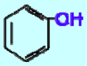
Alcohols

An alcohol consists of a carbon chain with a hydroxy group (-OH) attached

Methanol	CH_3-OH
Ethanol	CH_3-CH_2-OH
Propanol	CH_3-CH_2-CH_2-OH
Phenol	

Nomenclature

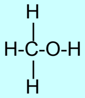
Nomenclature of Alcohols

a) Alcohols are named by dropping the e ending of the parent alkane and replacing with ol. The –OH group can also be named as a substituent using the group name, hydroxy.

b) Still another nomenclature involves naming the alkyl group followed by a space and the word alcohol

Nomenclature

- General formula of alcohols $C_nH_{2n+2}O$
- First member is Methanol
  - a) Displayed formula is



$$\begin{array}{c} H \\ | \\ H\text{-}C\text{-}O\text{-}H \\ | \\ H \end{array}$$

  - b) Systematic name: methanol (from : methan + ol)
  - c) Structural formula - CH_3OH
  - d) Molecular formula CH_4O

Nomenclature

Examples:

CH_3OH	**Methanol**
CH_3CH_2OH	**Ethanol**
$CH_3CH_2CH_2OH$	**propan-1-ol** or 1-**propanol**
$CH_3CH(OH)CH_3$	**propan-2-ol** or **2-propanol**

Nomenclature

if more than one hydroxyl is present, the prefixes di-, tri-, tetra-... are used the terminal "e" is retained on the parent alkane name.

$CH_2OHCH(OH)CH_2OH$

Common name is Glycerol and systematic name is 1,2,3-propanetriol.

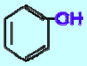
Nomenclature

Name the following molecules:

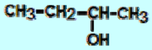
CH_3-OH

CH_3-CH_2-OH

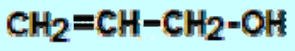
CH_3-CH_2-CH_2-OH



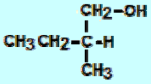
Nomenclature



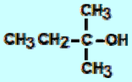
- **2-butanol**



- **2-propene-1-ol**



- **2-methyl-1-butanol**



- **2-methyl-2-butanol**

Alcohol Classification

Alcohols may be classified as

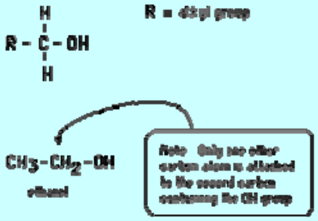
- **Primary**
- **Secondary**
- **Tertiary**

Depending on whether the carbon atom that is attached to the –OH group is surrounded by one, two or three other carbon atoms

Primary Alcohols

A primary alcohol is bonded to carbon atom that is bonded also to one or no carbon atom carbon atom.

Example

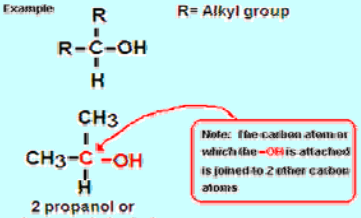


Note: Only one other carbon atom is attached to the second carbon containing the OH group

Secondary Alcohols

A secondary alcohol is attached to a carbon atom that is bonded also to 2 carbon atoms.

Example

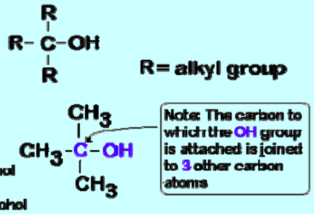


2 propanol or
isopropyl alcohol

Note: The carbon atom on which the –OH is attached is joined to 2 other carbon atoms

Tertiary Alcohols

A tertiary alcohol has three other carbons attached to the carbon on which the -OH group resides



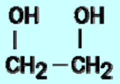
Example

2 methyl-2-propanol
or
tertiary butyl alcohol

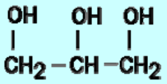
Note: The carbon to which the OH group is attached is joined to 3 other carbon atoms

Polyhydroxy alcohols

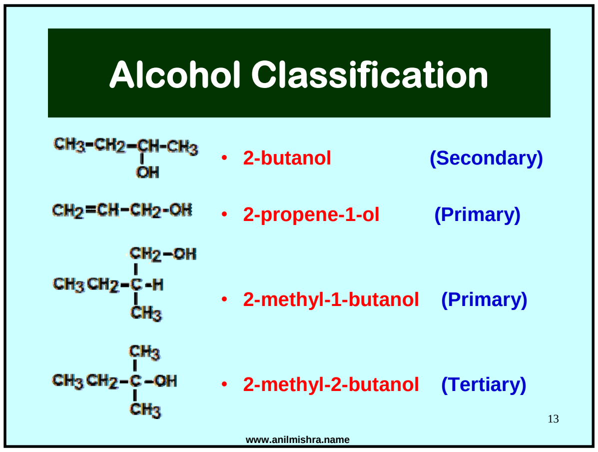
Alcohols that have more than one OH group are known as polyhydroxyl alcohols. Two examples are shown below



