less bulky ortho.

most acidic Bulky ortho

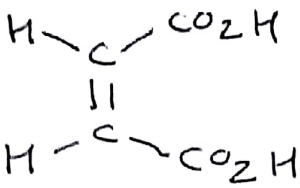
Hydrogen bonding



less acidic due to Intramolecular Hydrogen bonding.

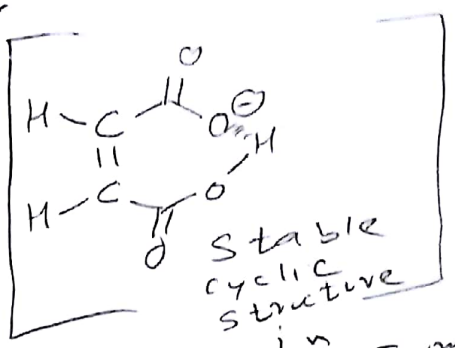
more acidic

Stereochemistry & Acidity.

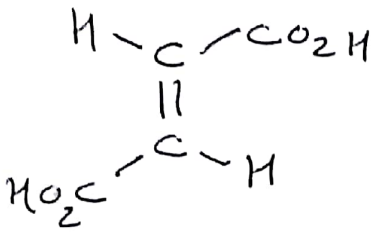


$pKa_1 = 2.04$

$pKa_2 = 6.23$

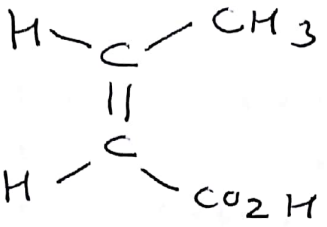


Stable cyclic structure in cis form

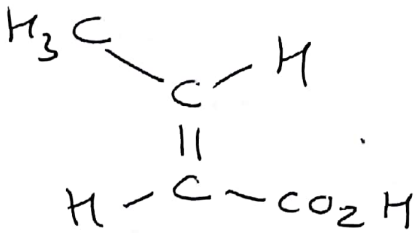


$pKa_1 = 3.02$

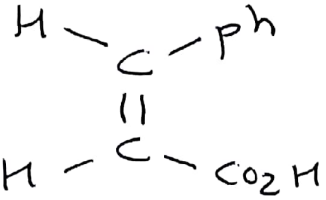
$pKa_2 = 4.38$



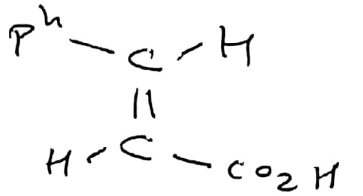
$pKa = 4.42$



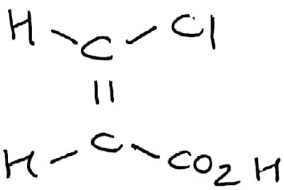
$pKa = 4.7$



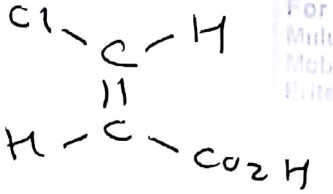
$pKa = 3.93$



$pKa = 4.50$

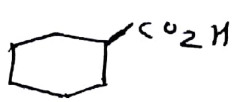


$pKa = 3.45$

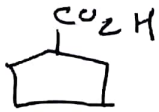


$pKa = 3.79$

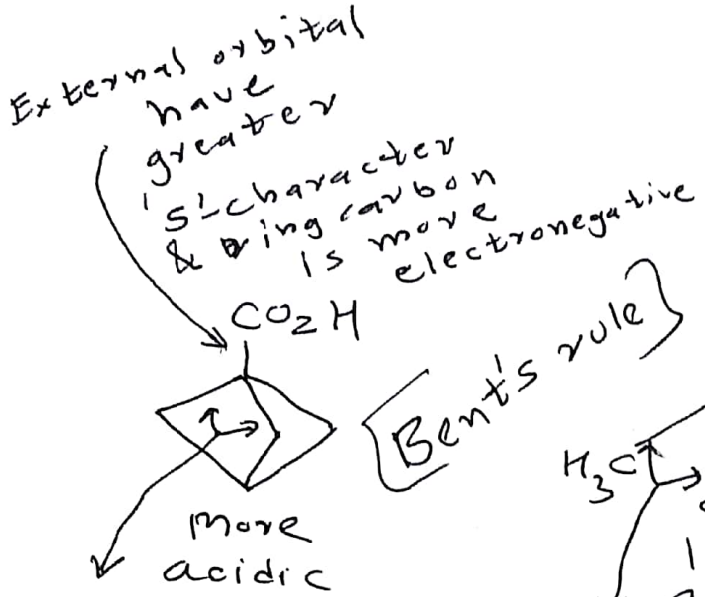
$pKa = \underline{4.83}$



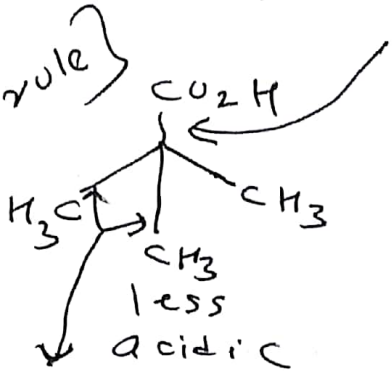
$pKa = \underline{4.91}$



$pKa = \underline{4.99}$



Bent's rule



C-C bond angles less than 109° due to ring size, Thus ring bonds have greater 'p' character

C-C bond angles greater than 109° due to steric-buttressing Thus C-C bonds have greater 's' character.

Miscellaneous examples on acidity, basicity, reactive intermediate Stability.

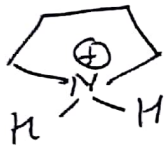
Q-1 → Correct order of pka values of conjugate acids.

a)  b)  c)  d) 

Soln :-

$$\left[pka \propto \frac{1}{acidity} \right]$$

 → Aromaticity is lost so try to regain it after H^+ donation so its a best acid among all

 → Its better base so its conjugate acid is weak & have highest pka among all.

 → Its poorer base and better acid than pyrrolidine due to angle strain & torsional Strain.

 → Its aromatic in nature even after donation of electron.

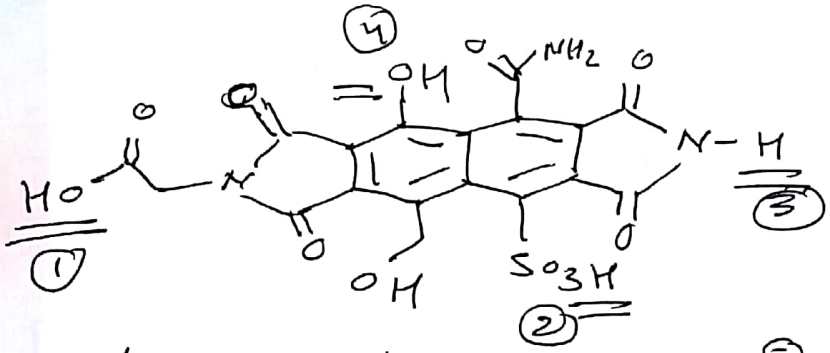
[Aromatic amine is poorer base & better acid than alicylic amine so its take 2nd position in acidity.]

{Conjugate acid of bases}

$$[c > b > d > a]$$ pka order using → Conjugate acid pka order

$$[c > b > d > a]$$ → Basicity order of bases.

Q→ Amount in grams of NaOH (m.w = 40) is required for complete neutralisation of one mole of following compound is

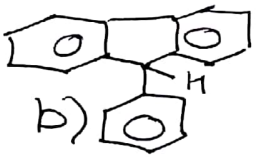


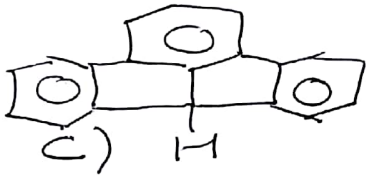
1 g eq H^+ & 1 g eq OH^- react to form H_2O.

There are 4 acidic H^+ ions

So amount of NaOH = 4 × 40 g = 160 g

Q→

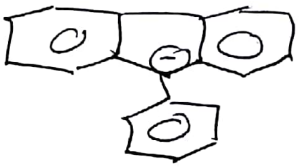




Acidity ?

Soln:- P c > b > a [acidity]

a > b > c [pKa]

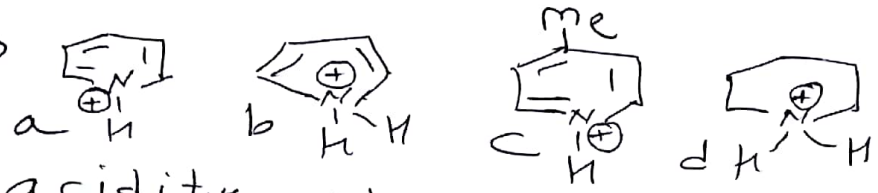


→ All conjugate bases are aromatic

→ Carbanions of 'b' & 'c' stabilised by three benzene rings resonance. but carbanion of 'c' is more planar than 'b'

→ Carbanion 'a' is planar & stabilized by two rings

→ ∴

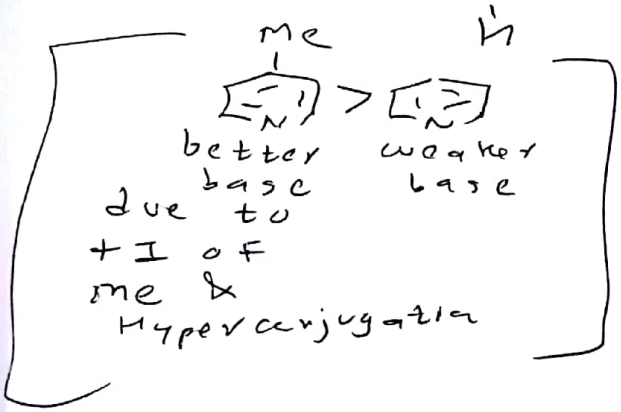
Q → 

acidity order

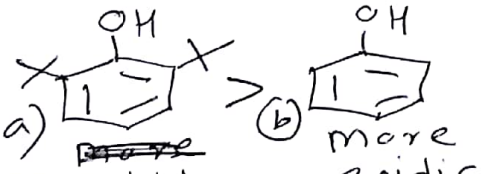
Soln :- b > a > c > d [acidity order]

[Better base have weaker acid]

d →  is best base

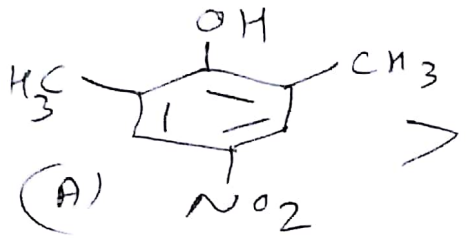


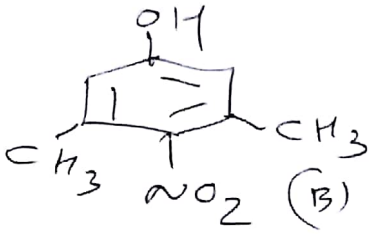
 → weakest base so best acid bcoz conjugate acid is antiaromatic.

