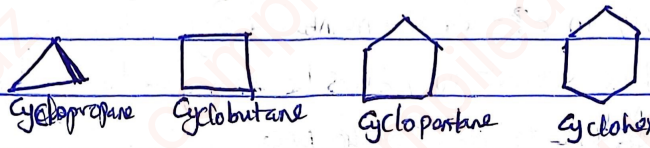
Alicyclic Compounds

The "Ali" part comes from aliphatic and the "cyclic" comes from carboxylic compounds in which the atoms of the rings are made up only carbon.

Therefore alicyclic compounds are compounds which includes saturated and unsaturated.

The behaviour of alicyclic compounds are similar to aliphatic hydrocarbon e.g properties of Δ is similar to C_3H_8

Example of alicyclic Compounds



Stereo Chemistry and Conformation in Alicyclic Compounds

(i) Cyclopropanes, cyclo butanes and Cyclopentanes: All these three classes of compounds are planar molecules; i.e their conformation and stereo chemistry is dependent on the substituent attached to the molecule.

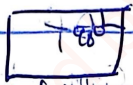
If we have a cyclobutane that is non planar the conformation will reduce the torsional strain. e.g in 1,3 dibromobutane

Euphetonial are stable

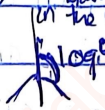
Types of Strains

(1) Bayer's Strains (Angular): For 3- or 4- membered ring, e.g cyclopropane & cyclobutane) we have bound to have strain in the molecule.

cyclopropane



cyclobutane



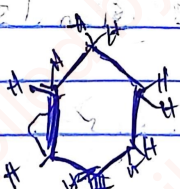
In an acyclic molecule, the tetrahedral angle of 109° about the sp^3 hybridized C is preferred to reduce C–C and C–H repulsion

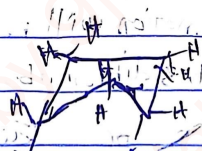
But, in a 3- or 4- membered ring, this cannot be achieved. This situation raises the energy of the system/molecule relative to an acyclic one.

This excess energy that is as a result of the constraint of the ring is called Bayer (Angular) strain.

(2) Pitzer or Torsional Strain: It occurs along rotation about carbon-carbon (C–C)

Any molecule that is forced to adopt an eclipsed conformation is said to suffer from torsional strain, because the molecule cannot rotate to avoid repulsion.





torsional strain is reduced

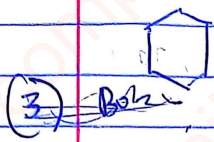
envelop conformation of cyclopentane

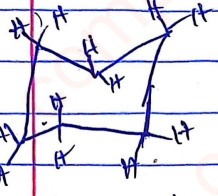
For cyclohexane (has: chair, boat & twisted boat conformation)

lowest energy (least torsional strain)

Chair < boat < twisted boat

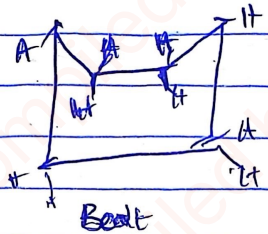
least stable with highest energy





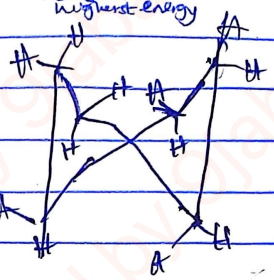
chair conformation

most stable in least energy



Boat

more stable higher Energy

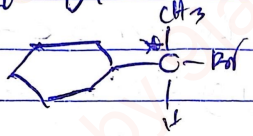


twisted boat

least stable higher Energy

Cyclic molecules can be chiral ($E-\underset{B}{\overset{A}{C}}-B$, $A \neq B \neq D \neq E$)

Identify the chiral molecle



3 chiral Centers

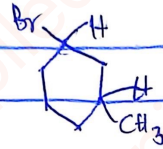
1-bromo-3-methylcyclohexane

To draw a stereoisomer;

For a cyclic system, the chiral centre must first be identified

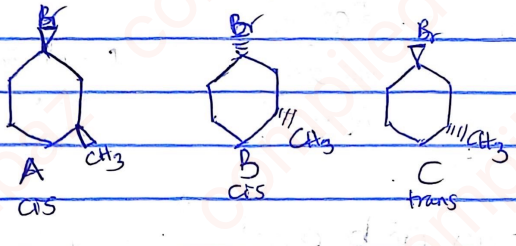
No of conformation $= 2^n$, where n is the number of chiral centers

So for,



$2^2 = 4$ stereoisomers/conformation is expected.

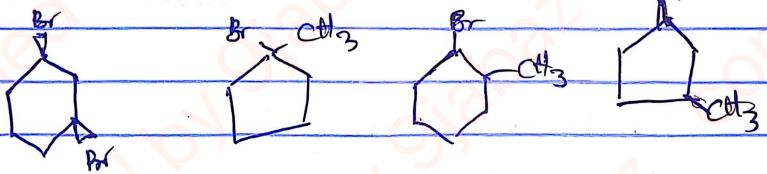
2 cis & 2 trans Conformation



Since cis bromomethylcyclohexane is a pair of enantiomer A&B while transbromo 3 methylcyclohexane is a pair of enantiomers C & D

Since A or B are each diastereomer to C or D, than cis and trans 1 bromo 3 methylcyclohexane are diastereomers of each other.

Read up R and S configuration



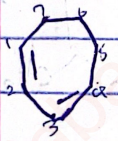
Give R & S configuration of the above

Nomenclature of Alicyclic Compound

(1) The prefix "cyclo" is used in naming alicyclic compounds when the structure contains more than one close ring, the prefix bicyclo, tricyclo, tetracyclo etc are used.

