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For haloBenzene :

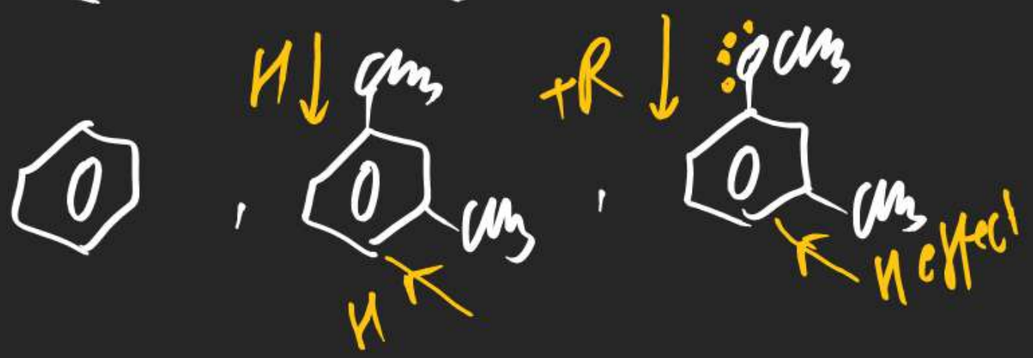
$-I$ effect of "X" $>$ $+R$ effect of "X" — For rate of Electrophilic Substitution

$+R$ 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) 

III > II > I

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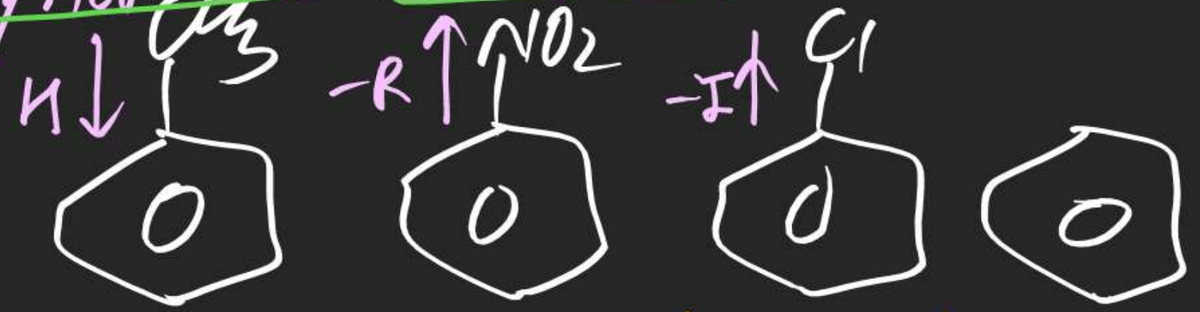
(c)

Highly Activated Mod. Activated

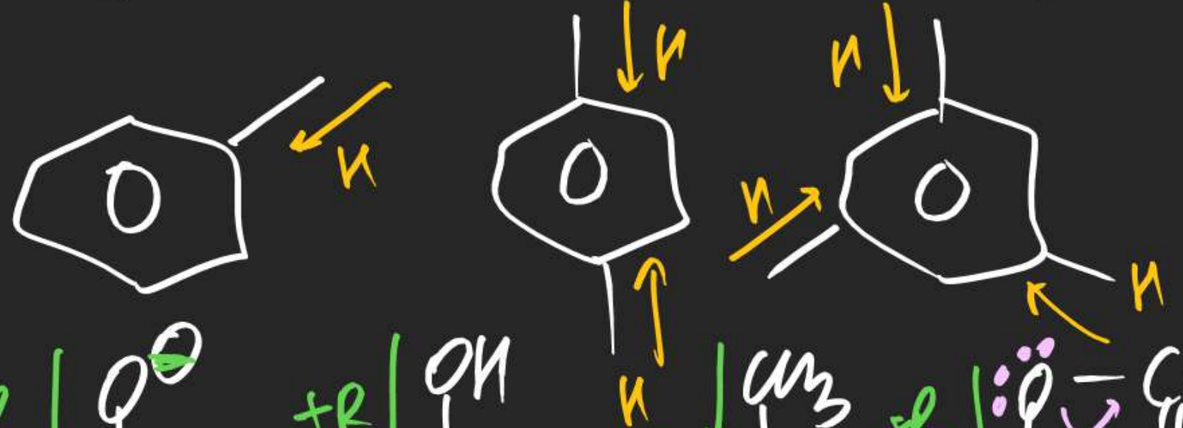
I > II > III > IV

(d)



