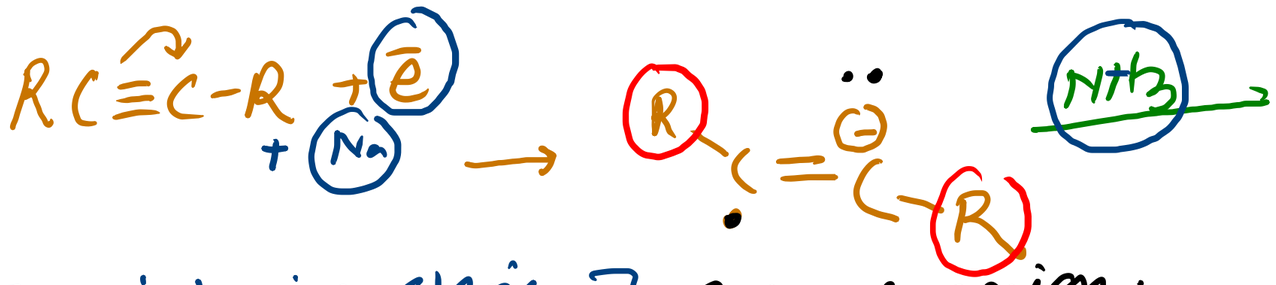
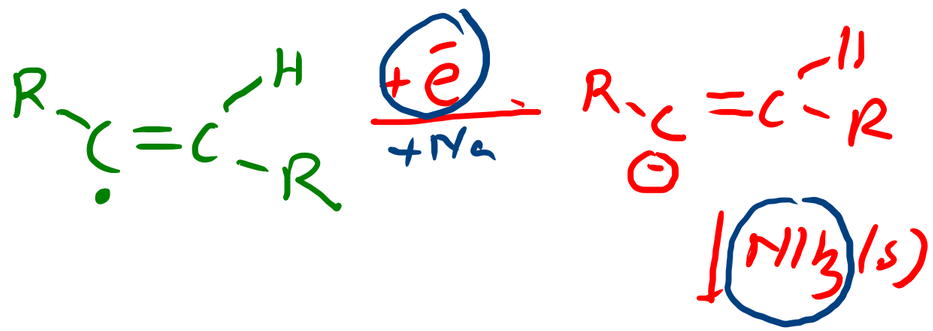
: Birch Reduction :



[To minimise steric repulsion between Rs']

Radical anion.

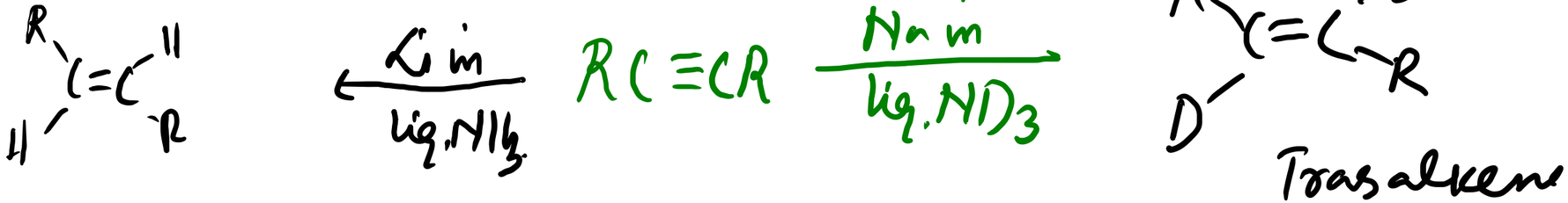
(To minimise repulsion)



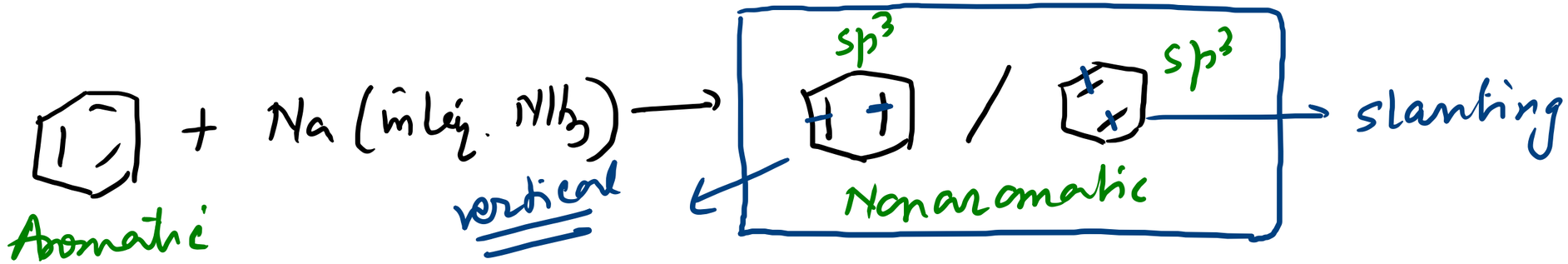
{ ē addition
H⁺ addition
ē addition
H⁺ addition.

