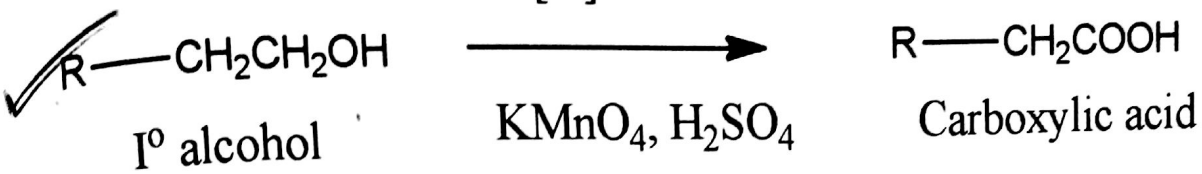
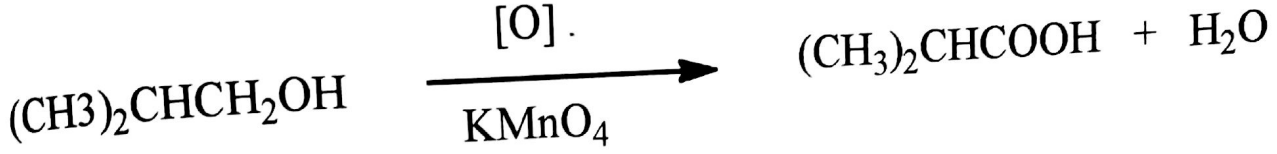
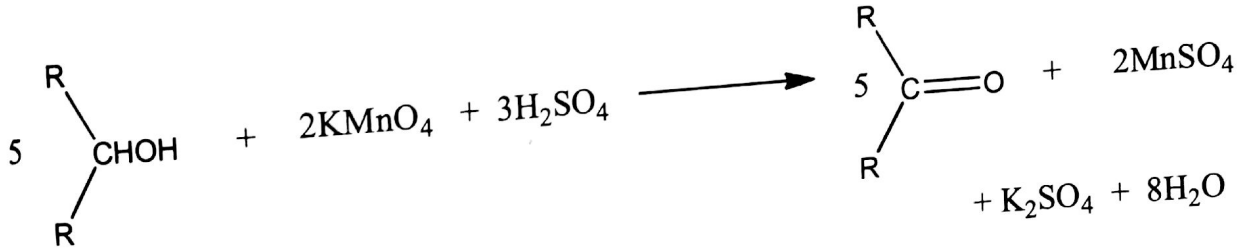


I° alcohol Carboxylic acid

For example, 2-methylpropan-l-ol is oxidized to 2-methylpropanoic acid with $KMnO_4$/ Na_2CO_3 solution in 76%.



However, secondary alcohols can be oxidised by $KMnO_4$ in acidic or alkaline conditions to give the ketones.



2° alcohol

The utility of this method lies in the fact that the product of oxidation (i.e. ketone) should be removed as the reaction proceeds by distillation.

(ii) Oxidation of alkenes

Alkenes on treatment with dilute $KMnO_4$ solution in presence of alkali give 1,2-diols. In this reaction, the purple $KMnO_4$ is reduced to MnO_2, a brown solid. This change in color is the basis of a test for the presence of double and triple bonds known as the Baeyer test for unsaturation.

of alkenes with $KMnO_4$ is carried out by Stirring

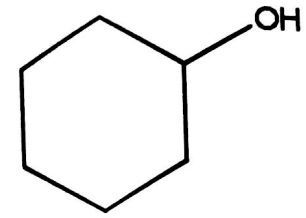
$3\ R_2CO + Na_2SO_4 + Cr_2(SO_4)_3 +$

$7H_2O$

In the above oxidation three moles of secondary alcohols react with
wo moles of Cr(VI) to yield three moles of ketones and two moles of Cr(III).

ome examples of oxidation with Cr(VI) reagents are given below:

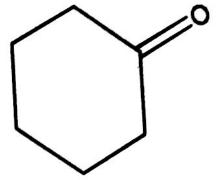
4



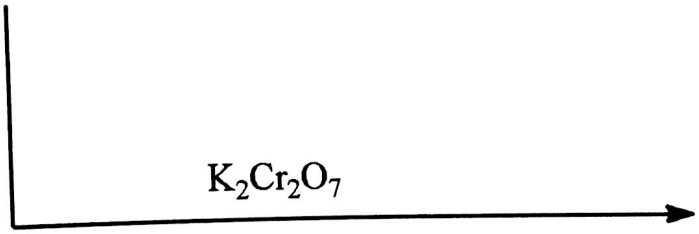
Cyclohexanol

$K_2Cr_2O_7$

H2SO4, 55°

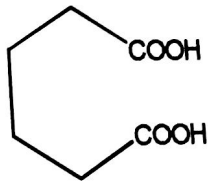


Cyclohexanone

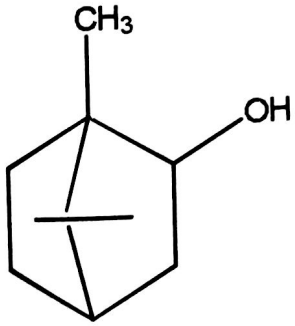


$K_2Cr_2O_7$

H_2SO_4, >60°



Adipic acid

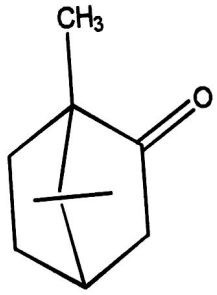


(-) Borneol

$Na_2Cr_2O_7$

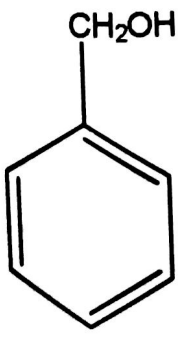
H_2O/H_2SO_4

Ether



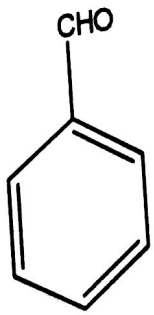
(-) Camphor
(83%)

2



$Na_2Cr_2O_7$, H_2SO_4

H_2O



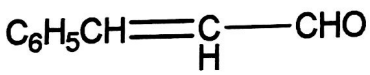
7.15.2 Lithium aluminium hydride

$LiAlH_4$ is prepared by the action of anhydrous aluminium chloride to a paste of lithium hydride in THF.

$$4LiH + AlCl_3 \xrightarrow[\text{Or dry ether}]{\text{THF}} LiAlH_4 + 3LiCl$$

It is one of the most important and useful reagent for the reduction of ketones, carboxylic acids, esters, acid chlorides, anhydrides, epoxides, nitriles and nitro compounds. Some typical examples are given below.

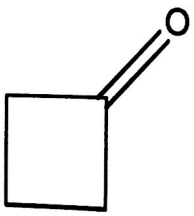
$$\underset{\text{Hexanal}}{CH_3(CH_2)_4CHO} \xrightarrow[2.\ H^+]{1.\ \text{LAH, Ether}} \underset{\text{Hexanol}}{CH_3(CH_2)_4CH_2OH}$$



Cinnamaldehyde

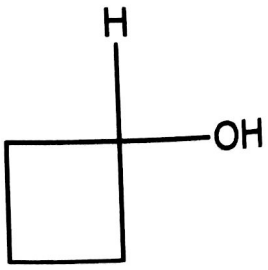
$$\xrightarrow[2.\ H^+]{1.\ \text{LAH, Ether}} \underset{\text{3-Phenyl-1-propanol}}{C_6H_5CH_2CH_2CH_2OH}$$

$$\underset{\text{Ethylacetoacetate}}{CH_3COCH_2COOC_2H_5} \xrightarrow[2.\ H^+]{1.\ \text{LAH, Ether}} \underset{\text{Butane-1-3-diol}}{CH_3CH(OH)CH_2CH_2OH}$$



Cyclobutanone

$$\xrightarrow[2.\ H^+]{1.\ \text{LAH, Ether}}$$



Cyclobutanol

Cyclohexanone

7.15.3 Sodium borohydride

Sodium borohydride is a very selective reducing agent and reduces aldehyde and ketones to alcohols. Groups like halogeno, cyano, amido and alkoxycarbonyl are unaffected. It is prepared by the reaction of sodium hydride with trimethylborate.

$$4\ NaH + B(OMe)_3 \xrightarrow{250^{o}} NaBH_4 + 3\ MeONa$$

$NaBH_4$ is insoluble in ether but soluble in alcohol and water. So it is used in hydroxylic solvents like alcohol, isopropanol etc. Some applications of $NaBH_4$ are given below.

$C_6H_5COCH_2CH_2COOR$ (R=H or C_2H_5) $\xrightarrow[MeOH]{NaBH_4}$ $C_6H_5CH(OH)CH_2CH_2COOR$ (R=H or C_2H_5)

$CH_3COCH_2CH_2COCH_3$ (Hexan-2,5-dione) $\xrightarrow{NaBH_4}$ $CH_3CH(OH)CH_2CH_2CH(OH)CH_3$ (Hexan-2,5-diol)

$CH_2OH(CHOH)_4CHO$ (Glucose) $\xrightarrow{NaBH_4}$ $CH_2OH(CHOH)_4CH_2OH$ (Sorbitol)

$NCCH_2CH_2CHO$ (3-Cyanopropionaldehyde) $\xrightarrow{NaBH_4}$ $NCCH_2CH_2CH_2OH$ (4-Hydroxy butyronitrile)

$RCOCl$ (Acid chloride) $\xrightarrow{NaBH_4}$ RCH_2OH (Alcohol)

7.15.4 Sodium liquid ammonia