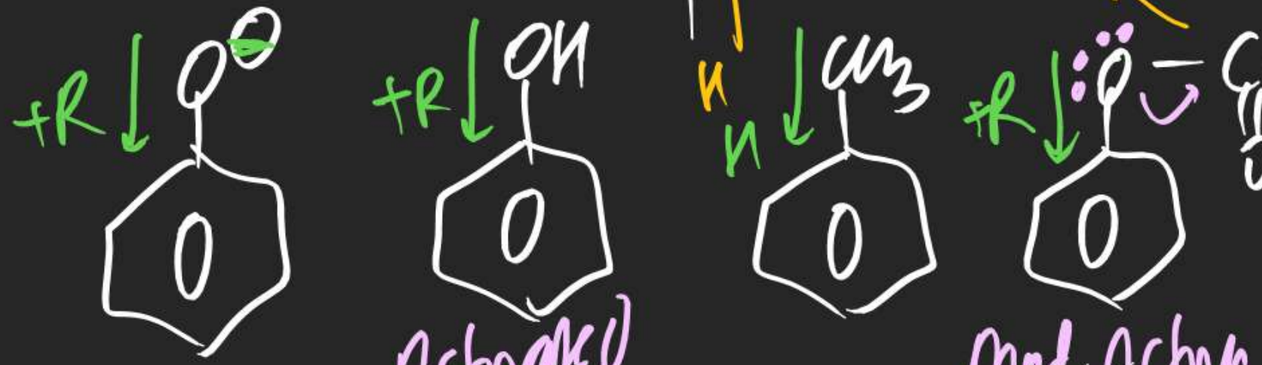
I > IV > III > II

(e)



III > II > I

(f)



Activated Mod. Activ

I > II > IV > III

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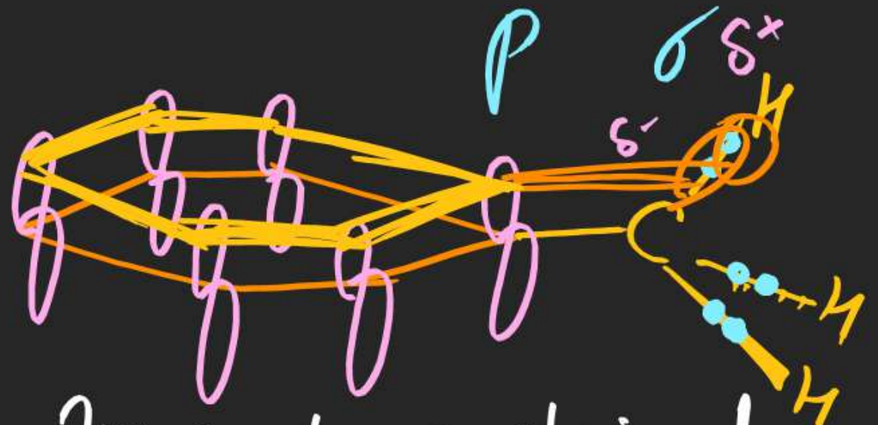
⇒ But Experiment shows actual order of Rate of electrophilic attack is

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.

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(vii) H effect is a weaker effect than R effect

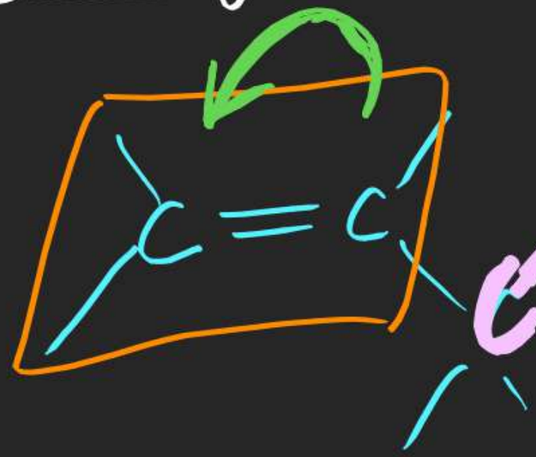
$$R > H > I$$

(viii) Permanent effect.

