Nishant Jindal

(#) Nucleophiles (Nucleophilic Reagents):

⇒ Nucleophiles

⇒ Nucleus + loving

⇒ Electron dense species [lone pair or π-Bond pair]

⇒ Electron donar

(i) Negatively charged Nucleophiles:

⇒ Nucleophiles having (−)ve charge

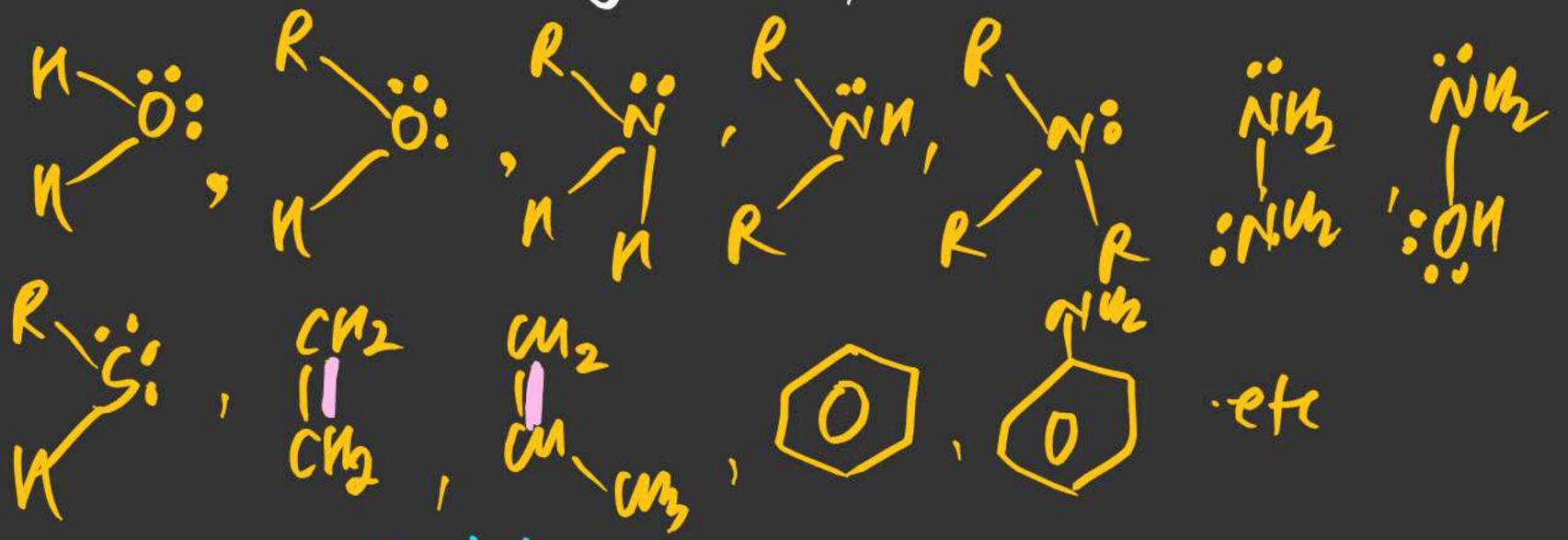
Ex: $H^{\ominus}$, $D^{\ominus}$, $T^{\ominus}$, $CH_3^{\ominus}$, $F^{\ominus}$, $Cl^{\ominus}$, $Br^{\ominus}$, $I^{\ominus}$, $OH^{\ominus}$, $OR^{\ominus}$, $NH_2^{\ominus}$ ..etc.