1,2 ethanediol
or ethylene glycol

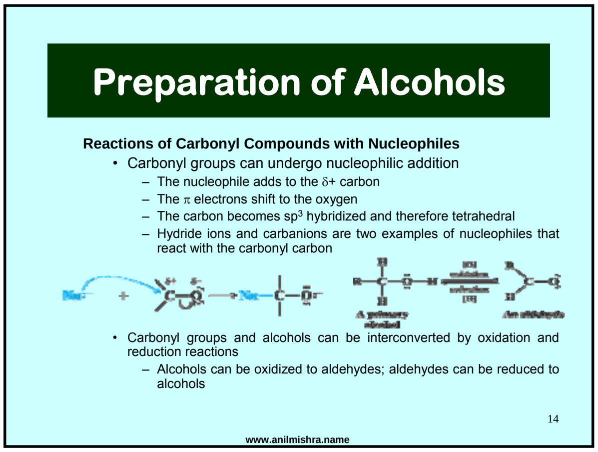


1,2,3 propanetriol
or glycerol



Alcohol Classification

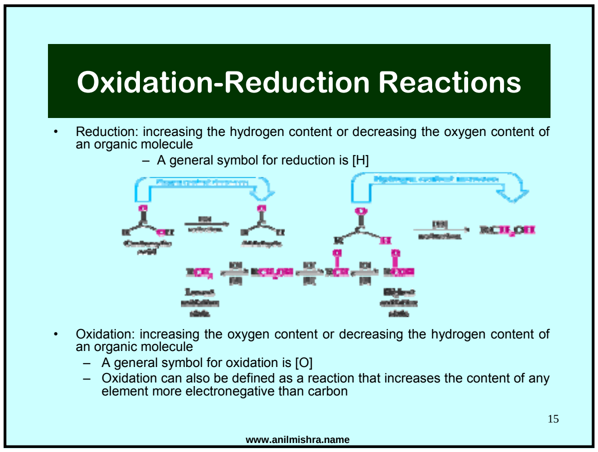
$CH_3-CH_2-\underset{\mid}{CH}-CH_3$ OH	• 2-butanol	(Secondary)
$CH_2=CH-CH_2-OH$	• 2-propene-1-ol	(Primary)
CH_2-OH CH_3CH_2-C-H CH_3	• 2-methyl-1-butanol	(Primary)
CH_3 CH_3CH_2-C-OH CH_3	• 2-methyl-2-butanol	(Tertiary)



Preparation of Alcohols

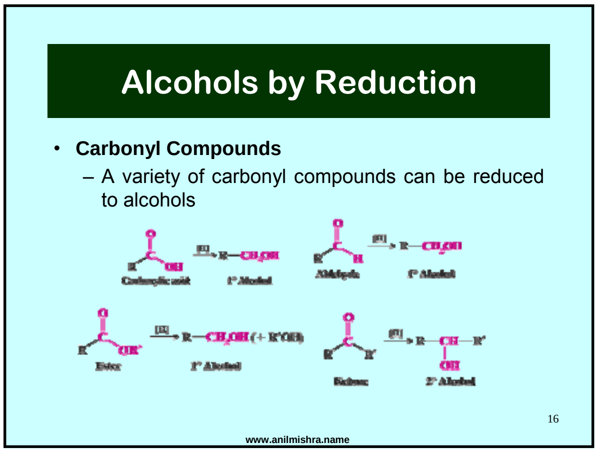
Reactions of Carbonyl Compounds with Nucleophiles

- Carbonyl groups can undergo nucleophilic addition
  - The nucleophile adds to the δ+ carbon
  - The π electrons shift to the oxygen
  - The carbon becomes sp^3 hybridized and therefore tetrahedral
  - Hydride ions and carbanions are two examples of nucleophiles that react with the carbonyl carbon
- Carbonyl groups and alcohols can be interconverted by oxidation and reduction reactions
  - Alcohols can be oxidized to aldehydes; aldehydes can be reduced to alcohols



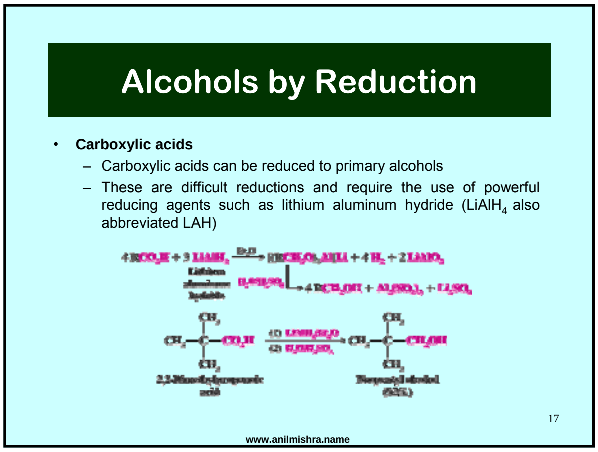
Oxidation-Reduction Reactions

- Reduction: increasing the hydrogen content or decreasing the oxygen content of an organic molecule
  - A general symbol for reduction is [H]
- Oxidation: increasing the oxygen content or decreasing the hydrogen content of an organic molecule
  - A general symbol for oxidation is [O]
  - Oxidation can also be defined as a reaction that increases the content of any element more electronegative than carbon



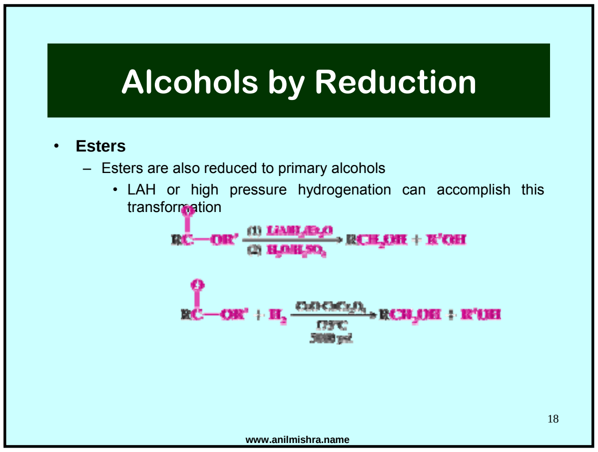
Alcohols by Reduction

- **Carbonyl Compounds**
  - A variety of carbonyl compounds can be reduced to alcohols



Alcohols by Reduction

- **Carboxylic acids**
  - Carboxylic acids can be reduced to primary alcohols
  - These are difficult reductions and require the use of powerful reducing agents such as lithium aluminum hydride ($LiAlH_4$ also abbreviated LAH)



Alcohols by Reduction

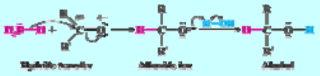
- **Esters**
  - Esters are also reduced to primary alcohols
    - LAH or high pressure hydrogenation can accomplish this transformation

Alcohols by Reduction

- **Aldehydes** and **ketones** are reduced to 1° and 2° alcohols respectively
  - Aldehydes and ketones are reduced relatively easily; the mild reducing agent sodium borohydride ($NaBH_4$) is typically used
  - LAH and hydrogenation with a metal catalyst can also be used

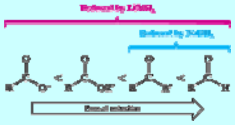
Alcohols by Reduction

- The key step in the reduction is reaction of hydride with the carbonyl carbon



Alcohols by Reduction

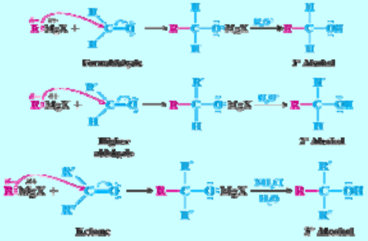
- Carboxylic acids and esters are considerably less reactive to reduction than aldehydes and ketones and require the use of LAH



