

## Oxidation

- (i) Increase in oxidation state
- (ii) gain of oxygen/any electronegative element
- (iii) loss of hydrogen/any electropositive element
- (iv) loss of electrons

An oxidising agent oxidises the substrate and must be reduced during the course of reaction

## Reduction

- (i) Decrease in oxidation state
- (ii) loss of oxygen/any electronegative element
- (iii) gain of hydrogen/any electropositive element
- (iv) gain of electrons

A reducing agent reduces the substrate and must be oxidised during the course of reaction

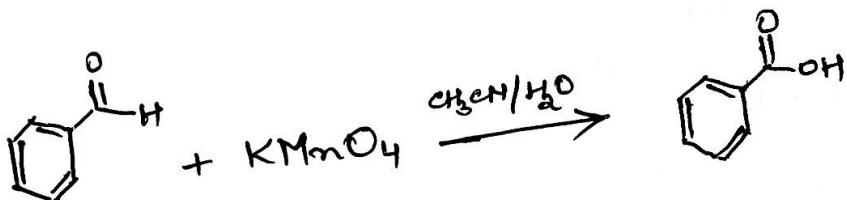
Oxidation and reduction, <sup>often</sup> occur simultaneously in a type of chemical reaction called as redox reaction.

Oxidising Agent KMnO<sub>4</sub> (Potassium Permanganate) Mn +7

Exhaustive oxidation of organic molecules by KMnO<sub>4</sub> will proceed until the formation of carboxylic acids. Therefore alcohols will be oxidized to carbonyls (i.e. aldehydes and ketones) and aldehydes (and some ketones also) will be oxidized to carboxylic acids.

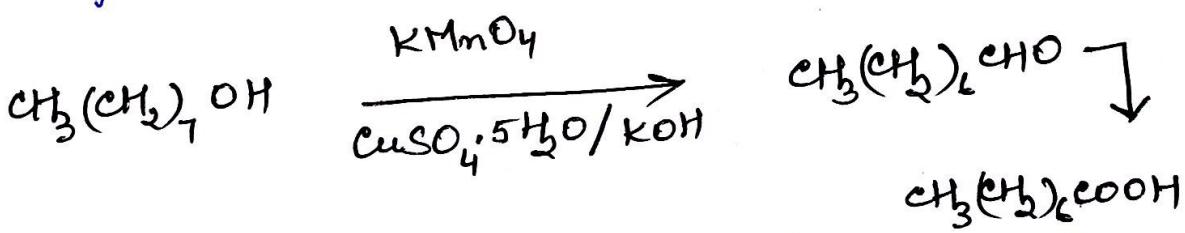
Aldehydes

Aldehydes are readily oxidized to carboxylic acids



Alcohols

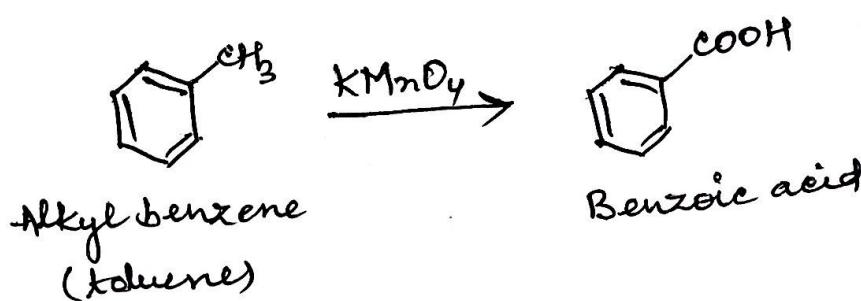
Primary alcohols can be oxidized efficiently by KMnO<sub>4</sub> in presence of basic copper salts. However the product is predominantly corresponding carboxylic acid (resulting from overoxidation of aldehyde product)



