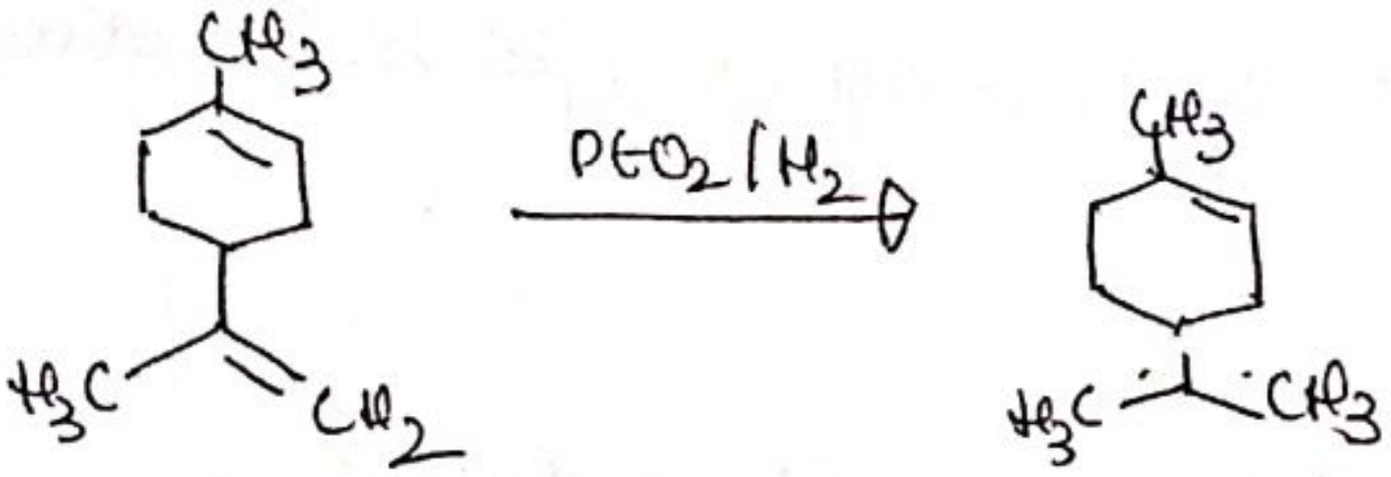
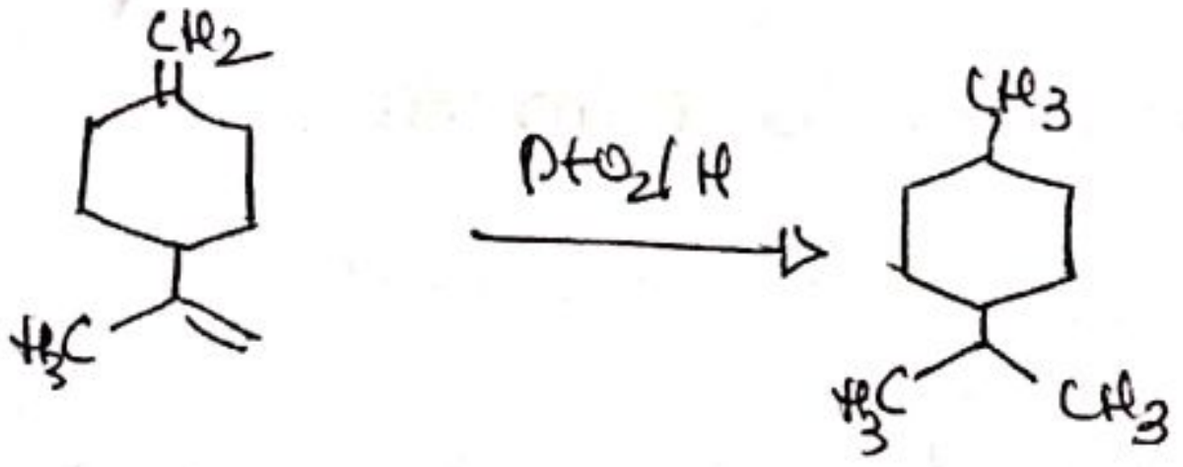
Heterogeneous hydrogenation.

① Platinum (Pt).

- Platinum is used in the form of its oxide, PtO_2 (Adams)
- It is used for reduction of alkenes, amides & azides.