Q → 

less acidic phenol

In a) → Large bulky group at ortho position produces steric crowding around C–OH band in 2,6-dit-butyl phenol as a result of which the –OH group goes out of the plane of ring. Steric hindrance persists in its conjugate base also. Since the $(O^{\ominus})$ unit remain out of the plane of the ring, lone pair orbitals of oxygen are no longer parallel to the π-orbitals of benzene ring. So resonance stabilization is not possible in this case whereas phenoxide ion formed from phenol is more stable. Thus 2,6-ditert butyl phenol becomes less acidic than phenol.

Q. 

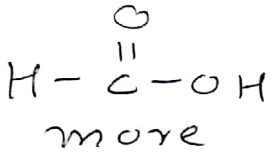
>


more acidic phenol

less acidic phenol

↓

[Due to SIR effect acidity ↓ses]

Q. 
>


more acidic

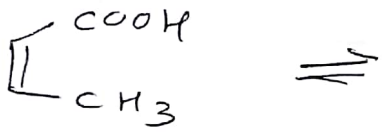
pka = 3.77

less acidic

pka = 4.2

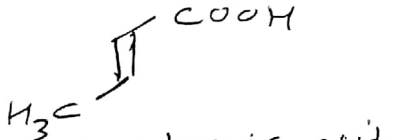
[Due to +R effect of phenyl ring acidity ↓ses]

Q. Isocrotonic acid is more acidic than crotonic acid. why?



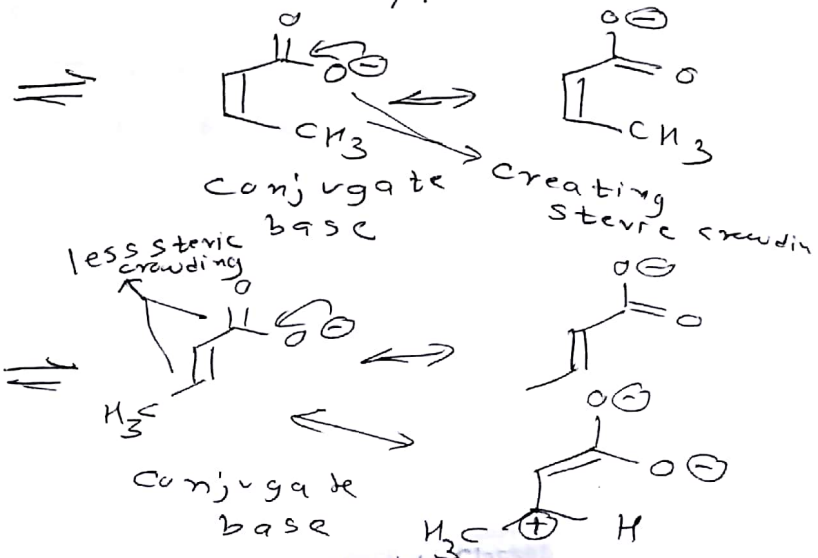
Isocrotonic acid

pka = 4.44

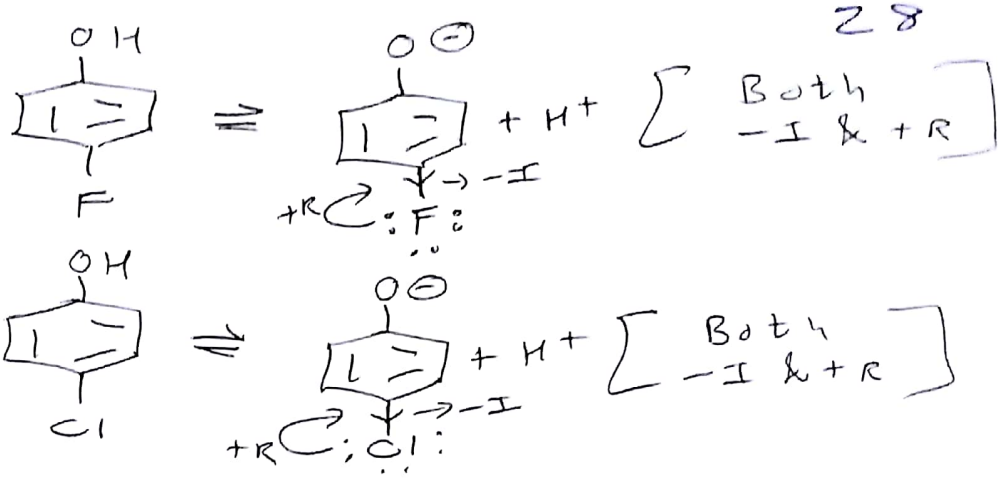


crotonic acid

pka = 4.69

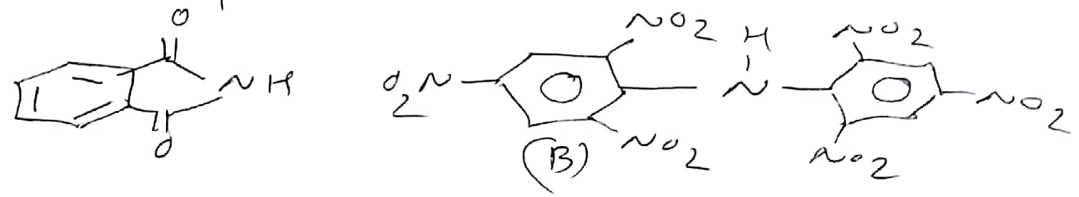


Q →



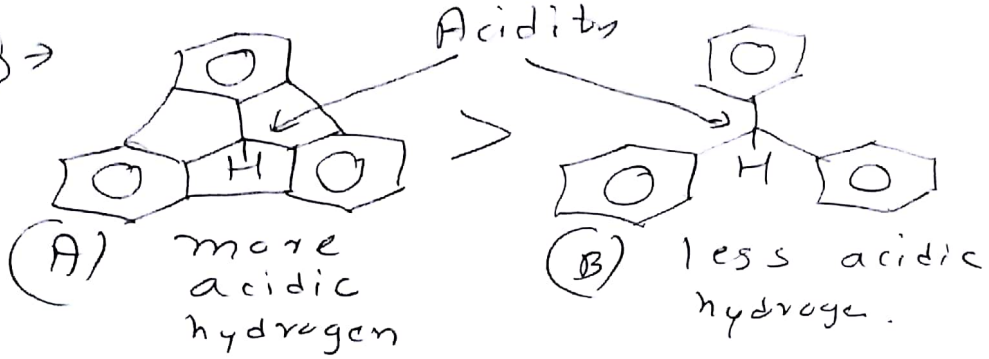
Both Halogen atom [Cl & F] have −I effect & +R effect.
Inductive effect becomes less pronounced as they are in para-position w.r.t −OH group. In this particular case resonance effect [+R] is deciding factor.
Fluorine is being smaller in size & its 2p orbital involved in resonance whereas chlorine is bigger in size & its 3p orbital involved in resonance. So Fluorine give effective delokalization of its lone pair electron with π-electron of benzene & thus +R effect of F dominates over Cl.
Hence para fluorophenol is less acidic than para chlorophenol.

Q →



Both (A) & (B) instead of being basic its acidic. & Due to stabllization of −ve charge on nitrogen of its conjugate base via electron withdrawing group.

Q→

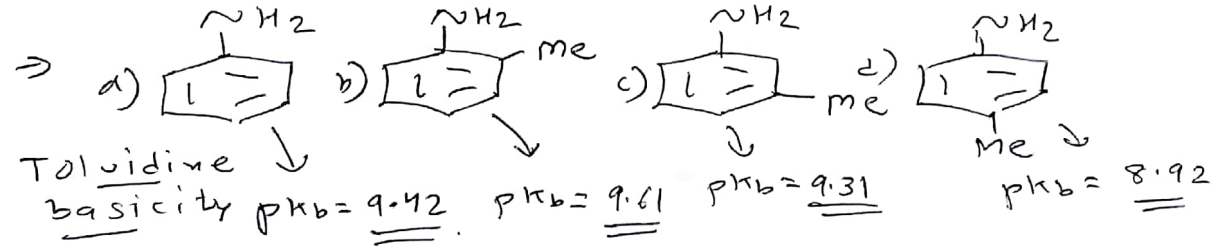


(A) more acidic hydrogen

(B) less acidic hydrogen.

→ Conjugate base of (A) is more stable bcoz carbionic (−ve) charge becomes delocalized into aromatic rings which are to be coplanar.
But in conjugate base (B) phenyl groups prefer to be in different planes for steric reasons & hence this carbanion become less stable due to lesser extent of delocalization.

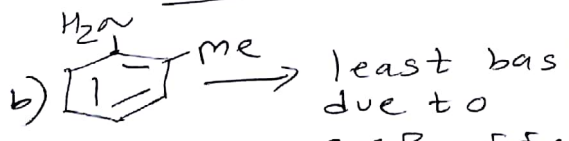
Q→



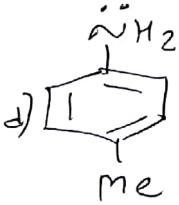
Toluidine basicity $pK_b = 9.42$ $pK_b = 9.61$ $pK_b = 9.31$ $pK_b = 8.92$

[Larger the value of K_b or smaller the value of pK_b, the stronger is the base.]

