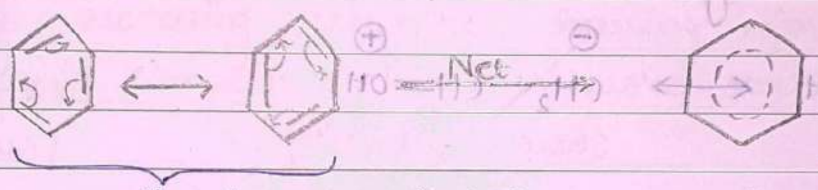
*2) Resonance effect:

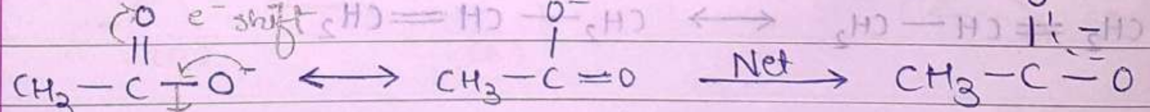
- delocalisation of 'π-electrons' in conjugated system is called Resonance.
- structure formed during resonance are known as "Resonance canonical structure".
- each conical structure contribute to form real structure.
- real structure is known as "Resonance hybrid structure".
- resonance hybrid is real whereas canonical is an ideal structure.

eg: 1) Structure of benzene:



canonical structure (ideal) ⟷ resonance hybrid structure (real)

II) structure of acetic ion:



$$CH_3-\overset{O}{\overset{\|}{C}}-O^- \longleftrightarrow CH_3-\overset{O^-}{\overset{|}{C}}=O \xrightarrow{Net} CH_3-\overset{O}{\overset{\vdots}{C}}\overset{..}{-}O$$

it makes val. e^- of C = 5

∴, C=O bond became unstable

∴, e^- shift to =O making

π shuffle again to

other side

⟹ **condition of resonance:**

- if 'π-bond' conjugated with another π-bond.

eg:

$$CH_2{=}CH-CH{=}CH_2 \longleftrightarrow \overset{\oplus}{C}H_2-CH{=}CH-\overset{\ominus}{C}H_2$$

$$\longrightarrow CH_2\text{==}CH\text{==}CH\text{==}CH_2$$

- if 'π-bond' conjugated with lone pair or negative ion than electron moves lone pair or negative ion to π-bond side.
- if 'π-bond' conjugated with vacant orbital (+ve) (positive charge).

eg:

$$\longrightarrow CH_2{=}CH-\ddot{O}H \longleftrightarrow \overset{\ominus}{C}H_2-CH{=}\overset{\oplus}{O}H$$

show neutrality.

lone pair = 2e⁻ (ownself e⁻'s)

$$\longrightarrow CH_2{=}CH-\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2-CH{=}CH_2$$

2e⁻ (bahar के किसी और के)

no ⊕ charge as no neutrality for LHS so, $-\delta-$ (LHS ≠ RHS)

$$\longrightarrow CH_2{=}CH-\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2-CH{=}CH_2$$

- if lone pair of negative charge conjugated with positive charge then lone pair or negative charge is moved towards positive charge (empty orbital)

eg: ⊕ stable ⊕ unstable.

$$\longrightarrow \overset{\oplus}{C}H_2-\ddot{O}H \longleftrightarrow CH_2{=}\overset{\oplus}{O}H$$

$$\longrightarrow \overset{\oplus}{C}H_2-\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2{=}\overset{\oplus}{C}H_2$$

- if 'π-bond' conjugated with electron deficient atom.

eg:

→ $CH_2=CH-BH_2 \longleftrightarrow \overset{\oplus}{C}H_2-CH=\overset{\ominus}{B}H_2$

- if 'π-bond' conjugated with free or odd electron.

eg:

→ $CH_2=CH-\dot{C}H_2 \longleftrightarrow \dot{C}H_2-CH=CH_2$

(2 electrons required for bond formation.)

