Toppersnotes
Unleash the topper in you

THE IIT - JEE SECRET

JEE MAINS AND JEE ADVANCED

ORGANIC CHEMISTRY

VOL - II

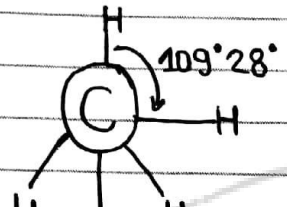
SIERRA INNOVATIONS
Private Limited

Contents

HYDROCARBON

CH=1 **Alkanes** C_nH_{2n+2} ≡ general molecular formula

also known as Paraffins (Very less reactive Compound)



Methane (CH_4)

→ sp^3 hybridisation

⇒ The Simplent alkane that Can Show Structure isomerism-

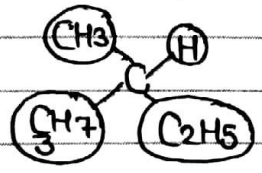
n-butane

$CH_3-CH_2-CH_2-CH_3$

iso-butane

$CH_3-CH(CH_3)-CH_3$

⇒ This Simplent alkane that is optically active :-



≡ $CH_3-\overset{H}{\underset{|}{C^{*}}}(CH_2-CH_3)-CH_2-CH_3$

CH_2

CH_3

⇒ This Simplent alkane that Can show isomerism

CH_3-CH_3 (ethane) ≡ Can show Conformational isomerism

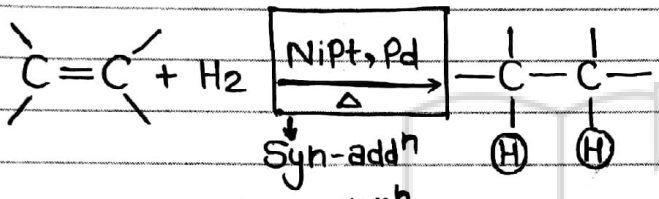
∴ ans: butane

not true isomerism

GENERAL METHOD OF PREPARATION OF ALKANES -

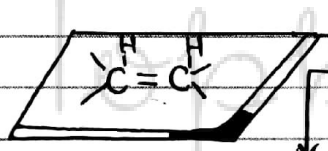
(1) → From alkenes - more substituted alkenes less reactive

(a) - Catalytic hydrogenation -



mrxⁿ → Can also reduce C-heteroatom/hal-hal multiple bond

4 MCTS

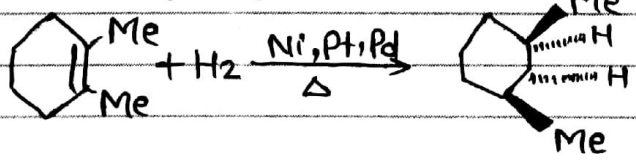


(Ni, Pt, are taken in V. finely divided particles)

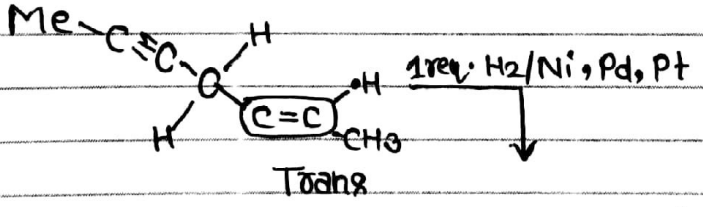
have Very good adsorbing properties

(1) - Catalytic hydrogenation is a Syn addition mrxⁿ.

(eg)-(1) →



(eg)-(2) →

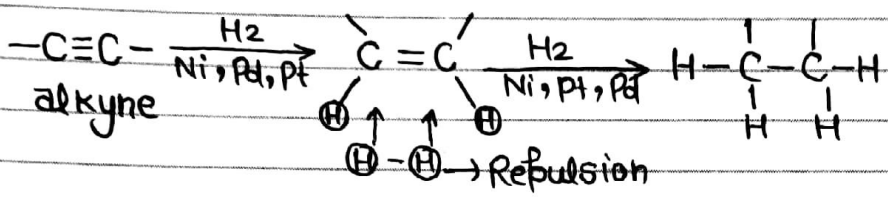


Trans

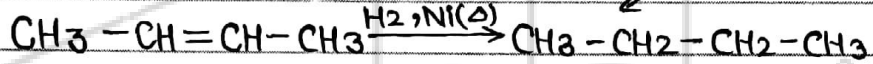
Hydrogenation ability of triple bond is more