(ix) Distance independent effect

Types of H effect:

(1) +Hyper Conjugation effect (+H effect) Permanent displacement of π e^- density away to directly attached alkyl group due to its σ (C–H) Bond e^-, is known as



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+H effect of that alkyl group.

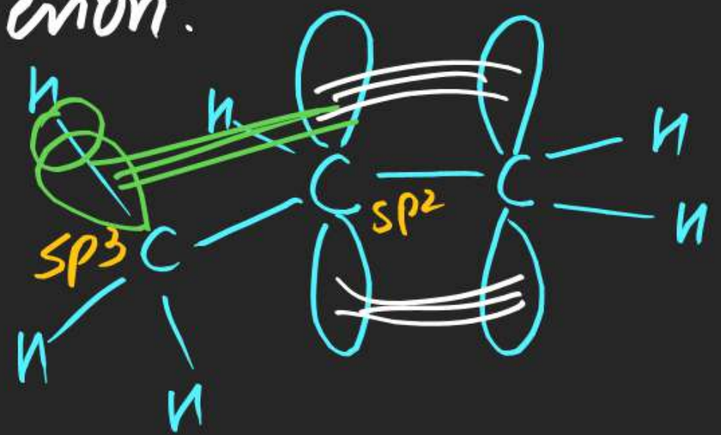
Ex:(1) which of the following contains H effect phenomenon.

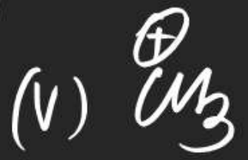
(i) ✓ $CH_3-CH=CH_2$

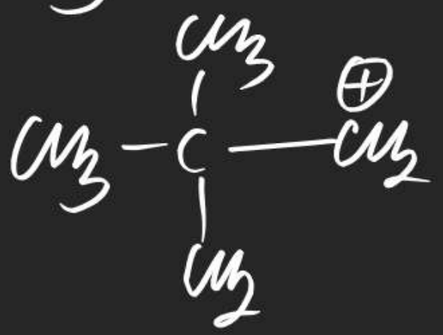
(ii) ✓ $CH_3-\overset{\oplus}{C}H_2$ (sp^3, sp^2)

(iii) ✓ $CH_3-\dot{C}H_2$ (sp^3, sp^2)

(iv) ✗ $CH_3-\overset{\ominus}{C}H_2$ (sp^3, sp^3)



(v) 

(vi) 

(vii)

(viii)

(ix)

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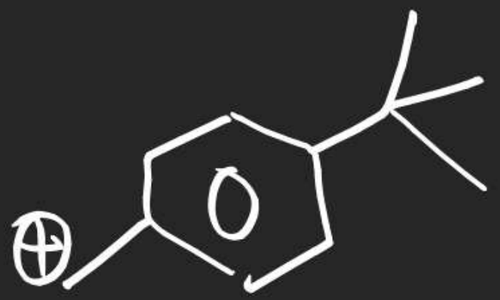
(x)

(xi) $CH_2=CH-CH=CH_2$

(xii) $H_3C-CH=O$

(xiii)

(xiv) 