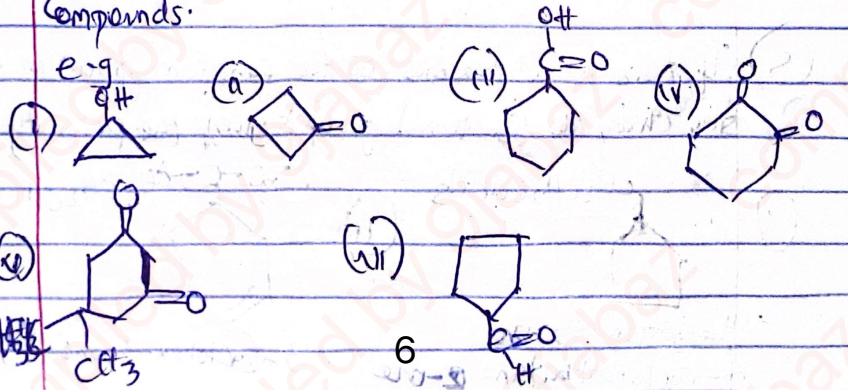
(2) The size of the ring is indicated by the use of standard IUPAC name for n-alkanes, alkenes or alkyne chains of different length
In case, of cycloalkenes containing several double bonds, the location of the bonds are located.

Example



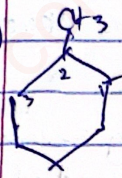
(3) Functional groups such as hydroxyl, Carbonyl, carboxylic acids are indicated as in corresponding acyclic compounds.

e.g

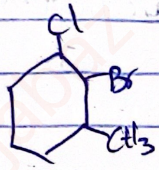


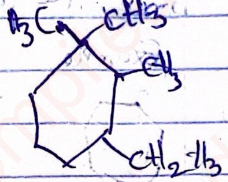
(4) If two or more substituents are present, the numbering is done from the substituent which comes first in the alphabetical order provided it satisfies the lowest sum rule

Example

(i) 

Methyl-2-methylcyclohexane

(ii) 

(iii) 

(iv) 

(5) If there is a presence of the functional group in a side chain, the functional group is given the priority

(i) 

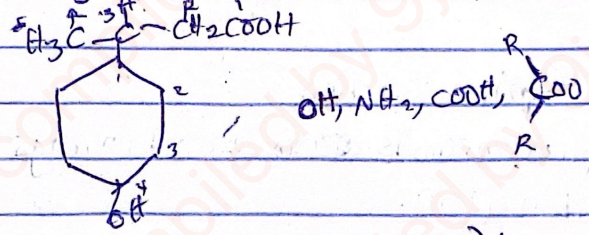
~~4-cyclopentan-2-one~~
4-cyclopentanbutan-2-one ?

(ii) 

3-(cyclohex-3-one-1-yl) butanol

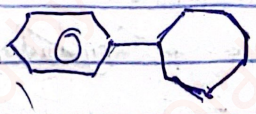
4

(6) If the alicyclic ring as well as the side chain contains the functional group - The compound is named as a derivative of the one which contains the principal functional group



3-(4-hydroxycyclohexanol-yl) butanoic acid

(7) If a compound contains an alicyclic ring and a benzene ring, then the compound is named as a derivative of alicyclic ring. If it contains more atom than the benzene, Hence the compound is named as derivative of benzene



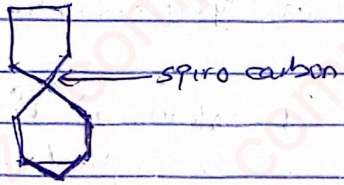
phenylcycloheptane

(8) If two alicyclic rings are attached, then the compound is made as a derivative of the one that contains greater number of carbons.

cyclopropylcyclobutane

Spiro Carbon

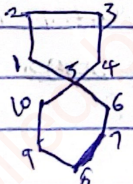
Spirocompounds occurs when two rings shares one carbon atom.



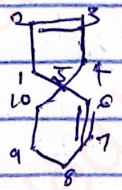
(1) The prefix 'Spiro' is used for the compounds in which one carbon is present between the two rings

(2) The number of carbon atom looked to the spiro atom in each ring is indicated in decending order.

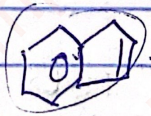
(3) The smaller ring is numbered first, then through the spir, then around the second ring.



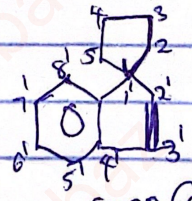
(4) When unsaturation is present the same enumeration pattern is used, but in such a direction around the rings that gives the double bond / triple bond the lowest number possible. (numbering pattern)



(5) If one or both of the spiro compound are fused polycyclic system, spiro is placed before the name of the component arranged in alphabetical order. The lowest number possible is given to the spiro atom and the number of the second component are marked with prime

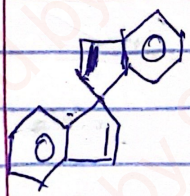


— indene



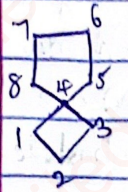
Spiro (Cyclo pentane)

1, 1' - indene



1, 1' - spirobiindene

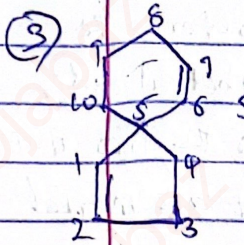
Examples

(1) 

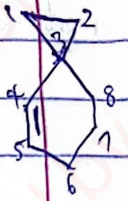
Spiro (4,3) octane

(2) 