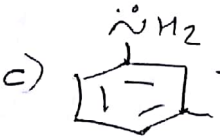
d > c > a > b



→ least basic due to SIP effect.

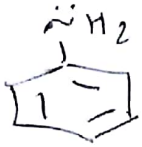
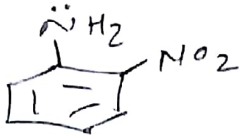


→ Most basic due to Hyperconjugation & Inductive effect.



→ Basic due to +I effect of methyl

→ less basic than meta due to devoid of methyl group.

Q→ a)  b)  c)  d) 

pK_b = 9.42 | 14.29 | 11.50 | 12.98

→ Basicity ∝ electron donating group

∝ $\frac{1}{\text{electron withdrawing group}}$

+R & +I & Hyperconjugation ↑ses basicity

−R & −I ↓ses basicity.

→ Aniline most basic due to devoid of electron withdrawing group.

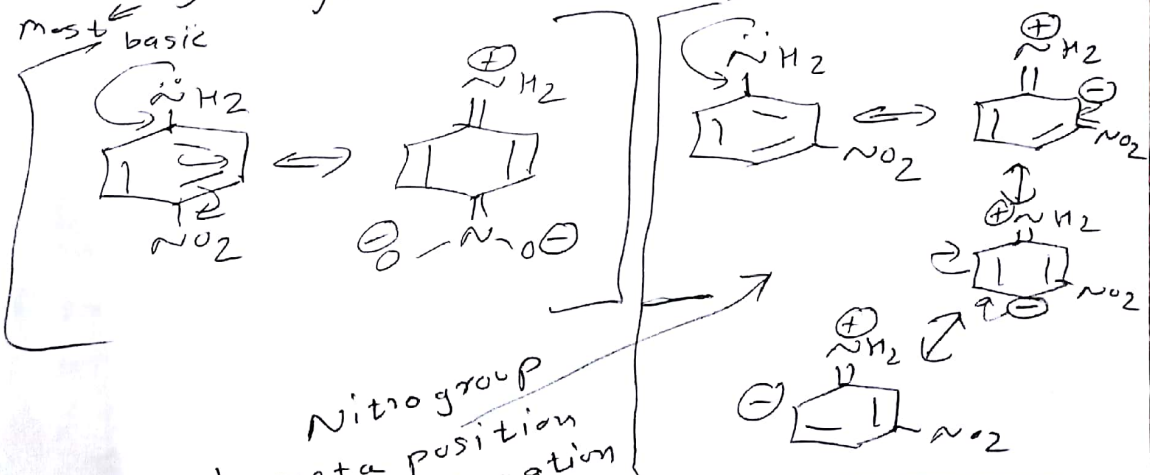
→ Orthonitro aniline is least basic due to SIR effect & −I effect.

→ Metanitroaniline is more basic then paranitroaniline due to presentee of only −I effect.

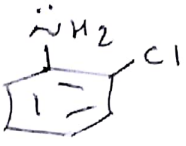
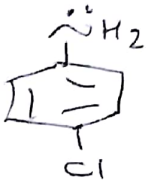
→ In paranitroaniline, nitrogen lone pair is ~~with~~ in conjugation ~~of~~ with nitro group so due to −R effect of nitro at para position its least basic than meta isome.

→ a) > c) > d) > b) → least basic

most basic ←



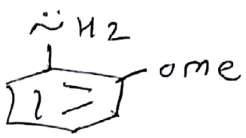
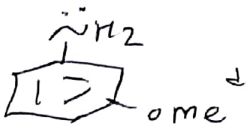
Nitro group at meta position is not in conjugation with $-\ddot{N}H_2$ group so we dont consider −R effect.

Q → a)  b)  c)  d) 

pK_b = 9.42 | 11.36 | 10.66 | 9.82

	−I SIP	−I	−I

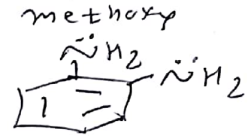
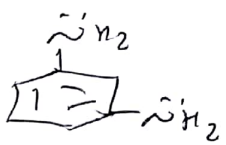
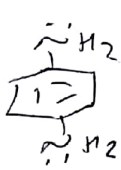
In case of halogen substituted amine, consider only **−I effect** of halogen.

Q → a)  b)  c)  d) 

pK_b = 9.42 | 9.51 | 9.8 | 8.82

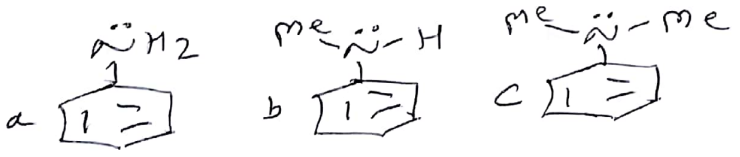
		−I	−I + R

[No SIP in methoxy]

Q → a)  b)  c)  d) 

pK_b = 9.42 | 9.53 | 9.12 | 7.96

	−I SIP	−I	−I + R

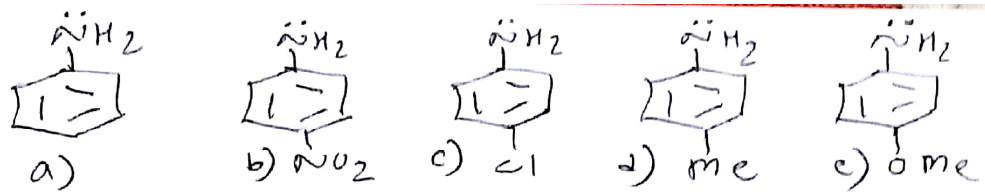
Q → 

a | b | c | d | e | f

g | h

Arrange basicity in decreasing order.

[h > e > d > c > b > a > f > g]

Q → 

32

Basic character → e > d > a > c > b

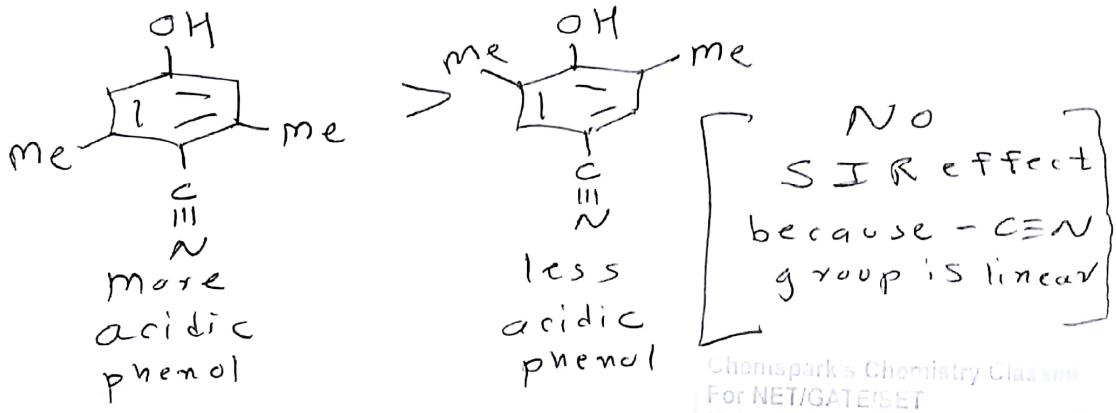
e: +R, −I [+R > −I]

d: +I & Hyper conjugation

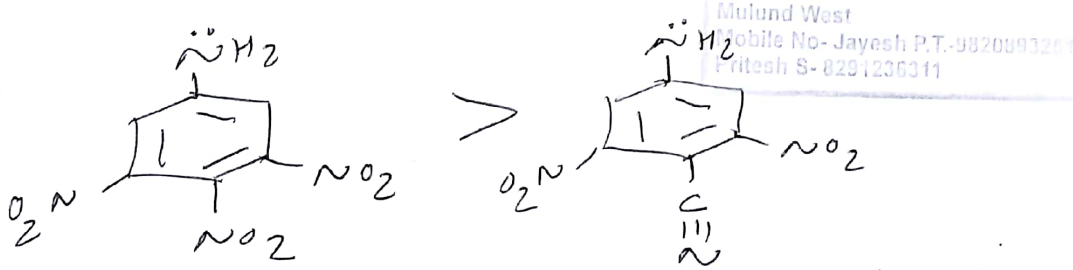
a: Standard

c: −I

b: −I, −R (−R > −I)

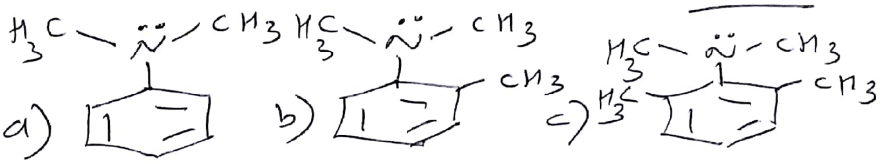
Q → 

No SIR effect because −C≡N group is linear

Q → 

more basic due to SIR

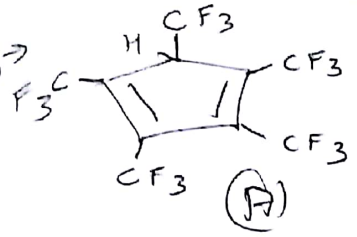
less basic due to absence of SIR

Q → 

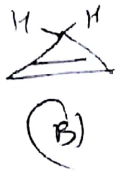
Basicity using order :- c > b > a

→ Steric hindrance so nitrogen ~~cannot~~ able to give electron to benzene ring & hence $e^{\ominus}$ is easily available for donation.

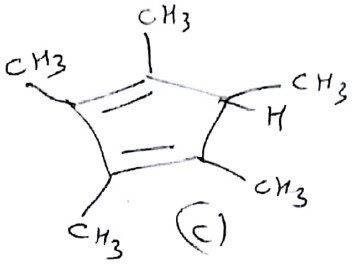
Q→



(A)



(B)



(C)

Acidity order :- A > C > B

Conjugate base is carbanion in all but 'B' carbanion  is least stable due to antiaromatic nature.