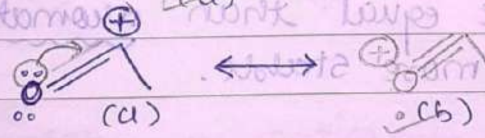
⟹ Rules for stability of resonating structure:

CASE:I if resonating structure having more number of 'π-bond' with complete octate, is more stable.

eg:

→ $\underset{(a)}{\ddot{N}H_2-\overset{\oplus}{C}H_2} \longleftrightarrow \underset{(b)}{\overset{\oplus}{N}H_2=CH_2}$ (b more stable)

→ $\underset{(a)}{CH_2=CH-CH=CH_2} \longleftrightarrow \underset{(b)}{\overset{\oplus}{C}H_2-CH=CH-\overset{\ominus}{C}H_2}$ (a more stable)

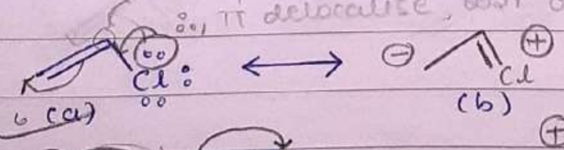
→ 

(b more stable)

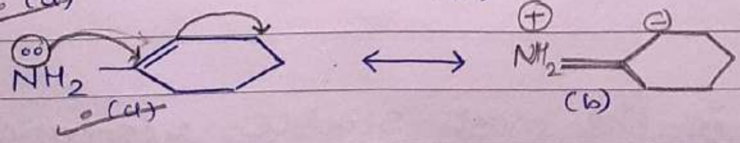
CASE:II if number of 'π-bonds' equal than less ionised structure is more stable.

eg:

lone pair જો જાય તો valency = 5
∴ π delocalise, [illegible] ⊖ [illegible].

→ 

(a more stable)

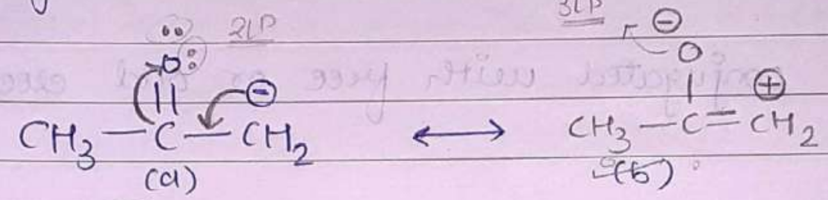
→ 

(a more stable)

1 minus charge = 2e⁻

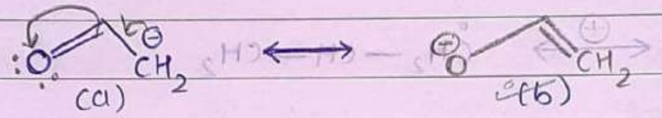
CASE: III If 'π-bonds' are equal and negative charges are available at same period of element then negative charge is more stable at more electronegative atom.

eg: →



(b more stable)

→

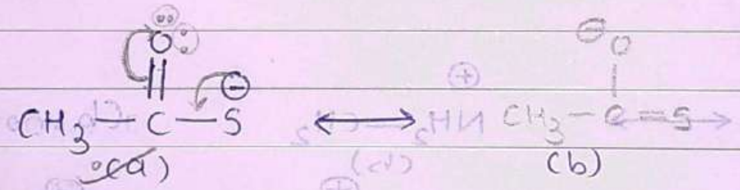


(b more stable)

O > C
(EN)

CASE: IV if number of 'π-bonds' are equal with availability of negative charge at elements of different periods than negative charge is more stable at larger sized atom.

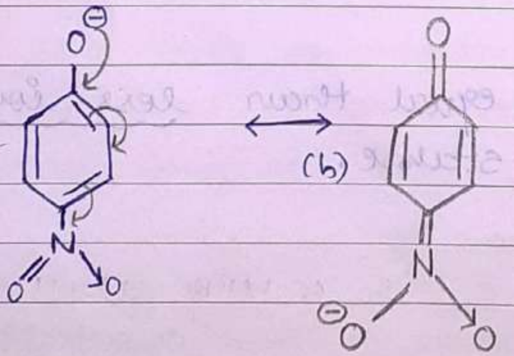
eg: →



(a more stable)

CASE: V if number of 'π-bonds' are equal than aromatic resonance structure is more stable.

eg: →



(a more stable)

→

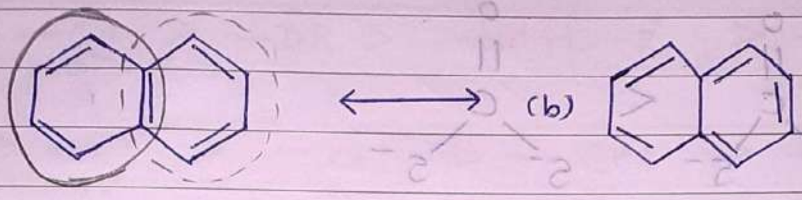
benzene is the most stable resonance compound.