- Lithium aluminium hydride is very reactive with water and must be used in an anhydrous solvent such as ether
  - Sodium borohydride is considerably less reactive and can be used in solvents such as water or an alcohol

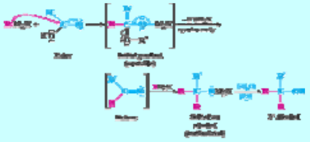
Alcohols from Grignard Reagents

- Aldehydes and ketones react with Grignard reagents to yield different classes of alcohols depending on the starting carbonyl compound



Alcohols from Grignard Reagents

- Esters react with two molar equivalents of a Grignard reagent to yield a tertiary alcohol
  - A ketone is formed by the first molar equivalent of Grignard reagent and this immediately reacts with a second equivalent to produce the alcohol
  - The final product contains two identical groups at the alcohol carbon that are both derived from the Grignard reagent



Properties of Alcohols

The physical properties of alcohols are similar to those of both water and hydrocarbons

The shorter chain alcohols such as methanol and ethanol are similar to water, in general they

-- have higher boiling points than hydrocarbons but lower than water

-- dissolve in water to some degree

-- are more polar than hydrocarbons but less polar than water

Physical Properties

- 1. **Boiling point is higher** than hydrocarbon. (Due to intermolecular H-bond)
- 2. **Spirituous odour** with burning taste.
- 3. Short chain alcohols, up till 4 carbon atoms are **soluble in water.**

Reactions of Alcohols

Alcohols undergo several types of reactions including:

- **Oxidation**
- **Dehydration**
- **Reactions with active metals**
- **Esterification**
- **Substitution**

Types of Alcohol Reactions

- Dehydration to alkene
- Oxidation to aldehyde, ketone
- Substitution to form alkyl halide
- Reduction to alkane
- Esterification
- Tosylation
- Williamson synthesis of ether

Reactions of Alcohols

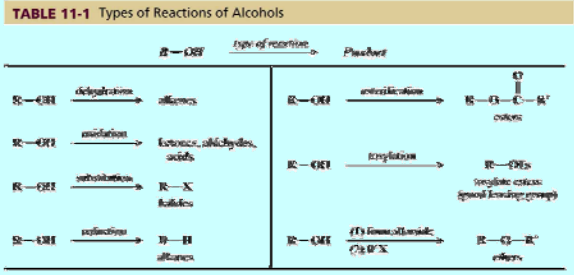
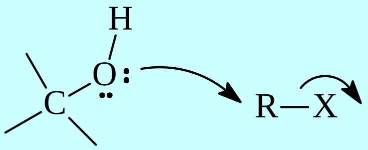


TABLE 11-1 Types of Reactions of Alcohols

$R{-}OH \xrightarrow{\text{type of reaction}} \text{Product}$

$R{-}OH \xrightarrow{\text{dehydration}}$ alkenes	$R{-}OH \xrightarrow{\text{esterification}} R{-}O{-}C({=}O){-}R'$ esters
$R{-}OH \xrightarrow{\text{oxidation}}$ ketones, aldehydes, acids	$R{-}OH \xrightarrow{\text{tosylation}} R{-}OTs$ tosylate esters (good leaving group)
$R{-}OH \xrightarrow{\text{substitution}} R{-}X$ halides	
$R{-}OH \xrightarrow{\text{reduction}} R{-}H$ alkanes	$R{-}OH \xrightarrow[\text{(2) } R'X]{\text{(1) form alkoxide}} R{-}O{-}R'$ ethers

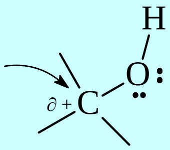
Alcohol as a Nucleophile



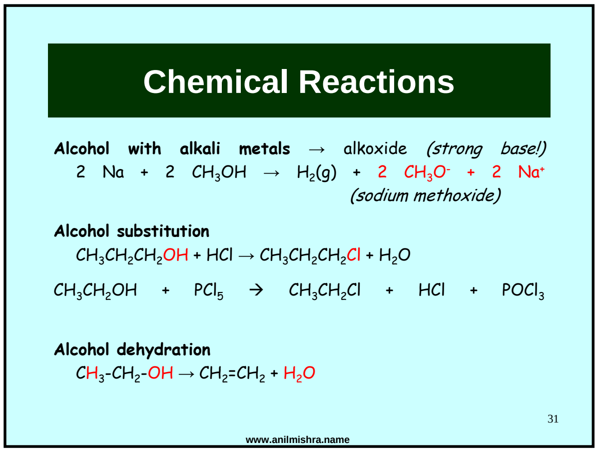
- ROH is weak nucleophile
- RO$^-$ is strong nucleophile
- New O-C bond forms, O-H bond breaks.

Alcohol as an Electrophile

- OH$^-$ is not a good leaving group unless it is protonated, but most nucleophiles are strong bases which would remove H$^+$.
- Convert to tosylate (good leaving group) to react with strong nucleophile (base)



C-Nuc bond forms,
C-O bond breaks



Chemical Reactions

Alcohol with alkali metals → alkoxide *(strong base!)*

$2\ Na + 2\ CH_3OH \rightarrow H_2(g) + 2\ CH_3O^- + 2\ Na^+$

(sodium methoxide)