Conjugate of (A) & (C) are aromatic but Carbanion of 'A' is more Stable due to −I effect of CF_3 group.

Q→ Decreasing order of reactivity towards Electrophile is

a) 

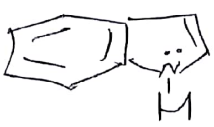
b) 

c) 

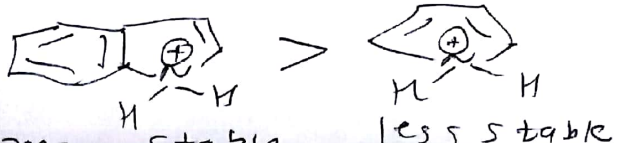
Nucleophilicity order :- a > b > c

Aromaticity order :- c > b > a [From resonance energy data]

Q Basicity order :-

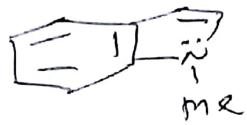
a)  b)  c)  d) 

Basicity order :- d > c > b > a

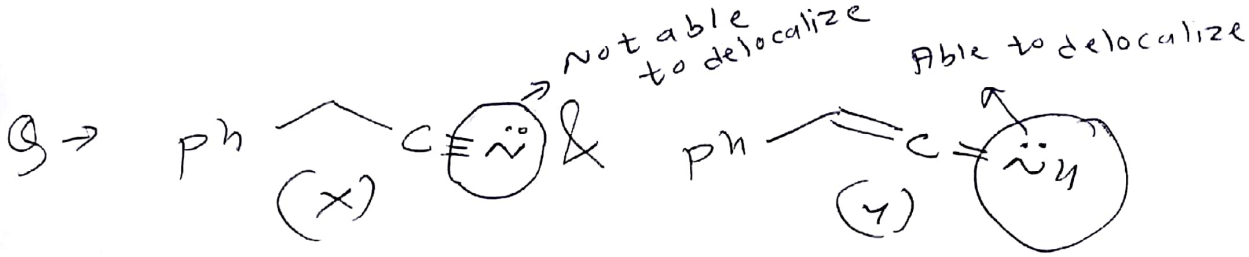
- Aliphatic amine is more basic than aromatic amine
- 

more Stable > less stable Conjugate acid

Q → Correct order for rates of Electrophilic substitution.

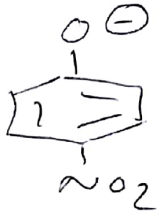
A)  B)  C) 

Nucleophilicity order :- A > C > B

Q → 

(x) & (y) are tautomers.

(x) is more basic than (y)

Q → A)  B)  C) 

B > C > A

Basicity of anion order :- B > ~~C~~ > A

A → −I, −R (−R > −I)
B → −I
C → −I, −R (−R > −I)

−R ↓ses basicity

In (c), conjugation length is linear & greater. So conjugate base (c) is more stable due to less available e⊖ pair on oxygen.

Q →  a)  b)  c)

Heat of hydrogenation ?

 d)

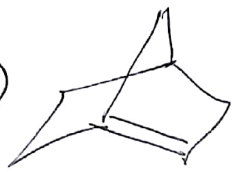
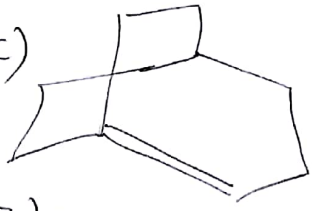
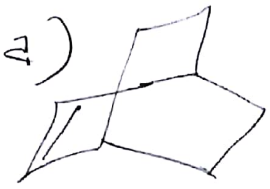
Solution :- a > c > b > d

Stability of alkene $\propto \frac{1}{\text{Heat of hydrogenation}}$

a → Two Hyperconjugation [2 α hydrogen]
b → Five Hyperconjugation [5 α hydrogen]
c → Five Hyperconjugation [5 α hydrogen]
d → Nine Hyperconjugation. [9 α hydrogen.

Trans alkene is more Stable than cis alkene.

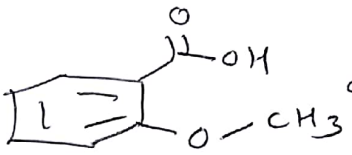
Q → Stability of alkene/olefin.

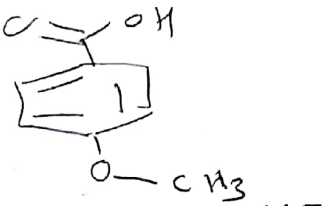
a) 
b) 
c) 
d) 

Stability order :- a > d > c > b

Bredt's rule → Applicable in (b) & (c).

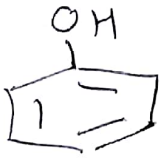
Q → a) 
pka = 4.18

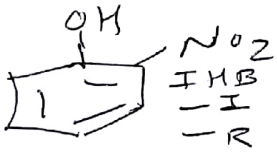
b) 
pka = 4.09

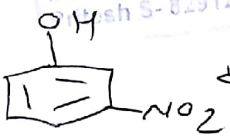
c) 
pka = 4.47

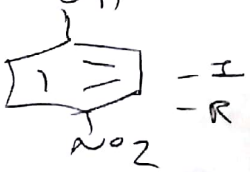
Acidity :- b > a > c
b → ortho effect
a → Standard
c → +R, −I (+R > −I)

+R & +I ↓ses acidity.
ortho effect ↑ses acidity.

Q → a) 
pka = 9.98

b) 
7.20

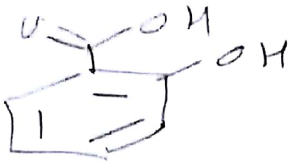
c) 
8.40

d) 
7.15

→ −R & −I ↑ses acidity

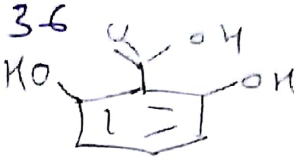
→ Intramolecular Hydrogen bonding present in (b) Structure so compare to para isomer its less acidic.

Q →

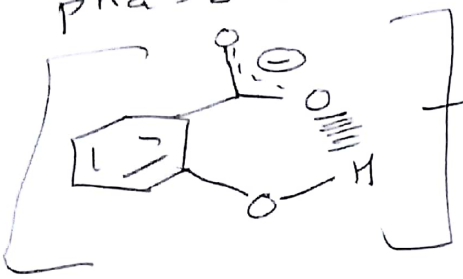


pKa = 2.98

pKa = 4.09

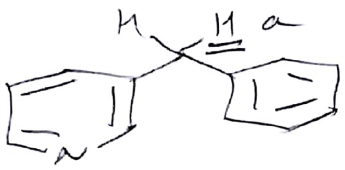


pKa = 2.30



→ Hydrogen bonding Stabilises conjugate base.

Q →

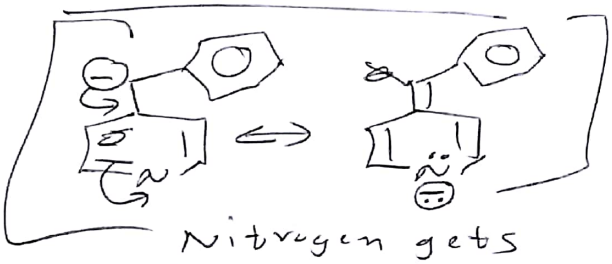


pKa = 30.1

less acidic 'H',

pKa = 26.7

more acidic 'H'



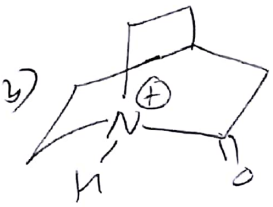
Nitrogen gets stabilized.

Q →

a)

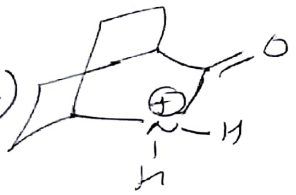
pKa = 1.0

b)



pKa = 5.33

c)



pKa = 0.14

Conjugate acid :- (b)

Stability

Not amide

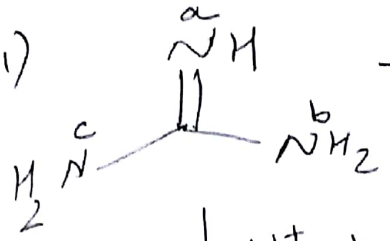
It is an amino ketone

↙

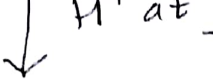
cannot tautomerize

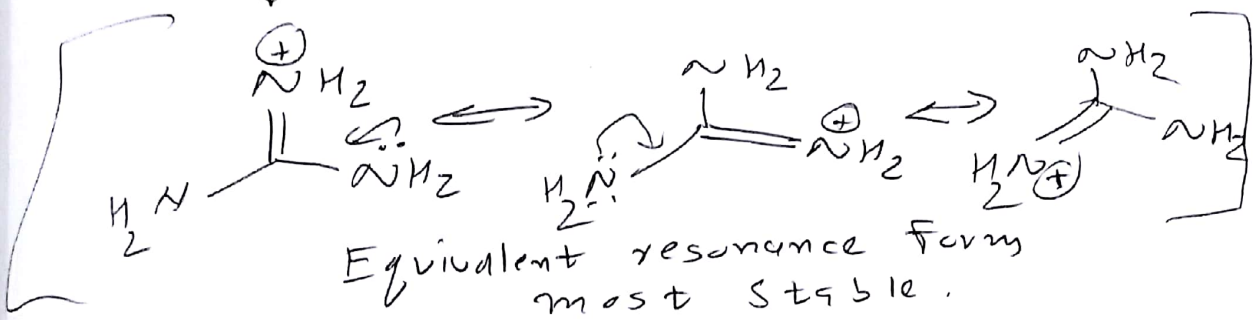
In (a) compound presence of methyl group ↓ses acidity.

Q → which Nitrogen is most basic?