* Benzene struc. given by Kakule.

CASE:VII in fused benzene ring structure with more number of Kakule benzene will be more stable.

eg: naphthalene

→ (a)



> (a more stable)

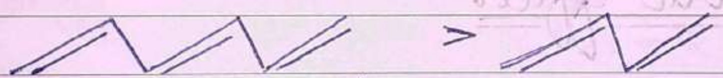
(NO. of Kakule benzene = 2) (No. of Kakule benzene = 01)

⟹ Stability of resonating structure of different molecule:

RULE:I larger the conjugation, more the stability is present.
(large conj. > smaller conj.)

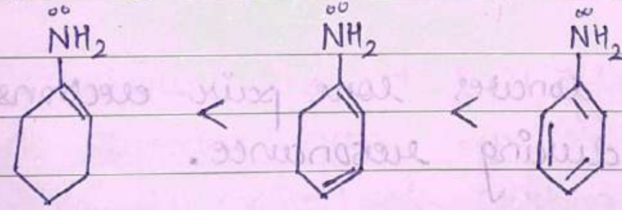
eg:

→



(no. of π's)

→

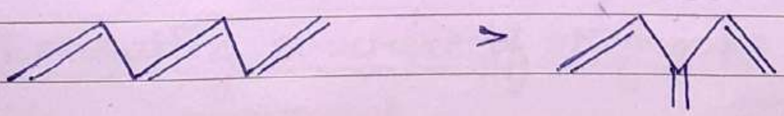


aromatic compounds are more stable (also, no. of π bond matters)

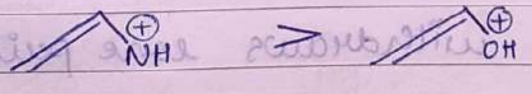
RULE:II Linear conjugation is more stable than cross-conjugation.

eg:

→



→

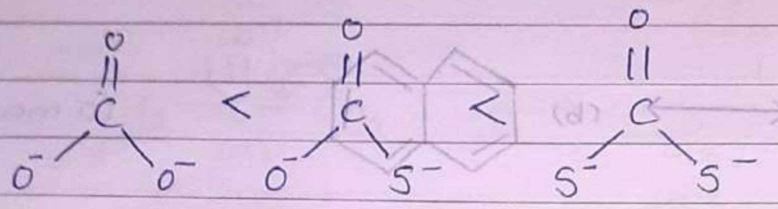


(OH on being electronegative can't bear +)

RULE:III more electronegative atom is less stable with positive (+ve) charge.

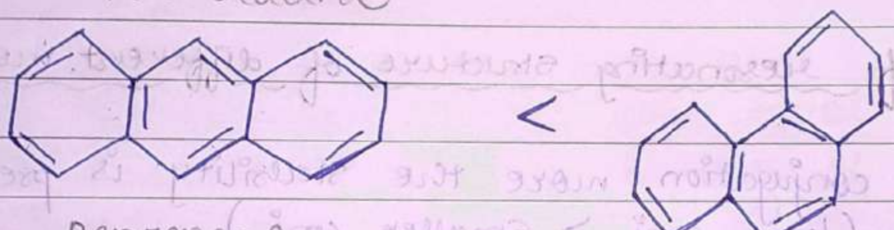
eg:

→



Anthracine

*



7π
16σ

Benzene = 2

Benzene = 3

* Types of mesomeric effect: / resonance effect

1.) +M effect:

- those groups which donates lone pair electrons or negative charge during resonance. (gain = '+' chrg)

eg:

→ $-\ddot{O}H$; $-\ddot{N}H_2$; $-\ddot{N}H-R$; $-\ddot{F}:$; $-\overset{\ominus}{C}H_2$

$-\overset{\ominus}{N}H$; $-\ddot{Cl}:$;

2.) -M effect:

- those groups which withdraws lone pair electrons during resonance. (gain '−' chrg)

