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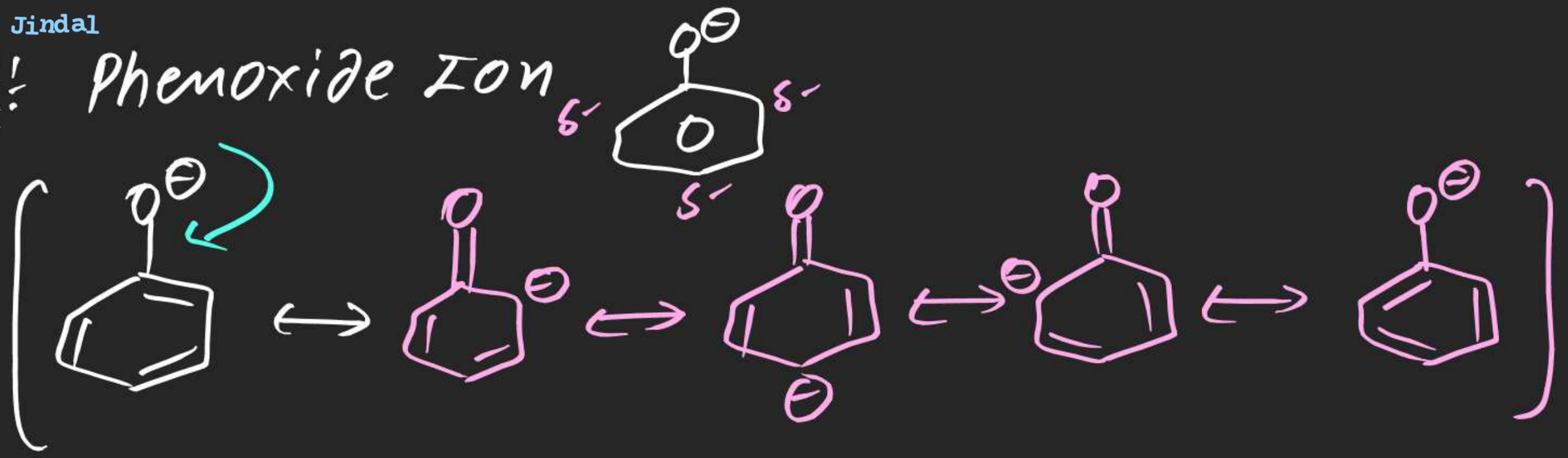
Ex: Phenoxide Ion



Note +R series

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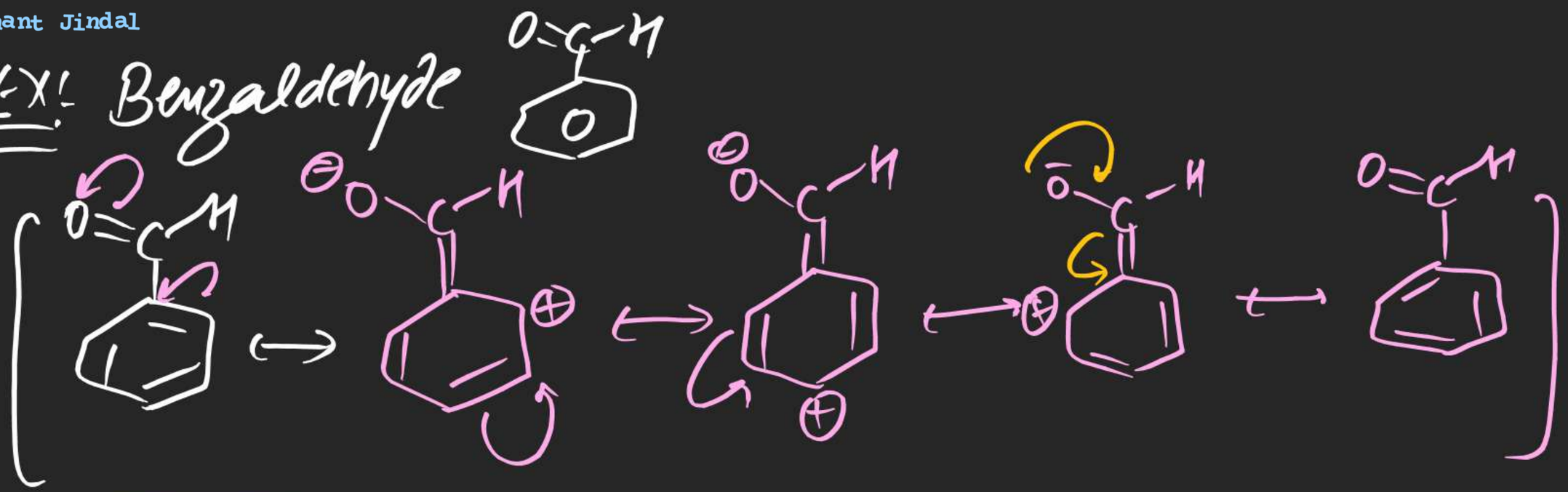
Ex: Benzaldehyde