1) 

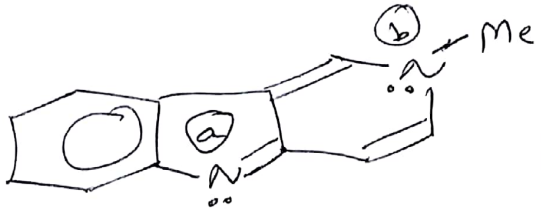
→ 'a' is most basic than 'b' 'c' nitrogen.



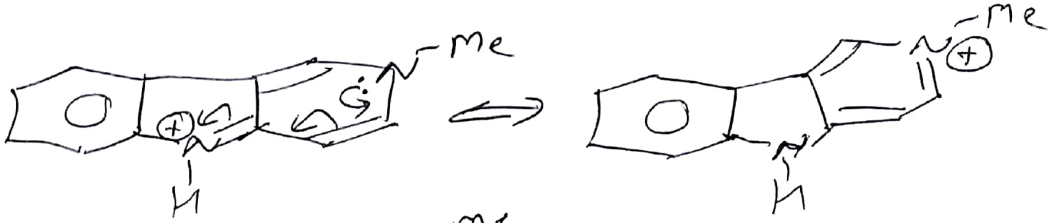


Equivalent resonance form most stable.

→ No stability at 'b' or 'c' nitrogen protonation.

2) 

(a) → most basic
(b) least basic

a) 

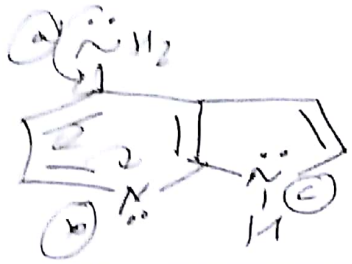
b) 

less stable conjugate acid.

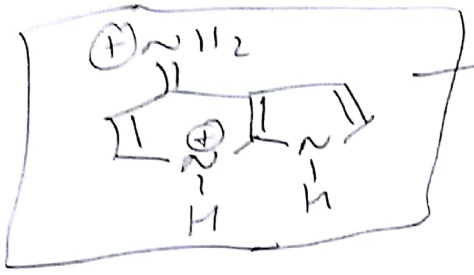
3) 

'a' is most basic then 'b'.

4)



Basicity :- b > a > c



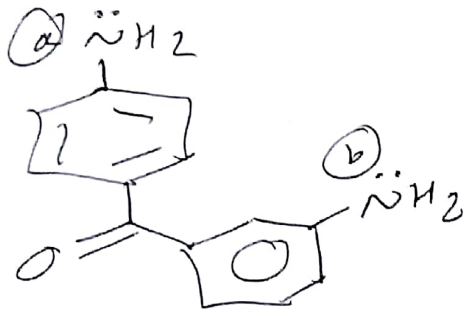
→ stable conjugate acid after protonation at (b) position nitrogen.

5)

(b) is more basic than (a)

→ Stable conjugate acid ~~of~~ after protonating at (b) N.

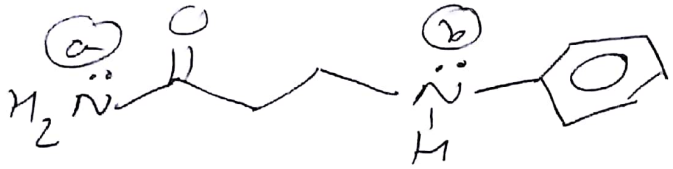
6)



(b) is more basic than (a)

'Na' is available with carbonyl conjugation.

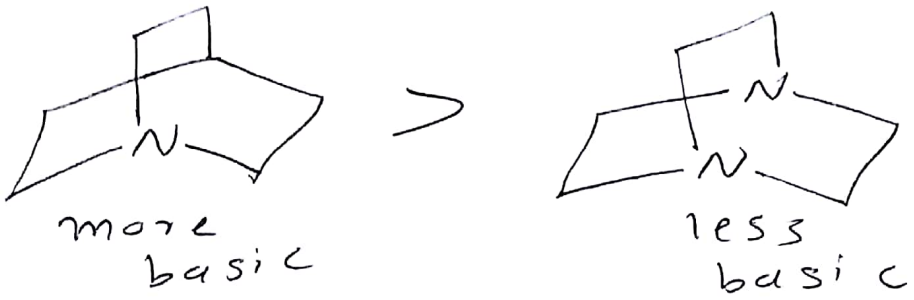
7)



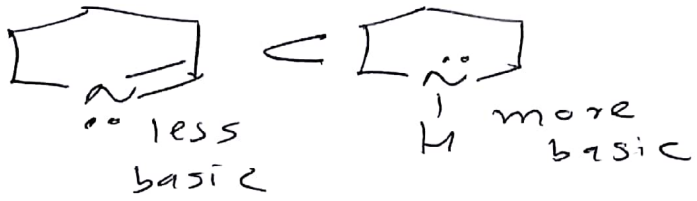
(b) more basic than (a).

'Na' is in resonance with carbonyl conjugation [ewg].

'Nb' is in resonance with aromatic ring conjugation.

Q → 

Q → 

Q → 

Q → a)  b)  c) 

Basicity :- a > b > c

Q → a)  pKa = 9.98 > b)  pKa = 7.15 c)  = 9.38 d)  = 10.14 e)  10.21

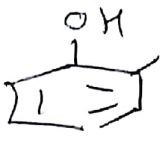
Acidity :- b > c > a > d > e

+R & +I group ↓ses acidity. [Cl, Me, OMe]

-R & -I group ↑ses acidity. [-NO2, -Cl, -OMe]

[Resonance > Hyperconjugation > Inductive effect
Dominating effects]

Hyperconjugation ↓ses acidity & ↑ses basicity.

Q → a)  b)  c)  d) 

pKa = 9.98 | 10.28 | 10.08 | 10.14

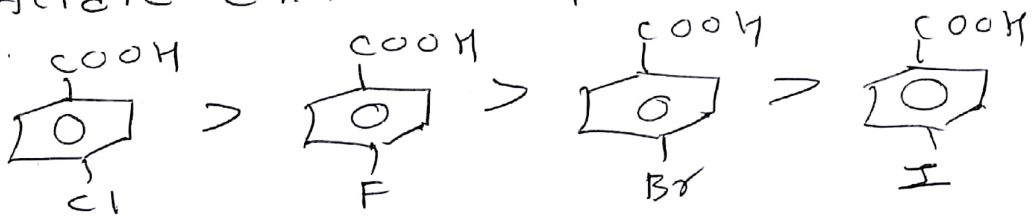
Acidicity :- a > c > d > b

→ Hyperconjugation & inductive effect both present at ortho & para methyl so its less acidic [b & d].

b have more +I effect.

→ 'c' only have +I effect.

Q → Acidic Character :-



less +R | more +R

Q → $CHCl_3$ is more acidic than $CFCl_3$.

$CHCl_3 \xrightarrow{-H^+} \overset{\ominus}{C}Cl_3$ → more stable carbanion due to empty 'd' orbital & filled 'p' orbital resonance

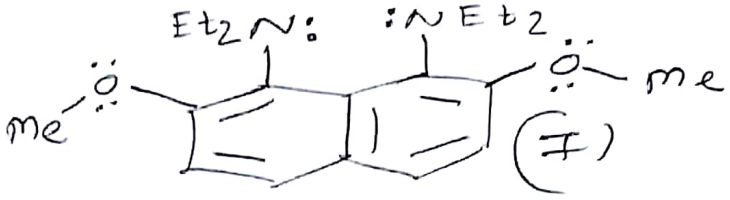
$CHF_3 \xrightarrow{-H^+} \overset{\ominus}{C}F_3$

only stabilised by −I effect

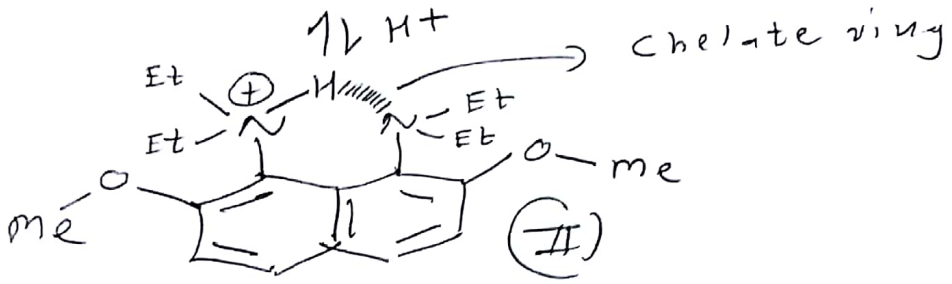
−I effect > −I effect

[dp resonance $\overset{\ominus}{C}Cl_3$ > $\overset{\ominus}{C}F_3$]

Proton Sponges



(I)



(II)

→ Compound (I) is an extremely strong organic base.

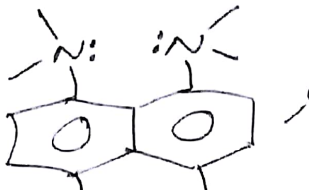
→ Neutral molecule (I) suffers from severe strain because two nitrogen lone pairs are forced to be near each other.

→ On protonation the conjugate acid (II) formed attains stability through intramolecular hydrogen bonding [one lp is connected to hydrogen]. As a result two large groups are held tightly by H-bridge & strain is releived.

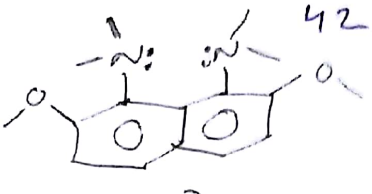
→ ∴ Protonation becomes 'energetically profitable' making (I) compound strongly basic. This type of compound known as 'Proton sponges'.

Q →

a)



b)



c)

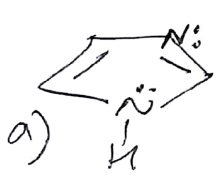
Basicity order :- b > a > c

b → +R, −I [+R > −I] No steric crowding due to methoxy.