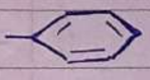
eg:

→ carbon containing func. groups i.e. $-\overset{O}{\overset{\|}{C}}-OH$; $-\underset{O}{\underset{\|}{C}}-NH_2$; $-\underset{O}{\underset{\|}{C}}-Cl$; $-\underset{O}{\underset{\|}{C}}-OR$; $-CN$; $-NO_2$ or $-N\begin{smallmatrix}=O\\ \to O\end{smallmatrix}$

*mesomerism = have func. grp compulsory.
resonance = no problem if no func. group
→ benzene without func. group can't use Mesomeric word.

⟹ Order of +M group: (show in ortho & para positions).

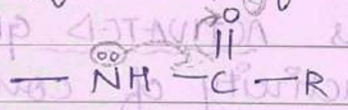
$-\overset{\ominus}{CH_2} > -NH^{\ominus} > -O^{\ominus} > -\ddot{N}H_2 > -\ddot{N}HR > -\ddot{N}R_2$ (bulky alkyl grp)

$> -\underset{..}{\ddot{O}}H > -\underset{..}{\ddot{O}}R > -\ddot{N}H-\overset{O}{\overset{\|}{C}}-R > -\underset{..}{\ddot{O}}-\overset{O}{\overset{\|}{C}}-R >$ 

$> -\underset{..}{\ddot{F}}: > -\underset{..}{\ddot{Cl}}: > -\underset{..}{\ddot{Br}}: > -\underset{..}{\ddot{I}}:$

Q:5 $-NH-\overset{O}{\overset{\|}{C}}-R$ group show less +M effect than NH_2 and OH group. Explain.

→ in —NH-COR group lone pair electrons are engaged with resonance to C=O bond also, making its electron quite difficult to form a resonance with benzene ring.



$-\ddot{N}H-\overset{O}{\overset{\|}{C}}-R$

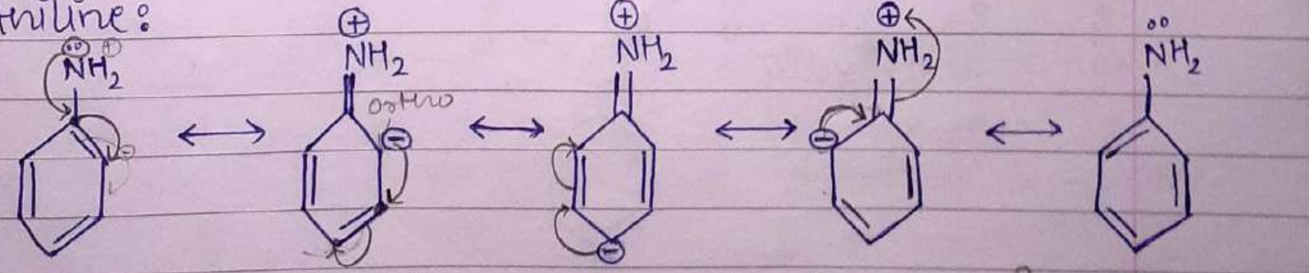
Q:6 $-\underset{..}{\ddot{F}}:$ show more +ve M effect than other halogens. Why?

→ As fluorine have 2p orbital which overlaps better with 2p orbital of carbon whereas on taking other orbitals i.e 3p, 4p, 5p... show energy difference for overlapping of lone pair making electrons difficult to form resonance.

⟹ Resonating structure of +M group:

Amino benzene

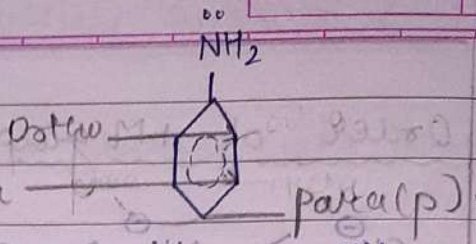
eg: Aniline:

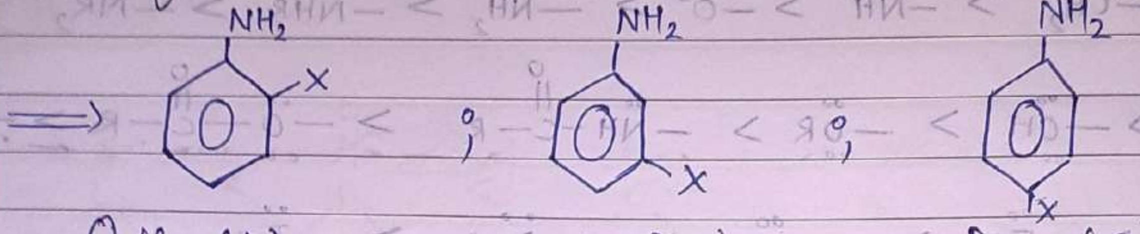


(both chrg)
(for neutrality)

∴ 5 resonating struc.
(all canonical) (hypothetical)

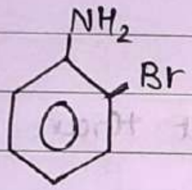
* <u>Resonance hybrid struc. for Aniline:</u>





Ortho (o) ; Meta (m) ; Para (p)

eg:

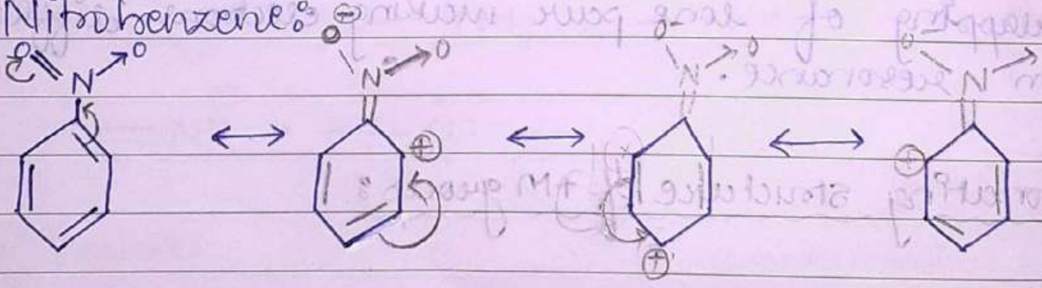


Name it (IUPAC):
Orthobromo Aniline.
or O-bromo aniline.

* **NOTE:**
- all +M groups (LP donors) in benzene ring are known as <u>ACTIVATED GROUPS</u> as they increase reactivity of compound.

⟹ <u>Resonating structure of -M group:</u> (show ~~on ortho~~/para.

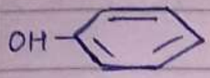
eg: Nitrobenzene:

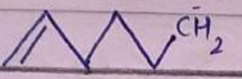


Finally

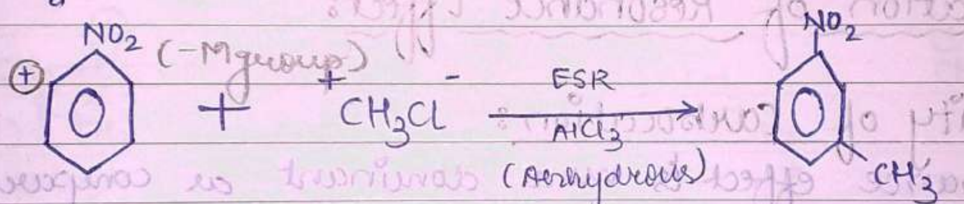
*** NOTE:**

 ⟶ no. func. group; Resonance ✓ Mesomer ✗



Or  ⟶ Resonance ✓ Mesomer ✓

⟹ +M group	−M group.
- −ve charge available over ortho and para positions.	+ve charge available over ortho and para positions.
- activated groups as it increases reactivity of benzene ring towards (ESR) electrophilic substitution rxn.	deactivated groups as it decreases reactivity of benzene ring towards (ESR) electrophilic substitution rxn
- ortho and para directing	- meta directing group.

eg: 

*** NOTE:**

if $G = -\ddot{O}H$; $-\ddot{N}H_2$; ~~$-CHO$~~ ; $-CN$; etc.
then, +M effect.