② Palladium.

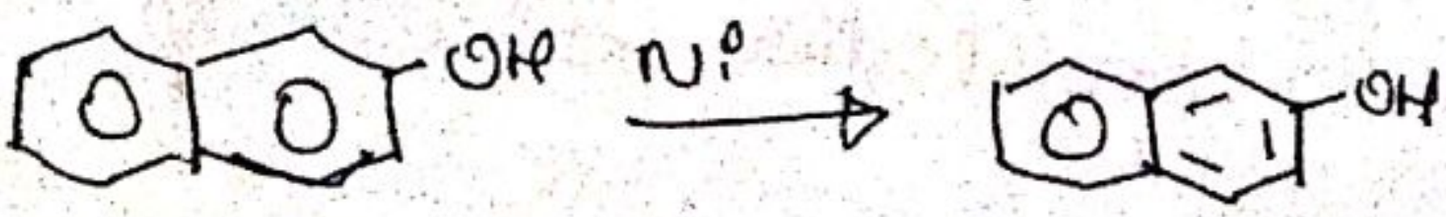
- $Pd/CaCO_3$ [Lindlar's catalyst].
- It is used for partial reduction of triple bond or double bonds.
- Partial hydrogenation of alkynes.

$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{Pd} R-CHO$$

$$H_3C-(CH_2)_2-C\equiv C-(CH_2)_3CH_3 \xrightarrow{Pd} H_3C-(CH_2)-\overset{H}{\underset{}{C}}=\overset{H}{\underset{}{C}}-(CH_2)_3-CH_3$$

③. Nickel.

- Raney nickel catalyst.
- Used for reduction of aromatic rings.



④ copper chromite.

• $CuCr_2O_4$ is obtained by thermal decomposition of copper ammonium chromate.

• Also catalyst effective at high temp (100-200°C) & pressure (200-300 atm).

• It reduces ester to alcohol & amides to amines.

• It can not reduce the aromatic nucleus.

Hydrogenolysis.

• Some functional groups can be removed under catalytic hydrogenation condition. This process is known as hydrogenolysis / reductive fission.

• There reaction proceed by addition of two electron from the metal to the bond to be broken.

• The ansion on protonation during working up give the product.

$$A-B \xrightarrow{2e^-} A^- + B^- \xrightarrow{2H^+} AH + BH.$$

certain groups like allylic & benzylic hydroxyl groups amine groups & carbon-sulphur single bonds readily undergo hydrogenolysis resulting in the cleavage of the bond b/n carbon & hetero atom.

$$RSCH_2C_6H_5 \xrightarrow[H_2]{\text{Raney Ni}} RSH + CH_3C_6H_5.$$

$$RNHSO_2C_6H_4CH_3\,(P) \xrightarrow[H_2]{\text{Raney Ni}} RNH_2 + HO_2SC_6H_4CH_3(P)$$

Reduction reactions involving - catalytic hydrogenation, complex metal hydrides, dissolving metals.

1. Catalytic hydrogenation / Heterogeneous hydrogen

- It is one of the most convenient method for the reduction of organic compounds.
- The method consists in stirring the substrate with a catalyst in a suitable solvent in an atmosphere of hydrogen.
- After the reduction is complete the catalyst is removed by filtration & the reduced product is obtained in pure state.
- common unsaturated groups such as C-C double bond, C-C triple bond, carbonyl group, carboxylic group, nitrile group, nitro group and aromatic hetero-cyclic nuclei can be reduced catalytically under appropriate conditions.
- A number of catalysts have been used for catalytic hydrogenation. They are used mainly as finely divided metals, metallic oxides or sulfides.
- The most common catalysts are the platinum metals (platinum, palladium, rhodium & ruthenium)

nickel and copper chromite.

- The catalytic reduction takes place between gaseous hydrogen and an organic compound.
- Transfer of hydrogen takes place from the catalyst to the molecule, resulting in reduction.
- In general it is found that hydrogenation takes place by the addition of hydrogen atoms to the less hindered side of the unsaturated site.

eg:- Platinum :- platinum is used in the form of its oxide, PtO_2 (Adam's catalyst).

Palladium :- palladium on $CaCO_3$ deactivated by lead acetate is known as Lindlar's catalyst. It is used for partial reduction of triple bonds to double bonds

Nickel :- The most important catalyst is Raney nickel which is obtained by the Raney's process, an alloy containing 50% of Ni and 50% of Al (known as Ni-Al alloy) is heated with aqueous NaOH solution at 50-100°C.