What will be the product (a) meso Compound (b) → a optically active Compound

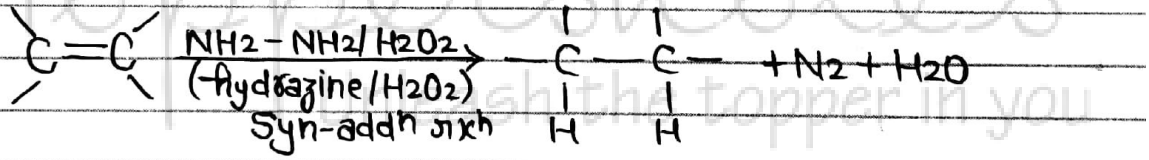
(2) – The rxn rate towards Catalytic hydrogenation of alkynes is greater than that of alkenes.



(3) – In Catalytic hydrogenation, if Ni is used as a metal Catlyst, the rxn is Called as Sabtier Senderen's rxn.

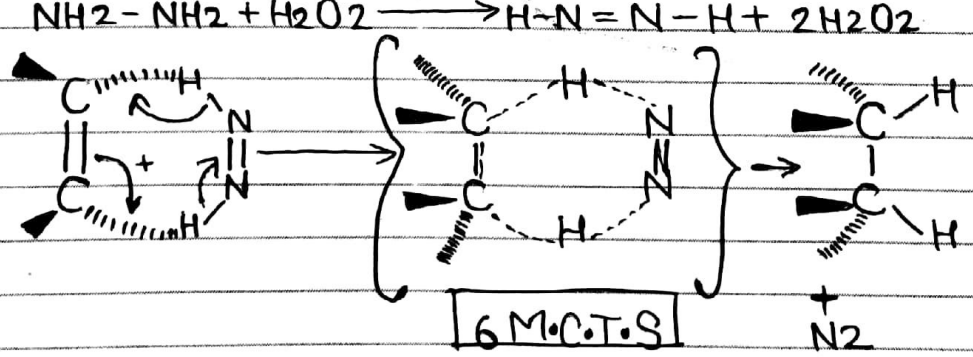


(b) – By transfer hydrogenation –



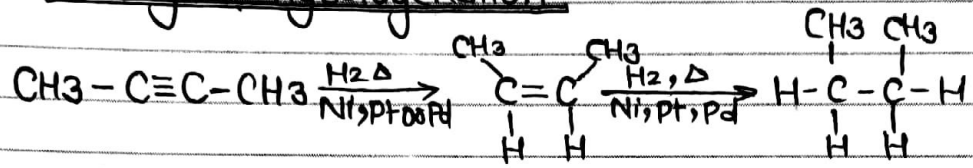
Cannot reduce chat atom mut bond.

Mechanism –



(2) From alkynes –

(a) Catalytic hydrogenation



Alkyne Alkenes Alkane

(3) → From alkye halids:–

(a) – wurtz rxn –

$$2R-X \xrightarrow[\text{dry ether}]{\text{(Na)}} R-R$$

(taken as Solventanly)

Mechⁿ – (1)

Radical mechanism – (3° more)

(1° < 2° < 3°)

$Na \longrightarrow Na^{\oplus} + 1e^{\ominus}$

$R\overset{\cdot}{-}X + 1e^{\ominus} \longrightarrow R^{\cdot} + X^{\ominus}$

$R^{\cdot} + R^{\cdot} \longrightarrow \boxed{R-R}$ alkane

$Na^{\oplus} + X^{\ominus} \longrightarrow NaX$

Mech – (2)

Ionic mechanism – (1° more)

$\boxed{1° > 2° > 3°}$

is more stable

$R-X \rightleftharpoons R^{\oplus} + X^{\ominus}$

$2Na \longrightarrow 2Na^{\oplus} + 2e^{\ominus}$

$R^{\oplus} + 1e^{\ominus} \longrightarrow R^{\odot} + 1e^{\ominus} \longrightarrow R^{\ominus}$

Carbocation — Carbonion

$R^{\ominus} + R\overset{\delta+}{-}X\overset{\delta-}{} \xrightarrow{SN} \boxed{R-R} + X^{\ominus}$

Important Points regarding wurtz rxn.