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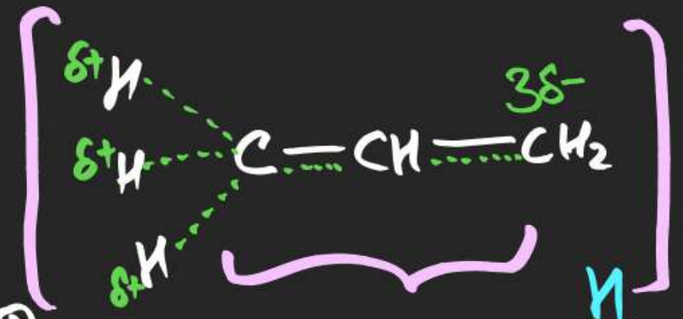
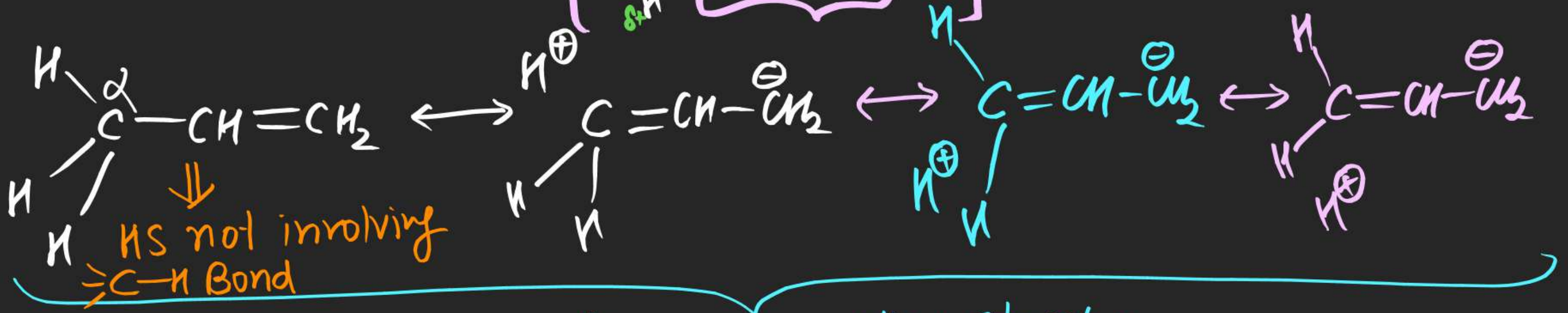
Ex-2: Propene:



Hyperconjugation Hybrid



⇓ HS not involving C—H Bond

Hyperconjugating structure.

Note: (i) +H effect is E Donating effect.

(ii) Total no. of HS = HS not involving C—H Bond + HS involving C—H Bond

$= 1 + N_{\alpha H}$

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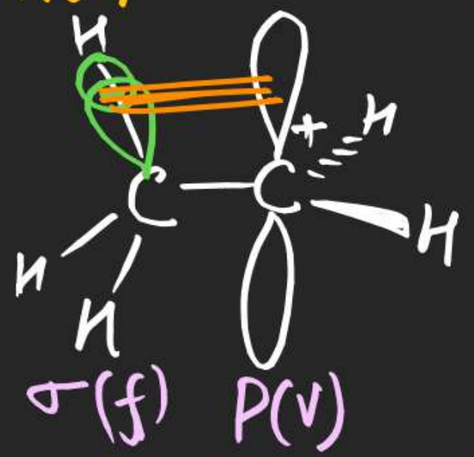
(iii) Total No. of Hs involving (C–H) Bond = $N_{\alpha H}$

(iv) +H effect increases e^- density at ortho & para position for electrophilic attack.