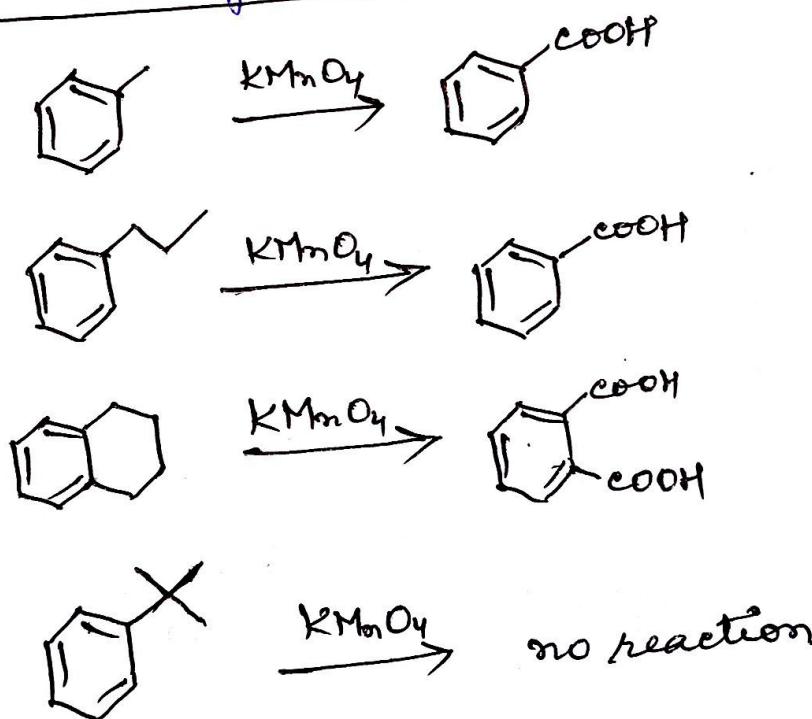
Although overoxidation is less of a problem with secondary alcohols, KMnO<sub>4</sub> is still not considered generally well-suited for conversion of alcohols to aldehydes or ketones.

## Aromatic side chains!

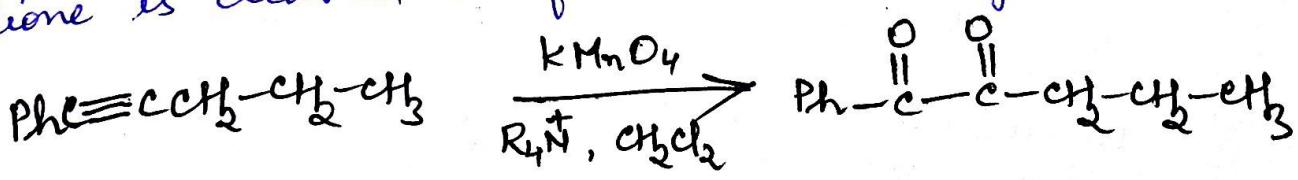
Treatment of an alkylbenzene with  $\text{KMnO}_4$  results in oxidation to give the benzoic acid.



The reaction only works if there is at least one hydrogen attached to the carbon. However, if there is at least one hydrogen, the oxidation proceeds all the way to the carboxylic acid.

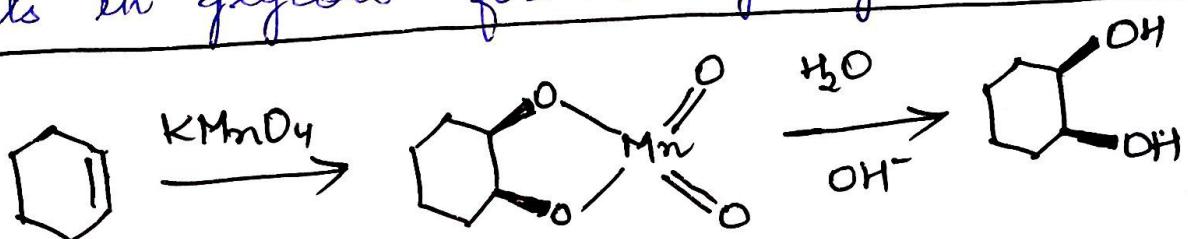


Alkynes Permanganate oxidation of alkynes leads to the formation of diones. (Under harsher conditions, the dione is cleaved to form two carboxylic acids)