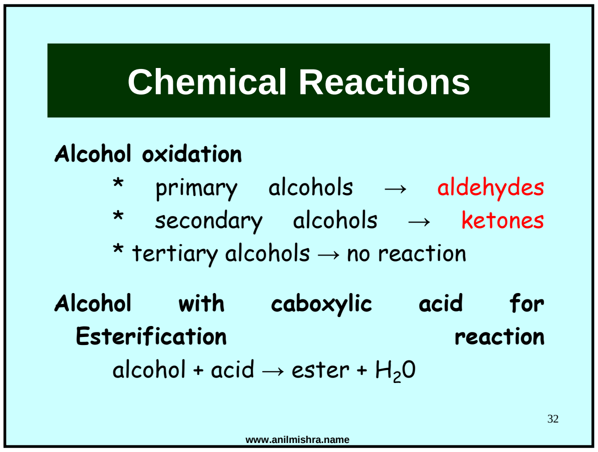
Alcohol substitution

$CH_3CH_2CH_2OH + HCl \rightarrow CH_3CH_2CH_2Cl + H_2O$

$CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + HCl + POCl_3$

Alcohol dehydration

$CH_3\text{-}CH_2\text{-}OH \rightarrow CH_2{=}CH_2 + H_2O$



Chemical Reactions

Alcohol oxidation

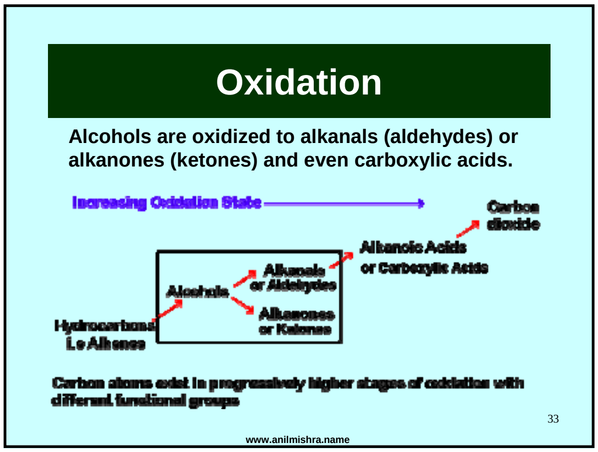
* primary alcohols → aldehydes

* secondary alcohols → ketones

* tertiary alcohols → no reaction

Alcohol with caboxylic acid for Esterification reaction

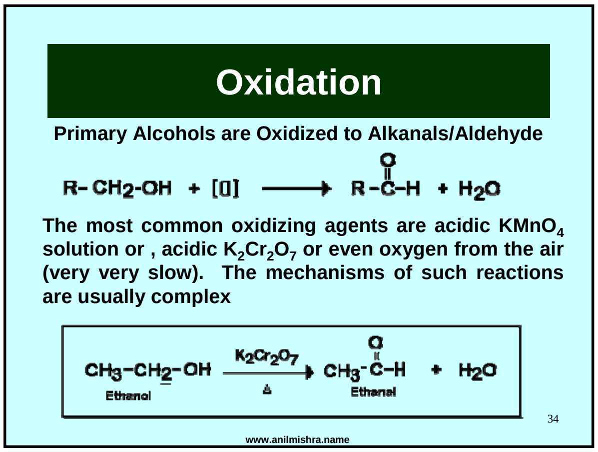
alcohol + acid → ester + H_2O



Oxidation

Alcohols are oxidized to alkanals (aldehydes) or alkanones (ketones) and even carboxylic acids.

Carbon atoms exist in progressively higher stages of oxidation with different functional groups



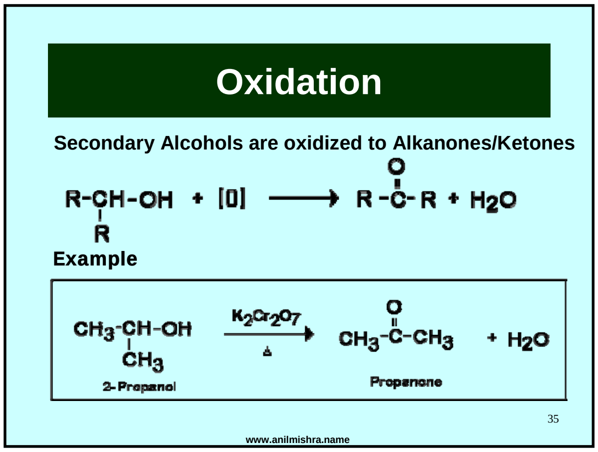
Oxidation

Primary Alcohols are Oxidized to Alkanals/Aldehyde

$$R\text{-}CH_2\text{-}OH + [O] \longrightarrow R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}H + H_2O$$

The most common oxidizing agents are acidic $KMnO_4$ solution or , acidic $K_2Cr_2O_7$ or even oxygen from the air (very very slow). The mechanisms of such reactions are usually complex

$$\underset{\text{Ethanol}}{CH_3\text{-}CH_2\text{-}OH} \xrightarrow[\Delta]{K_2Cr_2O_7} \underset{\text{Ethanal}}{CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}H} + H_2O$$



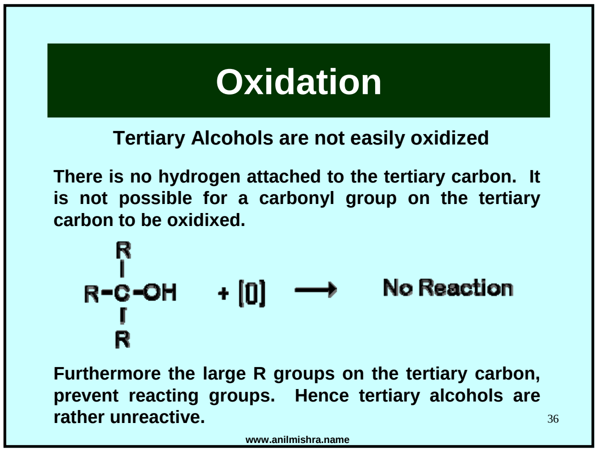
Oxidation

Secondary Alcohols are oxidized to Alkanones/Ketones

$$R\text{-}\underset{\underset{\displaystyle R}{|}}{C}H\text{-}OH + [O] \longrightarrow R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R + H_2O$$

Example

$$\underset{\text{2-Propanol}}{CH_3\text{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H\text{-}OH} \xrightarrow[\Delta]{K_2Cr_2O_7} \underset{\text{Propanone}}{CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3} + H_2O$$



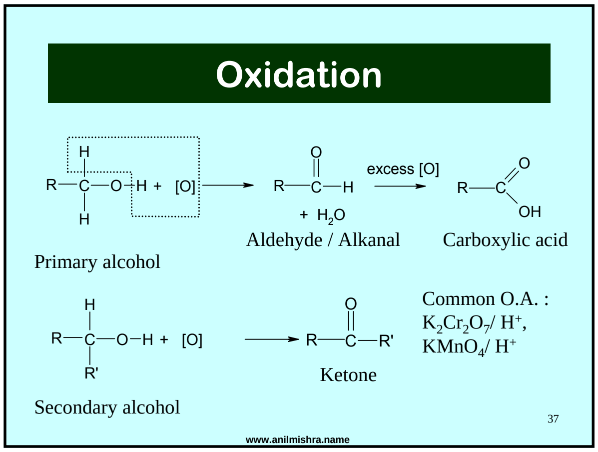
Oxidation

Tertiary Alcohols are not easily oxidized

There is no hydrogen attached to the tertiary carbon. It is not possible for a carbonyl group on the tertiary carbon to be oxidixed.

$$R\text{-}\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}\text{-}OH + [O] \longrightarrow \text{No Reaction}$$

Furthermore the large R groups on the tertiary carbon, prevent reacting groups. Hence tertiary alcohols are rather unreactive.



