For haloBenzene :

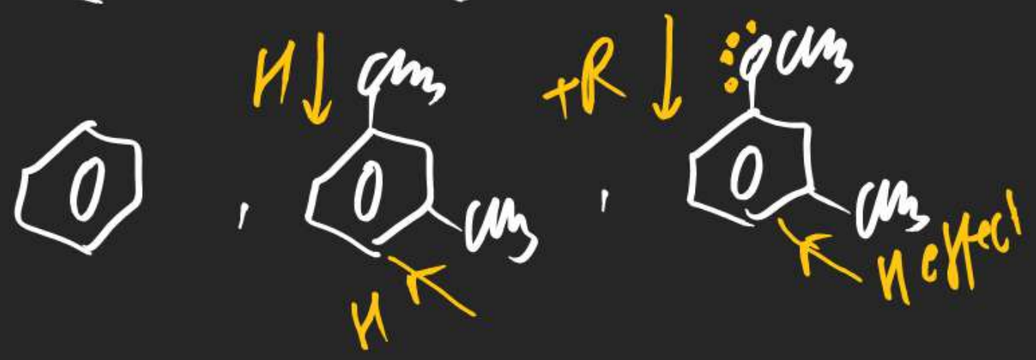
$-I$ effect of "X" $>$ $+R$ effect of "X" — For rate of Electrophilic Substitution

$+R$ 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

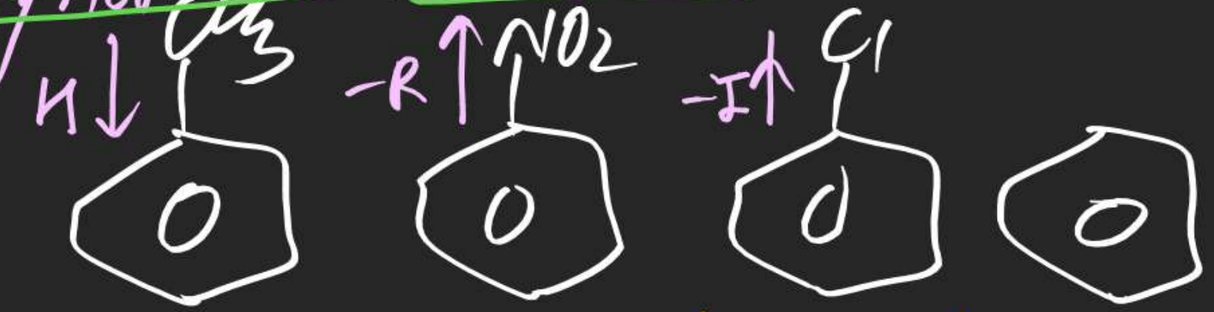
(b) 

III > II > I

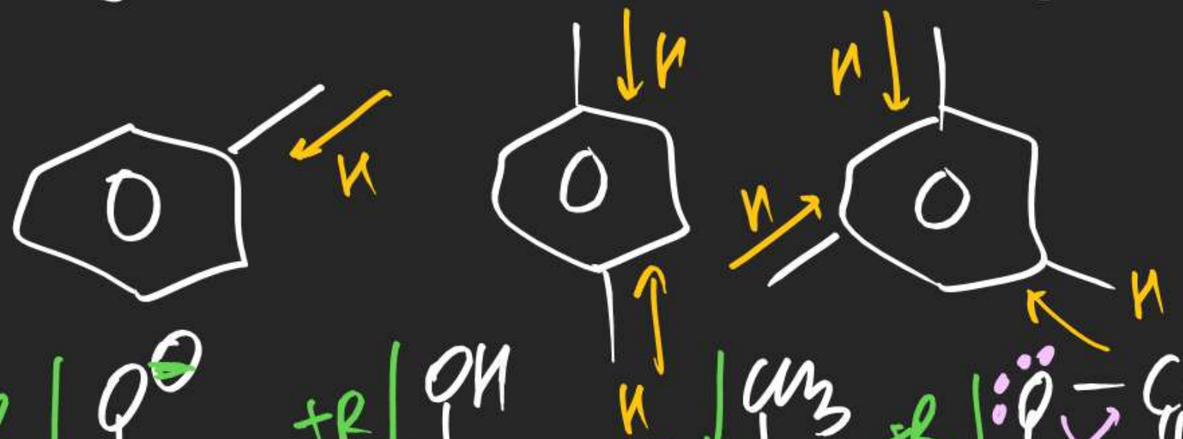
(c) 