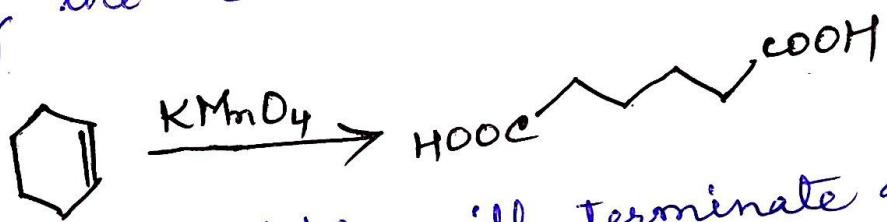


Alkenes Under mild conditions, potassium permanganate can effect conversion of alkenes to glycol. (The glycol may further oxidize leading to cleavage of the carbon-carbon bond, if reaction conditions are not controlled).

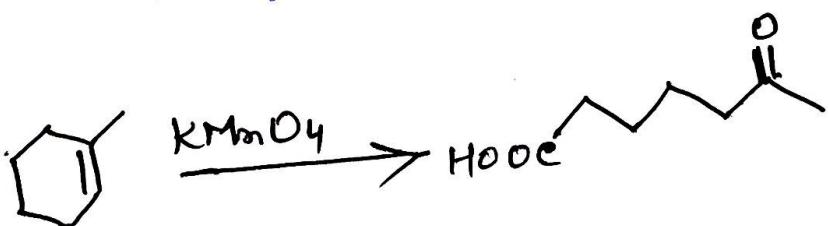
A cyclic manganese diester is an intermediate in these oxidations, which results in glycols formed by "syn addition".



With addition of heat and/or more concentrated  $\text{KMnO}_4$ , the glycol can be further oxidized, clearing the C-C bond.



More substituted olefins will terminate at the ketone



Oxidising Agent

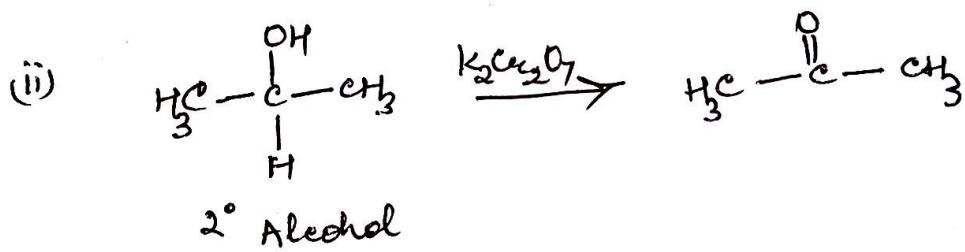
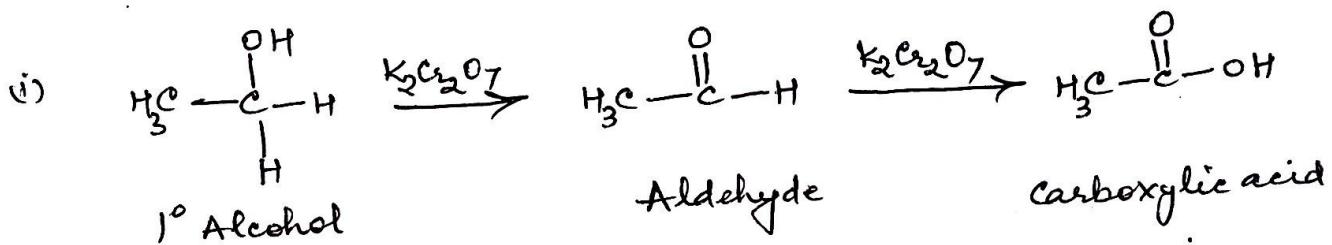
$K_2Cr_2O_7$

(Potassium Dichromate)

Cr + 6

Alcohols

$K_2Cr_2O_7$  oxidises primary alcohol into aldehydes and secondary alcohols into ketones which are further oxidised to carboxylic acids



2° Alcohol

Tertiary alcohols have no hydrogen atom attached to the carbon atom holding the -OH group, so they cannot be oxidized by  $K_2Cr_2O_7$ .