Spiro (5,4) decane

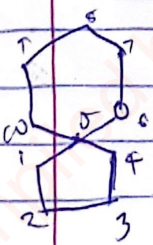
(3) 

Spiro [5,4]
deca-1-6-diene

(4) 

Spiro [5,2]
octan-4-ene

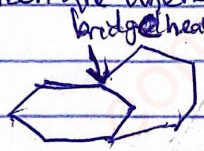
Questions

(1) 

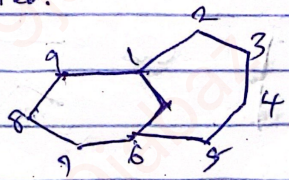
6-oxaspiro
(5,4) decane

Bicyclo compounds

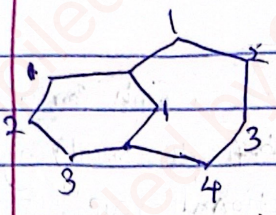
(1) The prefix "bicyclo" is used for such compound
(2) Number the larger ring first before the small ring
(3) Find the highest priority functional group, this will be the suffix, then count the total number of carbon in the molecule which gives the root name
(4) Identify the two rings of the bicyclic molecule (they should share a perimeter). The bridge head carbon are where these ring met



(5) The numbering beg ins at bridge head and follows the longest path to the second bridge head. Continue numbering along the longest until all carbons are numbered.



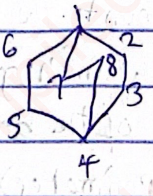
(6) Find all unique pathway between the bridge head carbons and count the number of carbons along the bridge pathway, then arrange in descending order.



4 - Carbon
3 - Carbon
1 - Carbon

Bicyclo[4,3,1]decane

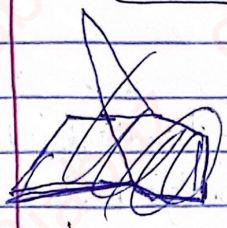
bicyclo(2,2,1)heptane



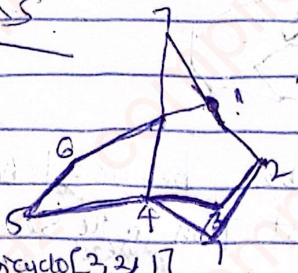
2 - Carbons
2 - Carbon
2 - Carbon

bicyclo(2,2,2)octane

Questions

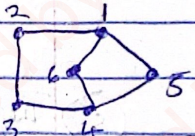


(1)



bicyclo[3,2,1] heptane

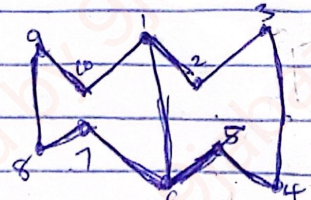
(3)



~~bicyclo[2,2,1]~~

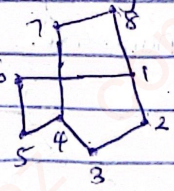
bicyclo[2,1,1]hexane

(2)



Bycle [4,4] decane

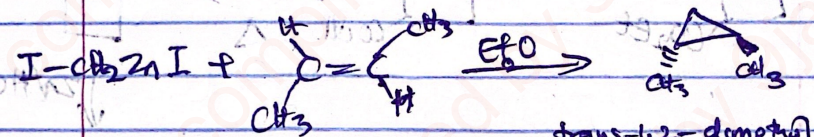
(4)



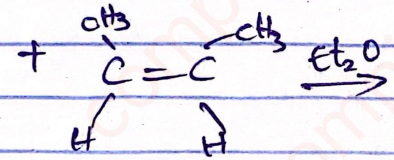
bicyclo[2,2,2]octane

Synthesis of Cyclopropane

Cyclopropanes are prepared by Simmons-Smith reaction, then dimerization reaction



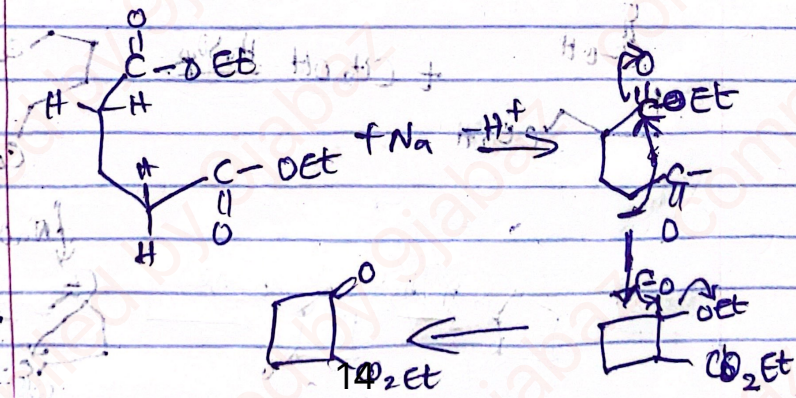
trans-1,2-dimethyl cyclopropane



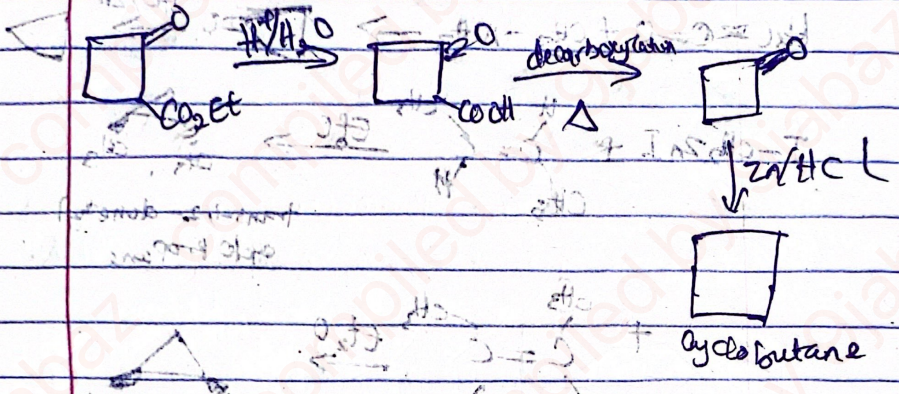
cis-1,2-dimethyl cyclopropane

Cyclobutanes

Cyclobutanes are prepared by Dieckmann Condensation reaction (intramolecular claisen condensation): Ide must have active methylene protons (acidic protons)

