(b) Oxymercuration-Reduction → reaction of alkene with mercuric acetate in aq THF

$R-CH=CH_2$ ① $Hg(OAc)_2, H_2O$ ② $NaBH_4$ → $R-\underset{OH}{CH}-CH_3$

[overall reaction to M. Rule]
[Addition of $Hg^{+}OAc$]

Mech

(I) $Hg(OAc)_2 \rightarrow Hg^{\oplus}OAc + AcO^{\ominus}$

(II) $R-CH=CH_2 + Hg^{+}OAc \rightarrow R-\underset{\oplus HgOAc}{CH}-CH_2$

(III) $R-\underset{H_2O}{CH}-CH_2 \rightarrow R-\underset{OH_2^{+}}{CH}-CH_2-HgOAc$ [S_N2 type]

(IV) $R-CH-CH_2-HgOAc \rightarrow R-\underset{OH}{CH}-CH_2HgOAc + AcOH$

(V) $R-\underset{OH}{CH}-CH_2HgOAc \xrightarrow{NaBH_4} CH_3-\underset{OH}{CH}-CH_3 + Hg + AcO^{\ominus}$

[$NaBH_4$ convert C–Hg to C–H bond]

(3) H₂O का addition more substituted carbon पर होता है

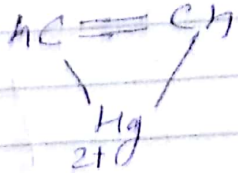
(4) Acid catalysed Hydration of alkyne

- Acc. to M. Rule
- Require mercuric ion

$HC\equiv CH \xrightarrow[H_2SO_4]{Hg^{2+},\ H_2O} CH_3CHO$

[Mech]

(I) $CH\equiv CH + Hg^{2+} \rightleftharpoons HC\equiv CH$ (Hg^{2+})



(II) $HC\equiv CH \xrightarrow{-H^+} HC=C-H$ (OH; Hg, +2)

$HC=C-H \xrightarrow{H^+} CH_3-C(=O)-H$ ← $CH_2=C-H$ (OH)

[aldehyde] — enol

Overall reaction

$R-C\equiv CH \xrightarrow[H_2SO_4]{Hg^{2+},\ H_2O} CH_3COOH$

$-C\equiv C- \xrightarrow[\text{catalyst}]{H_2}$ cis-alkene

Hydrogenation of alkene & alkyne

$>C=C<$ or $-C\equiv C-$

$+$

H_2

↓ Pt, Pd or Ni

alkane

alkene से reaction में अंतर

- It is catalytic hydrogenation
- Syn addition (cis-alkene)
- addition at less hindered side
- Stereospecific syn addition
- H–H bond की strength more होने से, कारण reaction के लिए enormous energy barrier होती है → [So without catalyst, barrier to the reaction would be enormous due to the strength of H–H bond, catalyst lower the energy by activation by breaking the H–H bond.]
- Pt or Pd are used as Pt/C or Pd/C ie adsorbed on charcoal
- Pt को PtO_2 की form में भी used होता है, It adam's catalyst.
- Hydrogenation reaction के दौरान released energy को heat of Hydrogenation कहते है

ie 'Heat of Hydrogenation' is exothermic
↳ It is indicated by (ΔH) (Kcal/mol)
↓
It is heat of reaction.

↳ Most stable alkene has the smallest heat of Hydrogenation (ie low -ve value)

as

(a) $CH_3-\underset{CH_3}{CH}-CH=CH_2$ (least stable) $\Delta H = -30.3$ E

(b) $CH_2=\underset{CH_3}{C}-CH_2CH_3$ -28.5 E

(c) $CH_3-\underset{CH_3}{C}=CH$ -26.9 more Sta

↳ Trans alkene > cis-alkene
↓
less ΔH°

→ Birch Red:

(A) alkyne → Na in liq NH3 → trans alkene

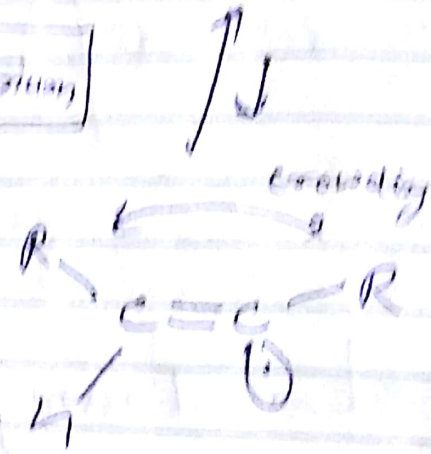
[Each] one e⁻ transfer

① $R-C\equiv C-R + Na \rightarrow Na^{+} + [R-\dot{C}=\ddot{C}-R]^{\cdot-}$ (radical anion)

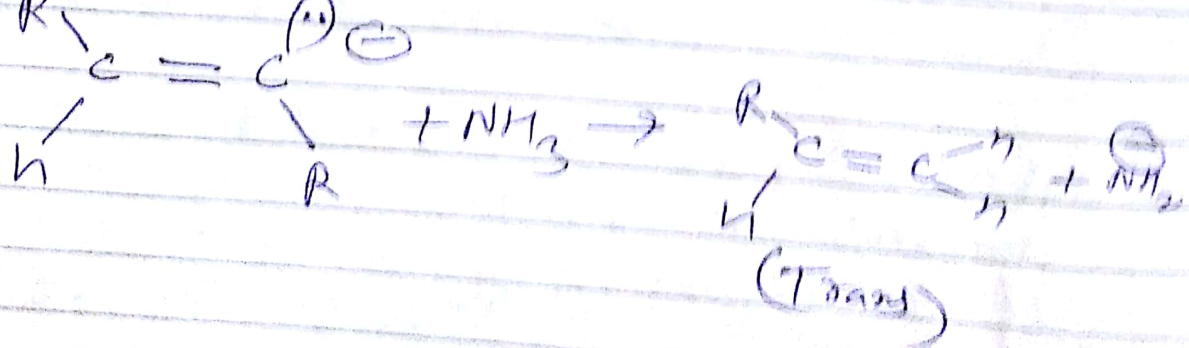
② $[R-\ddot{C}=\dot{C}-R]^{\cdot-} + NH_3 \rightarrow R-C=C(H)-R + {}^{\ominus}\ddot{N}H_2$

alkenyl radical (trans stable)

[They are in equilibrium]



③ [IInd protonation] →



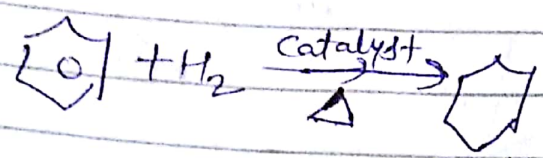
Hydrogenation of Aromatic ring

But require higher temp (100–200°C)