$LiAlH_4$, $NaBD_4$, Mg-mgcl

(ii) Neutral Nucleophiles :-

⇒ Nucleophiles having no any charge

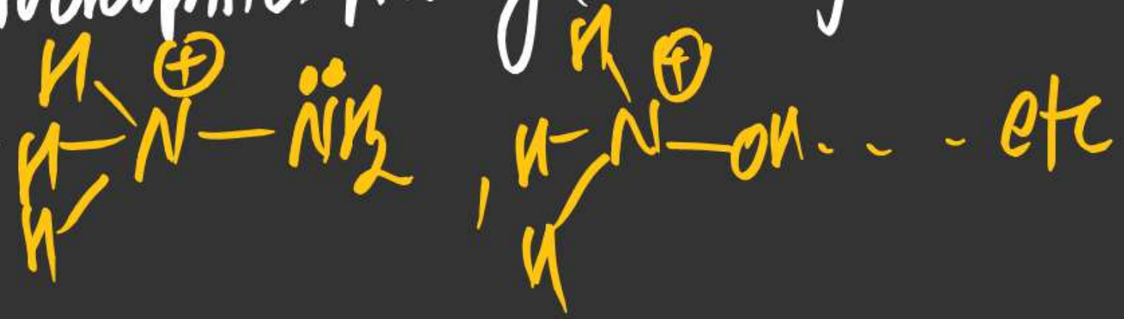
Ex :-



(iii) Positive Nucleophiles :-

⇒ Nucleophiles having (+)ve charge

Ex :-



Note (i) Alkali metal Cations are not Electrophile

$Na^{\oplus}$, $Li^{\oplus}$ - - - - -

(ii) Transitional metal Cations are Electrophiles

Ag^{+}, Hg^{+2}, Hg_2^{+2} - - - - - Electrophiles

(iii) Each Cation doesn't have vacant orbital But still may be electrophilic $\overset{\oplus}{N}H_4$, $H_3\overset{\oplus}{O}$ - - - Electrophiles

Formal charge

(iv) Each anion doesn't have lone pair But it may behave like Nucleophile

$\overset{\ominus}{B}H_4$, $\overset{\ominus}{B}F_4$ - - -

Formal charge

(v) on moving left to Right in Periodic table always analyse in terms of Electronegativity ⟶ En

(vi) on moving Top to Bottom in Periodic table always analyse in terms of Size

↓ Size

(vii) Negatively charged Nucleophiles are stronger Nucleophile than Neutral Nucleophile

(1) $^{\ominus}NH_2 > NH_3$

(2) $^{\ominus}OR > ROH$

(3) $HO^{\ominus} > H_2O$

(4) $^{\ominus}SH > H_2S$

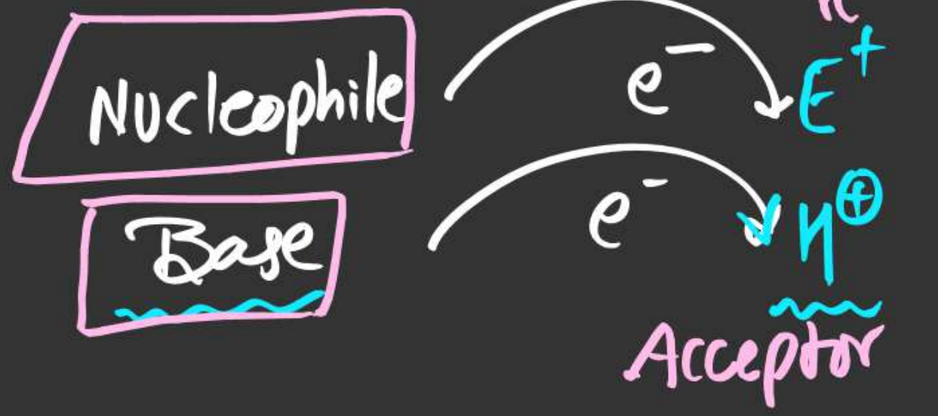
(viii) Nucleophile having higher No. of Nucleophilic sites are more Nucleophilic

(5) $^{\ominus}O-O-H > {}^{\ominus}OH$

(6) $H_2N-NH_2 > NH_3$

(ix) Basicity is a thermodynamic property & measured By Equilibrium Constant like(K_b)

$$\ddot{B} + H^{\oplus} \rightleftharpoons \overset{\oplus}{B}H$$



(x) Nucleophilicity is a kinetic property & measured By Rate Constant(k)

$$Nu^{-} + R-X \xrightarrow{k}$$

(xi) On moving left to Right in Periodic table Nucleophilicity & Basicity Both are parallel & decreases

IIT (7) $\overset{\ominus}{C}H_3$ $\overset{\ominus}{N}H_2$ $\overset{\ominus}{O}H$ $F^{\ominus}$

left → C N O F → Right

Nucleophilicity $\overset{\ominus}{C}H_3 > \overset{\ominus}{N}H_2 > \overset{\ominus}{O}H > F^{\ominus}$

Basicity $\overset{\ominus}{C}H_3 > \overset{\ominus}{N}H_2 > \overset{\ominus}{O}H > F^{\ominus}$

(xii) On moving Top to Bottom in Periodic table Nucleophilicity & Basicity Both are anti parallel, Nucleophilicity increases whereas Basicity decreases.