Highly Activated Mod. Activated

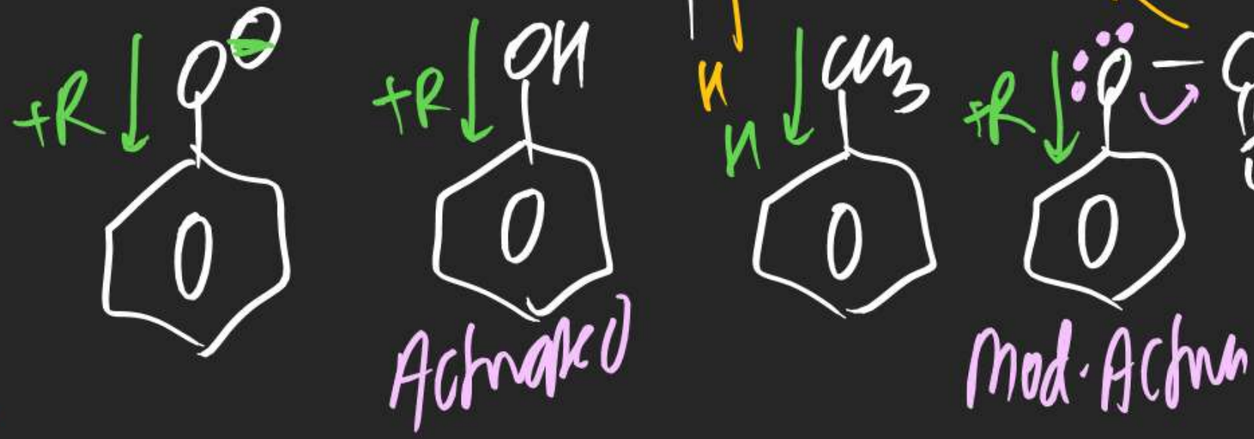
I > II > III > IV

(d) 

I > IV > III > II

(e) 

III > II > I

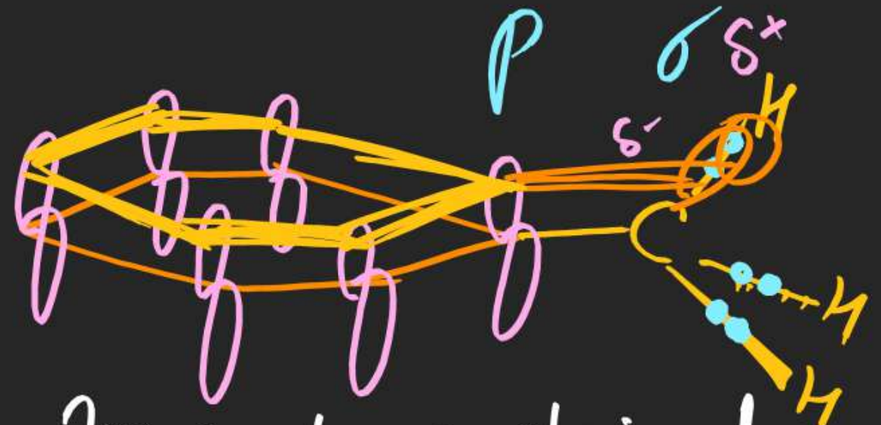
(f) 

Activated Mod. Activa

I > II > IV > III

⇒ 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.