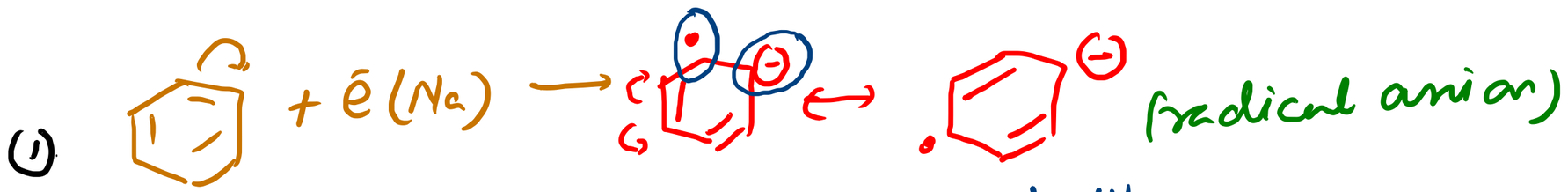
Trans alkene.

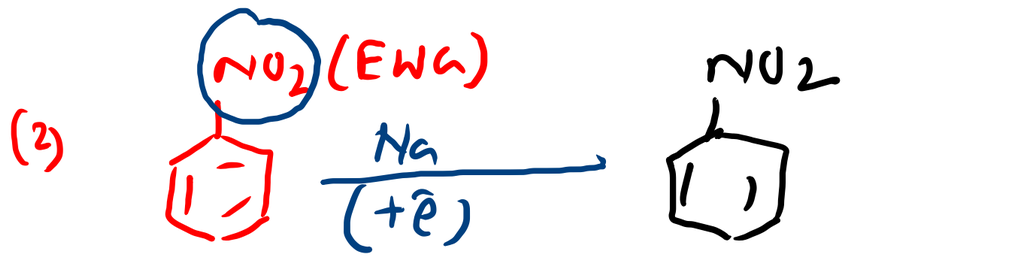
Birch reduction is not applicable for terminal alkyne (acidic H).

