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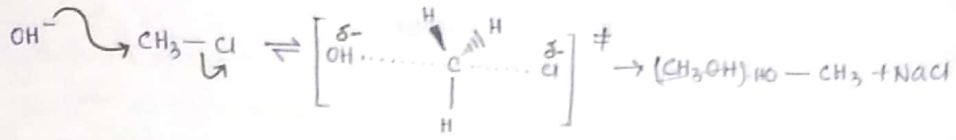
B.Sc(H) Chem
Sem-2 CC-4

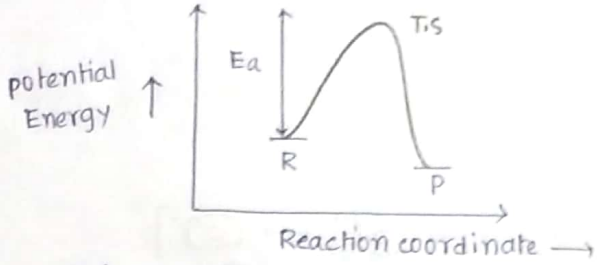
Reaction Mechanism

Reaction Mechanism is a detailed description how a bond is broken or formed in a chemical reaction when the starting meterial is converted into product.

$NaOH + CH_3Cl \longrightarrow NaCl + CH_3OH$ Nucleophile : OH^-



Transition state (pentacoordinated)



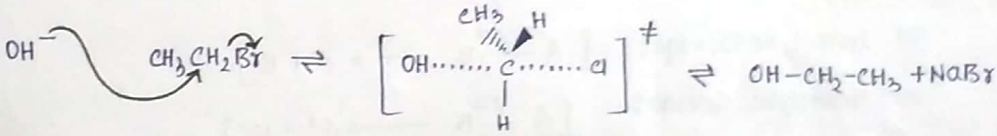
E_a = Activation Energy
R = Reactant
P = Product

It is an exothermic reaction.

Type of Reaction :

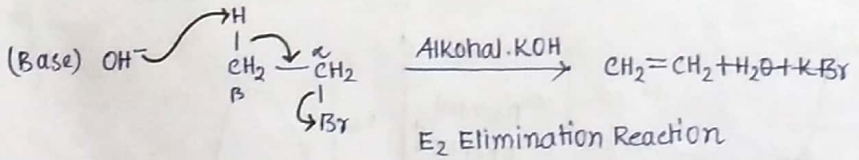
(i) Substitution Reaction :

$CH_3CH_2Br + aq.\ NaOH \longrightarrow CH_3CH_2OH + NaBr$

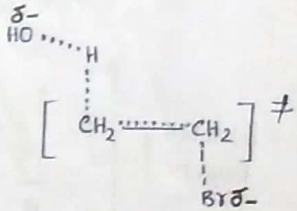


Transition state

(ii) Elimination Reaction :

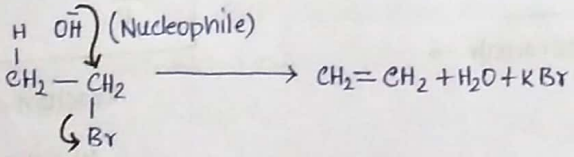


E_2 Elimination Reaction



Transition state

(a) OH^- reacts as a base when it reacts with H-atom.



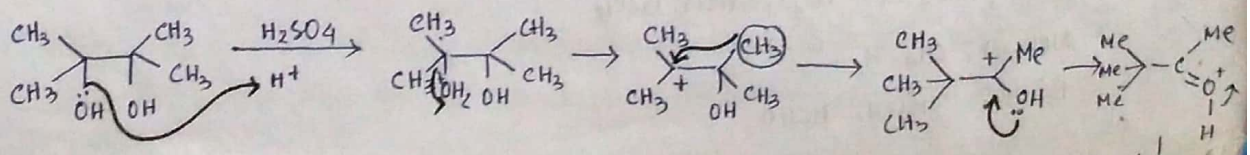
(b) OH^- acts as a nucleophile when it reacts with electrophilic carbon atom.

(iii) Addition Reaction : $CO + Cl_2 \rightarrow COCl_2$

$CH_2 = CH_2 \xrightarrow[CCl_4]{Br_2} CH_2(Br) - CH_2(Br)$

(iii) Rearrangement Reaction :

(Pinacol) $(CH_3)_2OH - (CH_3)_2OH \xrightarrow{H_2SO_4} CMe_3COMe$ (Pinacholon)

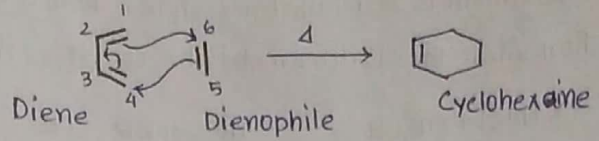


Here -Me group migrates with it's bonding electron pair.