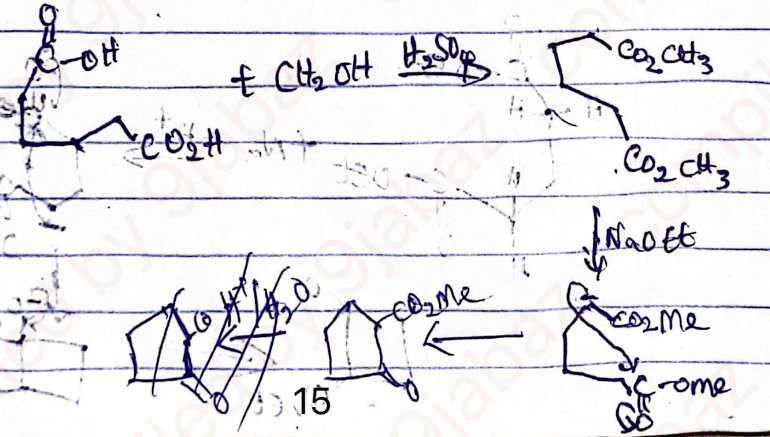


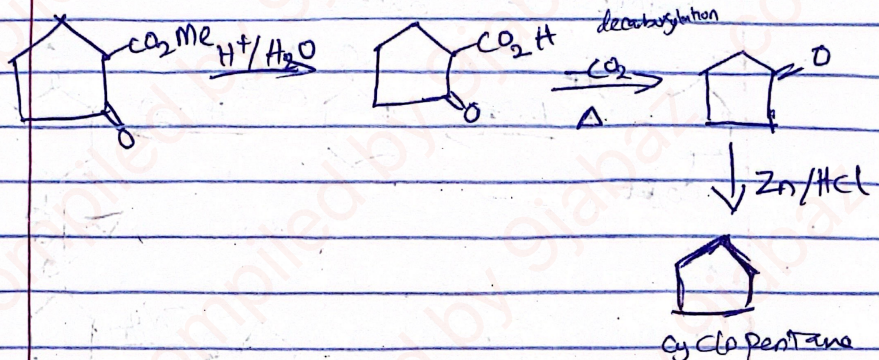
In the presence of a base such as Na or NaOEt, the protons can be extracted to form a carbanion



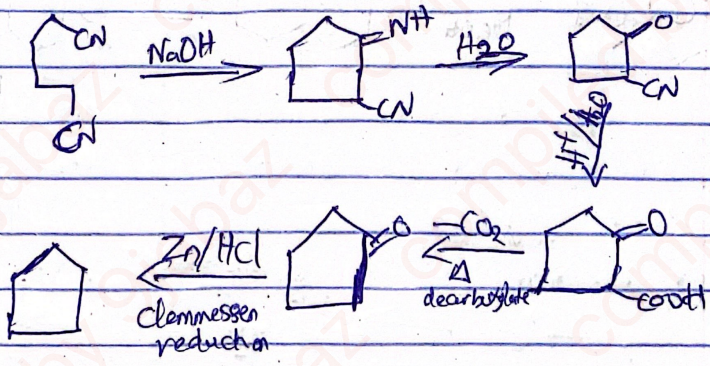
Cyclopentanes

Cyclopentanes are prepared by the same method, Dieckmann condensation (intramolecular claisen Condensation), but we are starting with a six membered carbon

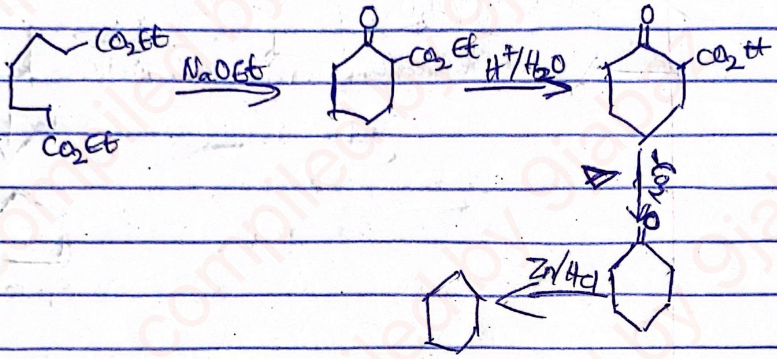




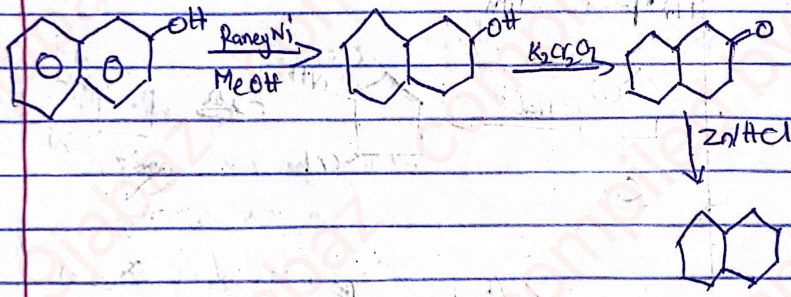
Another way to make cyclopentanes is through ~~Thorpe~~ reaction



Synthesis of Cycloheranes



Other Synthesis



Means we have two functional groups in the compound.