Copper Chromite : $CuCr_2O_4$, is obtained by thermal decomposition of copper ammonium chromate. This catalyst is effective at high temperature (100-200°C).

& Pressure [200-300 atm] (15)

It reduces esters to alcohols and amides to amines.

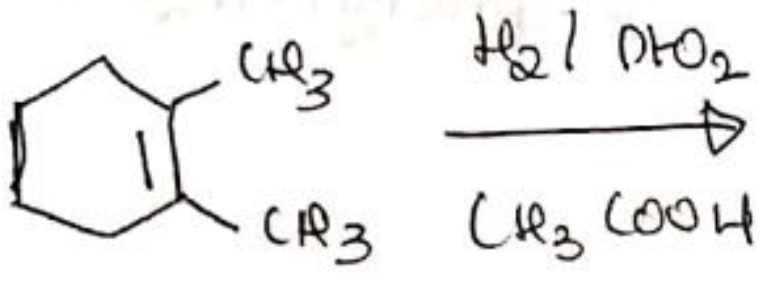
It can not reduce the aromatic nucleus.

Applications of Catalytic hydrogenation.

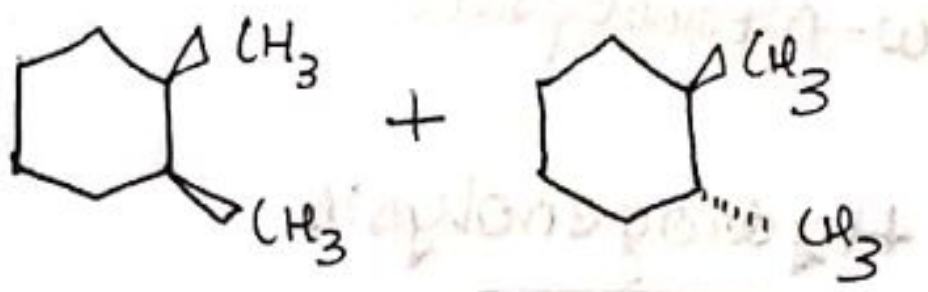
(1.) Reduction of alkenes.

$C_6H_5CH=CHCH_2OH \xrightarrow[EtOH]{Raney\ Ni/H_2} C_6H_5CH_2CH_2CH_2OH$

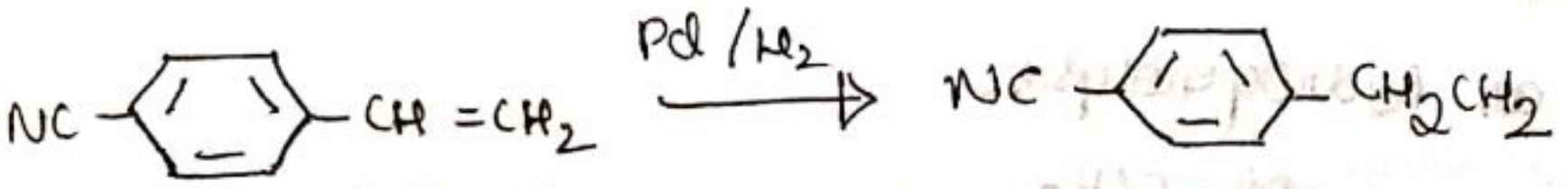
Cinnamyl alcohol — Dihydrocinnamyl alcohol.