(v) Orbital overlapping in

Ethyl Carbocation

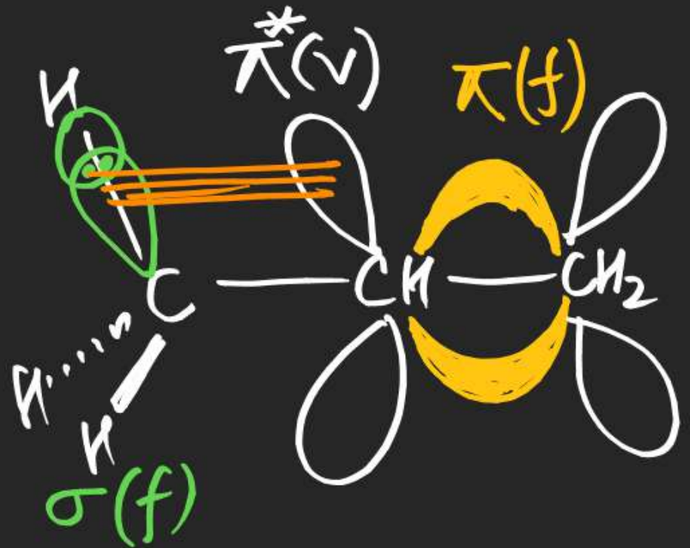
$\sigma(f)-P(v)$



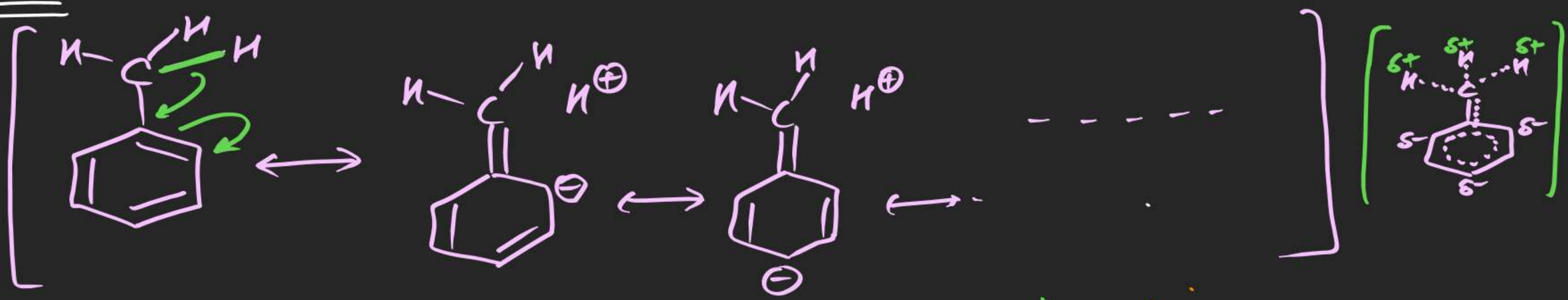
& in Propene

$H_3C-CH=CH_2$

$\sigma(f)-\pi^*(v)$



Ex-3:- Toluene



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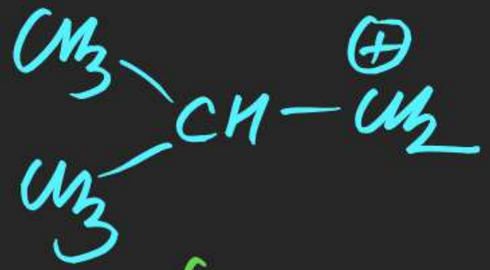
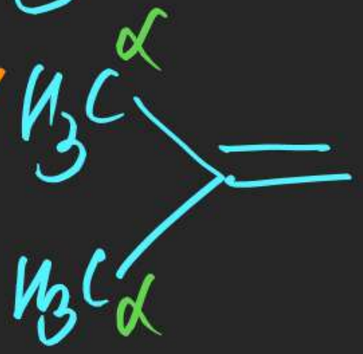
EX-4: Total no. of Hs str involving C–H Bond.

(i) $CH_3-\overset{\oplus}{C}H-CH_2-CH_3$

(ii) 

(iii) 

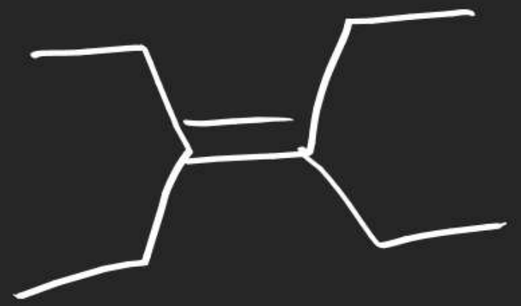
(iv)

5

(v)

(vi)

6

(vii) 

(viii)