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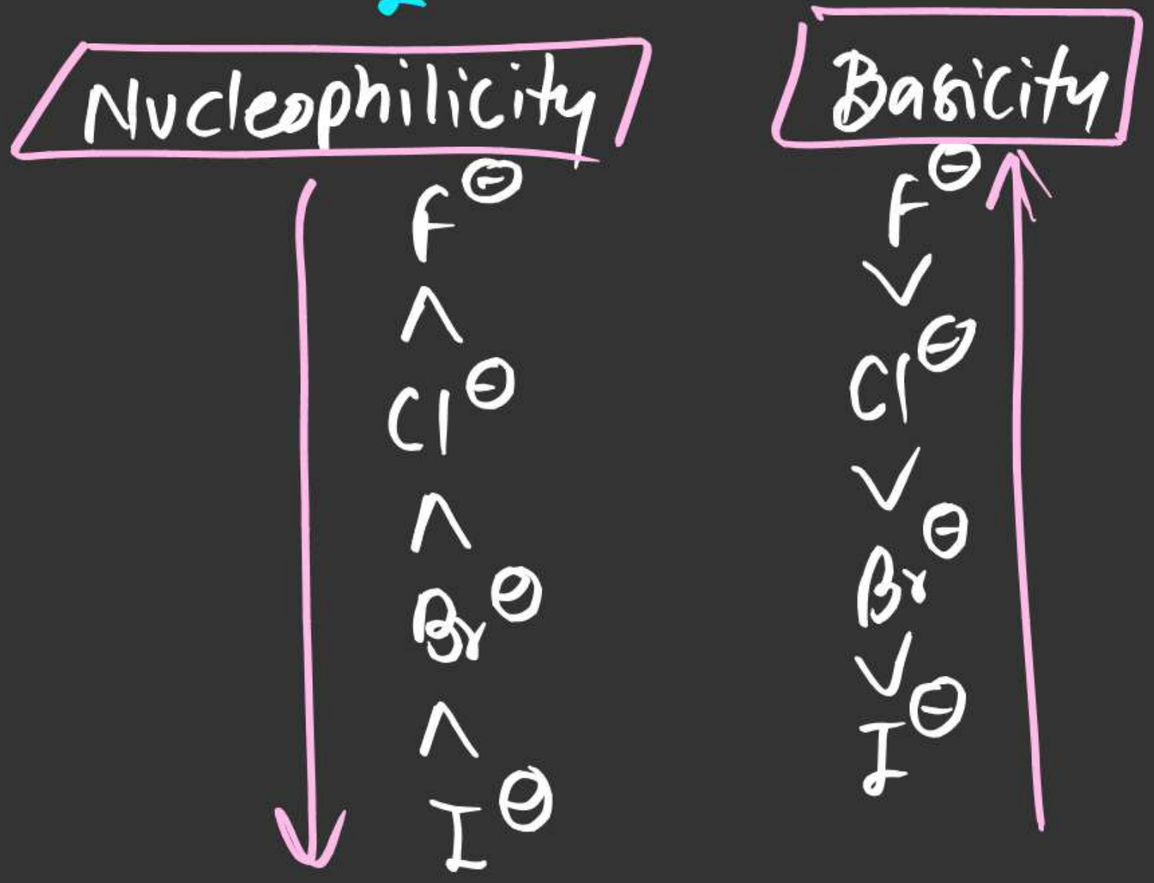
(8) $F^{\ominus}$ $Cl^{\ominus}$ $Br^{\ominus}$ $I^{\ominus}$