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

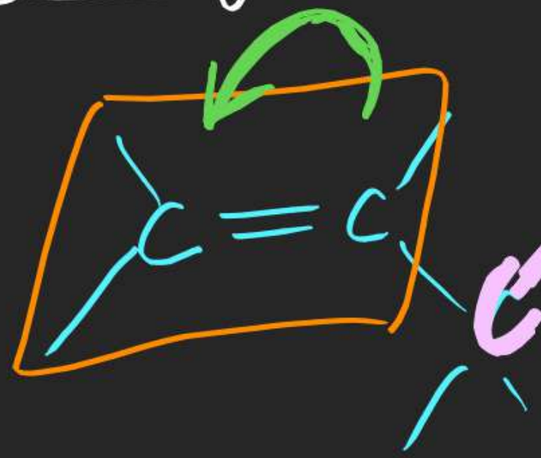
$$R > H > I$$

(viii) Permanent effect.

(ix) Distance independent effect

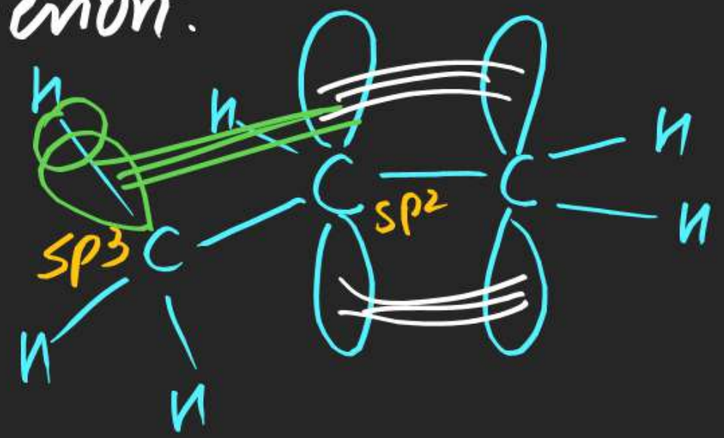
Types of H effect:

(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



+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) $\overset{\oplus}{C}H_3$

(vi) $CH_3-C(CH_3)_2-\overset{\oplus}{C}H_2$

(vii)

(viii)

(viii)

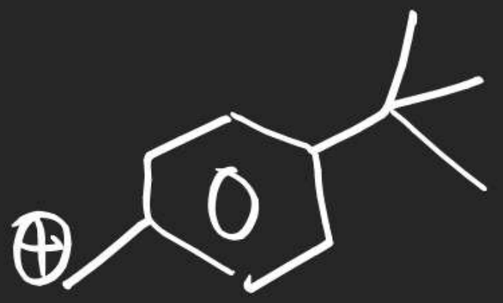
(ix)

(x) 