-R series :

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⟹ Order of Rate of electrophilic attack.

Activating Compounds: All compounds which show higher rate of electrophilic substitution than Rate of electrophilic substitution of Benzene, are known as Activating Compounds.

Highly Activating Groups

$-NR_2$, $-NHR$, $-NH_2$, $-OH$, $-O^{\ominus}$, $-CH_2^{\ominus}$, $-OR$

+R

Moderately Activating Groups

$-\ddot{N}H-\overset{\overset{O}{\|}}{C}-CH_3$ / $-\ddot{O}-\overset{\overset{O}{\|}}{C}-CH_3$

+R

Weakly Activating Group

$-CH_3$, $-CH_2-CH_3$, $-CH(CH_3)_2$, $-C(CH_3)_3$

+H / +I

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Note:

EDG

↓

("σ" e⁻s + "π" e⁻s)

I effect R effect

EDG:

+R & +I — Compound Activating

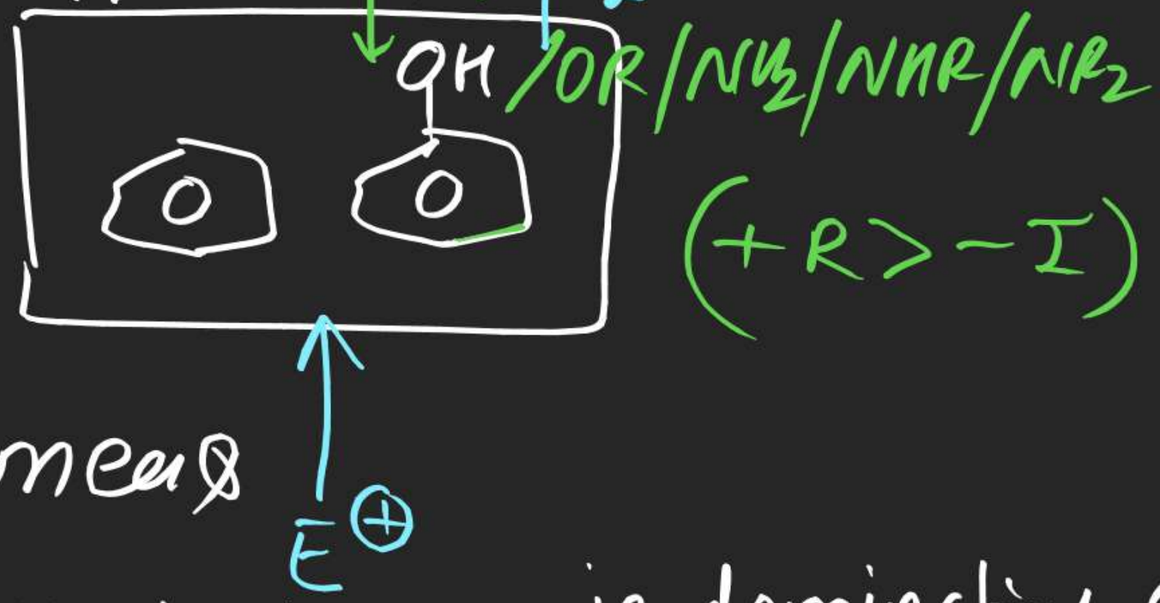
[+R > -I] +R & -I — Compound Activating

-R & -I — Compound deactivating

-R & +I — Compound deactivating (Hypothetical Combination)