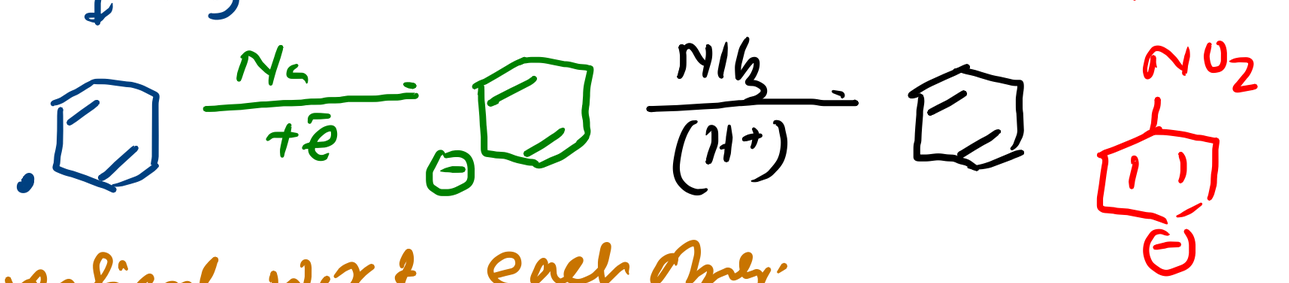


Trans alkene



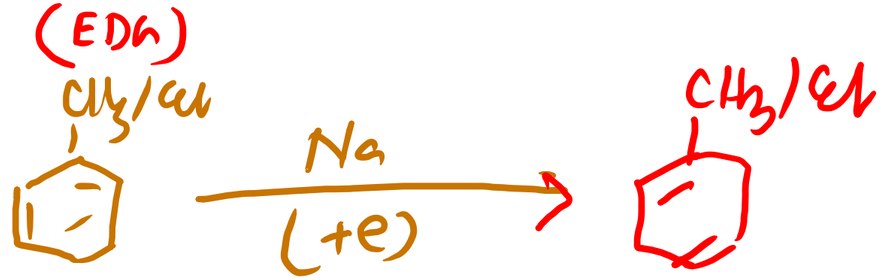


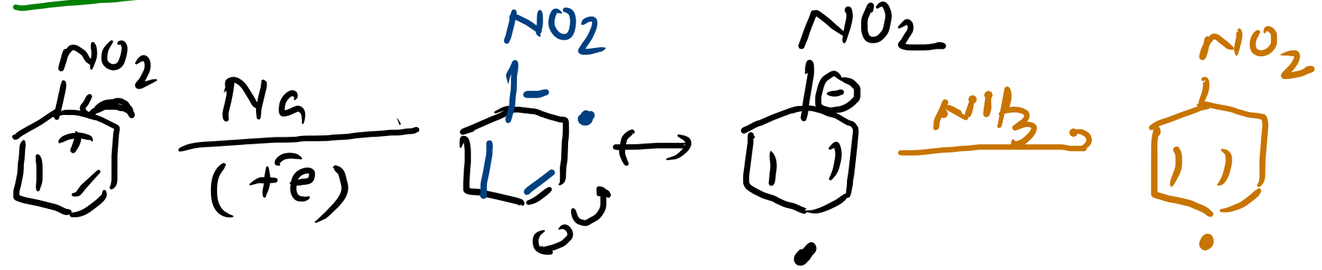


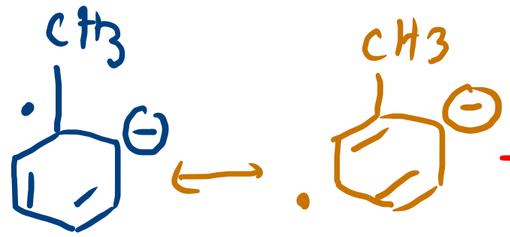
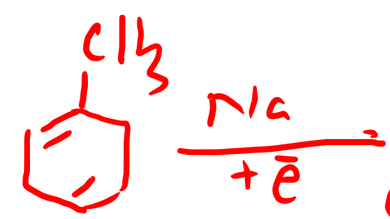
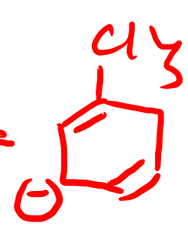


* Bond should be at vertical w.r.t each other.

: Explanation:





(EDA.)  $\xrightarrow[(Na)]{+\bar{e}}$  $\xrightarrow{NH_3}$  $\xrightarrow[+\bar{e}]{Na}$  $\xrightarrow[H^+]{NH_3}$ 

---

1) **M.P.V reduction:** [Aldehyde & ketone reduction] Meerwin-Ponndorf Verley reduction

[Aluminium Isopropoxide + Protic solvent

$$RCH=O \xrightarrow[+ROH]{Al(OCHMe_2)_3} RCH_2OH.$$

$$R\underset{\underset{O}{\|}}{C}-R' \xrightarrow[+ROH]{Al(OCHMe_2)_3} R_2CHOH.$$

$-O-CHMe_2$ Isopropoxide

(ii) **Bouveault Blanc Reduction** (IIT-Mains 2021)

$$RCH=O \xrightarrow[+EtOH]{Na} RCH_2OH$$

$$R_2C=O \xrightarrow[+EtOH]{Na} R_2CHOH$$

$$R-C\equiv N \xrightarrow[Na/EtOH]{} RCH_2-NH_2$$

$$R-\underset{\underset{O}{\|}}{C}-OEt \xrightarrow{Na/EtOH} RCH_2OH$$

$$R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow{Na/EtOH} RCH_2OH$$

$$R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R \xrightarrow{Na/EtOH} RCH_2OH$$

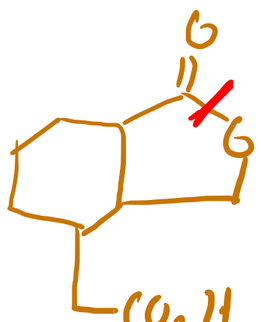
		$RCH=O$	$R_2C=O$	RCO_2H
: Alcohol :	i) LAH	✓ RCH_2OH	✓ R_2CHOH	✓
	ii) SBH	✓ RCH_2OH	✓ R_2CHOH	×
	iii) B_2H_6	✓ RCH_2OH	✓ R_2CHOH	✓ (yield is higher)
	iv) $H_2(Ni)$	✓ RCH_2OH	✓ R_2CHOH	×
[MPV]	v) $Al(OCHMe_2)_3 + ROH$	✓ RCH_2OH	✓ R_2CHOH	×
[Bouveault Blanc reduction]	vi) Na + EtOH.	✓ RCH_2OH	— R_2CHOH	spontaneous ⟹ ✓ $Sn^{2+} \rightarrow Sn^{4+} + 2e$ (less stable → more stable)

: $RCH=O$ ~~Bad~~ preparation by reduction process:

i) DIBAL-H (−78°C)

ii) $SnCl_2 + HCl$ (aq) Stephen reduction.

iii) Lindlar Catalyst (rosen method reduction)



$R(\equiv N$ — DIBAL-H/H_2O, −78°C. → $RCH=O$

$R-\underset{\underset{O}{\|}}{C}-NH_2$ — DIBAL-H, −78°C. → $RCH=O$

$R-\underset{\underset{O}{\|}}{C}-NMe_2$ — DIBAL-H, −78°C. → $RCH=O$

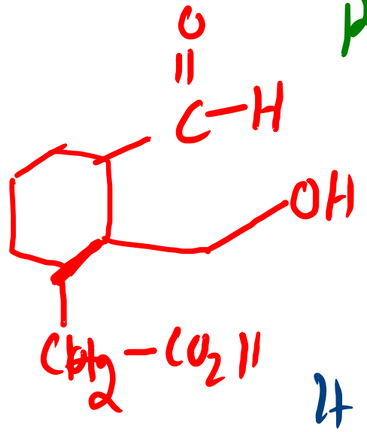
$R-\underset{\underset{O}{\|}}{C}-Cl$ (Acid chloride) — DIBAL-H, −78°C. → $RCH=O$

$R-\underset{\underset{O}{\|}}{C}-OR$ (Ester) — DIBAL-H, −78°C. [+ROH] → $RCH=O$

DIBAL-H
Diisobutyl aluminium hydride.