$C(CH_3)_3COMe$

(v) Pericyclic Reaction: (Converted cyclic shift of electron)

Dields-older reaction: Without formation of any intermidiate single step reaction



Diene Dienophile Cyclohexaine

cycloaddition reaction

Type of intermidiate:

(i) carbocation $[-\overset{+}{\underset{|}{C}}-]$

(ii) carboanion $[-\overset{-}{\underset{|}{C}}-]$

(iii) Carbene $[:C(-H)(-H)]$

(iv) Nitrine $[R-\ddot{N}:]$

(v) Benzyne $[\text{C}_6\text{H}_4 \; sp^2, sp^2 \leftrightarrow \text{C}_6\text{H}_4^{(-)(-)} \leftrightarrow \text{C}_6\text{H}_4:]$

(vi) σ - complex

(vii) π - complex

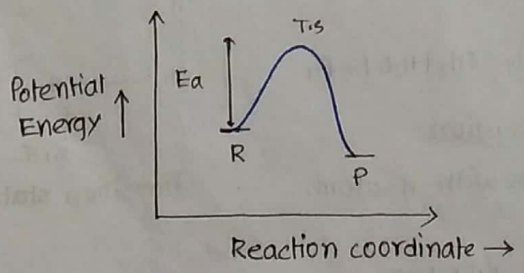
(viii) Free - radical

Bond clevage:

(i) Homolytic clevage: $[A-B \longrightarrow A^{\cdot} + B^{\cdot}]$

(ii) Heterolytic clevage: $[A-B \longrightarrow A^{+} + B^{-}]$

Exothermic curve

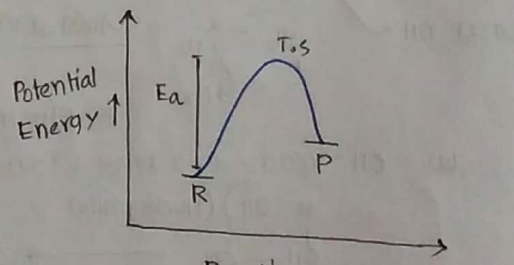


ΔH = -ve

i.e $\Delta H = H_P - H_R$

= -ve

Endothermic curve



ΔH = +ve

$\Delta H = H_P - H_R$

= +ve

2006 Which of the following species behave as a — (a) Nucleophile (b) Electrophile (c) Neither (d) Both.

I^-, $BeCl_2$, NH_3, Cr^{3+}, CH_4, H_2, CH_3CN, $SnCl_4$, NO_2^+, HCHO

Nucleophile: I^-, NH_3

Electrophile: Cr^{3+}, NO_2^+, $SnCl_4$, $BeCl_2$

Neither: CH_4, H_2

Both: CH_3CN, HCHO

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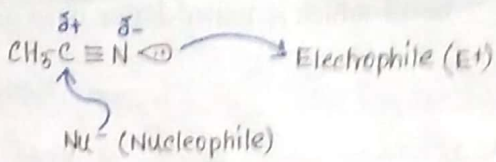
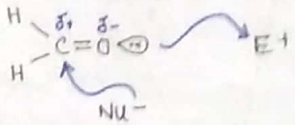
Both :



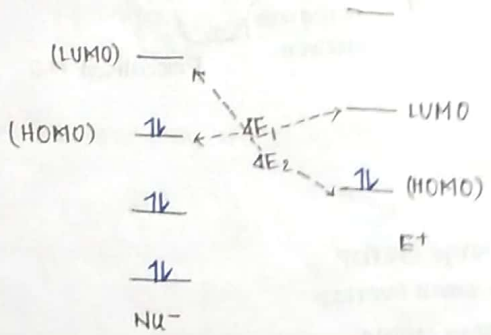


Molecule attract each other :

(i) Attraction of opposite charge.

(ii) Overlap of high energy filled orbital (HOMO) with Lower energy (LUMO) Empty orbital.

$Nu^- \rightarrow$ HOMO $\quad E^+ \rightarrow$ LUMO.