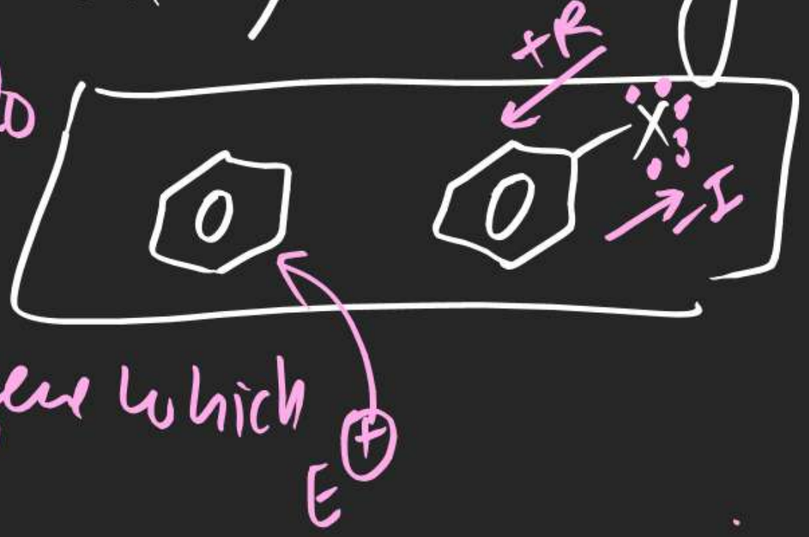
[+R < -I] +R & -I — Compound Deactivating (In case of halogens)

(ii) out of Benzene & Phenol Electrophile prefer to attack on phenol, it means



+R effect of -OH is dominating over -I effect of OH

(iii) out of Benzene & halo Benzene, Electrophile prefer to attack on Benzene which means



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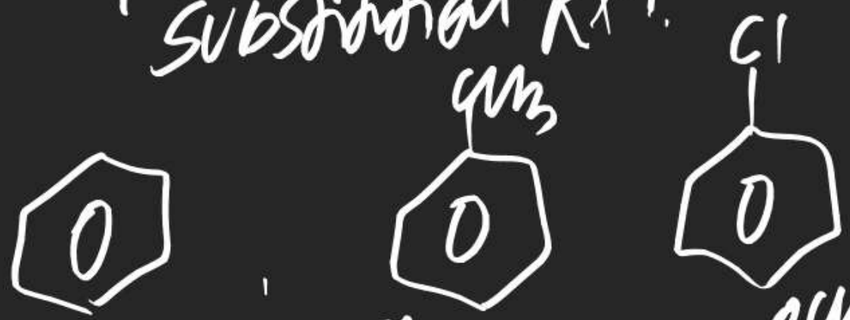
For haloBenzene :

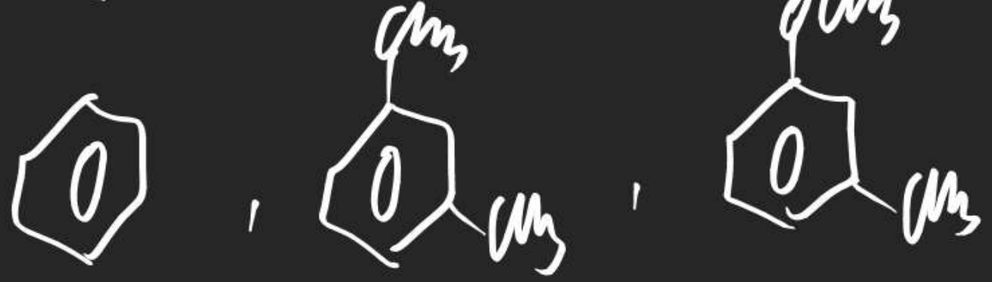
$-I$ effect of "X" $>$ $+R$ effect of "X" — For rate of Electrophilic Substitution