BIFUNCTIONAL COMPOUNDS

DIOLS

Diols are compounds containing two –OH group in the molecule. The common name is dihydric alcohols

Nomenclature:

The common names are assigned to individual diols after the name of the corresponding alkanes or the ~~dimeth~~ polymethylene from which they could be obtained directly by hydroxylation

	Formular	Common name	IUPAC
1.	$HO-CH_2-CH_2-OH$	Ethylene glycol	1,2-ethanediol / ethane-1,2-diol
2.	$HO-CH_2-CH_2-CH_2-OH$	Trimethylene glycol	1-3-propanediol
3.	$HO-CH_2-\underset{OH}{CH}-CH_3$	Propylene glycol	1,2-propanediol

Diols are designed as α, β, or γ according to relative positions of the two –OH groups

1,2-diols are α-glycol

1,3-diols — β-glycol

1,4-diols — γ-glycol

Properties

(1) The lower diols are colourless, viscous liquids which are soluble in water.

(2) Diols have higher boiling points than the corresponding monohydric alcohol of similar molecular weights.

E.g $OHCH_2CH_2OH$ $CH_3CH_2CH_2OH$

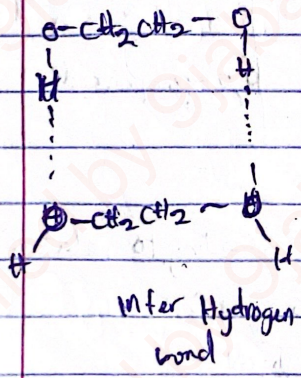
$C_2H_6O_2$ $C_3H_7O_7$

62 g/mol 60 g/mol why?

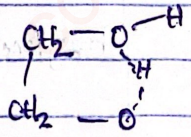
BP: 197°C 97°C

The difference in boiling point is due to extensive hydrogen bonding in the molecules as a result of the two -OH groups.

Hydrogen bond is the interaction between hydrogen and a small highly electronegative atom (F, O, N)



Inter Hydrogen bond



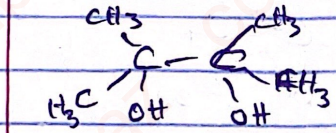
Intramolecular hydrogen bonding

1,2-diol	Propanol
high boiling point	Low boiling point
high viscosity	low viscosity

(3) The solubility of the diol is larger than the corresponding alcohol

Pinacol – Pinacolone Rearrangement

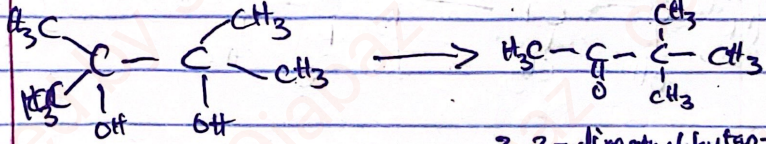
Completely substituted 1,2-diols, such as,



2,3-dimethyl butan-1,2-diol

are known as pinacols

They undergo dehydration and rearrangement in acid to form ketones



2,3-dimethyl butan-1,2-diol

Pinacol

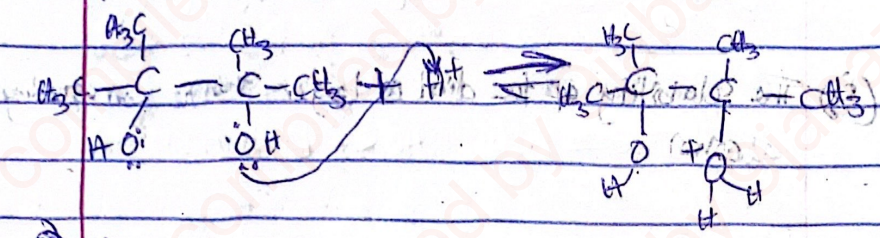
3,3-dimethyl butan-2-one

Pinacolone

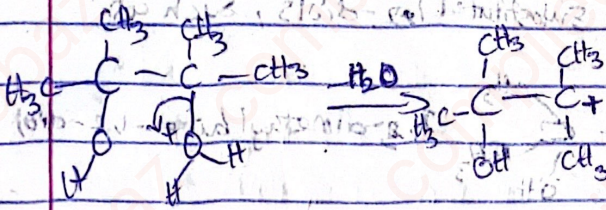
05-05-2025

The mechanism of the reaction involves four major steps.