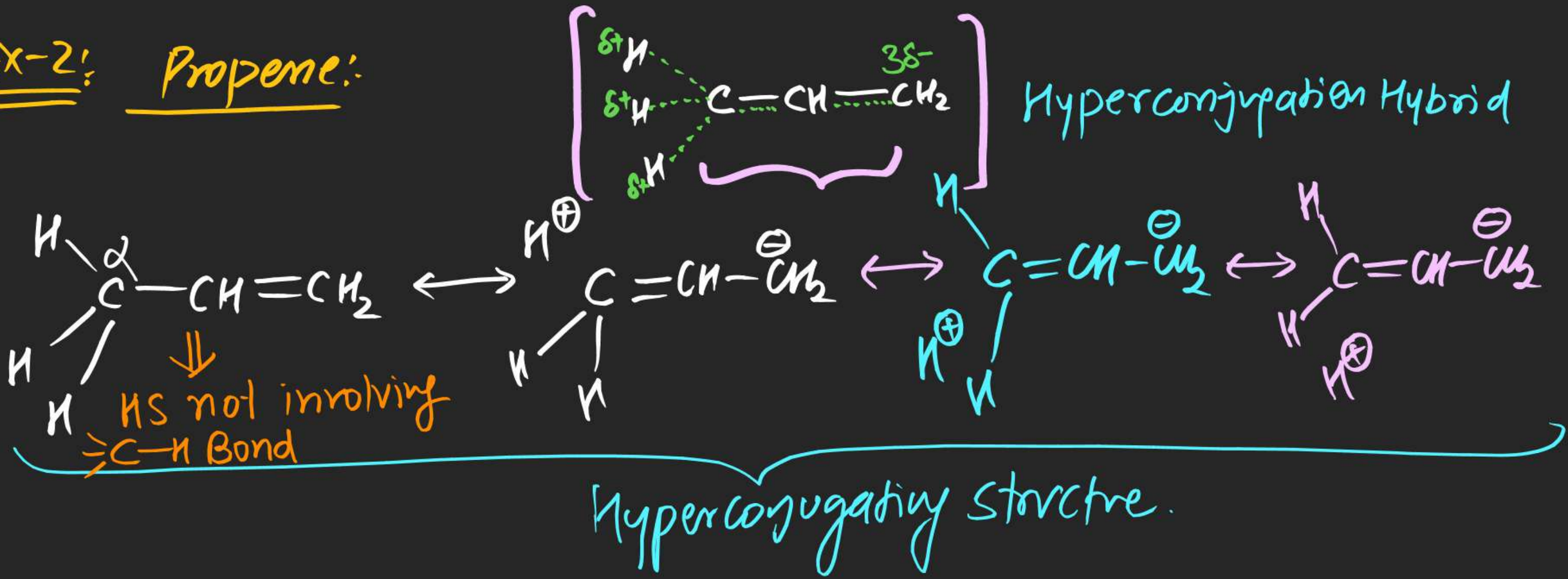
(xi) $CH_2=CH-CH=CH_2$

(xii) $H_3C-CH=O$

(xiii) 

(xiv) 

Ex-2: Propene:



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

(ii) Total no. of Hs = Hs not involving C–H Bond + Hs involving C–H Bond

$$= 1 + N_{\alpha H}$$

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

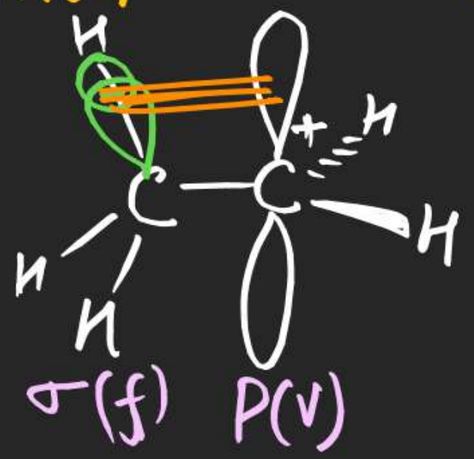
(iv) +H effect increases e^- density at ortho & para position for electrophilic attack.