Nu^- (HOMO) $\quad E^+$ (LUMO)

ΔE_1 = Lower energy gap between HOMO and LUMO. (Better interaction)

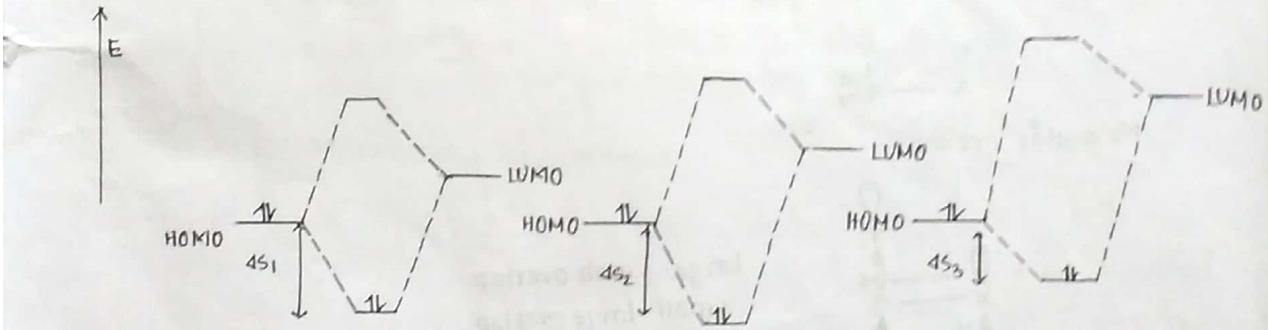
ΔE_2 = Nu^- (LUMO) $\quad E^+$ (HOMO)

Higher energy gap between HOMO and LUMO.

Since, $\Delta E_2 >> \Delta E_1$

$\therefore r_1 >> r_2$

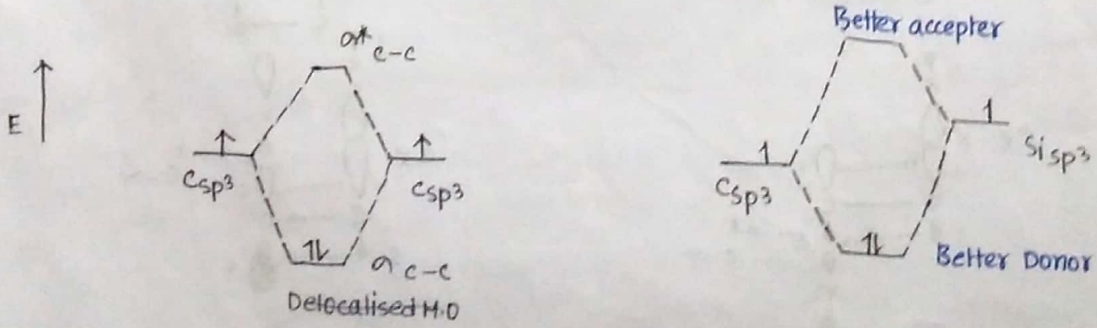
$r_1 = r_2$ = reaction rate



ΔS = Stabilization Energy

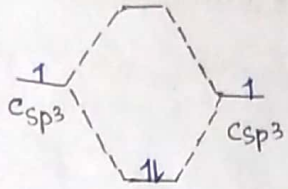
$\Delta S_1 > \Delta S_2 > \Delta S_3$

$r_1 > r_2 > r_3$



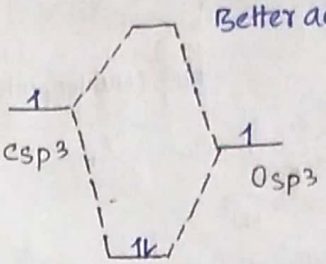
Weak bond will have correspondingly correspondingly low-lying antibonding state formation of weak bonds will leads to a correspondingly lower energy antibonding orbital. Such structure are reactive as both Nucleophile and Electrophile.

Between C–C and C–O bond which is better donor and accepter?



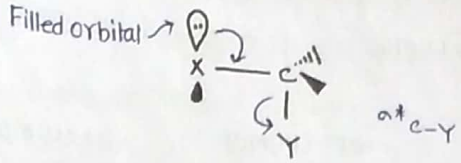
Better Donor

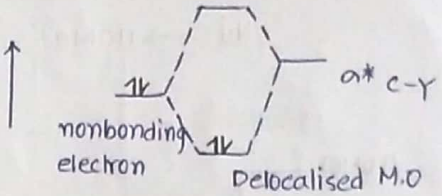
Better accepter



Lower energy of O because O is more electronegative than C atom.

Anti orientation filled and unfilled orbitals leads to a better overlap.