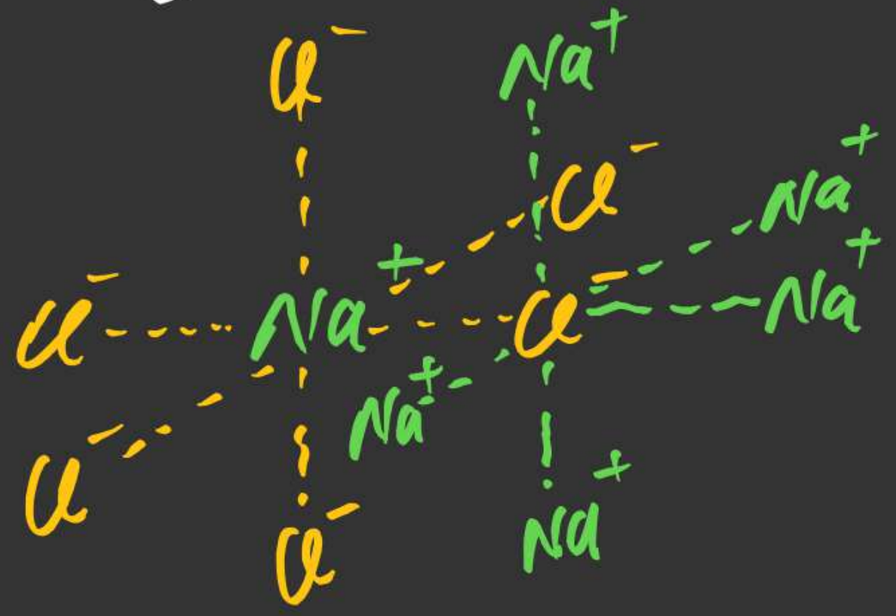


(xiii) Nucleophilicity depends upon type of Solvent used.

Ex: Discuss Nucleophilicity of following salts in Various Solvents.

(Ionic Salt) NaF, NaCl, NaBr, NaI

Soln: NaX Salt Crystallizes in a lattice



lattice can be dissociated by polar Solvents ($\mu \neq 0$)

Sol^n: (i) Non polar Solvent (CCl_4, CS_2, Benzene ....)
($\mu = 0$)

⇒ No dissociation of Salt
⇒ Salt Exist as a Ion pair

NaF NaCl NaBr NaI
Ionic

Nucleophilicity order

$Na^+ \cdots I^\ominus > Br^\ominus > Cl^\ominus > F^\ominus \cdots Na^+$
weak interaction — Strong interaction

(ii) Polar Protic Solvent (H_2O, ROH, RCOOH ... etc)
$\mu \neq 0$ (conform H Bond)

⇒ Salt gets dissociated
⇒ PPS solvated Both Cation & Anion

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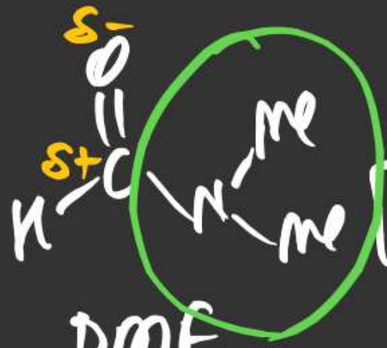
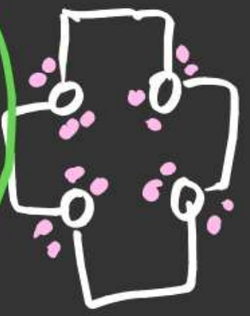
Nucleophilicity order in PPS

$$I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$$

(iii) Polar Aprotic solvent

$\mu \neq 0$ (Gain form H Bond)





[Dimethyl sulphoxide] [Tetra Hydro Furan] [Dimethyl formamide]