(1) - It is a Coupling rxn, therefore methane cannot be prepared by this method.

(2) - It is only useful for the preposition of Symmetrical alkanes (ewn no. of C-atoms)

(3) - It is not useful for preposation of unsymm alkanes as a no. of side products are formed.

$Me-Cl + Et-Cl \xrightarrow[\text{dry ether}]{Na} \underset{\text{ethane}}{Me-Me} + \underset{\text{butane}}{Et-Et} + \underset{\text{Propane}}{Me-Et}$

$Na^{\oplus}$ | ie^- $\quad$ $Na^{\oplus}$ | ie^-

$Me^{\odot}$ $NaCl$ $\quad$ $Et^{\odot}$ $NaCl$

$Me^{\odot} + Me^{\odot}$ $\quad$ $Et^{\odot} + Et^{\odot}$ $\quad$ $Me^{\odot} + Et^{\odot}$

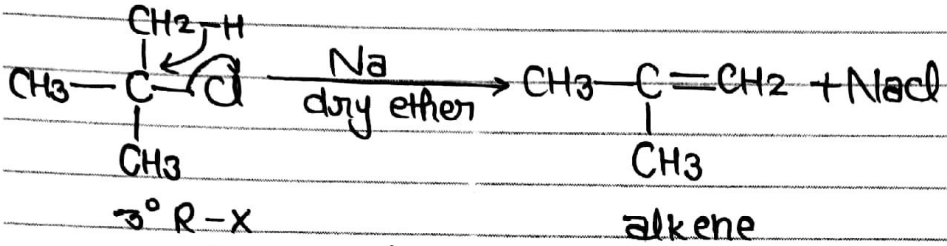
(4) - The reactivity of R-X towards wurtz rxn is ⇒

$\boxed{R-F < R-Cl < R-Br < R-I}$

or leaving group tendency

$\Rightarrow [F^{\ominus} < Cl^{\ominus} < Br^{\ominus} < I^{\ominus}]$

(5) → If 3° R-X is taken as the substrate in wurtz in wurtz rxn, alkane will be formed, as the major product



as 3° Carbon-ff-radical has has V. less prob. to Combine with 3° C-f-n.

1°/2°	R-X ⟶ alkane
3°	R-X ⟶ alkene

(eg)-(1) → $CH_3-CH_2-Br \xrightarrow[\text{dry ether}]{Na} CH_3-CH_2-CH_2-CH_3$ + $CH_2=CH_2 + CH_3-CH_3$

ethyl-bromide — n-butane — in traces.

$CH_3-CH_2-Br \xrightarrow{Na^{\oplus}+1e^{-}} CH_3-CH_2^{\oplus} + Br^{\ominus}$

Diamerisation → $CH_3-CH_2-CH_2-CH_3$ (major)

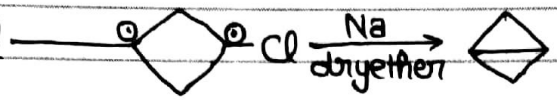
Disproportionation → $CH_3-CH_3 + CH_2=CH_2$ (minor)

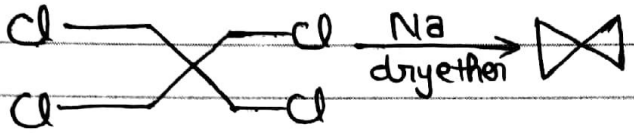
$CH_2-CH_2^{\oplus}$ (H)

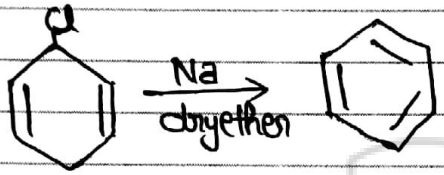
Intramolecular wurtz.