⟹ Order of −M group:

$$-NO_2 > -C\equiv N > -\overset{O}{\overset{\|}{C}}-H > -\overset{O}{\overset{\|}{C}}-R > -\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$$

$$> -\overset{O}{\overset{\|}{C}}-OR > -\overset{O}{\overset{\|}{C}}-OH > -\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 > -\overset{O}{\overset{\|}{C}}-O^- > -\overset{O}{\overset{\|}{C}}-NH^-$$

$$> -\overset{O}{\overset{\|}{C}}-CH_2^-$$

***NOTE:**

- higher the +ve charge [on c of carbonyl] more the −M effect is shown.

imp ## ***NOTE:**

- In case of Fluoro benzene: -I-effect is more dominant over +M effect.
- Toluene ($C_6H_5CH_3$) is ortho-Para directing due to hyper-conjugation effect as it does not show +M effect.

⟹ Application of Resonance Effect:

★(A) Stability of carbocation:

- resonance effect is more dominant as compared to inductive effect.
- number of resonating structure (↑) stability of ion (or free radicle) (↑)

eg: I $\boxed{CH_2=CH-CH_2}-\overset{\oplus}{C}H_2$ → no resonance −I- eff.

II $CH_2=CH-\overset{\oplus}{C}H_2$ have resonance

III $\boxed{CH_3}-CH_2-\overset{\oplus}{C}H_2$ no resonance +I-eff

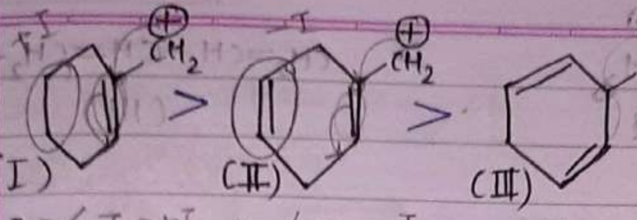
so, II > III > I

phenyl (C_6H_5)

eg: I $(C_6H_5)_2\overset{\oplus}{C}H$ II $(C_6H_5)_3\overset{\oplus}{C}$ III $CH_2=CH-\overset{\oplus}{C}H_2$

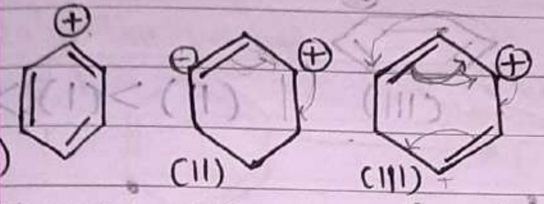
⟶ II > I > III

Stability of carbocation +I -I

Q:7 

(I) R = ✓ I = +I (II) R = ✓ I = -I (III) R = X I =

+I supports carbocation more hence I > II > III

Q:8 

(I) R = X (II) R = ✓ (III) R = ✓

Benzene with + or free radical it is highly unstable.

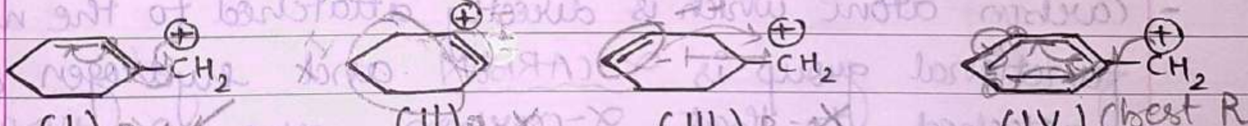
III > II > I

*** NOTE:**
- if any ion or free radical is present over BENZENE ring, i.e. makes the most unstable condition due to its impact over Aromaticity of Benzene. most stable condition

Q:9 (I) $CH_3\rightarrow\overset{\oplus}{C}-CH=CH_2$ with CH_3 below C (in reson.) (II) $CH_3-\overset{\oplus}{CH}-CH=CH_2$ (in resonance) (III) $\overset{\oplus}{CH_2}-CH=CH_2$

R = ✓ I = +I I = +I R = ✓ I = -I (not consi

→ I > II > III

Q:10 

(I) R = ✓ (II) R = X (III) R = X (IV) (best R). R = ✓ (branch have +).