$\Rightarrow$ Salt gets dissociates

$\Rightarrow$ PAS mainly Solvates Cation

Nucleophilicity order

$$F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$$

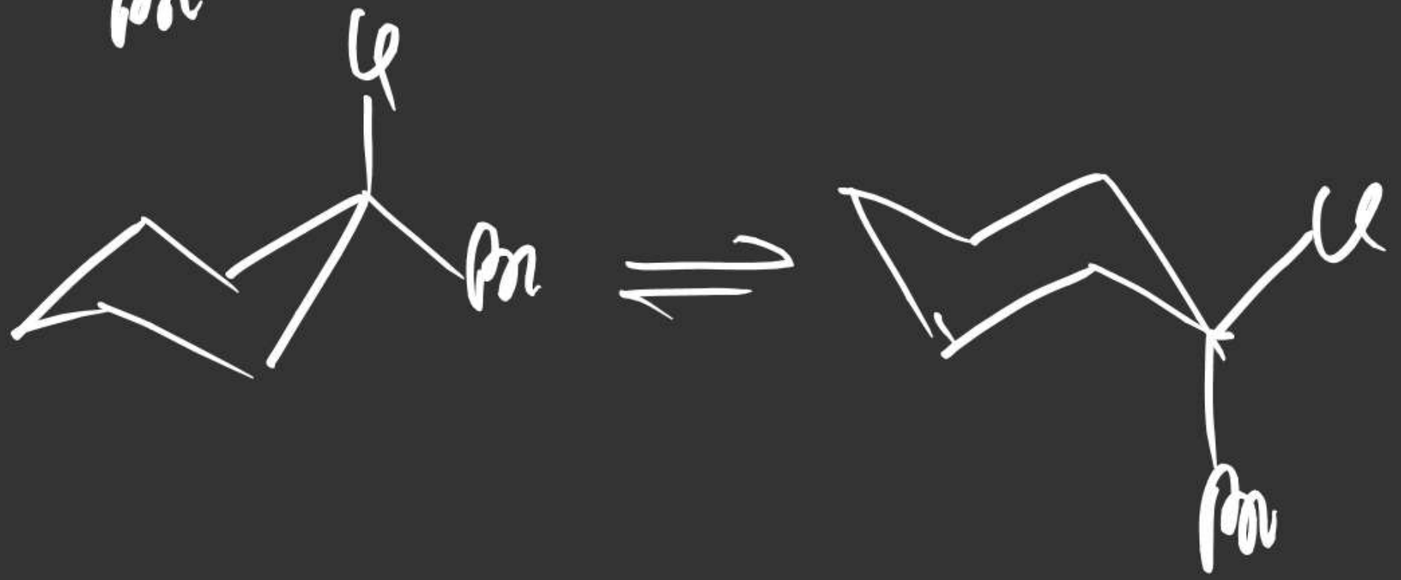
(6)

$K_{eq} > 1$

(7)

$K_{eq} > 1$

(8)



$K_{eq} > 1$

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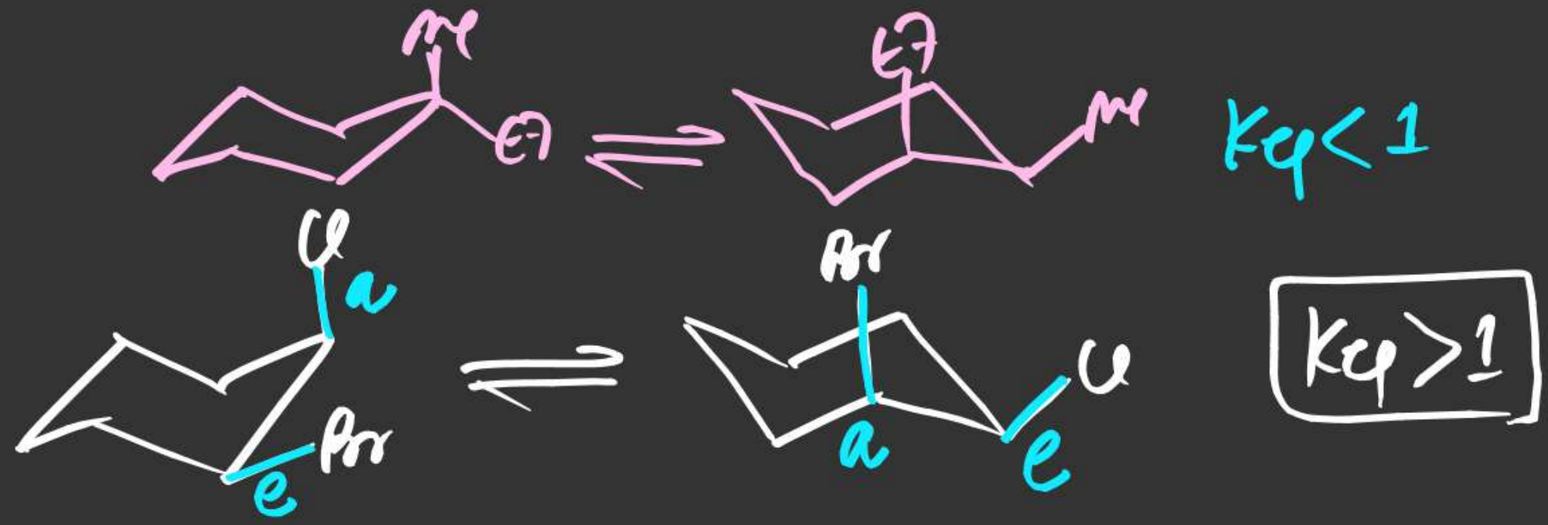
HW (discussion)
Conformation