Catalytic hydrogenation

reaction ~~x~~ नहीं होती है

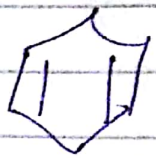
ie



यह reaction alkene से aromatic ring को तुलना में easily होती है

Birch reduction

Birch



1,4-dihyd
benze

→ 1,4-addit
H_2

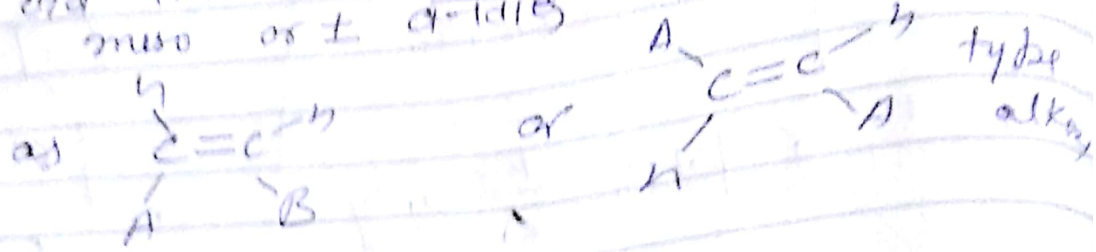
→ alkene aromatic are more reduced

Stereochemistry of alkene

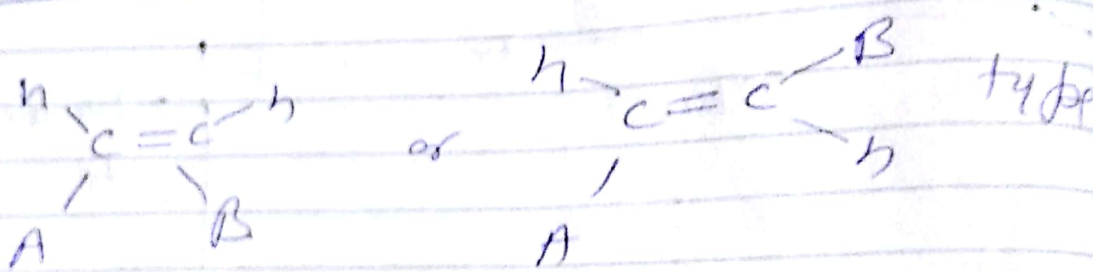
(A) When both ends are same

cis-alkene + syn addition → meso
trans alkene + syn → ± (racemic mix)

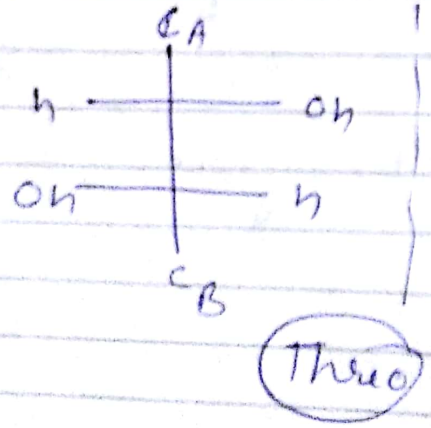
एक ही C पर substituent same हैं तो meso or ± नहीं बनेगा

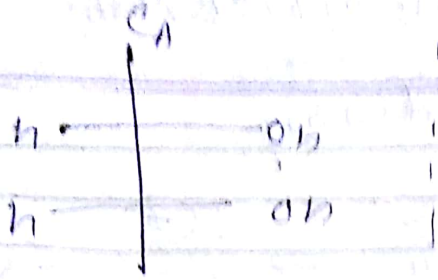


(B) When both ends are differ as:

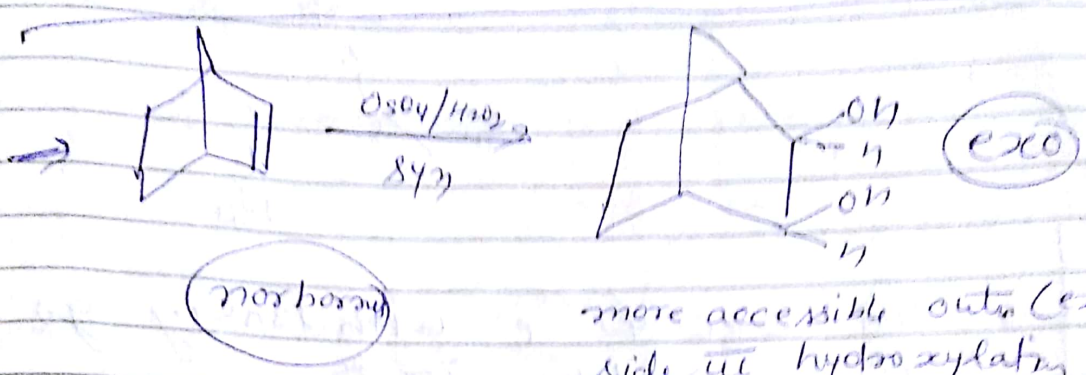


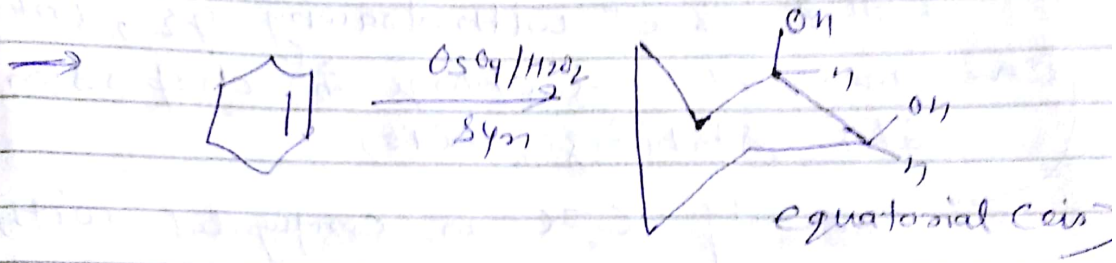
Then trans + anti addition → erythro
" + syn " → Threo