$R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R$ (Anhydride) — DIBAL H, −78°C. → $RCH=O$

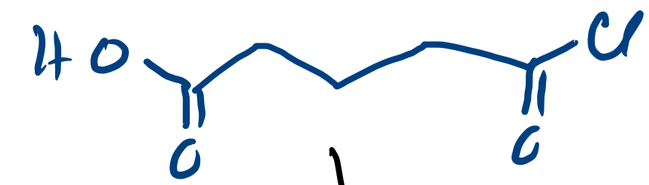
DIBALH (−78°C)



$R(\equiv N \xrightarrow[[H]]{+[H]} RCH=NH \xrightarrow{+H_2O} RCH=O + NH_3\uparrow$

$HAl(CH_2-CHMe_2)_2$

a)



DIBAL-H, −78°C. →

H_2 (Lindlar)

αAH (xs) = $HOCH_2-CH_2-CH_2-CH_2-CH_2OH$

H_2 (Ni) = $HO-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OH$

: **Stephen Reduction**: [only applicable to prepare aldehyde from alkyl cyanide]

??

$$R-C\equiv N \xrightarrow[+HCl(aq)]{SnCl_2} RCH=O + NH_3$$

??✓

$$R-C\equiv N \xrightarrow[+HCl(g)]{SnCl_2} RCH=NH \xrightarrow{+H_2O} RCH=O + NH_3\uparrow$$

$$R-\ddot{C}\equiv\ddot{N} + H-Cl \longrightarrow R-C\equiv\overset{+}{N}H \xrightarrow[Sn^{2+}\rightarrow Sn^{n+}]{+2\bar{e}} R\overset{\ominus}{C}=NH \xrightarrow{HCl} RCH=NH$$

is the final pdt when HCl(g) is used.

But if HCl(aq) is used, then imine formed undergo hydrolysis. $RCH=NH + H_2O \longrightarrow RCH=O + NH_3$.

$$R-C\equiv N \xrightarrow[HCl(g)]{SnCl_2} X \xrightarrow{LiAlH_4} Y.$$

$$R-C\equiv N \xrightarrow[HCl(aq)]{SnCl_2} X' \xrightarrow{LiAlH_4} Y'$$

X: $RCH=NH$.