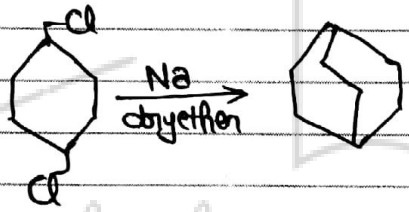
(eg-(1) ⇒

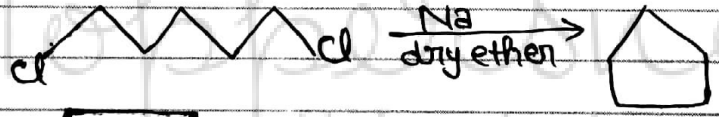
$2Na - 2Na^{\oplus} + 2e^{\ominus}$

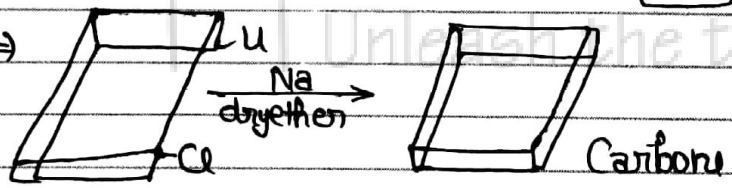
(eg)-(2) 

(eg)-(3) 

(eg)-(4) 

(eg)-(5) → 

(eg)-(6) ⇒ 

(eg)-(7) ⇒ 

(b) **Frankland Reaction** –

$$R_2Zn + R'-X \xrightarrow{\text{ether}} R-R' + ZnX_2$$

alkane

R_2Zn (diakyl zinc) ≡ Frankland Reagent

Organometalic Compound

↳ breaks as R⊖

Q- Write mechanism also -

$(CH_3)_2Zn + CH_3-\overset{\delta+}{CH_2}-\overset{\delta-}{Br} \longrightarrow CH_3-CH_2-CH_3 + ZnBx^2$

n- Propane

Mechanism -

$(CH_3)_2Zn \longrightarrow 2CH_3^{\ominus} + Zn^{+2}$

$CH_3 + CH_3-CH_2-Br \xrightarrow[rxn]{SN} CH_3-CH_2-CH_3 + Br^{\ominus}$

NOTE:-

(1)- Frankland rxn is useful for Preparation of Symmetrical as well as unsymm. alkane.

(2)- On taking 1° & 2° alkye halids as the rxn substrate, the major product will be alkanes whereas taking 3° alkyl halide as rxn Salestrate, the major product will be alkene

(C) ⇒ Corry-House Synthesis -

$R_2CuLi + R^1-X \longrightarrow R-R^1 + a|B + LiX$

R_2CuLi = Gileman's reagent

↳ Organometalic Compound :. $R^{\ominus}$

Mechn : $R-X + 2Li \longrightarrow RLi + LiX$

$2Li + CuX \longrightarrow R_2CuLi + LiX$

$\underbrace{R_2CuLi}_{R^{\ominus}} + R^1-X \longrightarrow R-R^1$

★ Both above notes are valid for Carry-house rxn as well.

(eg) → $(CH_3CH_2)_2CuLi + CH_3-CH_2-Br \rightarrow CH_3-CH_2-CH_2-CH_3 + CuBr + LiBr$

(d) → From Grignard Reagent – (RMgX)

(i) $RMgX + R'-X \xrightarrow{Sn\ rxn'} R-R' + MgX_2$

eg ⊕ – $CH_3-CH_2-Br \xrightarrow[Et_2O]{Mg} CH_3CH_2MgBr$

Preparation of RMgX

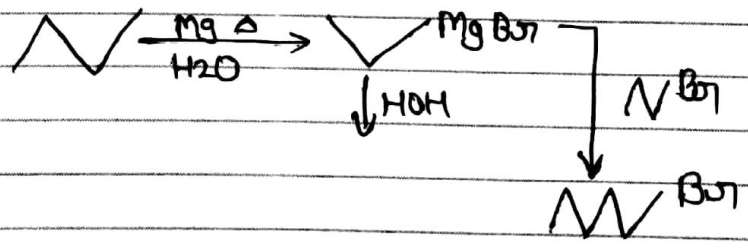
$\xrightarrow{SN\ rxn}$ $\overset{St}{CH_3}-\overset{S-}{Br}$

$CH_3-CH_2-CH_3 + MgBr_2$

(ii) $\overset{\ominus}{R}/\overset{\oplus}{Mg}X + \overset{St}{H}-\overset{S-}{A} \longrightarrow R-H + Mg(A)\swarrow$