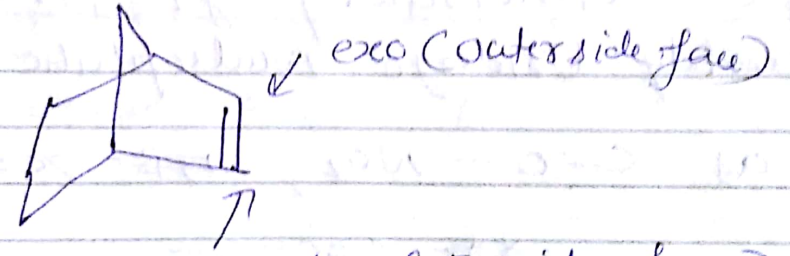




[eclipsed]

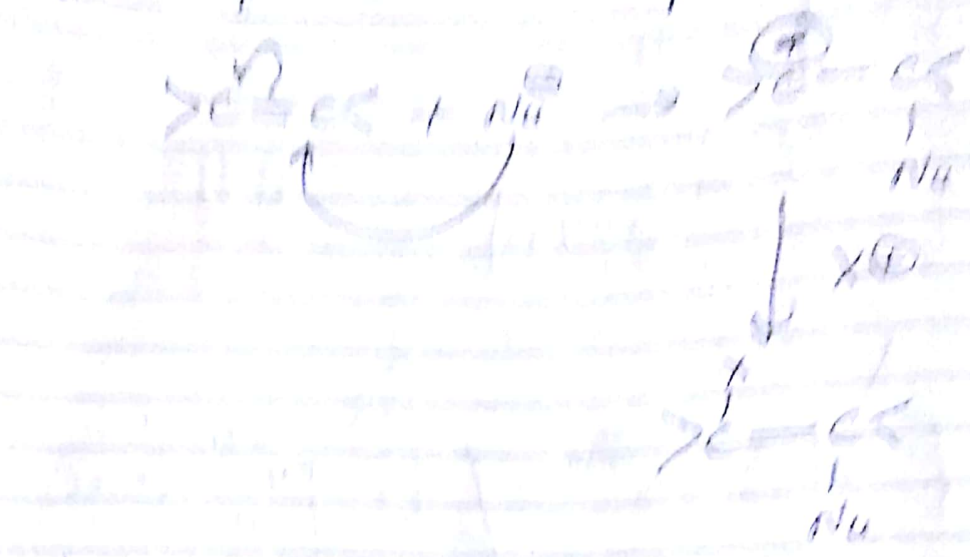






1° Mode of Electrophilic addition

Nucleophilic addition



→ यदि C=C पर e⁻ withdrawing gr. हो तो यह addition देता है,

→ Since इसमें carbanion intermediate बनता है 2 e⁻ withdrawing gr. carbanion को और अधिक charge का dispersion करते stabilize करते,

→ So यदि C=C is conjugated with e⁻ withdrawing gr., then it readily undergo Nucleophilic addition,

as C=C-NO₂, C=C-CHO

C=C-C(=O)-, C=C-COOH

Nucleophilic addition

(A) Michael addition

(B) Cyanoethylation

(B) Cyanoethylation

acrylonitrile + C_2H_5OH

↓ Strong base

Product

↳ It is 1,4- addition of acrylonitrile

$CH_2=\overset{2}{C}H-CN \xrightarrow[Base]{C_2H_5OH} C_2H_5O-CH_2CH_2-CN$

↑

यहां से attack होता है (β-C पर attack)

Mech →

C_2H_5OH + Strong Base → $C_2H_5O^{\ominus}$

$CH_2=\overset{\beta}{C}H-C\equiv N \rightarrow$ [$EtO-CH_2-\overset{\alpha}{C}H-C\equiv N$ ⟷ $EtO\,CH_2-CH=C=N^{\ominus}$]

↓ C_2H_5OH

$C_2H_5O-CH_2CH_2-CN$

(A) Michael addition