Oxidation

$$R{-}\overset{H}{\underset{H}{C}}{-}O{-}H + [O] \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}H + H_2O \xrightarrow{\text{excess } [O]} R{-}C(=O)OH$$

Primary alcohol

Aldehyde / Alkanal

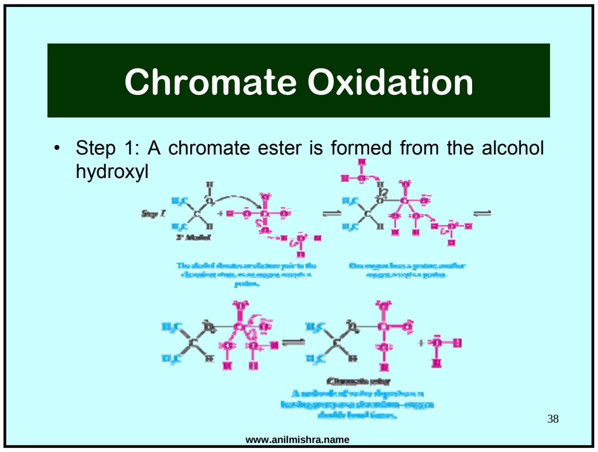
Carboxylic acid

$$R{-}\overset{H}{\underset{R'}{C}}{-}O{-}H + [O] \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}R'$$

Secondary alcohol

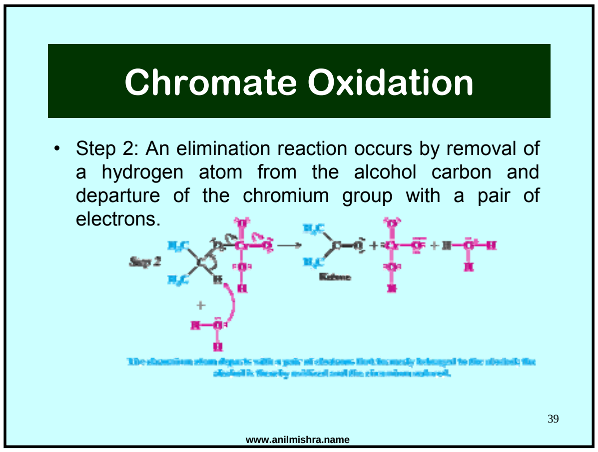
Ketone

Common O.A. : $K_2Cr_2O_7$/ H^+, $KMnO_4$/ H^+



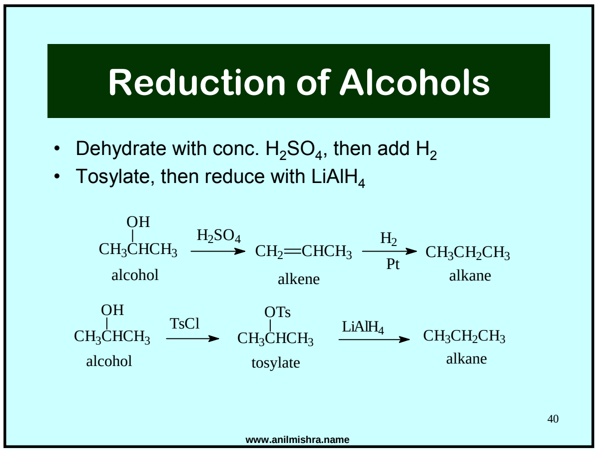
Chromate Oxidation

- Step 1: A chromate ester is formed from the alcohol hydroxyl



Chromate Oxidation

- Step 2: An elimination reaction occurs by removal of a hydrogen atom from the alcohol carbon and departure of the chromium group with a pair of electrons.



Reduction of Alcohols

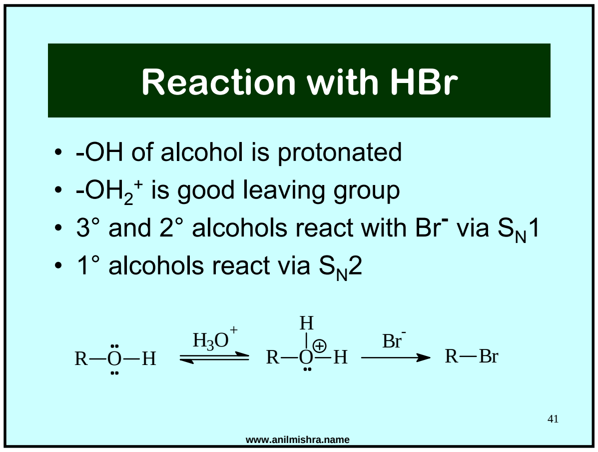
- Dehydrate with conc. H_2SO_4, then add H_2
- Tosylate, then reduce with $LiAlH_4$

$$CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow{H_2SO_4} CH_2{=}CHCH_3 \xrightarrow[Pt]{H_2} CH_3CH_2CH_3$$

alcohol — alkene — alkane

$$CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow{TsCl} CH_3\overset{OTs}{\overset{|}{C}}HCH_3 \xrightarrow{LiAlH_4} CH_3CH_2CH_3$$

alcohol — tosylate — alkane



Reaction with HBr

- -OH of alcohol is protonated
- $-OH_2^+$ is good leaving group
- 3° and 2° alcohols react with Br^- via S_N1
- 1° alcohols react via S_N2

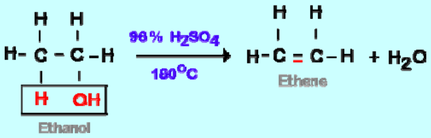
$$R{-}\ddot{\underset{\cdot\cdot}{O}}{-}H \underset{}{\overset{H_3O^+}{\rightleftharpoons}} R{-}\overset{H}{\overset{|}{\underset{\cdot\cdot}{O}}}{}^{\oplus}{-}H \xrightarrow{Br^-} R{-}Br$$

Reaction with HCl

- Chloride is a weaker nucleophile than bromide.
- Add $ZnCl_2$, which bonds strongly with -OH, to promote the reaction.
- The chloride product is insoluble.
- Lucas test: $ZnCl_2$ in conc. HCl
  - 1° alcohols react slowly or not at all.
  - 2° alcohols react in 1-5 minutes.
  - 3° alcohols react in less than 1 minute.