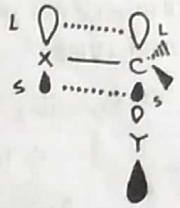




Delocalised M.O

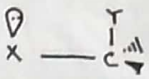
Molecular orbital :

Anti orientation

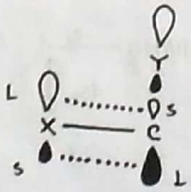


Large-large overlap
small- small overlap
more stable

Syn Orientation

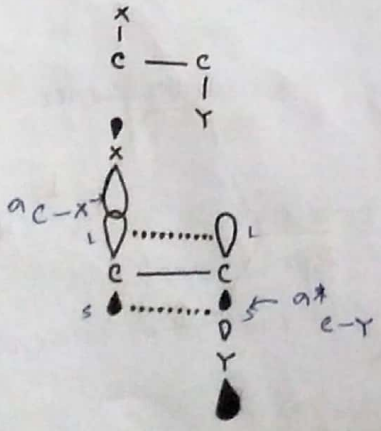


Molecular orbital



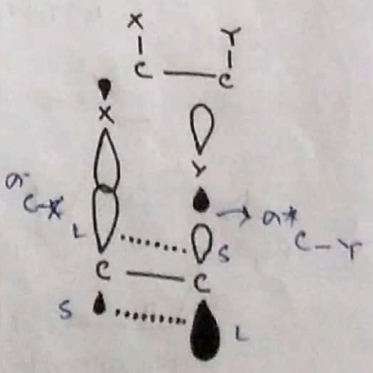
Large-small overlap
small-large overlap

Anti orientation



Better interaction

Syn- Orientation



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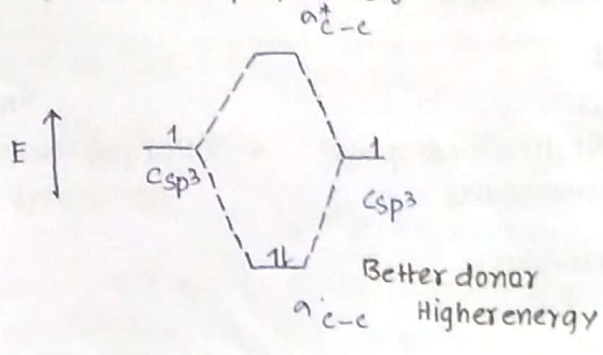
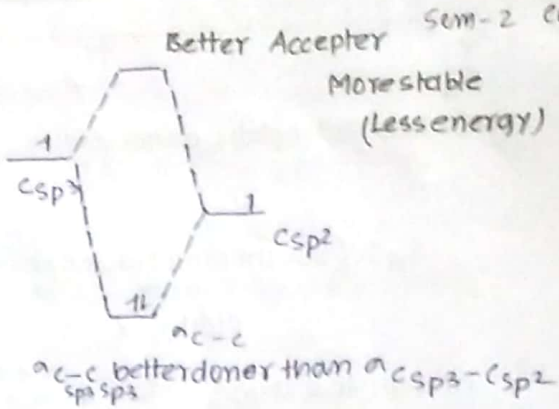
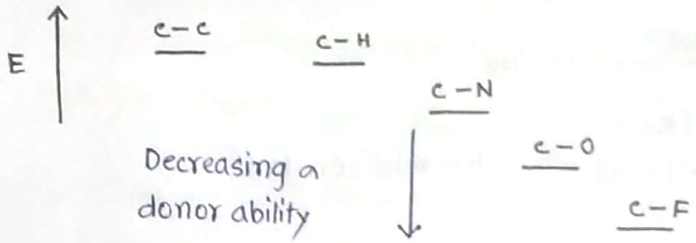
Donor accepter properties :



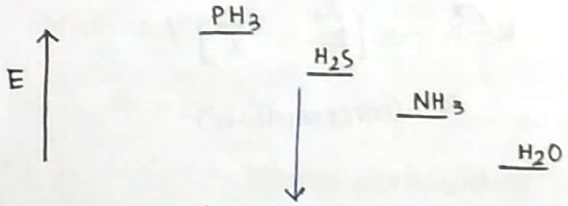


σ- doner ability

σ_{C-C} better doner than $\sigma_{C_{sp^3}-C_{sp^2}}$

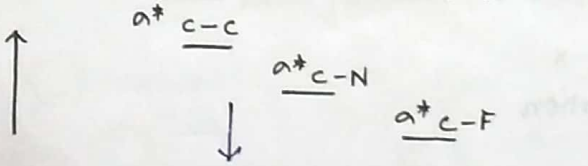


Non-bonding donor ability



Decreasing donor ability of non bonding electron.

Accepter ability of σ^*_{C-X} bond



σ^* accepter ability increases