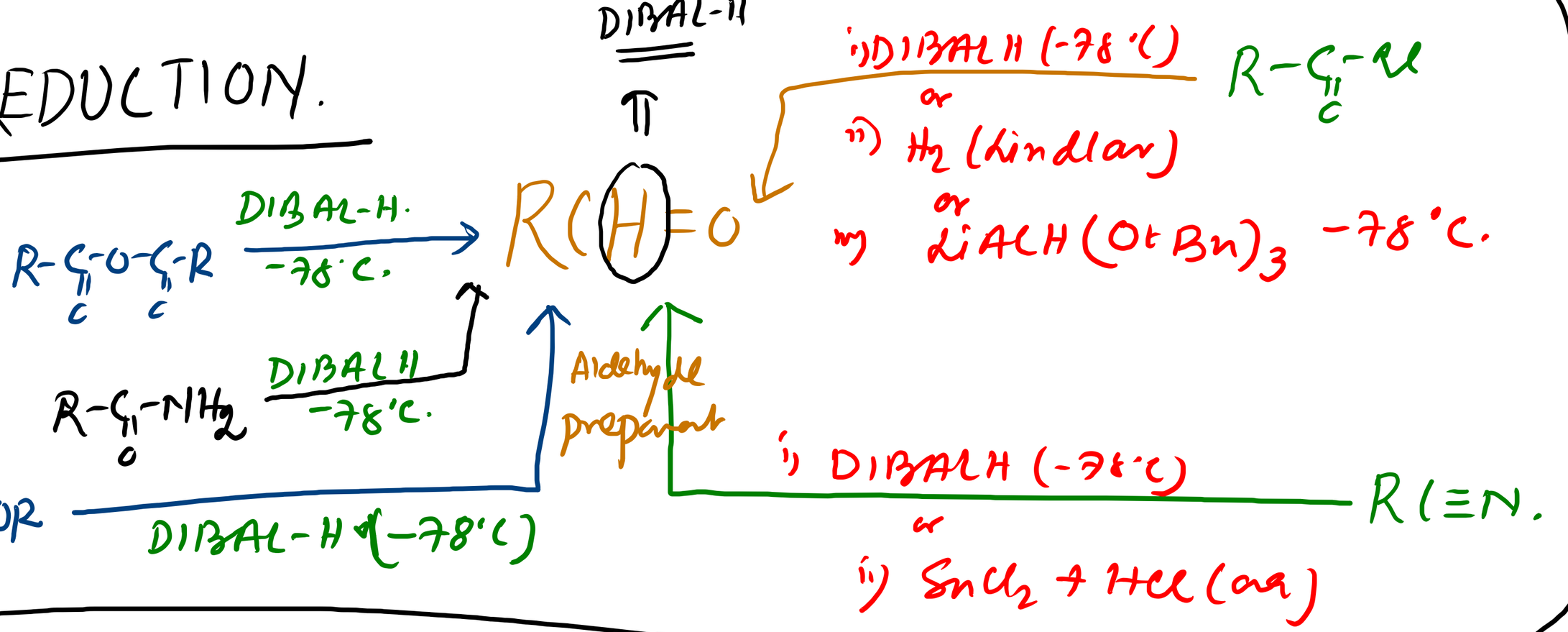
Y: RCH_2-NH_2

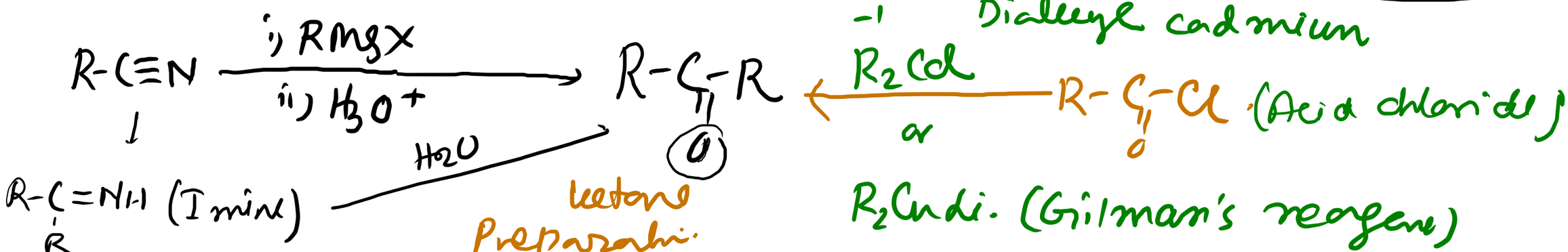
X': $RCH=O$.

Y': RCH_2OH

REDUCTION.

H_2 (Lindlar or DIBAL-H)





: Hydrocarbon Preparation:

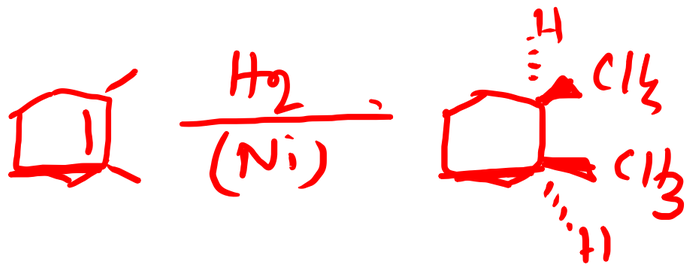
: Alkene preparation:

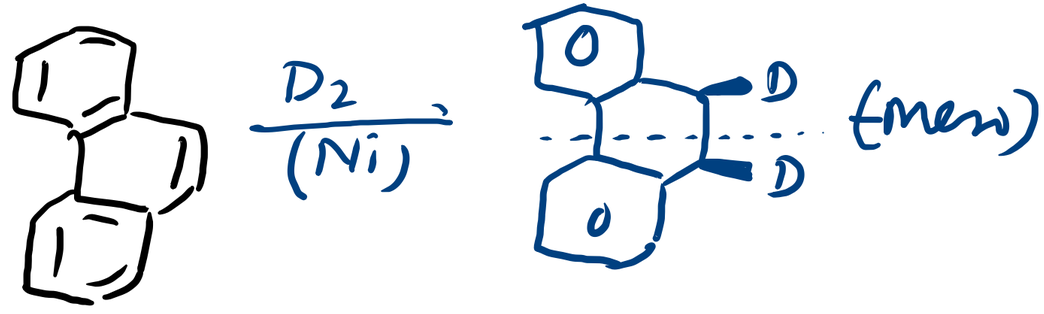
(i) $R-C\equiv C-R$ — H_2 (Lindlar) → (syn addition) → $\underset{H}{\overset{R}{}}C=C\underset{H}{\overset{R}{}}$ (cis)