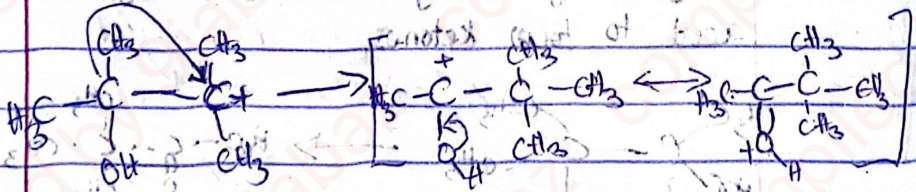
(i) protonation



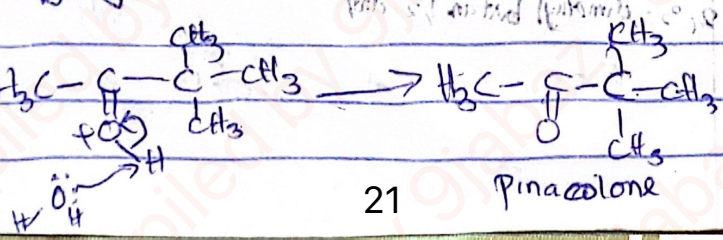
(ii) Loss of water



(iii) 1,2-alkyl shifts

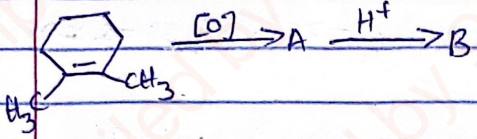


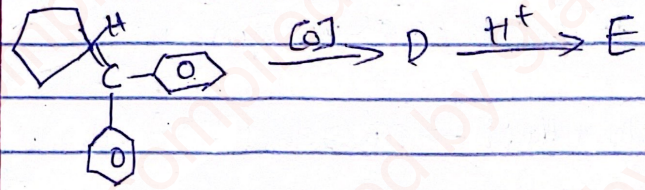
(iv) Deprotonation



Pinacolone

Assignment

(i) 

(ii) 

Write the possible structure for lettered A-E

Ethylene glycol

Ethylene glycol is the simplest of dihydrate alcohol and is referred to as glycols CH_2OHCH_2OH

Preparation

(i) By hydroxylation of ethene: ethyleneglycol can be prepared by adding ethene into cold dilute $KMnO_4$ in the presence of Na_2CO_3

$$CH_2CH_2 + H_2O + [O] \xrightarrow[Na_2CO_3]{KMnO_4} OHCH_2CH_2OH$$

(2) ~~By~~

(2) By hydrolysis of 1-2, dibromoethane with aqueous Na_2CO_3

$CH_2BrCH_2Br + Na_2CO_3(aq) \rightarrow OHCH_2CH_2OH + 2NaBr + CO_2$

(3) From hydrolysis of ethylene chloro hydrin: ~~Ethylene~~ chloro hydrin is prepared from the reaction of ethene with HOCl

$CH_2CH_2 + HOCl \rightarrow OHCH_2CH_2Cl \xrightarrow{NaHCO_3} CH_2OHCH_2OH + NaCl + CO_2$

ethylene chloro hydrin

Physical properties

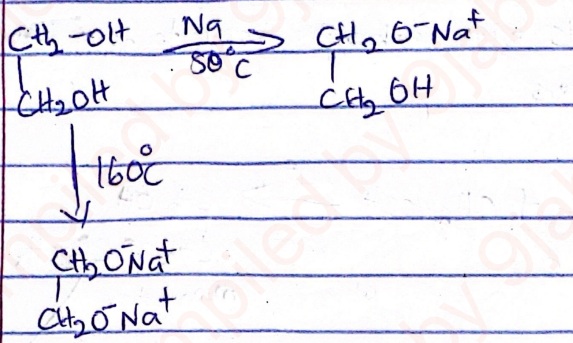
(1) Ethylene glycol is a colourless viscous liquid liquid with bp 147°C and mp 11.5°C, specific gravity of 1.11g/cm³

(2) It has a sweet taste and it is miscible with water and ethanol in all proportion, but insoluble in other

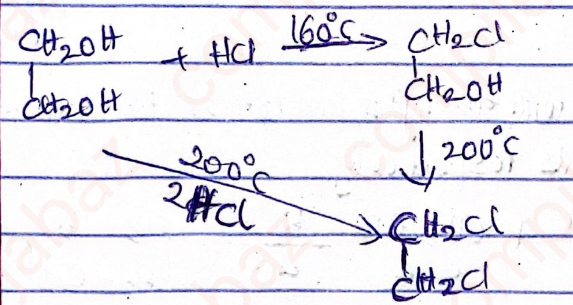
(3) It is toxic, just like methanol when taken orally

Reactions

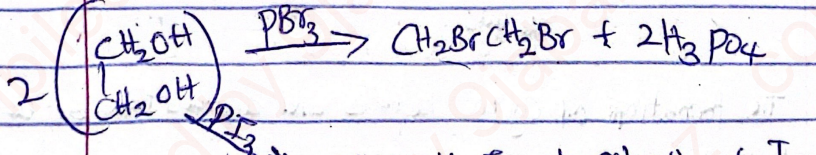
(1) ~~Ethylene~~ glycol reacts with sodium at 50°C to form the mono alkoxide, and dialkoxide, when the temperature is raised to 160°C, ~~it forms dialkoxide~~



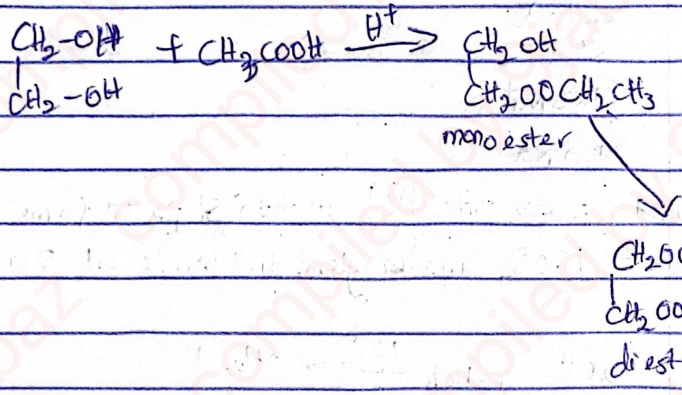
(2) It reacts with HCl in two steps to form chlorohydrin at 160°C and ethylene dichloride at 200°C