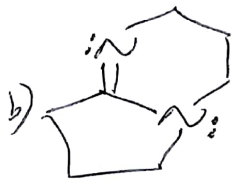
c → +R, −I [+R > −I], −I more than in 'b'

Steric crowding more due to methoxy group at ortho position with N,N'-dimethyl.

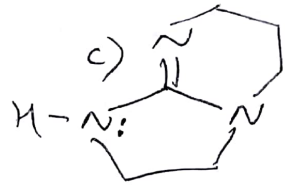
Q →



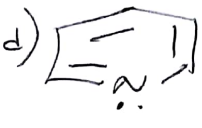
a)



b)



c)



d)

Basicity order :- c > b > a > d

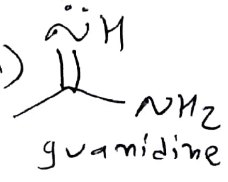
c → Refer guanidine

b → Refer amidine

'a' → more basic than 'd' due to +R effect

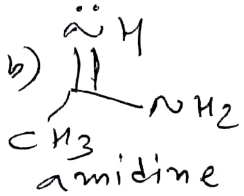
Stabilization by −NH group in imidazole.

Q → a)



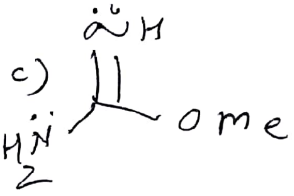
guanidine

b)

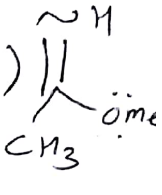


amidine

c)



d)

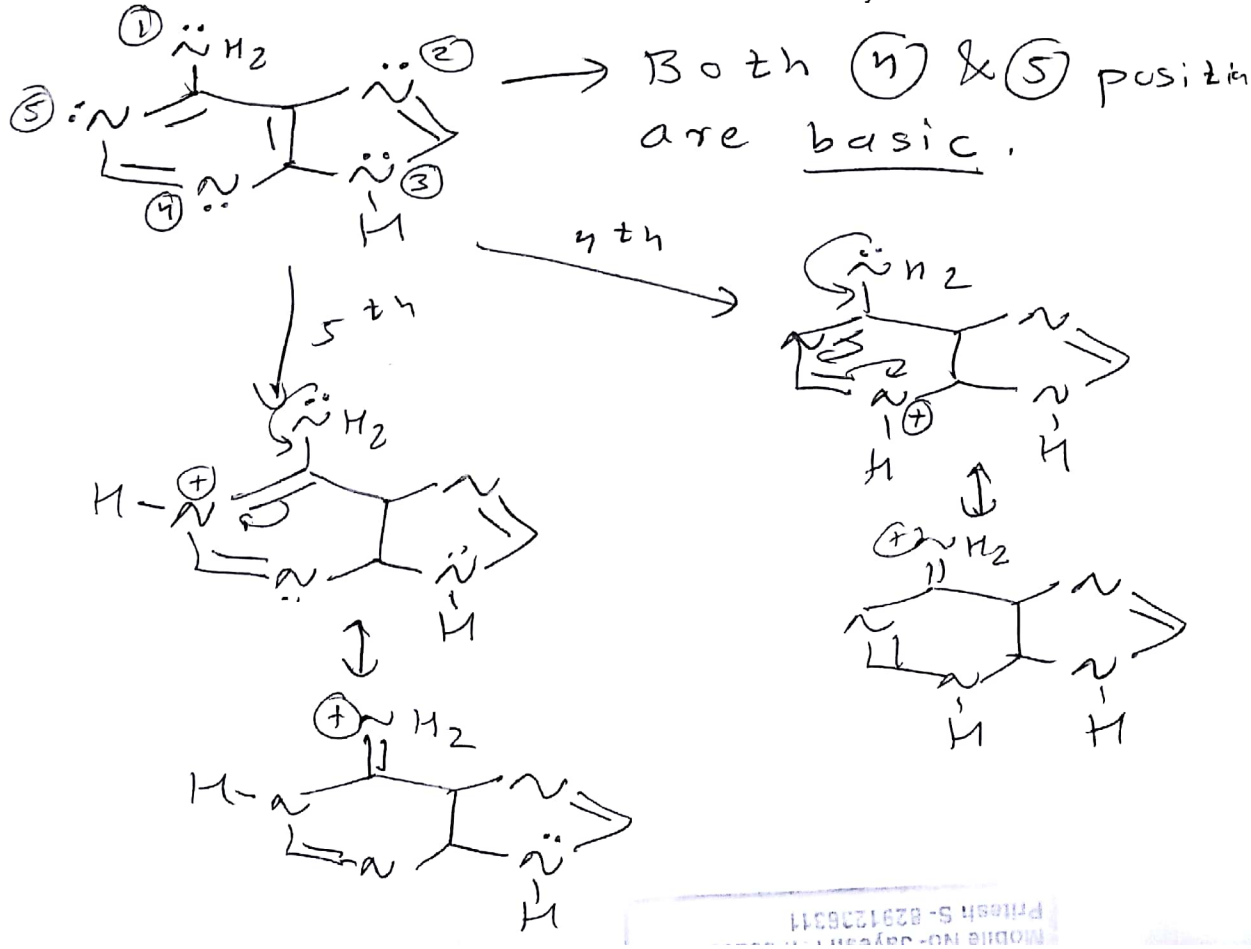


Basicity order :- a > c > b > d

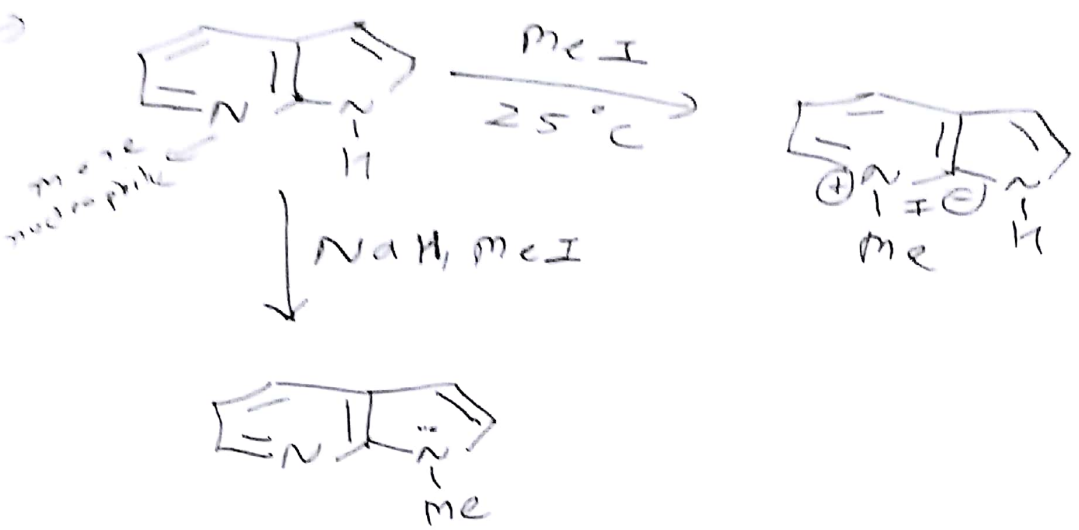
Q → Major product formed in the reaction of guanosine with one equivalent of methyl iodide is:

N-7 nitrogen is most nucleophilic bcoz its not in resonance with other ~~ca~~ elements.

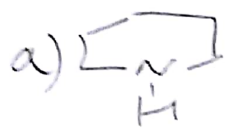
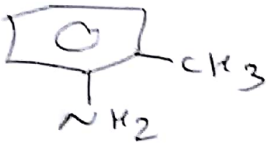
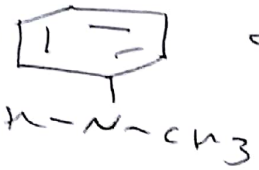
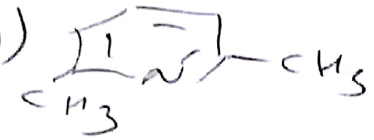
Q → Monoprotonation of Adenine (X) in acidic solution mainly occurs at



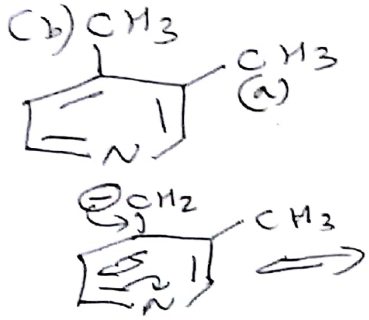
Q →



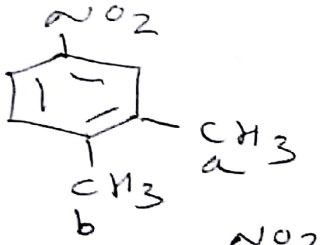
Q → Compare basic strength increasing order.

a) 
b) 
c) 
d) 

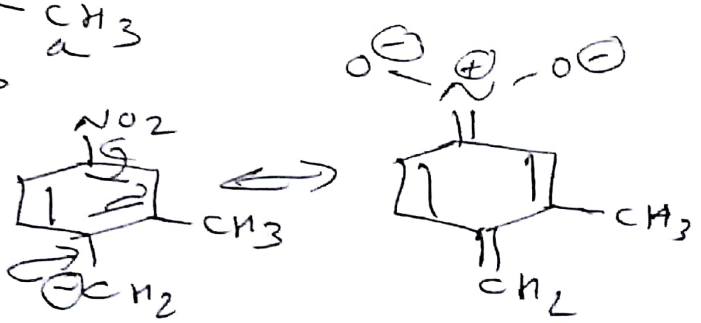
Soln:- a b < c < d < a

Q → 

(b) ⇒ acidic proton



b ⇒ acidic proton



Q → Select stronger base in each pairs

I) $CH_3S^{\ominus}$ & $CH_3O^{\ominus}$

$CH_3O^{\ominus}$ is stronger base than $CH_3S^{\ominus}$ bcoz CH_3-SH is a strong acid than CH_3OH.