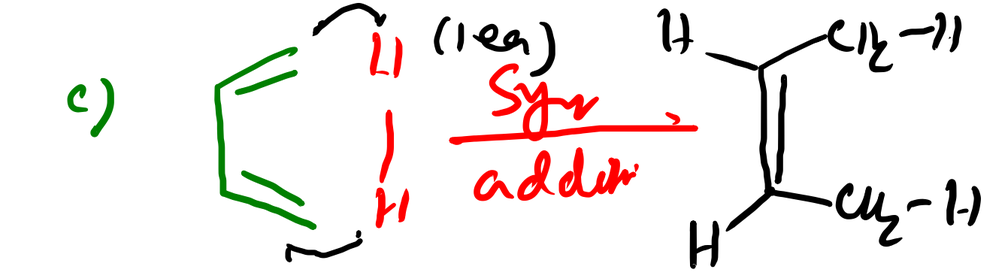
H_2 (P-2 catalyst)

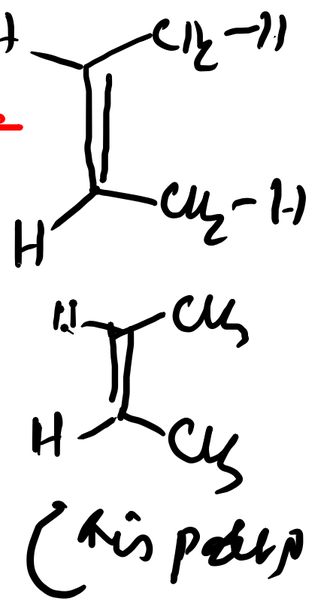
ii) $R-C\equiv C-R$ — Na (liq. NH_3) → $\underset{H}{\overset{R}{}}C=C\underset{R}{\overset{H}{}}$ (trans)

Li (liq. NH_3)

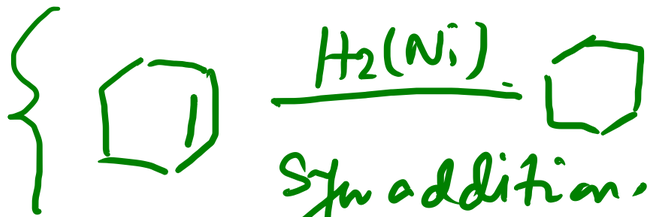
a) 

b) 

c) 



Alkene → Alkane

Hydrogenation:  H_2 (Ni) → Syn addition. or H_2 (Pd/Pt)

ROH ⟶ RCl.

$CH_2=CH_2 + HCl \rightarrow CH_3CH_2Cl$

Carbonyl cpd ⟶ Alkane Preparation (IIT- Mains Compulsory)

a) $RCH=O \longrightarrow RCH_3$

b) $R-\underset{\underset{O}{\|}}{C}-R \longrightarrow RCH_2-R$.

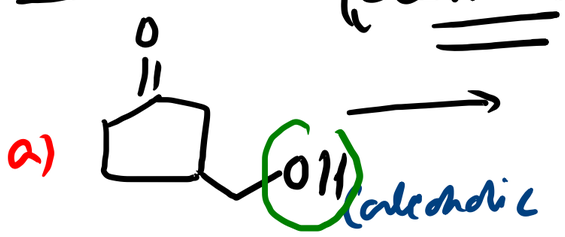
always coming in IIT-JEE

$HC\equiv C-CH_3 \rightarrow CH_2=CH_2$

: Limitation (clemenson) can't be used

i) $N_2H_4 + \bar{O}H / O\bar{R} / \Delta$ (ethylene glycol is used as solvent)
Wolff-Kishner Reduction.

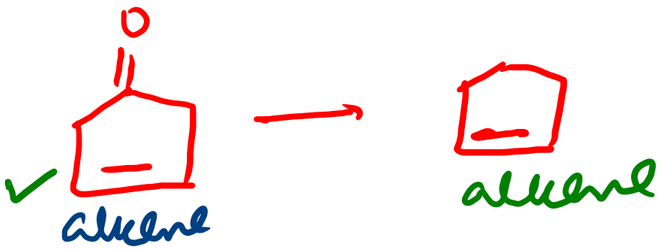
ii) $Zn(Hg)$ + conc. HCl
Clemenson Reduction

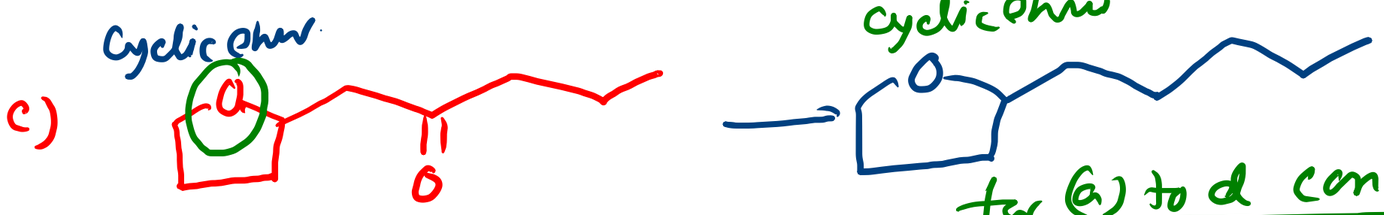
a) 

(alcoholic)

m) CH_2SH, twice. raney Ni / H_2.
CH_2SH
Mosingo reduction.
Ethylene dithiol

never coming in IIT

b) 

c) 

for (a) to d conversion.