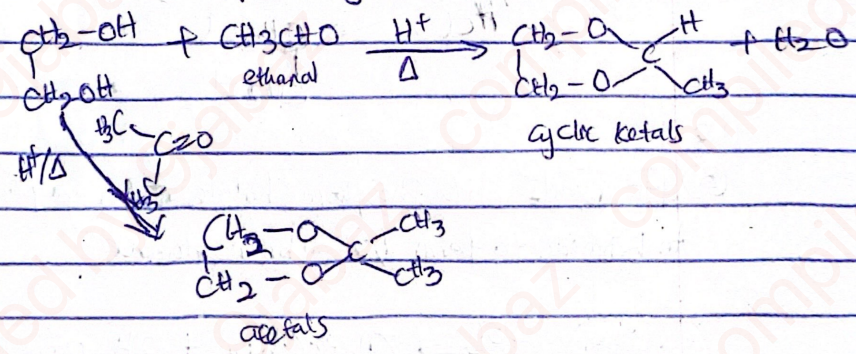
(3) It reacts with Phosphoras halide, such as Phosphorus tribromide to form 1,2-dibromoethane



(4) It reacts with carboxylic acid (→ e.g. ethanoic acid) to form mono esters and diesters



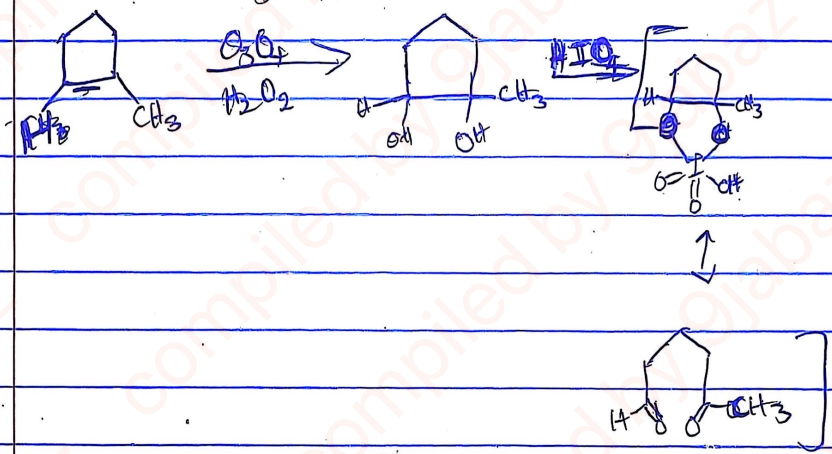
5. It reacts with aldehydes and ketones to form ~~ethers~~ ketals and acetals respectively



The formation of cyclic ketals and acetals can be used to protect carbonyl group when the reaction is carried out in alkaline

The carbonyl can be regenerated by action of periodic acid.

(6) Periodic Cleavage of diols



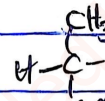
9th May, 2025

Lactic Acid

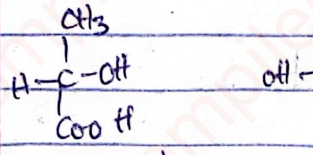
α-hydroxyl propranic acid ($CH_3CH(OH)COOH$)

Lactic acid is the main constituent of sour milk. It is found in the blood and muscle tissue where it is found by decomposition of glycogen. ($C_6H_{10}O_5$).

This reaction produce the energy needed for muscular work. The lactic acid molecule is assymetric;



Therefore, exhibit optical isomerism. It is prepared as a racemic mixture of: D-lactose acid and L-lactic acid



L-lactic acid — D-lactic acid

2(R)-hydroxyl propanic acid — 2(S)-hydroxyl propanic acid.

Preparation of lactic Acid ⟹ or propanoic acid

(1) By bromination of propionic acid followed by hydrolysis when heated with dilute NaOH solution

$$CH_3CH_2COOH + Br_2 \xrightarrow[\Delta]{NaOH} CH_3CH(OH)COOH$$

(2) In the industry, it is prepared by hydrolysis of acetalaldehyde cyanohydrin which is obtained from a reaction of acetalaldehyde.

$$CH_3CHO + KCN + HCl \longrightarrow CH_3-\underset{OH}{\overset{|}{C}}-CN \xrightarrow[\text{Complete hydrolysis}]{HCl} CH_3CH(OH)COOH$$

3- By oxidation of propyleneglycol with dilute HNO_3 (nitric acid) - a mild oxidizing agent

$CH_3CH(OH)CH_2OH \xrightarrow{HNO_3} CH_3CH(OH)COOH$

4- By fermentation of sucrose. Sucrose can be hydrolysed to glucose and fructose

$C_{12}H_{12}O_{11} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$

$C_6H_{12}O_6 \xrightarrow[\text{acidification}]{\text{Bacillus}} CH_3CH(OH)COOH$

(BAC)

Properties

① It is colourless, crystalline solid.

The two enantiomeric form form (D & L) melt at at 53°C while the racemate melts at 16°C at ordinary temperature and pressure

The commercially available lactic acid is a syrupic liquid having a sour taste. It is hygroscopic and miscible with water, ethanol and ether

Optically pure lactic acid has a specific rotation of +3.82 of D- lactic acid and

-3.82 for L-lactic acid

Reactions

(1) Reaction with NaOH: It reacts with excess NaOH to form a salt.