Periodic table

L ⟶ R Basicity ↑ses

T ⟶ B Basicity ↓ses

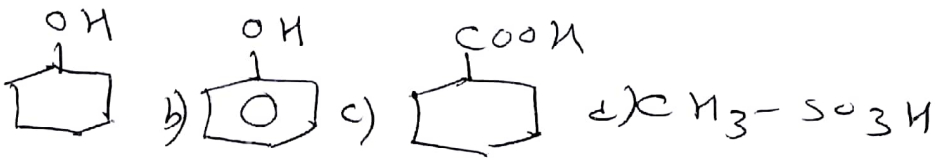
II) $CH_3-\overset{\ominus}{N}H$ & $CH_2=CH-\overset{\ominus}{N}H$

$CH_3-\overset{\ominus}{N}H$ is stronger base bcoz in $CH_2=CH-\overset{\ominus}{N}H$, anion is resonance stabilized.

III) $CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus}$ < $HO-\overset{O}{\overset{\|}{C}}-O^{\ominus}$

Strong base

IV) Q →



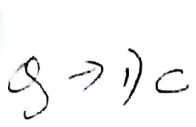
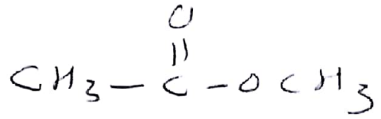
a) b) c) d) CH_3-SO_3H

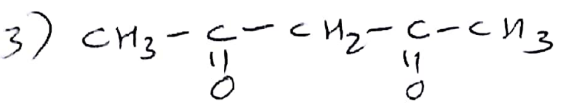
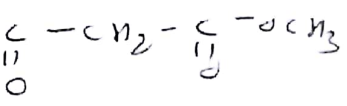
Increasing pKa order.

Stronger the acid, higher the Ka & smaller the value of pKa.

$pKa = -\log Ka$

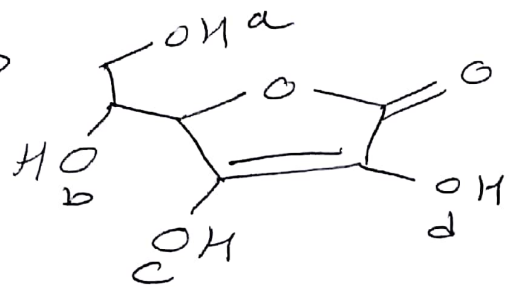
d < c < b < a

Q → 1)  2) 

3)  4) 

Increasing pka order.

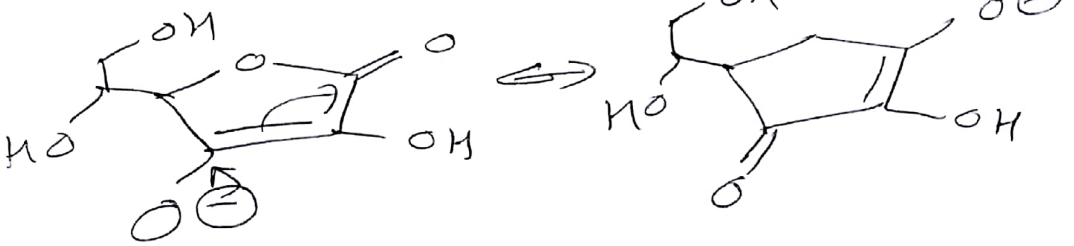
$$3 < 4 < 1 < 2$$

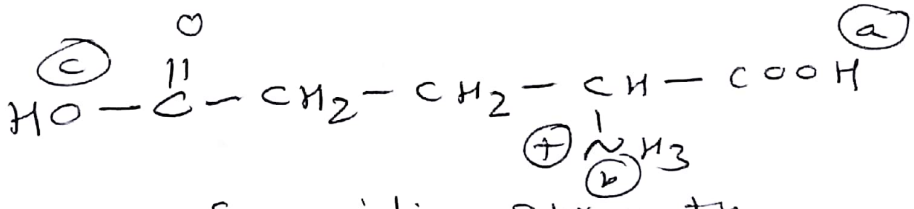
Q → 

ascorbic acid.

most acidic proton.

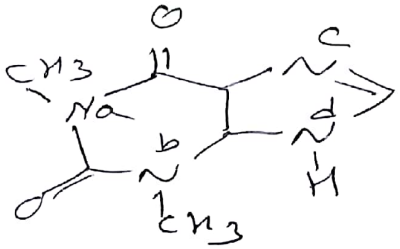
(c) → most acidic



Q → 

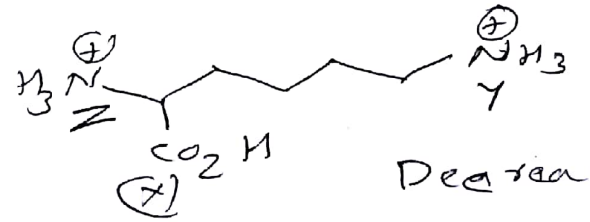
order of acidic strength

$$\boxed{a > c > b}$$

Q → 

Increasing order of basicity.

$$a < b < d < c$$

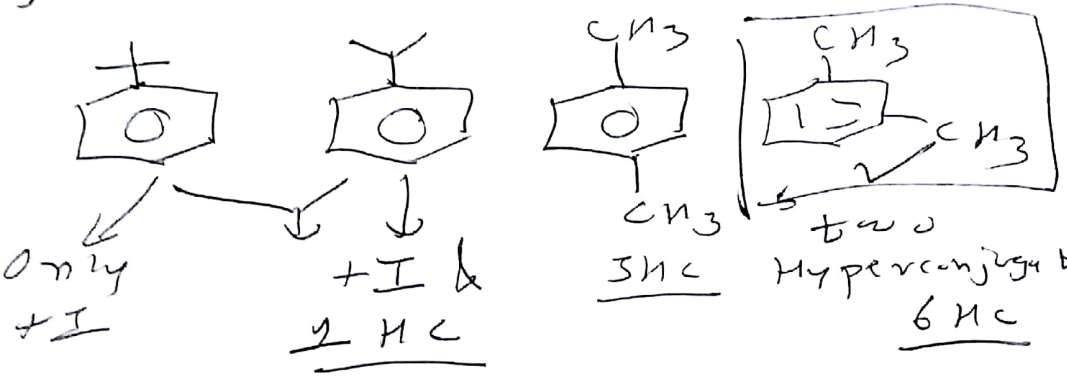
Q → 

Decreasing order (acidity)

$$\underline{x > y > z}$$

Q → which of the molecules has highest electron density in phenyl rings?

Soln.



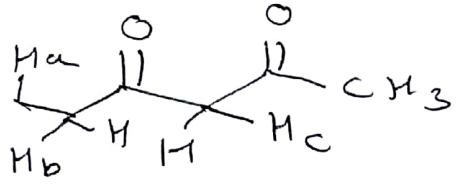
HC = Hyperconjugation

Q →

Heat of combustion

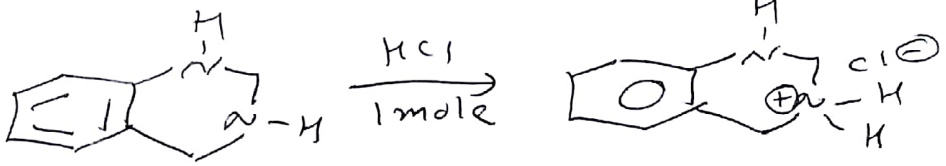
a > b > c

Q →

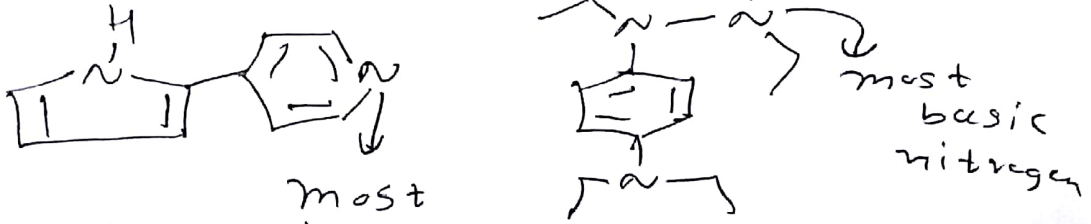


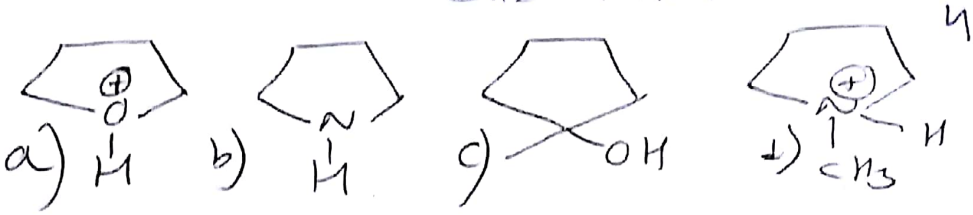
acidity order :- c > b > a

Q →



Q →

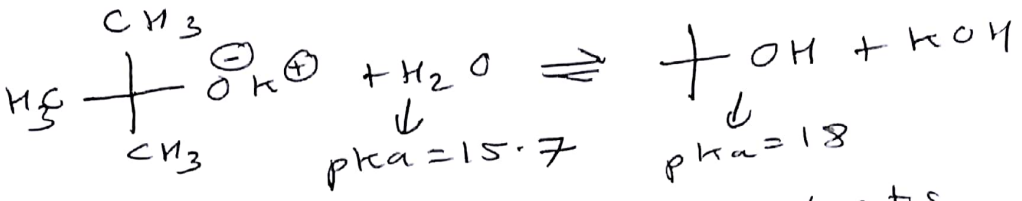


Q→ 

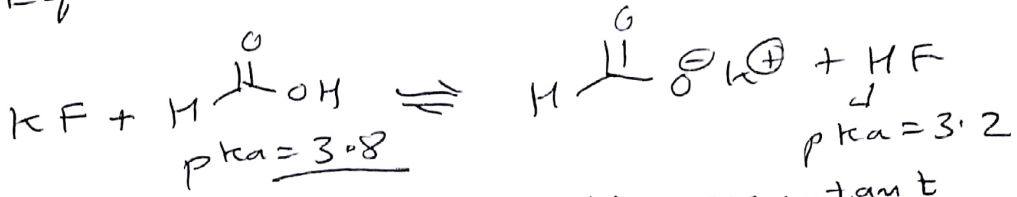
acidic strength :- a > d > c > b

Q→ a  b  c 

Heat of combustion :- 3⇒ c > b > a

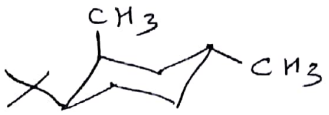
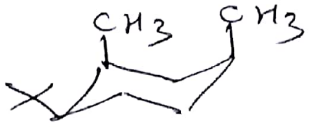
Q→ 

Equilibrium favours the products

Q→ 

Equilibrium favours the reactant

Q→ Smallest heat of combustion?

a)  b) 

c)  d) 

Molecular formula & substituents are same.