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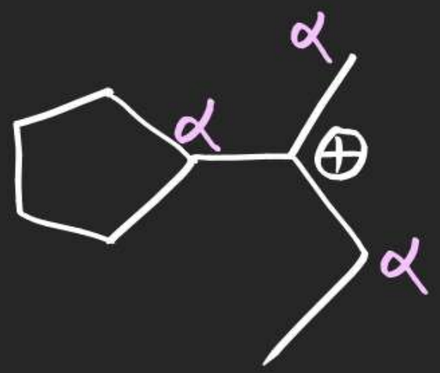
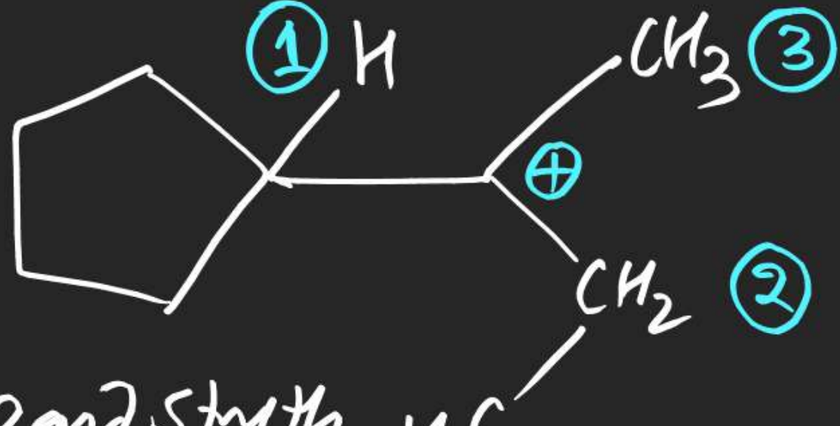
(ix)



$\Longrightarrow$



6

Ans

Note: H effect depends on Bond strength

Arrange following in ↓ order of **+H effect** when attached with a "sp^2" Carbon

(a) $-CH_3$, $-CD_3$, $-CT_3$ $\quad (I > II > III)$

Bond strength order: C–T > C–D > C–H

(b) $-CH_3$, $-CH_2D$, $-CHD_2$, $-CD_3$ $\quad (I > II > III > IV)$

(c) $-\overset{3}{C}H_3$, $-\overset{2}{C}H_2-CH_3$, $-\overset{1}{C}H(CH_3)-CH_3$, $-\overset{0}{C}(CH_3)_3$ $\quad (I > II > III > IV)$

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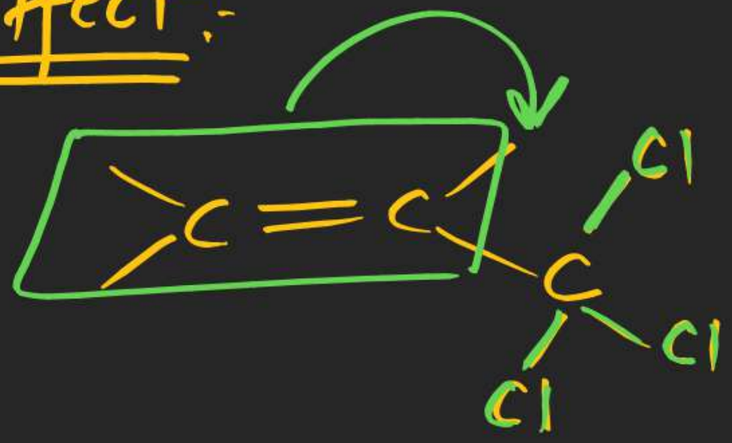
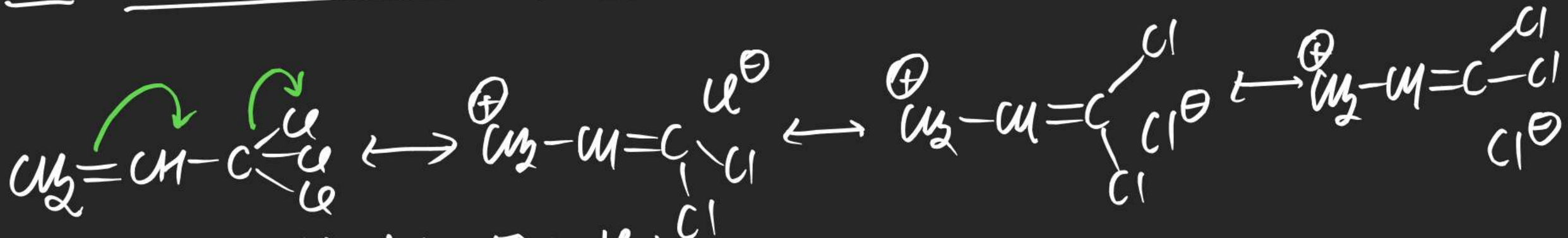
(#) −H effect :-



when πe^- density gets displaced towards attached group ($-CCl_3$) it is known as − H effect of $-CCl_3$.

EX: 3,3,3-Tri Chloro Propene :



Note (i) −H effect is EW effect.