$CH_3CH(OH)COOH \xrightleftharpoons{NaOH} CH_3CH(OH)COO^-Na^+$

(2) It reacts with alcohol to form esters

$CH_3CH(OH)COOH \xrightarrow[\text{(ii) dry } HCl_{(g)}]{\text{(i) } CH_3OH} CH_3CH(OH)C(=O)OCH_3$

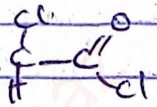
Methyl lactate

(3) Reaction with H_2SO_4

$CH_3CH(OH)COOH + H_2SO_4 \xrightarrow{130^\circ C} CH_3CHO + CH_2O_2$

ethanal formic acid

(4) Reaction with PCl_5 dp

$CH_3CH(OH)COOH \xrightarrow{PCl_5}$ 

(5) With Ag_2O (oxidation reaction)

$CH_3CH(OH)COOH \xrightarrow[[O]]{Ag_2O} CH_3-C(=O)-COOH$

pyruvic acid

(6) It is reduced by HI

$$CH_3CH(OH)COOH \xrightarrow[126^\circ C]{HI} CH_3\underset{I}{CH}COOH \xrightarrow[126^\circ C]{HI} CH_3CH_2COOH$$

(7) Iodoform reaction

$$CH_3-\underset{H}{\overset{OH}{C}}-COOH \xrightarrow{I_2} CH_3\overset{O}{C}-COOH \xrightarrow[OH^-]{3I} 2CI_3COOH$$

$$CHI_3 + [COO^-Na^+]_2 \xleftarrow{2NaOH}$$

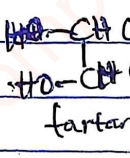
Uses

(1) As mordant for drying woods.
(2) As acidulant in candles
(3) As calcium and iron lactate in medicine to make up for calcium ion (Ca^{2+}) and iron deficiency in the body
(4) As ethyl and butyl lactate which are used in plastic industry

Tartaric Acid

α, α' - dihydroxyl succinic Acid a

Iupac: 2, 3-dihydroxyl butan-1, 4-dioic acid



tartaric acid

D-tartaric acid is the most widely distributed plant acid. It occurs in grapes, tamarind and in other fruits, either free or as a potassium acid tatarate (ester)

During the later stage of fermentation of grape juice to wine, the potassium acid tartarate is thrown out as a reddish brown crust called algol

Isolation of Tartaric Acid from Algol

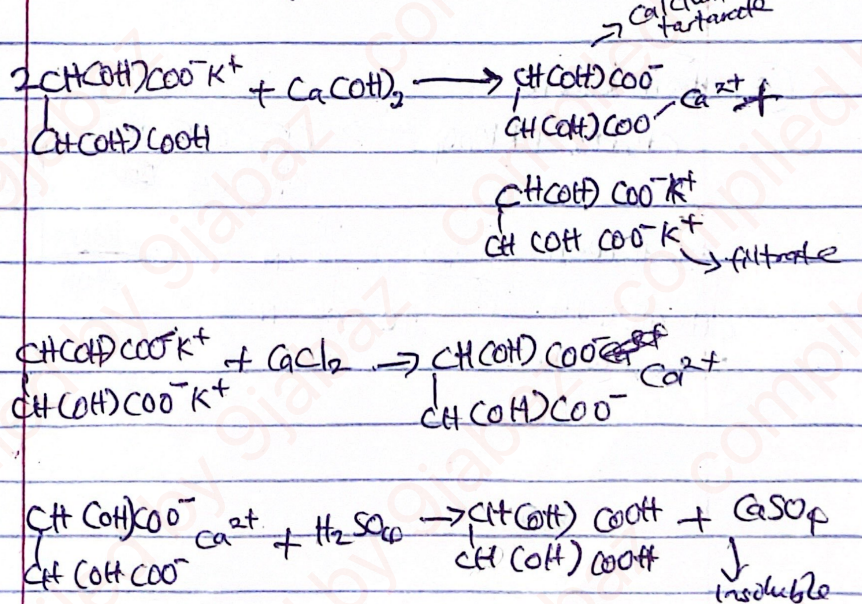
Tartaric acid was first isolated from algol. Algol is first recrystallize to give a purer form which is called cream of tartar.

The cream of tartar is dissolved in boiling water and the solution is nearly neutralized with milk of brine ($Ca(OH)_2$). The potassium acid tartarate react with lime to give normal potassium tartarate

and an insoluble calcium tartarate. The precipitated calcium tartarate is filtered off and $CaCl_2$ is added to the filtrate to obtain a fresh crop of calcium tartarate.

The calcium tartarate from the two lot is combined and decomposed to calculated quantities of dil. H_2SO_4

The precipitated calcium sulphate is removed by filtration. The tartaric acid is obtained as a white crystalline solid.



Laboratory Preparation

(1) From ethyne: It can be prepared from the reaction of carbon and hydrogen

$$2C + H_2 \rightarrow CH \equiv CH \xrightarrow[H_2]{Pd/BaSO_4} CH_2 = CH_2$$

$$CH_2 = CH_2 \xrightarrow[CCl_4]{Br_2} CH_2Br \cdot CH_2Br \xrightarrow[C_2H_5OH]{KCN} CH_2CN \cdot CH_2CN \xrightarrow[H_2SO_4/H_2O]{hydrolysis} CH_2COOH \cdot CH_2COOH$$

$$CH_2COOH \cdot CH_2COOH \xrightarrow[H_2O_2]{Br_2} CHBrCOOH \cdot CHBrCOOH \xrightarrow{AgOH} CH(OH)COOH \cdot CH(OH)COOH$$

(Energy)

1,2-dibromo succinic acid

dextaric acid

(2) From ethene

$$CH_2CH_2 + KMnO_4 \rightarrow CH_2(OH) \cdot CH_2(OH) \xrightarrow{HNO_3} CHO \cdot CHO$$

glyoxal

$$CHO \cdot CHO \xrightarrow[EtOH]{KCN} H-C(OH)-CN \cdot HO-CH-CN \xrightarrow[H^+/H_2O]{hydrolysis} CH(OH)COOH \cdot CH(OH)COOH$$

tartaric acid.