Phenols

$K_2Cr_2O_7$  can be used to oxidize a number of different organic compounds, including phenols. Hydroquinone, for example, is oxidized to benzoquinone.

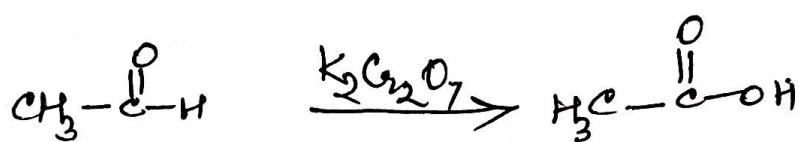
- ozone



Hydroquinone

Benzoquinone

Aldehydes  $\xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7}$  oxidizes aldehydes into carboxylic acids.



## Reducing Agent NaBH<sub>4</sub> (Sodium Borohydride)

Sodium borohydride is a reagent mainly used for the reduction of ketones and aldehydes. (it will also reduce acid halides). It reduces by transfer of hydride ions to substrates as in case of lithium aluminium hydride.

Reduction :- (i) conversion of ketones to secondary alcohols.



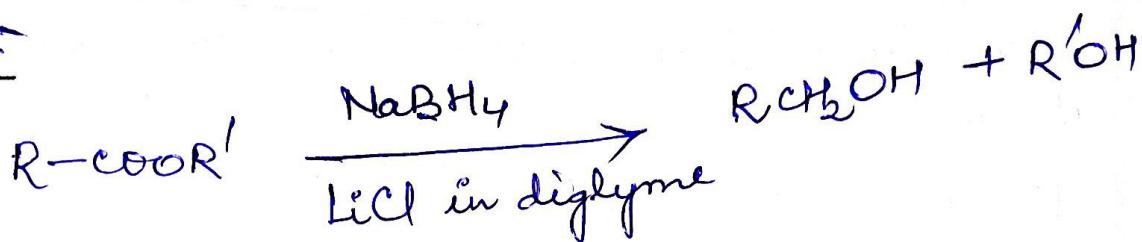
Reduction :- (ii) conversion of aldehydes to primary alcohols.



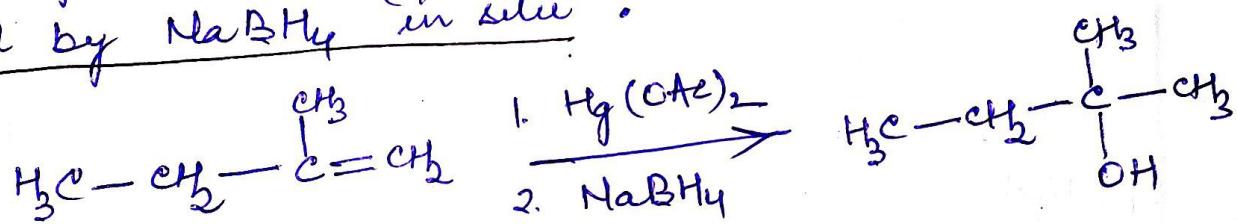
Reduction :- (iii) Reduction of carbon-nitrogen double bond  
Although NaBH<sub>4</sub> does not reduce nitriles, it reduces carbon-nitrogen double bond.



(iv) Reduction of esters: Ester groups are unaffected by  $\text{NaBH}_4$  but in presence of  $\text{LiCl}$  or  $\text{AlCl}_3$  in diglyme, they are reduced to alcohols.



(v) Hydration of Olefins Olefins are hydrated under mild conditions without rearrangement in high yield on treatment with mercuric acetate followed by  $\text{NaBH}_4$  'in situ'.