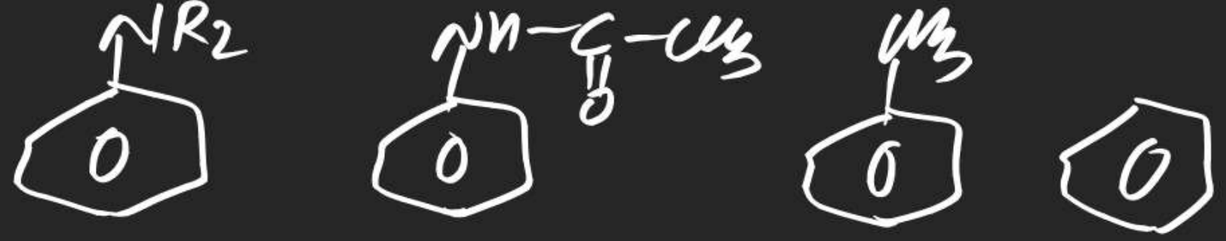
$+R$ effect of X $>$ $-I$ effect of X — For orientation of electrophile

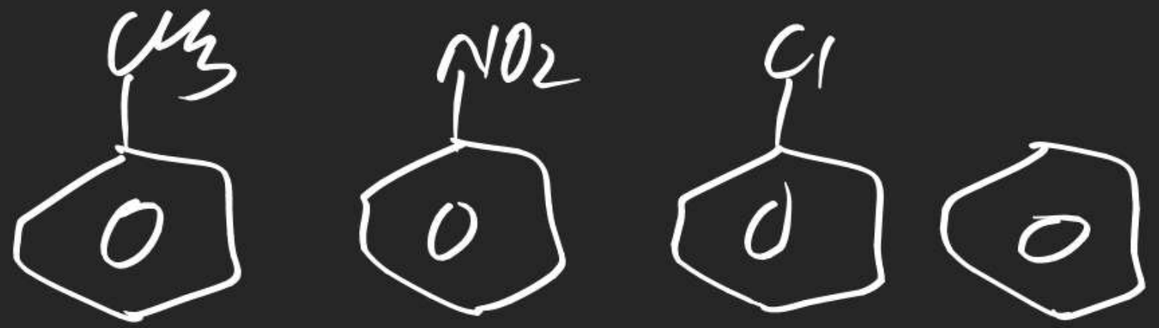
Ex: (1) Arrange following in decreasing order of rate of electrophilic substitution Rxn.

(a) 

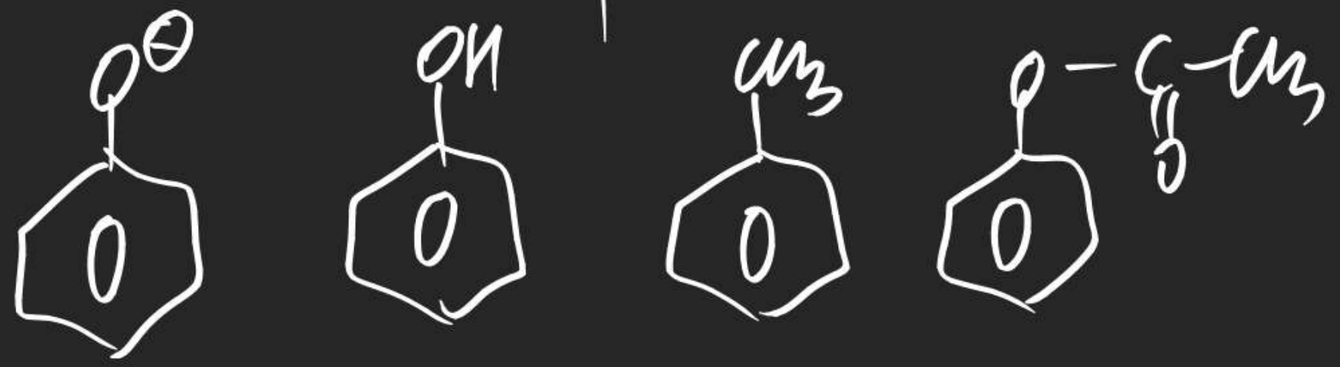
II > I > III

(b) 