Dehydration

- **Many alcohols undergo intramolecular dehydration, removing water to form alkenes.**



Dehydration

Definition: removal of water from a molecule.

Extra info: H and OH are removed from two adjacent carbons.

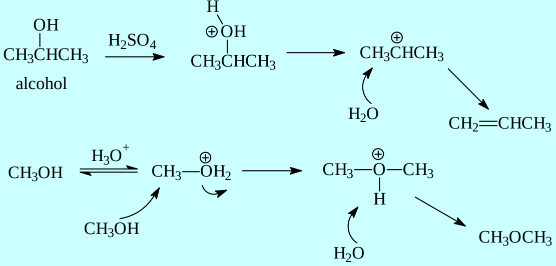
Reagent and conditions: Dehydrating agents

- Conc H_2SO_4, heat
- Conc H_3PO_4, heat
- Solid SiO_2, heat
- Solid Al_2O_3, heat
- Solid ceramic or solid pumice, heat

Dehydration Reactions

- Conc. H_2SO_4 produces alkene
- Carbocation intermediate
- Saytzeff product
- Bimolecular dehydration produces ether
- Low temp, 140°C and below, favors ether
- High temp, 180°C and above, favors alkene

Dehydration Mechanisms



Reactions with Metals

- **Alcohols are far less acidic than water but they react with highly reactive metals such as potassium and sodium.**
- **The metal replaces the hydrogen atom in the alcohol group forming a salt and hydrogen gas**

$$2\,R\text{-}OH + 2\,Na \longrightarrow 2\,R\text{-}O\text{-}Na + H_2$$

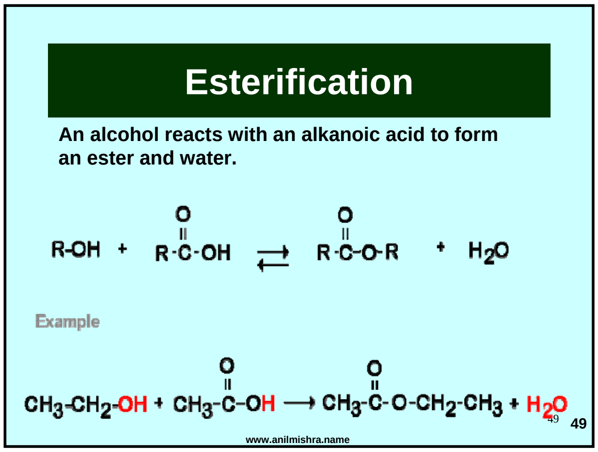
Example

$$2\ CH_3\text{-}CH_2\text{-}OH + 2\,Na \longrightarrow CH_3\text{-}CH_2\text{-}ONa + H_2(g)$$

Ethanol Sodium ethoxide

Reactions with Metals

Note that the reaction between Na, sodium solid and alcohol at room temperature releases colourless gas of H_2. This indicates the presence of OH hydroxy group in alcohols.



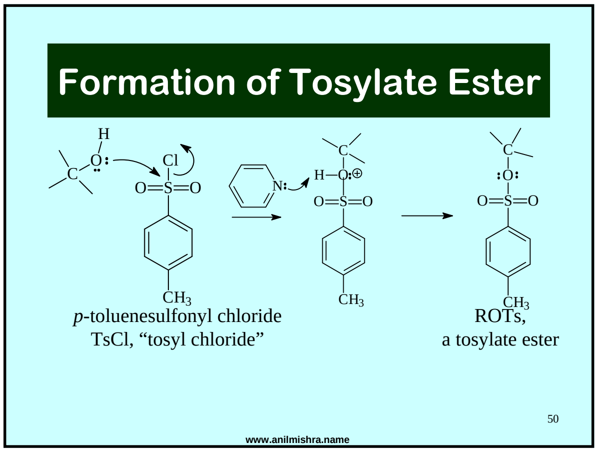
Esterification

An alcohol reacts with an alkanoic acid to form an ester and water.

$$R\text{-}OH + R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \rightleftarrows R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R + H_2O$$

Example

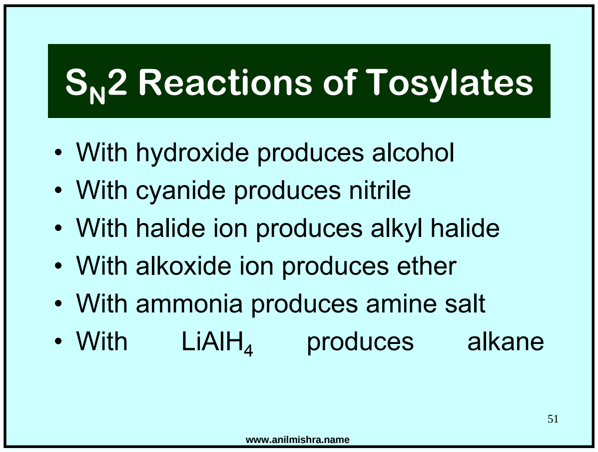
$$CH_3\text{-}CH_2\text{-}OH + CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \longrightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2\text{-}CH_3 + H_2O$$



Formation of Tosylate Ester

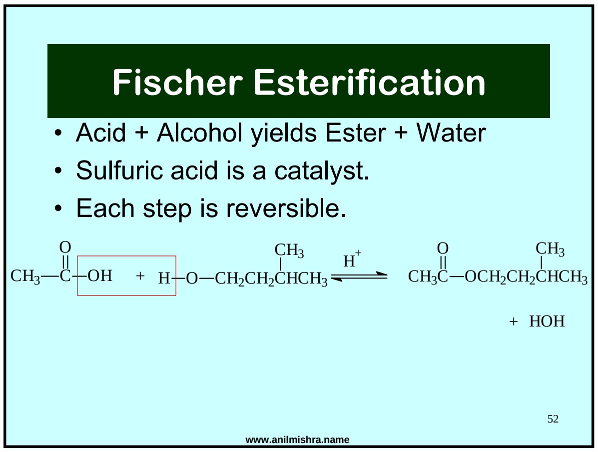
p-toluenesulfonyl chloride
TsCl, “tosyl chloride”