H–OH
H–NH_2
H–OR
H–O–C(=O)–R
H–C≡C–R
H–X
H–NH–R

CH_4 can prepared by this method only → read.

eg ⊕ – 

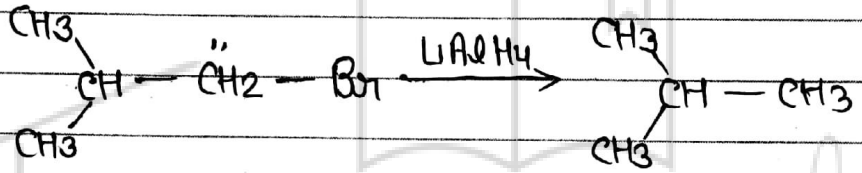
(e) By reduction of R-X (alkye houide)

(i) → Reaction by $LiAlH_4$ —

$$R\text{-}X \xrightarrow{LiALH_4} R\text{-}H$$
(1°/2°x) alkane

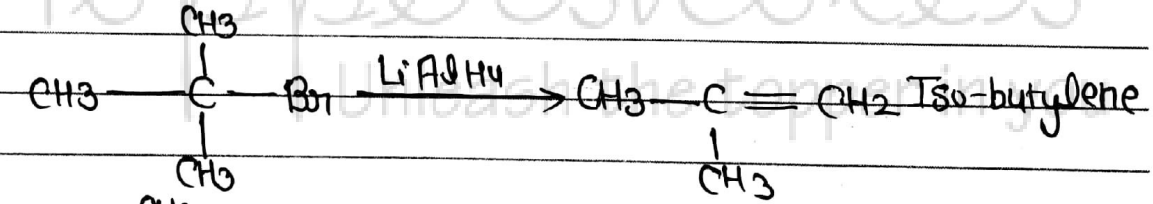
$$R\text{-}X \xrightarrow{LiAlH_4} \text{alkene}$$
(3°Rx)

(eg)-(1)

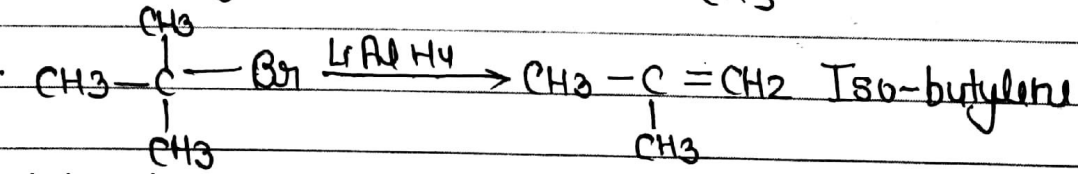


Isobutyl Promide — Isobutane

(eg)-(2) -



(eg)-(2)-



t-butyl bromide — alkene

$LiAlH_4$ & $NaBH_4$ → not react with 1°
↳ more reaction with all
also Ph_3SnH

TH

NOTE:- $LiAlH_4$ is a strong reducing agent & is used to reduce 1° & 2° Rx into alkanes R–H, where as 3° Rx are reduce to alkenes by this.

(ii) **reduction by $NaBH_4$ –**
(Sodium borohydride)

$R-X \xrightarrow{NaBH_4} X$ (no rxn)

$R-X \xrightarrow{NaBH_4}$ alkanes

eg-(1) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Br \xrightarrow{NaBH_4} X$ (no rxn)

eg-(2) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-\overset{3^\circ}{Br} \xrightarrow{NaBH_4} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$
(Isobutane)

NOTE

⇒ $NaBH_4$ is a mild reducing agent as Compared to $LiAlH_4$. $NaBH_4$ reduces Only 2°/3° Rx into alkane.

(iii) ⇒ **Reduction by Red P + HI –**

$R-X \xrightarrow[\Delta]{Red\ P-HI} R-H$

Red P is used to eliminate I_2, from the product, because I_2 will react red with alkane to given RI.

$R-H + I_2 \rightleftharpoons R-I + HI$ – to be Continued

$Red\ P + I_2 \longrightarrow PI_3$

(4) ⇒ By reduction of Carbonye group - (—C—)

(a) Clemenson reduction – This removes (reduces) -OH also C=C.