(v) Orbital overlapping in

Ethyl Carbocation

$H_3C-\overset{\oplus}{C}H_2$

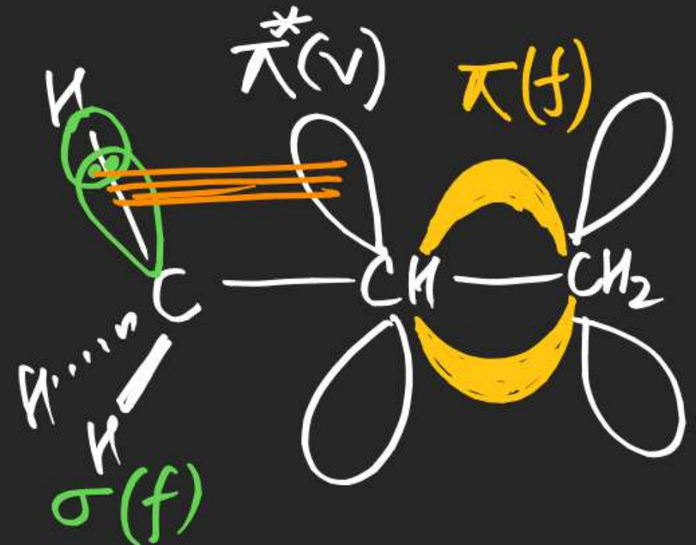
$\sigma(f)-P(v)$



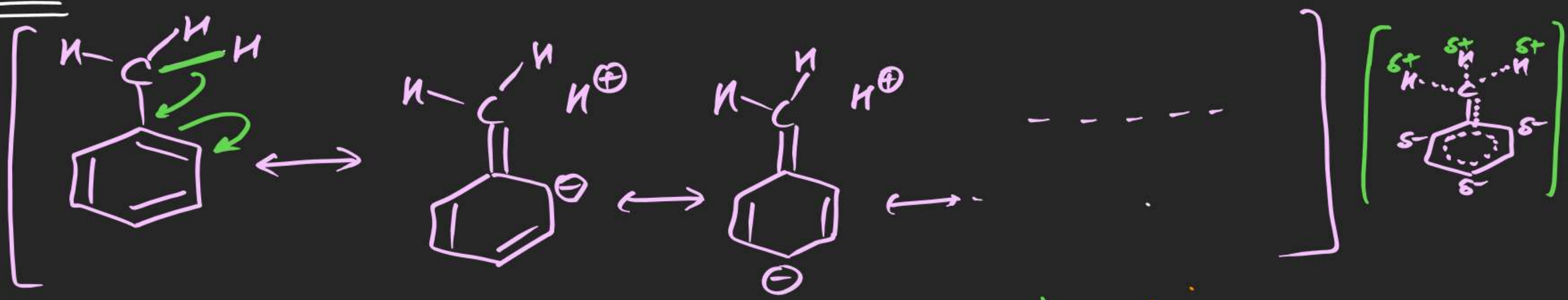
& in Propene

$H_3C-CH=CH_2$

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

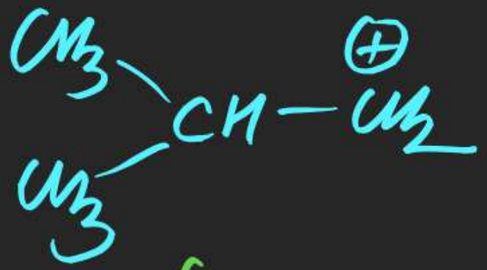


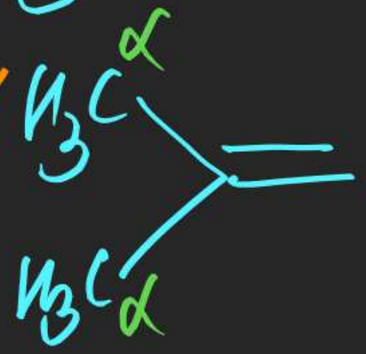
Ex-3:- Toluene

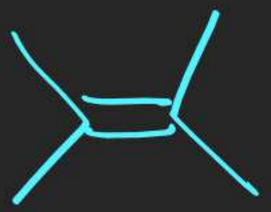


EX-4: Total no. of Hs str involving C–H Bond.

(i) 

(ii) 

(iii) 

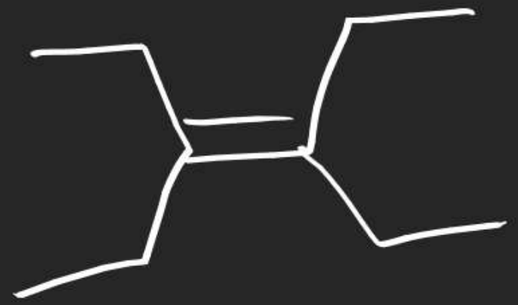
(iv) 