ROTs,
a tosylate ester



S_N2 Reactions of Tosylates

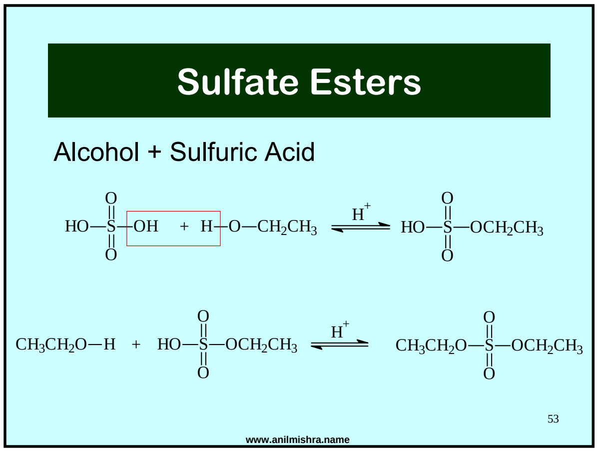
- With hydroxide produces alcohol
- With cyanide produces nitrile
- With halide ion produces alkyl halide
- With alkoxide ion produces ether
- With ammonia produces amine salt
- With $LiAlH_4$ produces alkane



Fischer Esterification

- Acid + Alcohol yields Ester + Water
- Sulfuric acid is a catalyst.
- Each step is reversible.

$$CH_3\text{—}\overset{O}{\overset{\|}{C}}\boxed{\text{—}OH \quad + \quad H\text{—}}O\text{—}CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3 \xrightleftharpoons{H^+} CH_3\overset{O}{\overset{\|}{C}}\text{—}OCH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3 + HOH$$

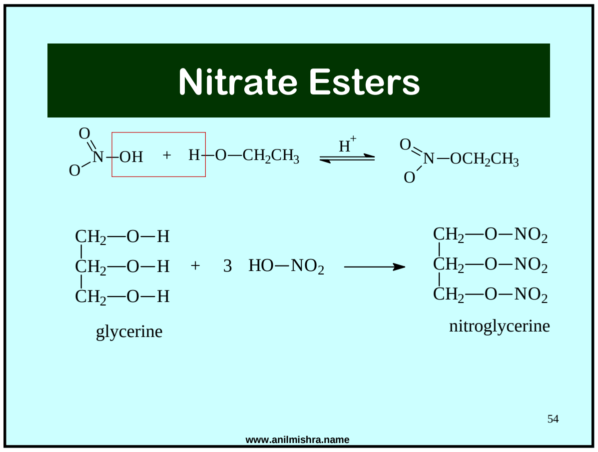


Sulfate Esters

Alcohol + Sulfuric Acid

$$HO\text{—}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\boxed{\text{—}OH \quad + \quad H\text{—}}O\text{—}CH_2CH_3 \xrightleftharpoons{H^+} HO\text{—}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{—}OCH_2CH_3$$

$$CH_3CH_2O\text{—}H + HO\text{—}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{—}OCH_2CH_3 \xrightleftharpoons{H^+} CH_3CH_2O\text{—}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{—}OCH_2CH_3$$



Nitrate Esters

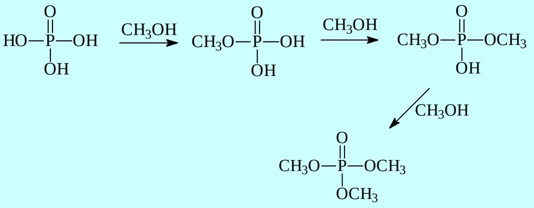
$$\overset{O}{\underset{O}{N}}\boxed{\text{—}OH \quad + \quad H\text{—}}O\text{—}CH_2CH_3 \xrightleftharpoons{H^+} \overset{O}{\underset{O}{N}}\text{—}OCH_2CH_3$$

$$\begin{array}{l} CH_2\text{—}O\text{—}H \\ | \\ CH_2\text{—}O\text{—}H \\ | \\ CH_2\text{—}O\text{—}H \end{array} + 3 \quad HO\text{—}NO_2 \longrightarrow \begin{array}{l} CH_2\text{—}O\text{—}NO_2 \\ | \\ CH_2\text{—}O\text{—}NO_2 \\ | \\ CH_2\text{—}O\text{—}NO_2 \end{array}$$

glycerine

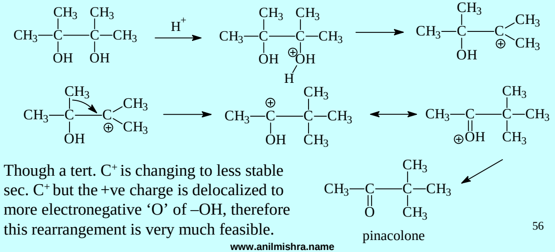
nitroglycerine

Phosphate Esters



Unique Reactions
Pinacol-Pinacolone Rearrangement

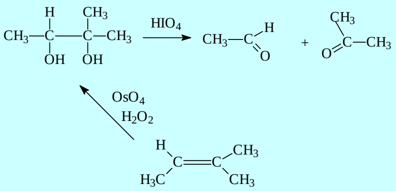
- Pinacol: 2,3-dimethyl-2,3-butanediol
- Dehydration with sulfuric acid



Though a tert. C^+ is changing to less stable sec. C^+ but the +ve charge is delocalized to more electronegative 'O' of –OH, therefore this rearrangement is very much feasible.

Periodic Cleavage of Glycols

- Same products formed as from ozonolysis of the corresponding alkene.

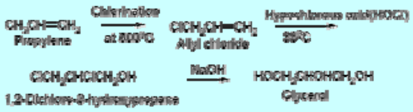


Trihydric Alcohol: Glycerol (1,2,3-Propantriol)

- Glycerol is commonly known as glycerine. It occurs in nature in oils and fats, which are mixtures of esters of glycerol (glycerides) with higher fatty acids and unsaturated acids.