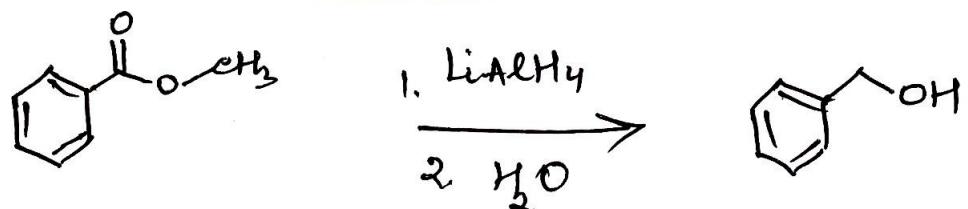
## Reducing Agent

LiAlH<sub>4</sub>

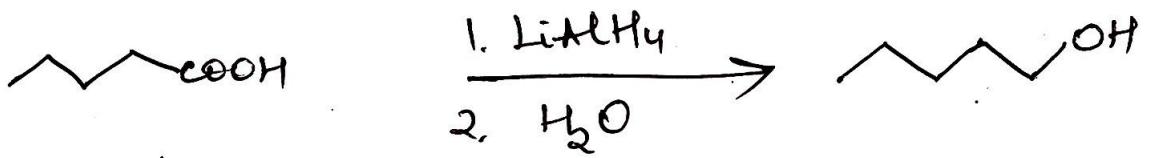
(LAH) Lithium aluminium hydride

Lithium aluminium hydride is very strong reducing agent. It will reduce aldehydes, ketones, esters and carboxylic acids to alcohols; amides and nitriles to amines and open epoxides to give alcohols. It reduces the substrate by transfer of hydride ions.

(i) Reduction: conversion of esters to primary alcohols.



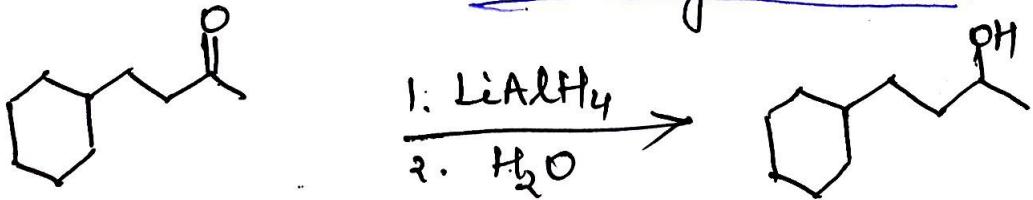
(ii) Reduction:- conversion of carboxylic acids to primary alcohols



(iii) Reduction : conversion of amides to primary amines

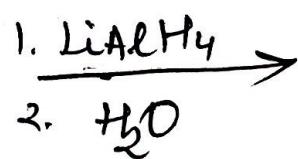


(iv) ~~con~~ Reduction : conversion of Ketones to secondary alcohols.



(v) Reduction:-

Conversion of nitriles to primary amines.

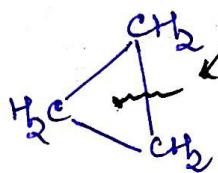


## Ring opening Reactions

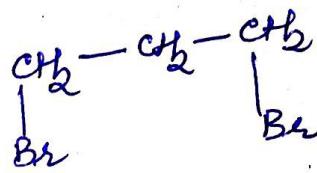
### (i) Addition of $\text{Cl}_2$ and $\text{Br}_2$

addition products.

Ring splits open



cyclopropane reacts with  $\text{Cl}_2$  and  $\text{Br}_2$  in the dark to form



1,3-dibromopropane

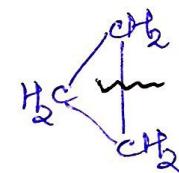
Similar reaction with chlorine.

Cyclobutane and higher members do not undergo this reaction.

### (ii) Addition of $\text{HBr}$ and $\text{HI}$

cyclopropane reacts with conc.  $\text{HBr}$  and  $\text{HI}$  to

yield 1-bromopropane and 1-iodopropane respectively.



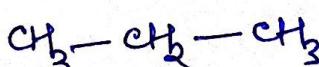
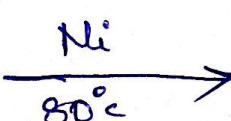
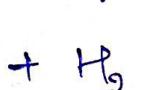
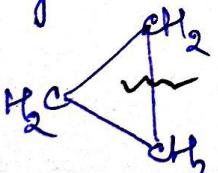
1-Bromopropane

Similar reaction with  $\text{HI}$ .

Cyclobutane and higher members do not give this reaction.