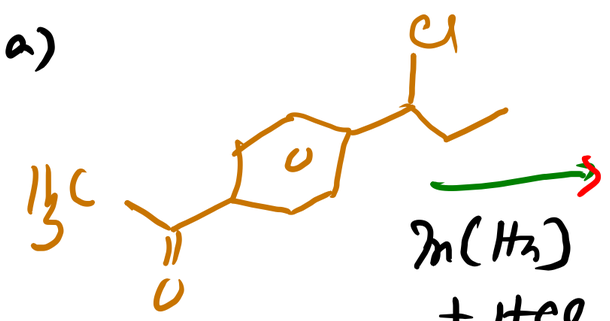
Best reagent : NH_2-NH_2 to OH

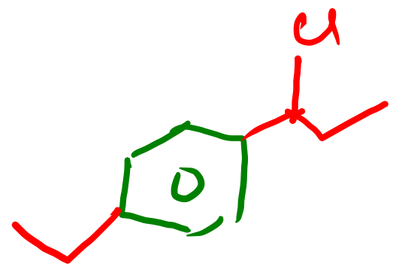
d) 

Acid sensitive group.

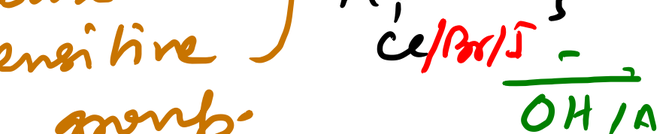
: Limiting Wolff Kishner:

a)



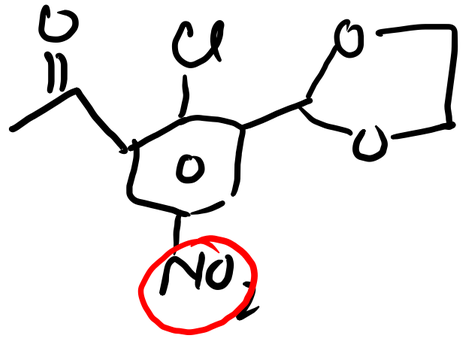


(base sensitive group)

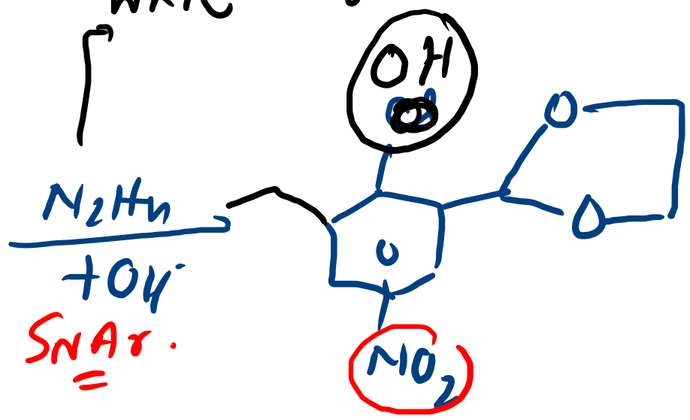


Here WKR can not be used.

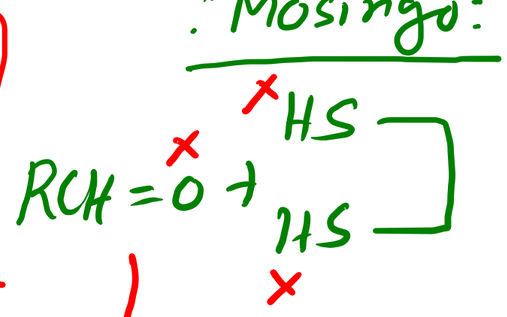
b)



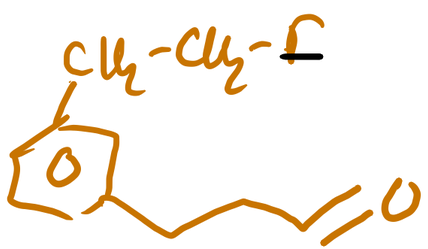
WKR reagent is used, -Cl group is substituted by -OH.

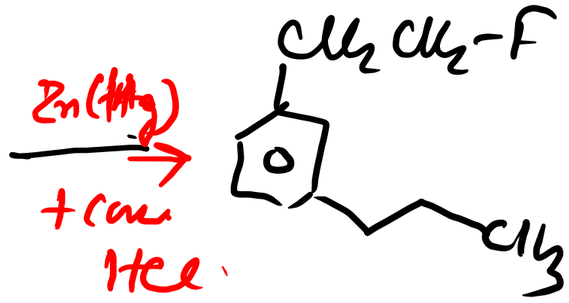


: Mosingo:



c)





: Red P + HI : (very strong reducing reagent)