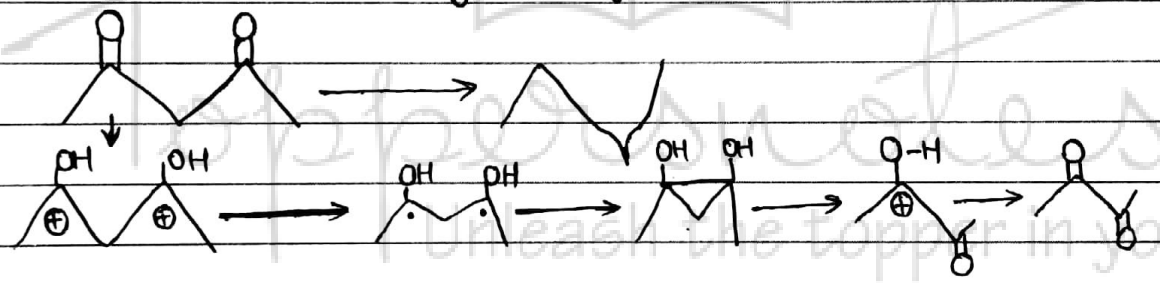
$$R-\underset{\underset{O}{\|}}{C}-H \xrightarrow[Conc.-HCl]{Zn-Hg} R-CH_3$$

(Aldehyde) Via formation of Cation

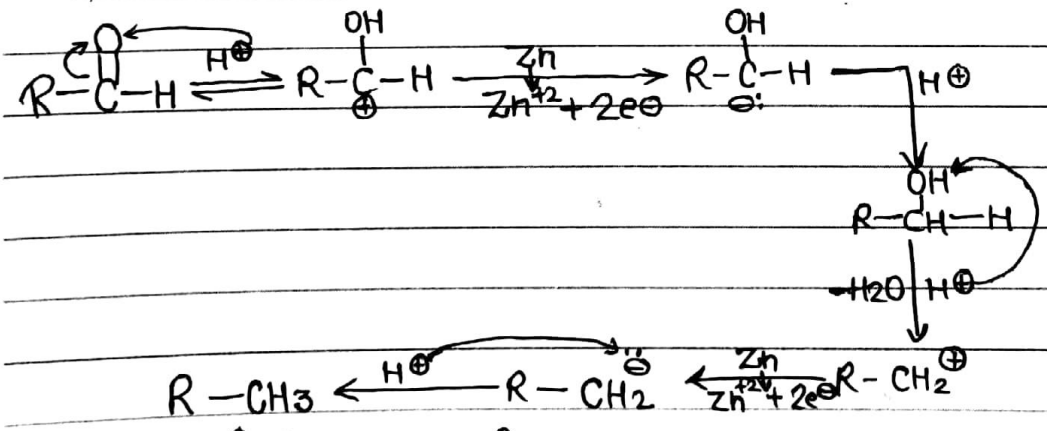
$$R-\underset{\underset{O}{\|}}{C}-R \xrightarrow[Conc.HCl]{Zn-Hg} R-CH_2-R$$ ∴ rearrn taken place.

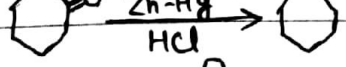
reagent used ⟶ [Zinc-amalgem in Conc. HCl]
(Protic medium)

↓
auoy of Zn & Hg



Mechanism

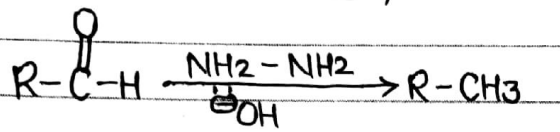


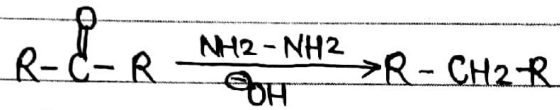
eg (1) ⇒ 

eg (2) ⇒ $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-H \xrightarrow[HCl]{Zn-Hg} CH_3-CH_2-CH_3$.