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Resonance effect > Hyperconjugation effect > Inductive effect

ED effect	+R effect	+H effect	+I effect
EW effect	−R effect	−H effect	−I effect

Stability of Reaction Intermidiates :-

(*) Stability of Carbocation $\propto$ ED groups $(+R, +H, +I) \propto \frac{1}{-I, -H, -R}$

(*) Stability of Carbon free Radical $\propto$ ED groups $(+R, +H, +I)$ $\propto$ EW group $(-R)$ $\propto \frac{1}{-I, -H, -R}$

(*) Stability of Carbanion $\propto$ EW groups $(-R, -H, -I) \propto \frac{1}{+I, +H, +R}$

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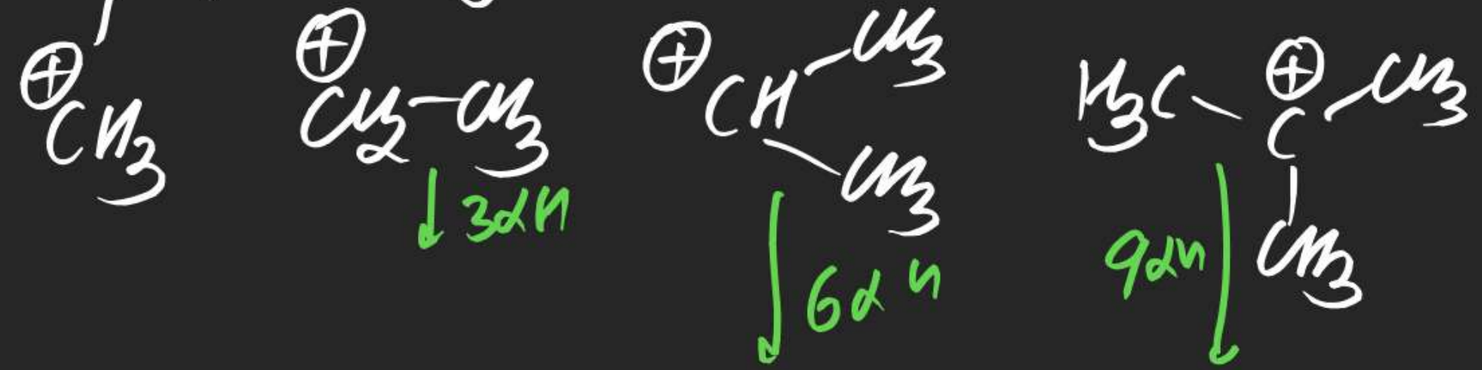
(#) Arrange following in ↓ order of stability

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

↓ 3α H $\quad$ ↓ 6α H $\quad$ ↓ 9α H

IV > III > II > I
(due to +H effect)



(2) $\dot{C}H_3$ $\quad$ $\dot{C}H_2-CH_3$ $\quad$ $\dot{C}H(CH_3)_2$ $\quad$ $H_3C-\dot{C}(CH_3)_2$

IV > III > II > I
(due to +H effect)

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

I > II > III > IV

(4) $\overset{\oplus}{C}H_2-CH_3$ $\quad$ $\overset{\oplus}{C}H_2-CD_3$ $\quad$ $\overset{\oplus}{C}H_2-CT_3$

(5)

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(6)

(7) $\overset{\oplus}{C}H_2-CD_3$ $\overset{\oplus}{C}H_2-CHD_2$ $\overset{\oplus}{C}H_2-CH_2D$ $\overset{\oplus}{C}H_2-CH_3$

(8)

(9)

(10) $\overset{\oplus}{C}H_3$ $\overset{\oplus}{C}D_3$ $\overset{\oplus}{C}T_3$

(11)

(12)

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(13)

(14)

(15)

(16)

(17)

(18)

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(19)

(20)

(21)

(22)

(23)

(24)

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(25) $\overset{\oplus}{C}H_3$ $\overset{\oplus}{C}Cl_3$

(26)

(27)

(28)

(29)

(30)

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(31) $m_3 - \overset{\oplus}{m_2}$ $m_2 = \overset{\oplus}{m_1}$ $HC \equiv \overset{\oplus}{C}$

(32)

(33)