→ (IV) > (I) > (III) > (II)

distance of ± (-minus) from ⊕ starts

*(B) ⇒ Stability of carbanion:

eg: (I) $\overset{\ominus}{CH_2}=CH=CH_2$ (II) $CH_3-\overset{\ominus}{CH_2}$ (III) $CH_2=\overset{\ominus}{CH}$

R = ✓ R = X I = +I R = X I = -I

→ (I) > (III) > (II)

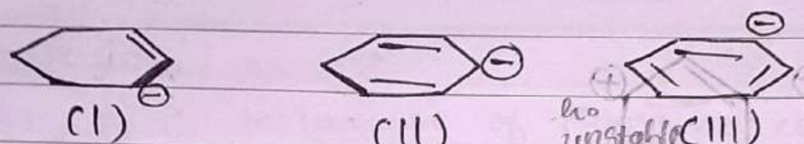
-I ↑ to stability of carbanion ↑.

Q:11 $(C_6H_5)_3\overset{\ominus}{C} > (C_6H_5)\overset{\ominus}{C}H_2 > CH_2=CH-CH=CH_2-\overset{\ominus}{C}H_2$

(I) (II) (III)

→ 3 benzene ring 1 ring

Q:12



(I) (II) no unstable (III) benzene with '−' chrg:

(II) > (I) > (III)

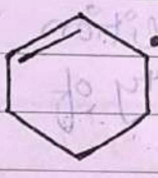
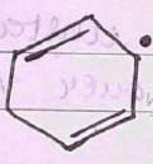
Q:13 $CH_2=CH-\dot{C}H_2$ $CH_2=\dot{C}H$ $CH_2=CH-\dot{C}H-CH=CH_2$

(I) (II) (III)

→ R✓ R× R✓

(III) > I > II

Q:14

(I)  (II)  more R (III)  Benzene with '•'

→ (III) > (I) > (II)

✱ α-Carbon and α-Hydrogen:

- carbon atom which is directly attached to the main functional group is α-CARBON and hydrogen atom attached to that α-carbon are α-HYDROGEN.

eg: $\underset{\gamma}{CH_3}-\underset{\beta}{CH_2}-\underset{\alpha}{CH_2}-CHO$ $\underset{\alpha}{CH_3}-\underbrace{CH=CH_2}_{F.G}$

Q:15 find no. of α-H in the following compounds:

⟹

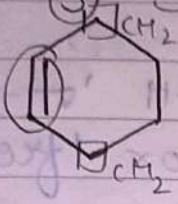
1) $\overset{\alpha}{C}H_{③}\overset{\oplus}{C}H_2 \longrightarrow 3$

2) $\overset{\alpha}{C}H_{③}\overset{\ominus}{C}H_2 \longrightarrow 3$

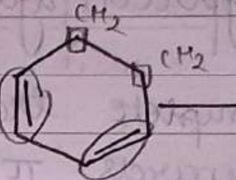
3) $CH_3-CH_2-\overset{\alpha}{C}H_{②}-CHO \longrightarrow 2$

4) $CH_2=CH_2 \longrightarrow 0$

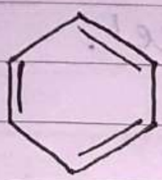
5.) $\overset{\alpha}{CH_{③}}-\underbrace{CH=CH}_{FG}-\overset{\alpha}{CH_{③}} \longrightarrow 6$

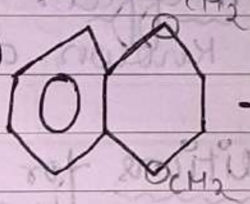
6.)


$\longrightarrow 4$

7.)


$\longrightarrow 4$

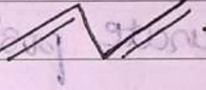
8.)

$\longrightarrow 0$

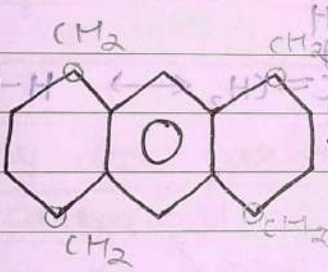
9.)


$\longrightarrow 4$

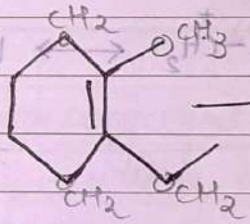
10.)


$\longrightarrow 0$

11.)

$\longrightarrow 0$

12.)


$\longrightarrow 8$

13.)


$\longrightarrow 9$

14.) $HCHO \longrightarrow 0$

15.) $CH_3\overset{\alpha}{C}H_2\dot{C}H_2 \longrightarrow 2$

α-H ↑ ∝ Stability ↑ ∝ H-eff ↑