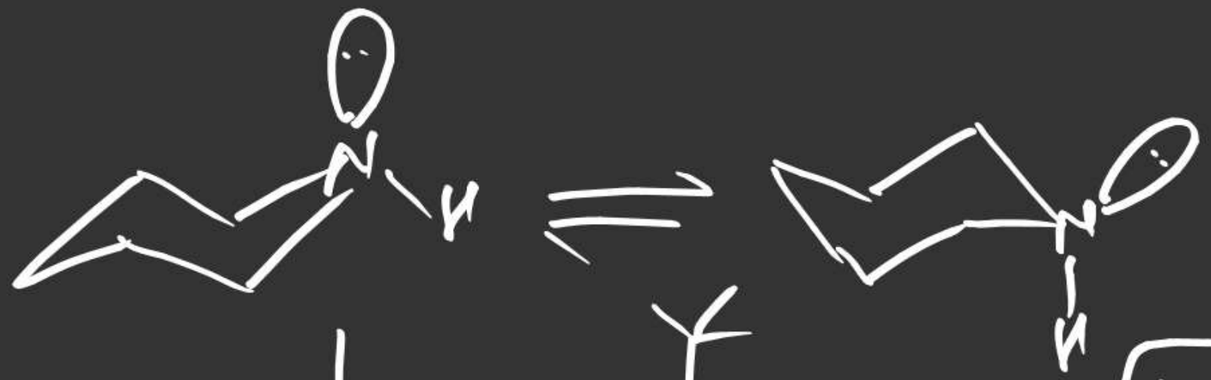
(9)



$K_{eq} < 1$

$K_{eq} > 1$

(10)



$K_{eq} < 1$

(11)