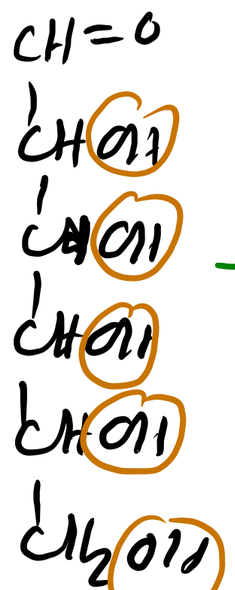
a) $RCH=O \longrightarrow RCH_3$

b) $R-\underset{\underset{O}{\|}}{C}-R \longrightarrow R_2CH_2$

c) $RCO_2H \longrightarrow RCH=O \longrightarrow RCH_2OH \longrightarrow RCH_3$.

d) $R-X \longrightarrow R-H$.

c)



$\xrightarrow[+HI]{red\ P}$ n-hexane.

D-glucose.

$\xrightarrow[(NCERT)]{HI/\Delta}$ n-hexane.

i) $N_2H_4 + \bar{O}H$: WKR

R.A O.A

ii) $N_2H_4 + H_2O_2$: It reduce

$HN=NH + H_2O$ & non polar multiple bond

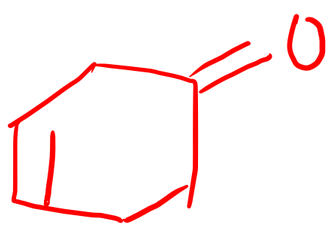
[Supplying H] like $C=C$ (alkene)

$C\equiv C$ (alkyne)

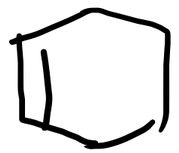
$N=N$. (azo group)

(multiple polar bond)

multiple nonpolar bond.



$N_2H_4 + OH^-$ (WKR)



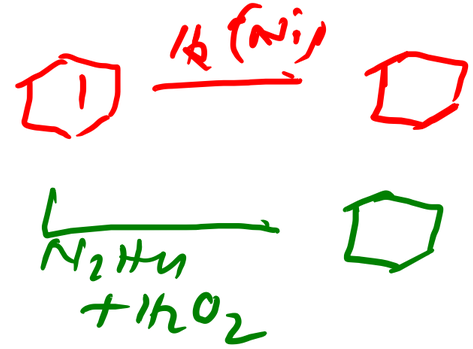
$N_2H_4 + H_2O_2$

Alkene → Alkane.

a) H_2 (Ni)

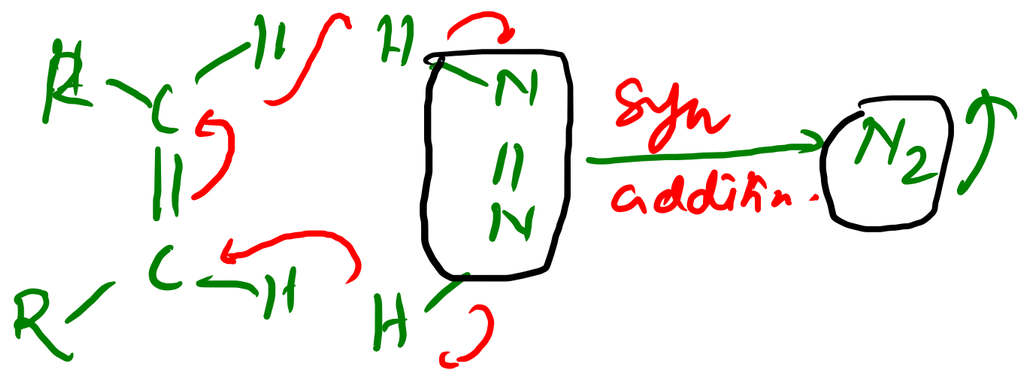
b) H_2 (Pd)

c) H_2 (Pt)



$$\overset{-2}{N_2H_4} + \overset{-1}{H_2O_2} \longrightarrow \overset{-1}{HN}=\overset{-1}{NH} + \overset{-2}{H_2O}$$

R.A O.A



alkane $N_2 H_2 + H_2$

e) HN = NH

diimine.

i) MPV.

ii) NaBH4/EtOH (Bonvealt Blanc)

iii) DIBALH (-78°C)

iv) $SnCl_2$ + HCl (Stephen)

v) $LiALH(OtBu)_3$ (-78°C)

last class discussion

vi) H_2 (Lindlar) (Rosenmund)

vii) R_2Cd (Dialkyl cadmium)

viii) R_2CuLi (Gilman's reagent).

ix) Zn(Hg) + conc HCl (Clemmensen reduction)

x) $N_2H_4 + OH/OR/\Delta$ (Wolff Kishner reduction)

Today's class:

New Reducing agent / Reagents

xi) CH_3SH Raney Ni (H_2)
CH_2SH.
Mosingo reduction.

xii) red P + HI.
(very strong reducing agent)

xiii) $N_2H_4 + H_2O_2$ (reduce multiple nonpolar bond)