### (iii) Addition of $\text{H}_2$

cyclopropane and cyclobutane react with hydrogen in the presence of  $\text{Ni}$  catalyst to give propane and n-butane respectively.

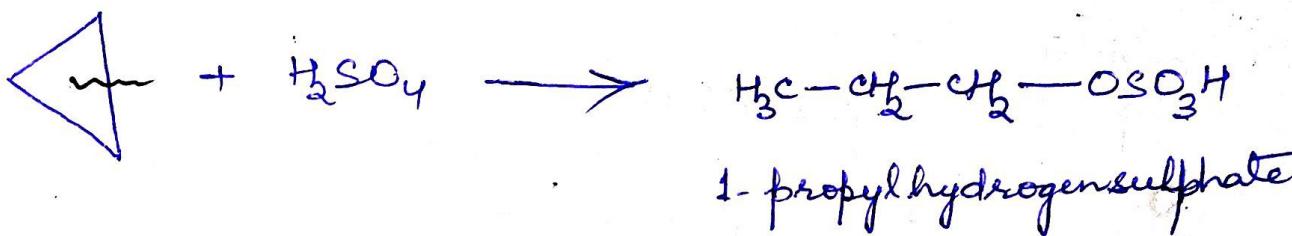


Propane

(iv) Addition of sulphuric acid cyclopropane reacts

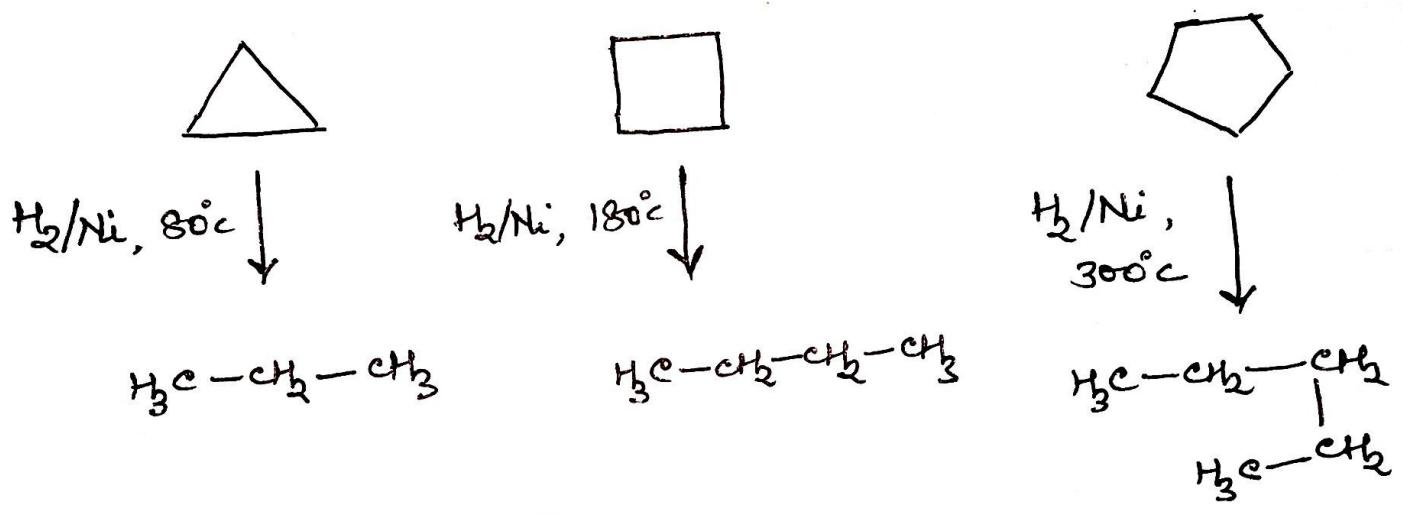
with  $H_2SO_4$  to yield

1-propylhydrogensulphate.



## Reactions Driven by the Strain of Small Rings

The ring strain of cyclopropane is the driving force for ring-opening reactions. Thus catalytic hydrogenation of cyclopropane yields propane. With increasing ring size, much higher temperatures are required for this reaction to occur:



(Highest Ring Strain)  
in cyclopropane