$K_{eq} \ll 1$

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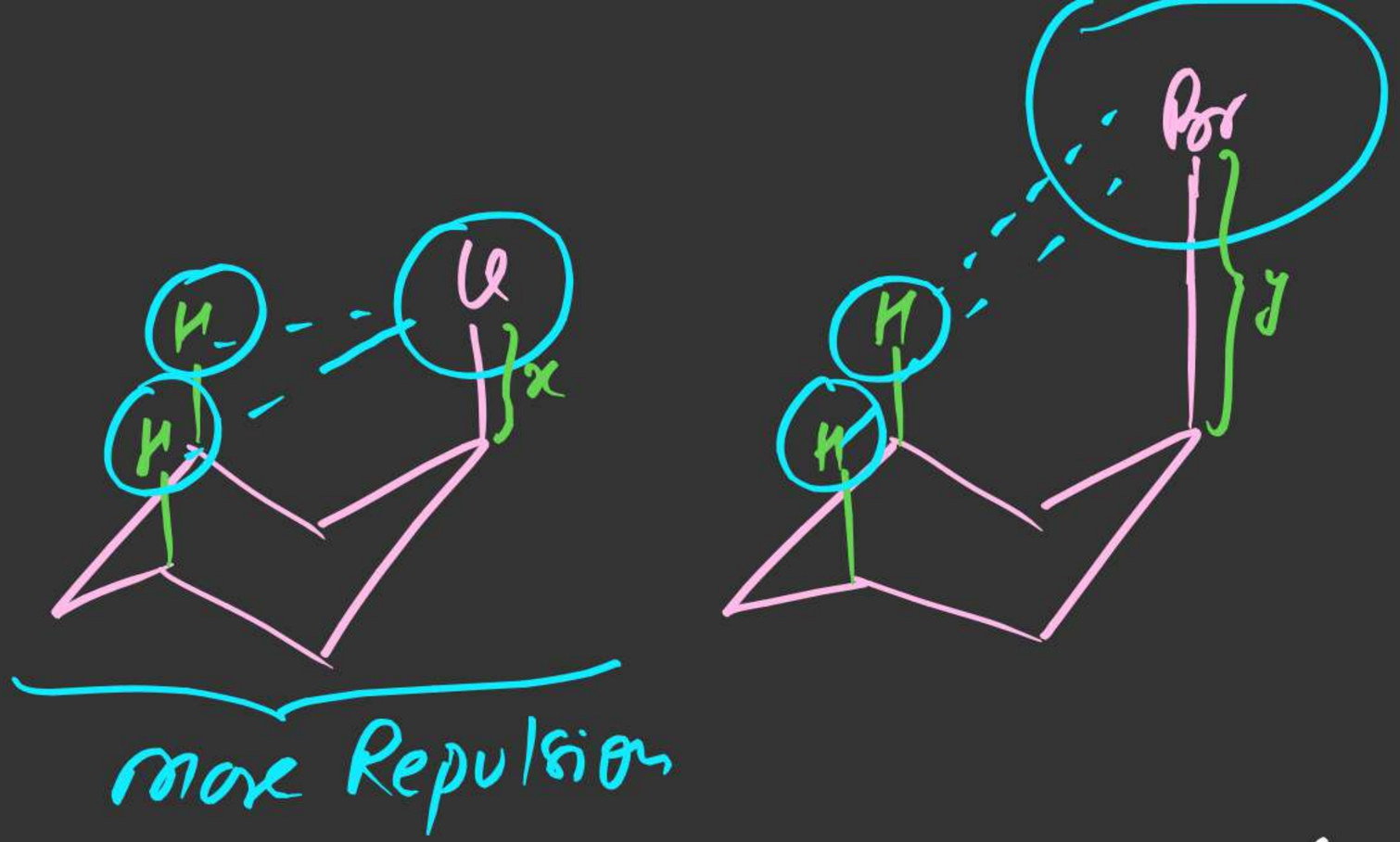
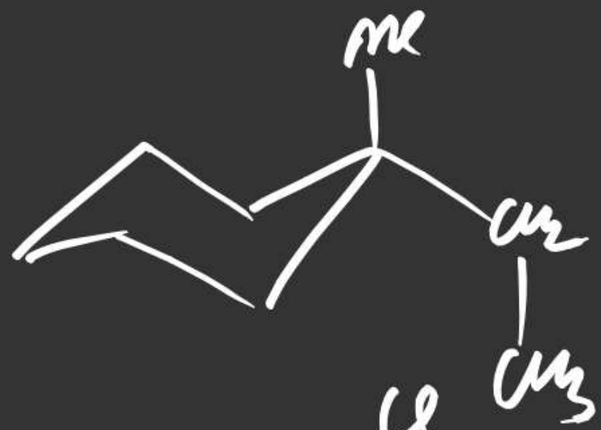


⇒ If any halogen has to be at axial, keep larger halogen atom at axial for maximum stability

Most stable conformation

(4)



(6)

(7)

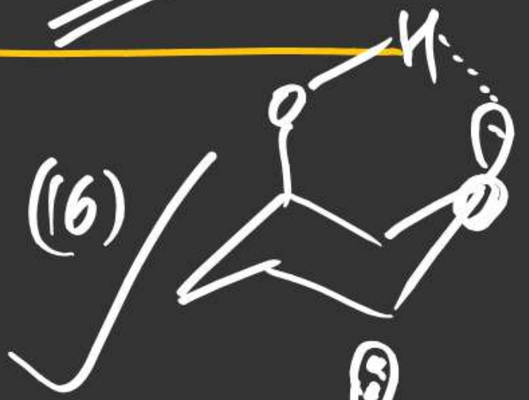
(8)

(10)

(14)

(15)

(16)



(17)