Manufacture

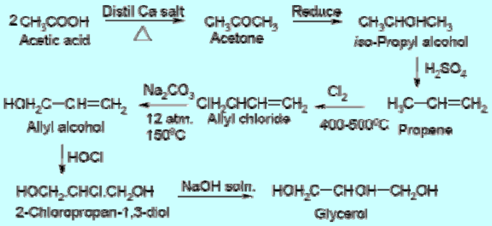
- Glycerol is obtained in large quantities as a by-product in the manufacture of soap.
- **Glycerol from petroleum by synthetic method**. Large quantities of glycerol are now synthesized from propylene obtained from petroleum.



Glycerol
Complete synthesis

- The synthesis of glycerol is of great theoretical importance, because glycerol is present in plants and animals, and also because this synthesis constitutes a step in the synthesis of simple sugars.
- Starting with carbon and hydrogen, we may obtain acetylene and then acetaldehyde and acetic acid.
- Glycerol can be synthesized through the following series of reactions from acetic acid.

Glycerol Complete synthesis

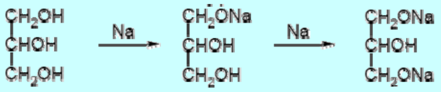


Physical properties

- Glycerol is a colourless syrupy liquid which, when pure, freezes to a crystalline solid (m.p. 17°C) and boils at 290°C. If however, impurities are present, it can be distilled only under reduced pressure without decomposition.
- It has sweet taste and is soluble in alcohol and water but is insoluble in ether.

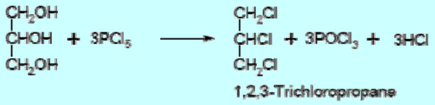
Chemical Properties

- **Action of sodium metal**.
  - Sodium metal reacts with primary alcoholic groups to form mono-sodium and di-sodium glycerollate.



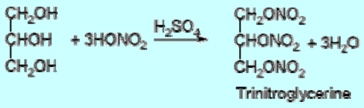
Chemical Properties

- **With PCl3**.
  - Glycerol reacts with PCl5 to give a trichloro derivative.



Chemical Properties

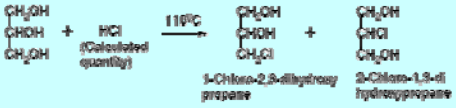
- **Action with acids.**
  - **With nitric acid**. With cold mixture of Conc. HNO3 and H2SO4, it gives trinitroglycerine.



- In fact it is glycerol trinitrate and is known as *Noble's oil*. It is a colourless, poisonous oily liquid. It is highly explosive and used in the formation of dynamite.

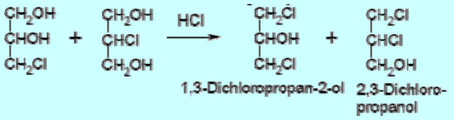
Chemical Properties

- **Action with acids.**
  - **Action of HCl gas**. When HCl gas is passed into glycerol, heated to 110°C, a mixture of two monochloro derivatives is obtained.



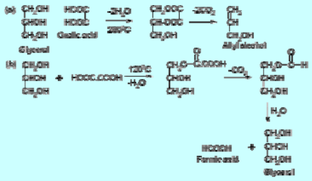
Chemical Properties

- On passing more HCl gas, keeping the same temperature, a mixture of two dichloro derivatives (1,3dichloropropan-2-ol and 2,3-dichloropropanol) is obtained, provided the quantity of HCl is 25% more than the calculated quantity.



Chemical Properties

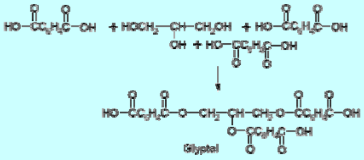
- **Action with acids.**
  - **Action of oxalic acid**. It gives allyl alcohol at 260°C and formic acid at 120°C.



  - Thus it is a continuous process to get formic acid from oxalic acid.

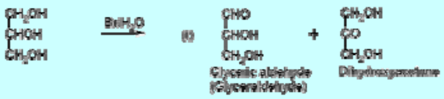
Chemical Properties

- **With phthalic acid**. Glyptals or alkyl resins are formed which are useful for the manufacture of paints and lacquers.



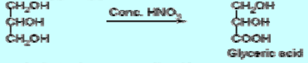
Chemical Properties

- **Oxidation**.
  - It gives different oxidation products depending on the nature of the oxidizing agent used. Thus,
    - Bromine water gives glyceric aldehyde and dihydroxyacetone.

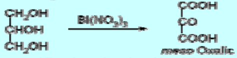


Chemical Properties

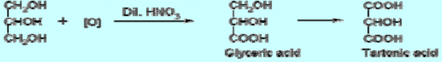
(b) Conc. HNO_3 gives glyceric acid.



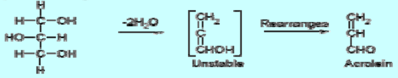
(c) Bismuth nitrate gives meso-oxalic acid.



(d) Dil. HNO_3 oxidizes it to glyceric acid and then tartronic acid.



(5) On heating with $KHSO_4$ it loses two water molecules and acrolein is formed.



Nitro Glycerine

Nitroglycerine. It is manufactured by adding glycerol gradually to a cold mixture of fuming nitric acid and concentrated sulphuric acid.

$$CH_2OH{-}CHOH{-}CH_2OH + 3HONO_2 \longrightarrow CH_2ONO_2{-}CHONO_2{-}CH_2ONO_2 + 3H_2O$$

Nitroglycerine is a poisonous colourless, oily liquid, and is insoluble in water. When ignited, it usually burns quietly. When heated rapidly, struck, or detonated, it explodes violently. The decomposition, which accompanies explosion, gives gaseous products occupying about 11,000 times the volume of nitroglycerine.

$$4C_3H_5(ONO_2)_3 \longrightarrow 12CO_2 + 10H_2O + 6N_2 + O_2$$

It is used in the manufacture of dynamite, by absorbing it in wood pulp and adding solid ammonium nitrate. Nitroglycerine is mixed with gun-cotton (cellulose nitrate) to make blasting gelatin or gelignite. A mixture of nitroglycerine, gun-cotton, and Vaseline is cordite (the smokeless powder). Another use of nitroglycerine is in the treatment of angina pectoris.