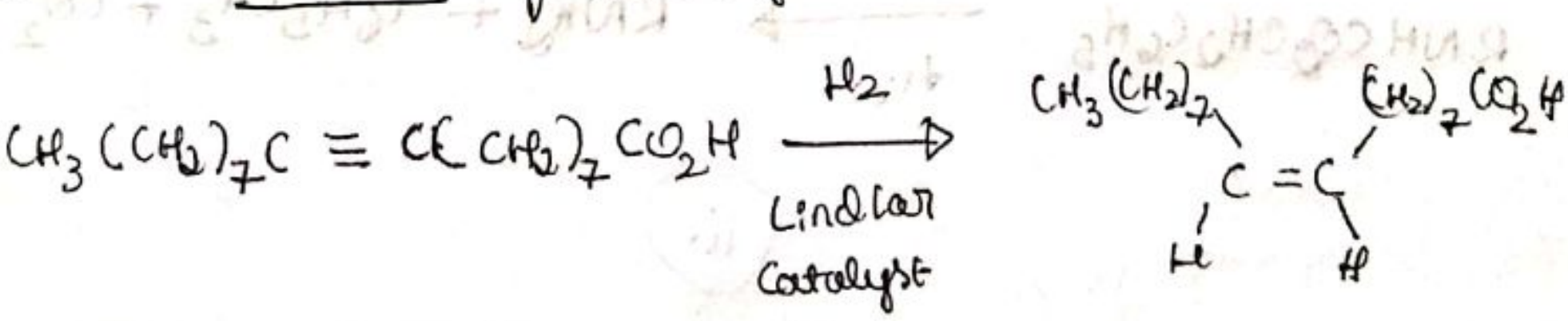
1,2-Dimethyl cyclohexene



cis-1,2-Dimethyl cyclohexane + trans-

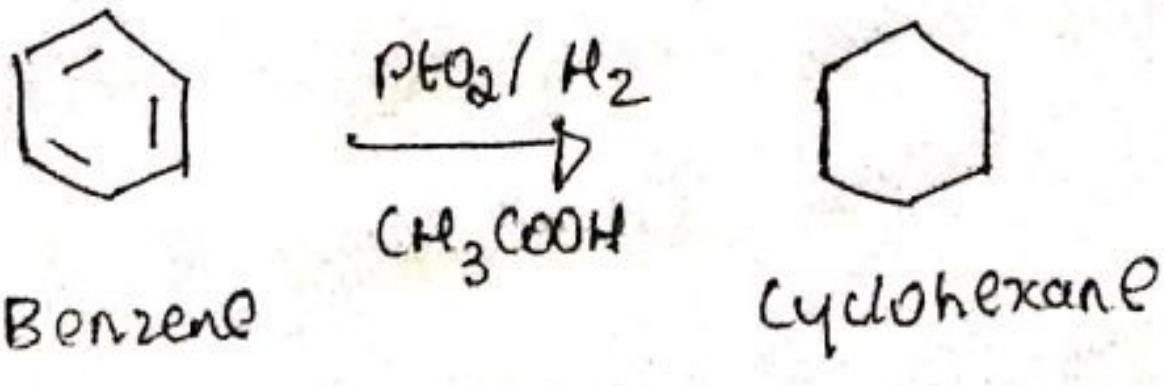


(2.) Reduction of alkynes.



Lindlar catalyst ($\equiv \rightarrow =$)

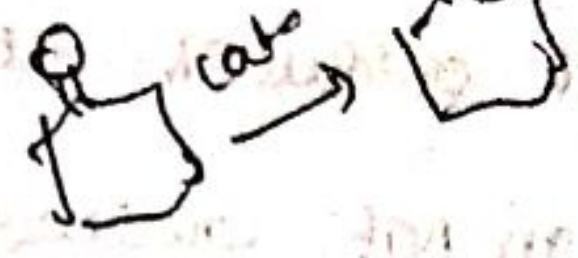
(3.) Reduction of aromatic compounds.



Benzene — Cyclohexane

④. Reduction of aldehydes & ketones

$$R\,CHO \xrightarrow[Ni\,/\,Pd]{PtO_2/H_2} R\,CH_2OH$$



⑤. Reduction of Nitriles, Oximes & nitro compounds

$$RC \equiv N \xrightarrow[C_2H_5OH]{H_2,\,PtO_2} [RCH=NH] \longrightarrow RCH_2NH_2$$

Nitriles

$$C_6H_5CH=CH\,NO_2 \xrightarrow[C_2H_5OH]{H_2,\,Pd-C} C_6H_5CH_2CH_2NH_2$$

ω-Nitrostyrene

β-phenylethylamine

⑥. Hydrogenolysis

Some functional groups can be removed under catalytic hydrogenation conditions. This process is known as hydrogenolysis.

$$R\,O\,CH_2C_6H_5 \xrightarrow{Pd-C/H_2} R\,OH + CH_3C_6H_5$$

$$RNHCO_2CH_2C_6H_5 \xrightarrow[H_2]{Pd-C} RNH_2 + C_6H_5CH_3 + CO_2$$