5

6

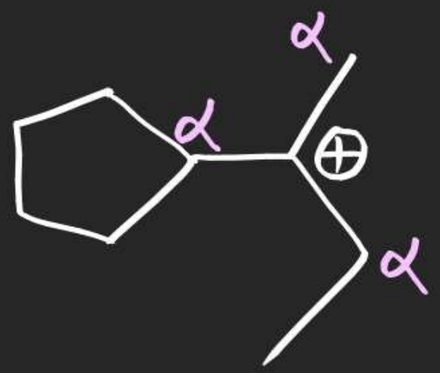
(v) 

(vi) 

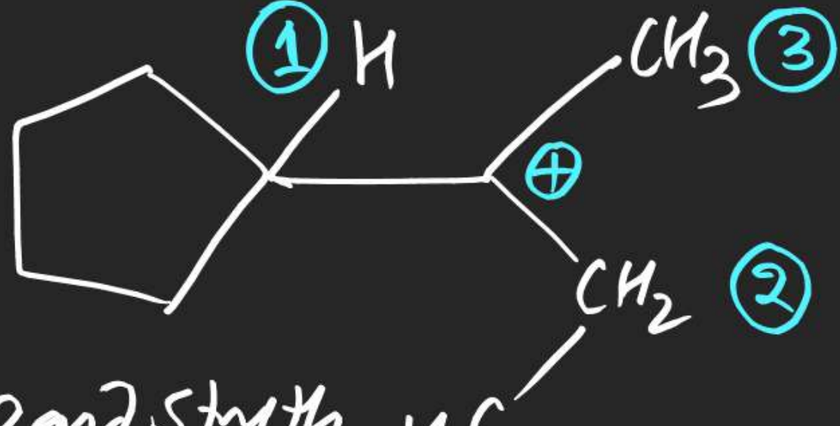
(vii) 

(viii) 

(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

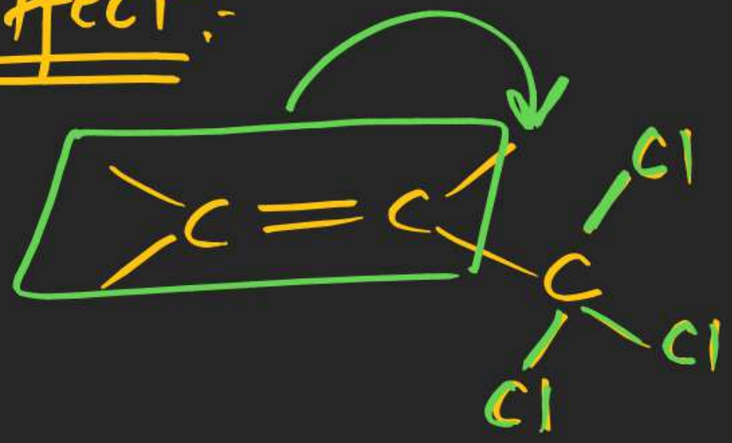
(a) $-CH_3$, $-CD_3$, $-CT_3$ $\quad (I > II > III)$

Bond strength order $C-T > C-D > C-H$

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

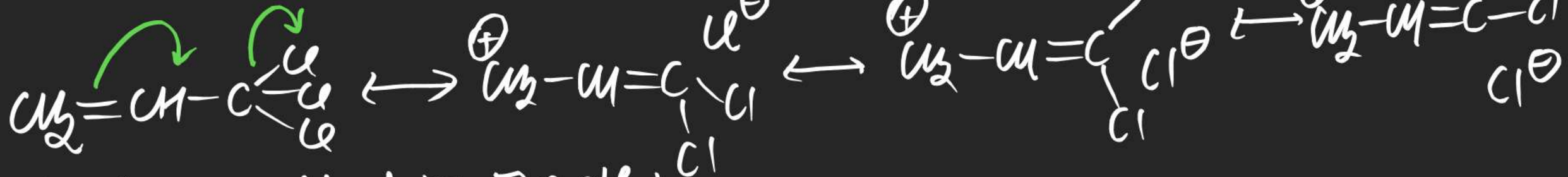
(c) $\overset{3}{-CH_3}$, $\overset{2}{-CH_2-CH_3}$, $\overset{1}{-CH(CH_3)-CH_3}$, $\overset{0}{-C(CH_3)_3}$ $\quad (I > II > III > IV)$

(#) −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.