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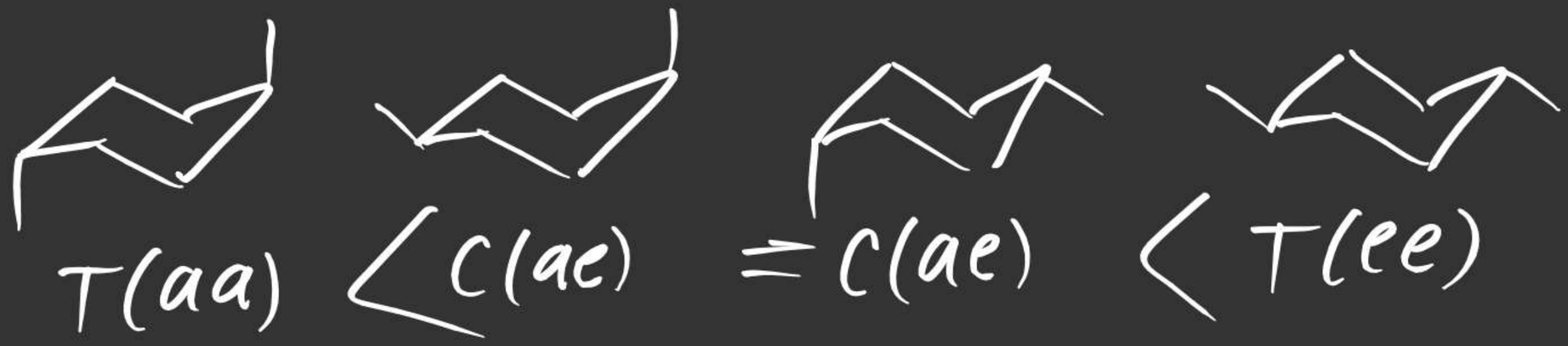
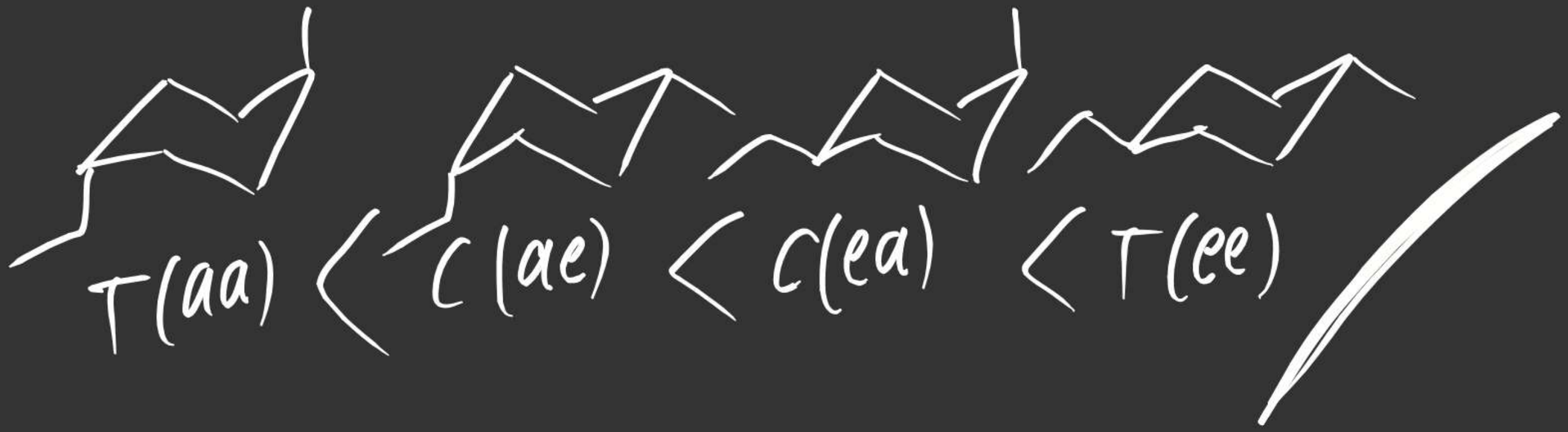
(19)

(20)



$T(aa) < C(ae) = C(ae) < T(ee)$

(21)



$T(aa) < C(ae) < C(ea) < T(ee)$