(b) ⇒ Wolf - Kishner reduction -

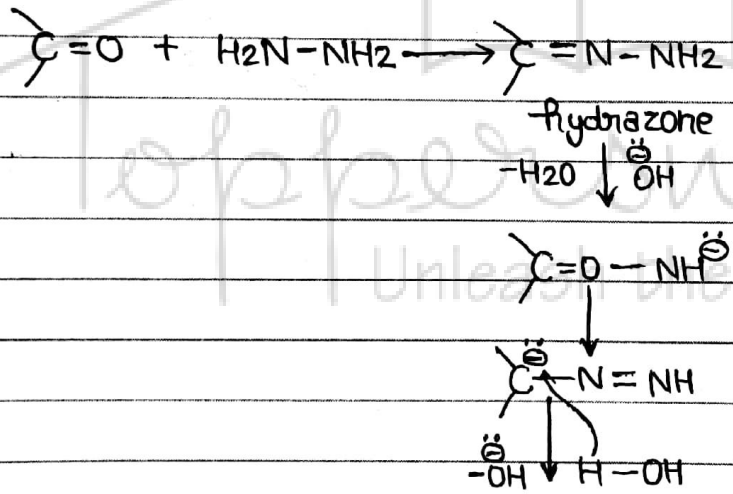
reducing agent - NH_2-NH_2/KOH
[Hydrazine in basic medium]

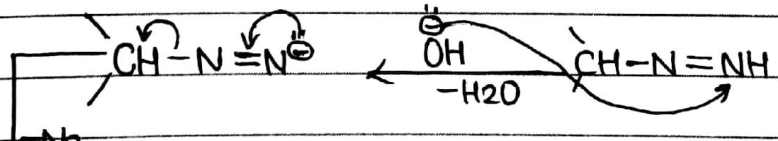


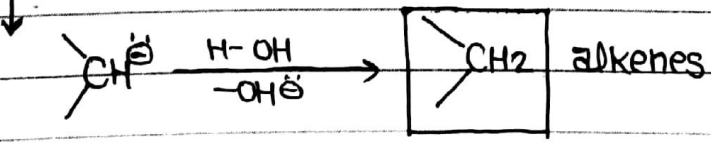


Ketone

Mechanism -







(eg)-(1) Ph-C(=O)-H $\xrightarrow[(ii)\ \ominus OH/HOH]{(i)\ NH_2-NH_2}$ Ph-CH_3

Benzaldehyde — Toluene

(eg) (2) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[(ii)\ OH^{\ominus}]{(i)\ NH_2-NH_2} CH_3-CH_2-CH_3$

NOTE - $NH_2-NH_2/\ddot{O}H$ Only reduces Carbonye group. It does not reduce any other fune. group.

⇒ When ⊖ is present, alkene is formed instead of alkane.

$$CH_3-\underset{Cl}{CH}-\overset{O}{\overset{\|}{CH}} \longrightarrow CH_3-\underset{Cl^{\ominus}}{CH}-\overset{\ominus}{CH} \longrightarrow CH_3-CH=CH$$

(C) → By Red P + HI -

$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\Delta]{Red\,P+HI} R-CH_3$$

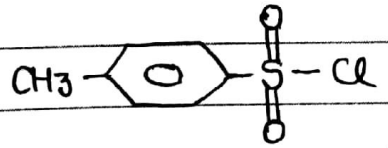
$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow[\Delta]{Red\,P+HI} R-CH_2-R$$

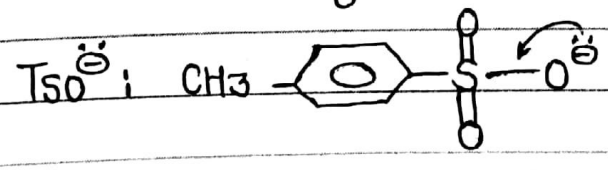
(5) ⇒ From Carboxylic acid -

★ Extra: Reductions of alcohals -

(i) ⇒ $R-OH \xrightarrow{Red\,P+HI} R-H$

(ii) ⇒ $R-OH \xrightarrow{Ts\,Cl} R-\boxed{OTS} \xrightarrow{LiAlH_4} R-H$





NOTE: Alcohal When try to Convert into alkans, by redn of $LiAlH_4$ Instead of redⁿ, acid-base rxⁿ occurs, To avoid this, the above Written method is used.