Resonance effect > Hyperconjugation effect > Inductive effect

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

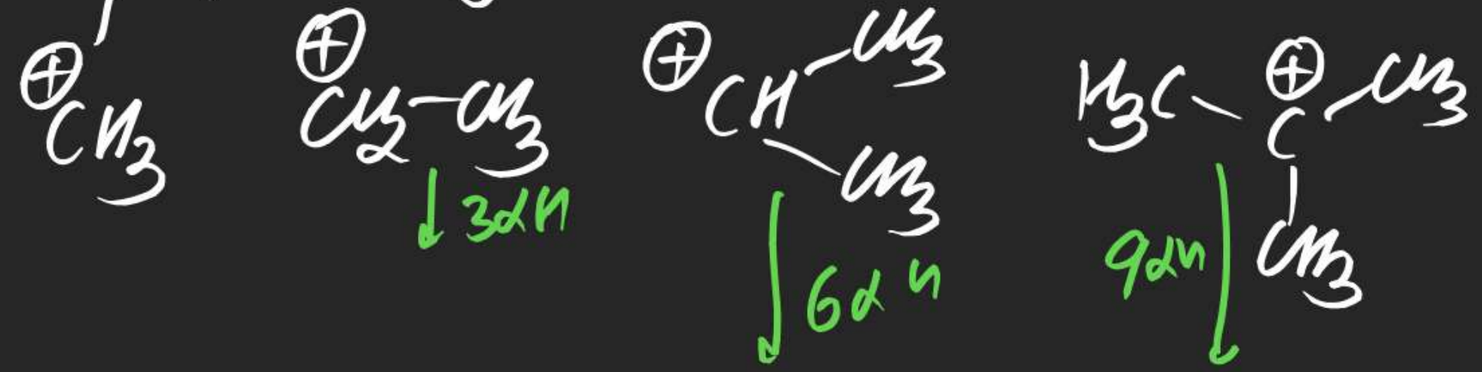
Stability of Reaction Intermidiates :

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

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

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

(#) Arrange following in ↓ order of stability

(1) 

3 α H

6 α H

9 α H

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

(2) 

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

(3) 

I > II > III > IV

(4) 

(5)

∴

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

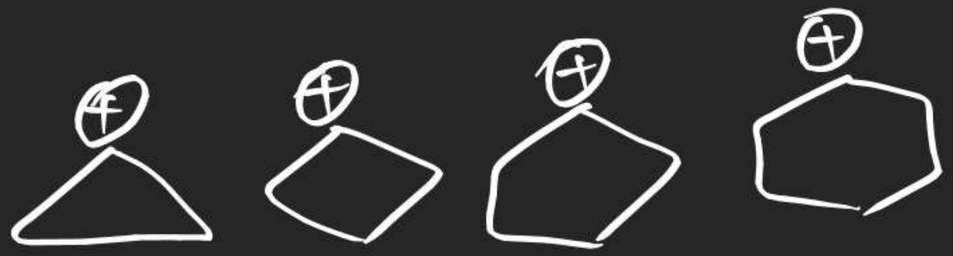
(11)

(12)

(13) 

(14)

(15)

(16) 

(17)

(18)

(19) 

(20)

(21)

(22) 

(23)

(24)

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

(26)

(27)

(28) 

(29)

(30)

(31) $m_3 - \oplus m_2 \quad m_2 = \oplus m_1 \quad HC \equiv \oplus C$

(32)

(33)