So stability of compound $\propto \frac{1}{\text{Heat of combustion}}$

(C) → Smallest heat of combustion due to high stability.

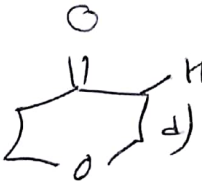
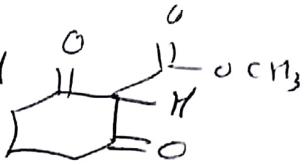
Q → Decreasing order of Heat of combustion.

a)  b)  c)  d) 

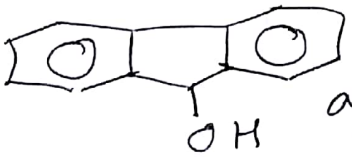
Soln:- b > d > a > c

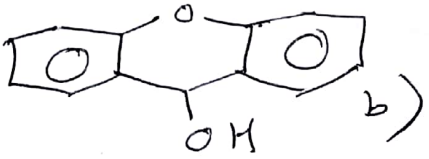
b → least stable, so High HOC

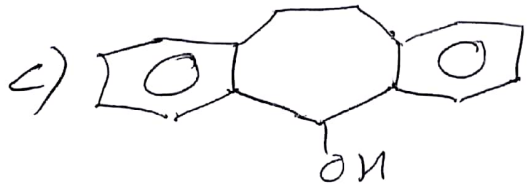
c → most stable, so least HOC

Q → a)  b)  c)  d) 

acidity order:- d > a > c > b

Q → 

a) 

b) 

c)

Decreasing order of ease of ionization under acidic conditions.

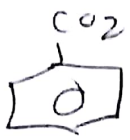
Soln:- b > c > a

Q → a) $\overset{\ominus}{C}H_3$ b) $\overset{\ominus}{N}H_2$ c) $\overset{\ominus}{O}H$ d) $\overset{\ominus}{F}$

Basicity order:- a > b > c > d

L → R Basicity ↓ses

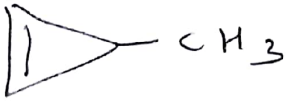
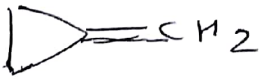
Q→ Compound which not give effervescence with Na_2CO_3.

a)  b)  c)  d) 

Soln :- Phenol (c) → weak acid

Q→ Most stable ~~X~~ylenes

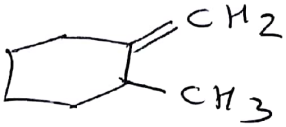
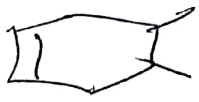
 meta xylene most thermodynamically stable xylene

Q→ a)  b)  c) 

Heat of hydrogenation :- ~~a → b > c~~

a > c > b → most stable

a ← least stable

Q→ a)  b)  c) 

Heat of hydrogenation :- ~~b → c → a~~

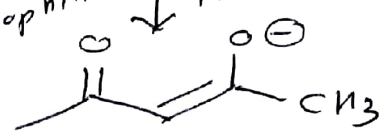
b > c > a

b ← least stable

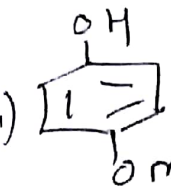
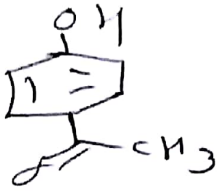
a → most stable.

Q→ 

more nucleophilic, H^+ ↓



[anion which form last, react first with Electrophile]

Q → a)  b)  c) 

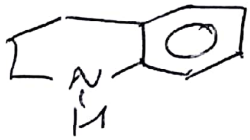
Acidity order :- c > b > a

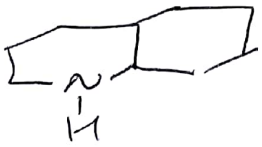
Q 

Rank the nonbonding electron indicated by arrow in order of increasing energy & basicity.

Increasing energy :- a > b > c

Basicity :- a > b > c

Q → a)  b)  c) 

d) 

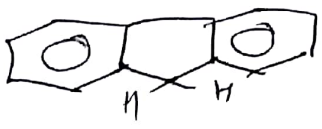
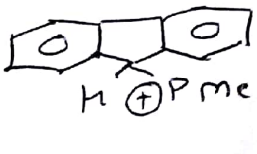
Basicity order :- d > b > c > a

Q → a) NaOH b) $NaOOCCH_3$ c) $NaOCH_3$

d) $NaNH_2$

most basic → (d)

least basic → (b)

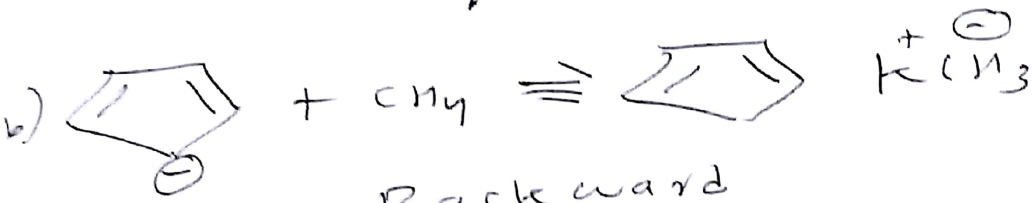
Q → a)  b)  c) 

acidity order :- c > b > a

ylide + aromatic — ylide + aromatic — aromatic

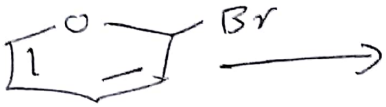
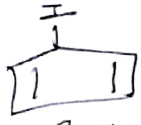
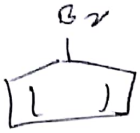
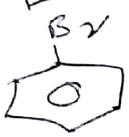
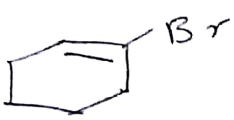
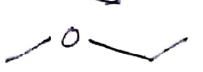
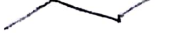
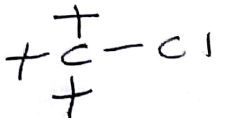
Q) a) 

Forward Equilibrium →

b) 

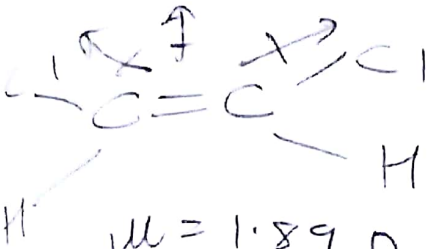
Backward Equilibrium ←

Q → Among the given pairs, which is more reactive towards AgNO3 or solvolysis.

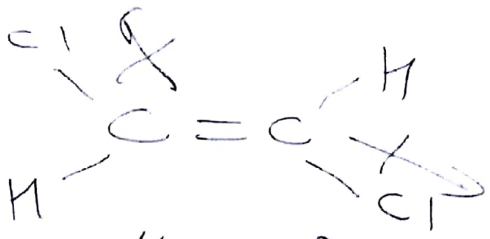
Compound A	Compound B	Answer
		B
		A
		B
		A
		B
		B
		A
		A

Polarity

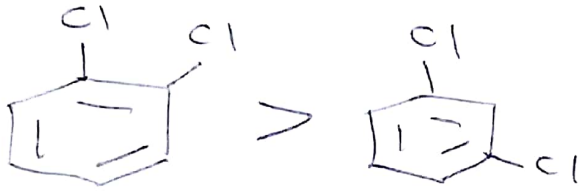
CHEMSPARK



$\mu = 1.89$ D

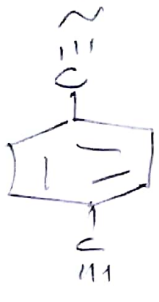


$\mu = 0$ D

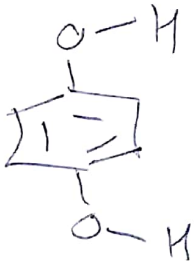


High dipole

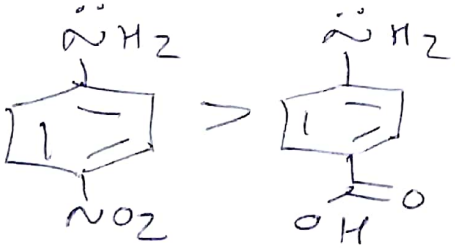
least dipole.



$\mu = 0$



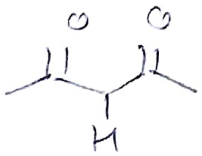
$\mu = 1.4$ D



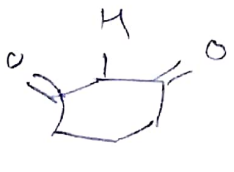
High dipole

less dipole

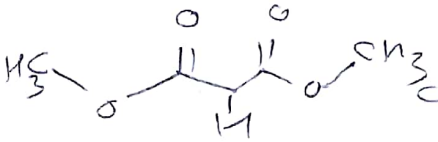
Q →



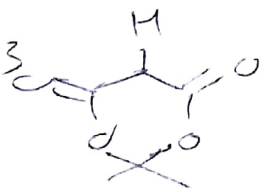
pka = 13.3



pka = 11.2



pka = 15.9



pka = 7.3