(c) 

(d) 

(e) 

(f) 

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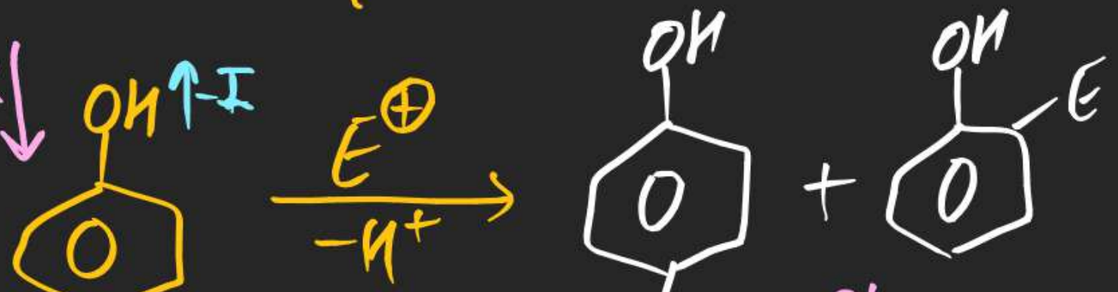
EX-2 Write product of following Reaction

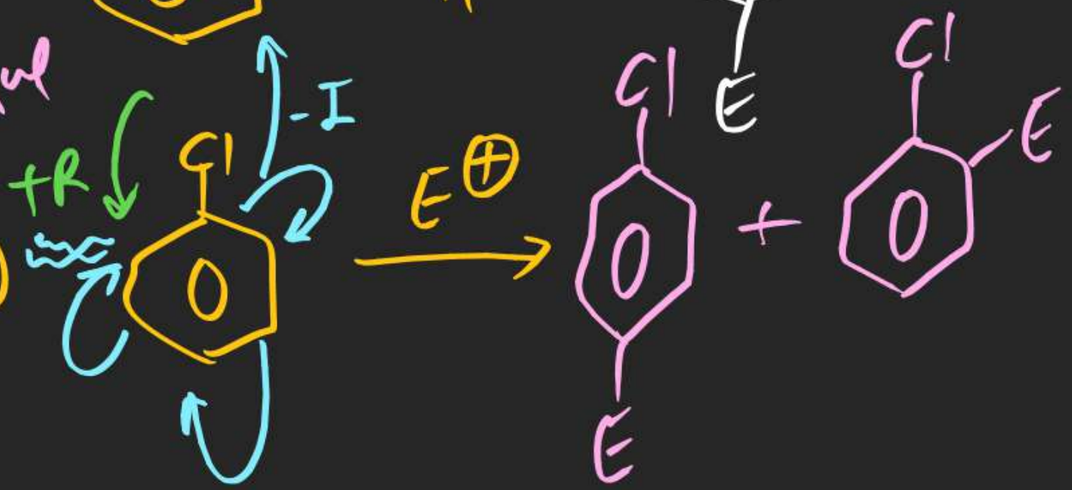
(a)

Activating (+R) (b)



(O & para)

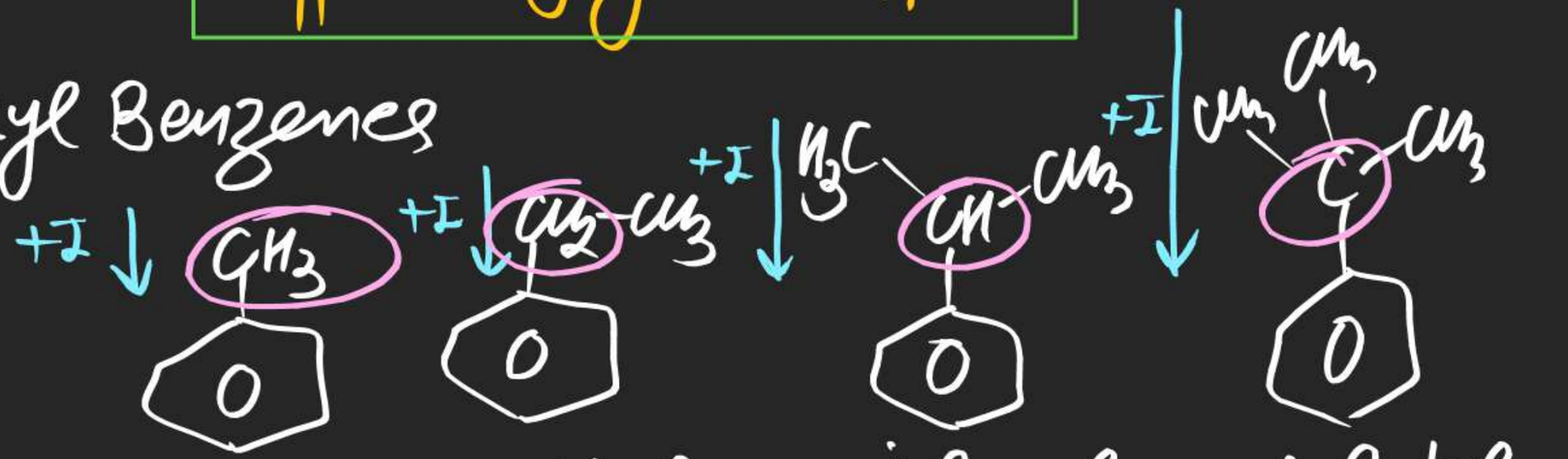
deactivating (c)



(ortho & para)

Hyperconjugation effect

For alkyl Benzenes



Nathan Bakes

Toluene (A)

Ethyl Benzene (B)

i-Propyl Benzene (C)

t-Butyl Benzene (D)

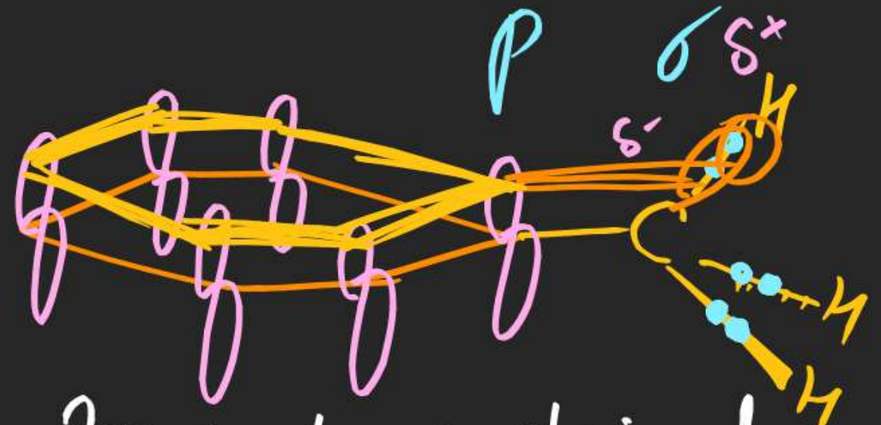
Order of rate of electrophilic substitution should be

जलत है $\times$ $D > C > B > A$ [Acc. to +I effect]

Nishant Jindal

⟹ But Experiment shows actual order of Rate of electrophilic attack is

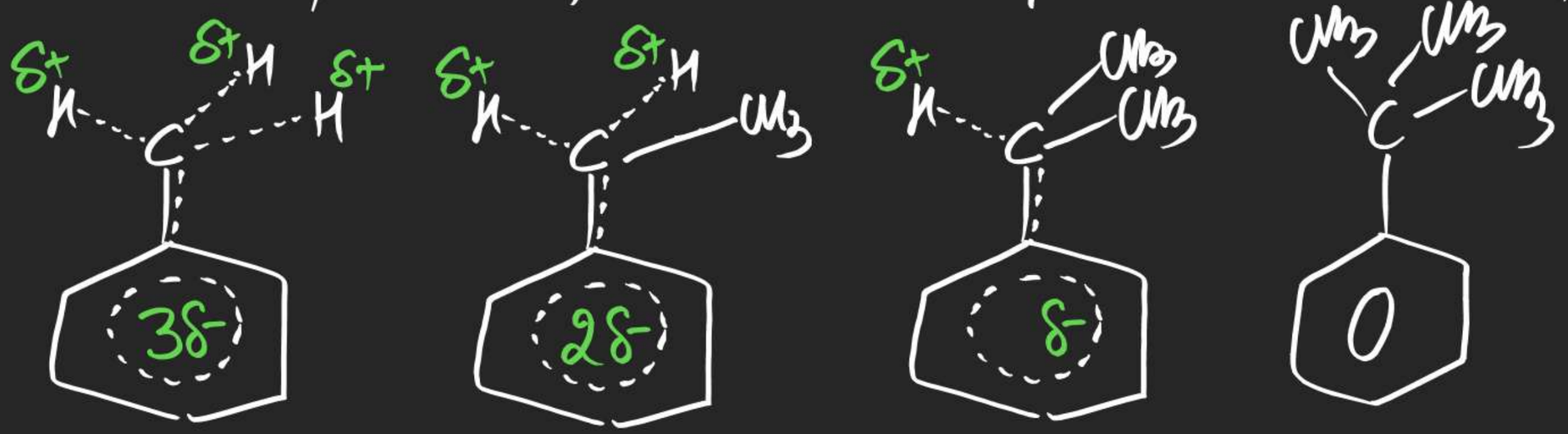
सही है $\boxed{A > B > C > D}$ (due to effect)



$BO(C-H) \in (0, 1)$

this order can be explained by overlapping b/w "P" orbital of Benzene with σ orbital of C–H Bond of directly attached alkyl group.

higher the No. of such $\geq C-H$ Bonds higher would be such



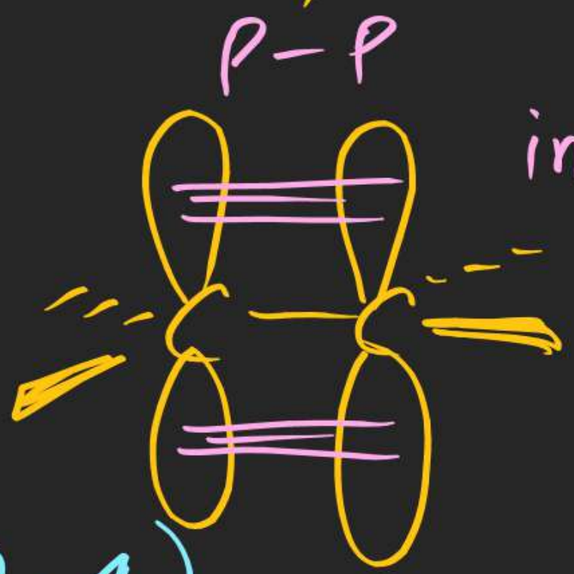
(A) (B) (C) (D)

overlapping & higher wd be electron density in Ring.

Note (1) This phenomenon is known as hyperconjugation & effect is known as hyperconjugation effect.

(ii) hyperconjugation involves ($\sigma - P$) overlapping

(iii) Condition of hyperconjugation.



in Resonance

(iv) Bond angle of C–H Bond $\in (0, 1)$

(v) Also known as Nathan Baker effect.

(vi) H effect is stronger effect than Inductive effect (I effect)

$(H > I)$

(vii) H effect is weaker effect than R effect

$$R > H > I$$

(viii) Permanent effect.

(ix) Distance independent effect.