

# ORGANIC CHEMISTRY

The name organic chemistry came from the word organism. In 1828 all organic compounds can be obtained from organisms or their remains. Jöns Jacob Berzelius in 1807 first coined the term organic chemistry for the study of compounds derived from biological sources. Although in the earlier 19th century naturalists & scientists observe critical differences between compounds that were derived from living things and those that were not.

The scientific philosophy back then, was that synthesis of organic compounds could only be produce within living matters. While inorganic compounds were synthesized from non-living things. A theory known as vitalism stated that a vital force from living organisms was necessary to make an organic compound. But in 1828, a German chemist Friedrich Wöhler amazed the science community by using an inorganic compound (ammonium cyanate  $\text{NH}_4\text{OCN}$ ) to synthesize urea ( $\text{H}_2\text{NCONH}_2$ ), an organic substance found in the urine of many animals. This led to the disappearance of vitalism theory. Wöhler mixed silver or lead cyanate with ammonium nitrate. This was supposed to use ammonium as a result of exchange in reaction according to his dualism theory. Wöhler however discovered that the end-product of this reaction is ammonium cyanate ( $\text{NH}_4\text{OCN}$ ) an inorganic salt.



chains of carbon atoms can be thousands of carbon atom long as in ~~polyethylene~~ polyethylene.  
 \* Another factor that makes carbon be unique is ISOMERISM.

Isomers are classified as structural isomers who have the same no. of atom, element and the same atomic weight but differ in the arrangement of <sup>atoms</sup> carbon in the molecule.

$C_2H_6O$  has 2 compounds  $C_2H_5OH$   $CH_3CH_2OH$ .

one is the ~~colorless~~ colorless liquid alcohol. The other is di-methyl ether, <sup>boil at  $13.6^\circ C$</sup>  which is  $CH_3OCH_3$  - a colorless gaseous ether.

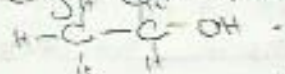
### COMPARISON OF PROPERTIES OF ORGANIC & INORGANIC COMPOUNDS.

PROPERTIES OF ORGANIC	ORGANIC	INORGANIC
Bonding between molecules	usually co-valent	mainly ionic.
Forces between molecules	generally weak	very strong.
Physical state	can be gas, liquid or <sup>low melting</sup> solid	high melting solids
Flammability	often flammable	not flammable
Solubility in $H_2O$	often low	often high.
conductivity of aqueous solns	non-conductors	conductors.
rate of chemical rxn	usually slow	usually fast.

matter behave in 2 way like particles or wave.  
(small size like particles) (large size like waves)

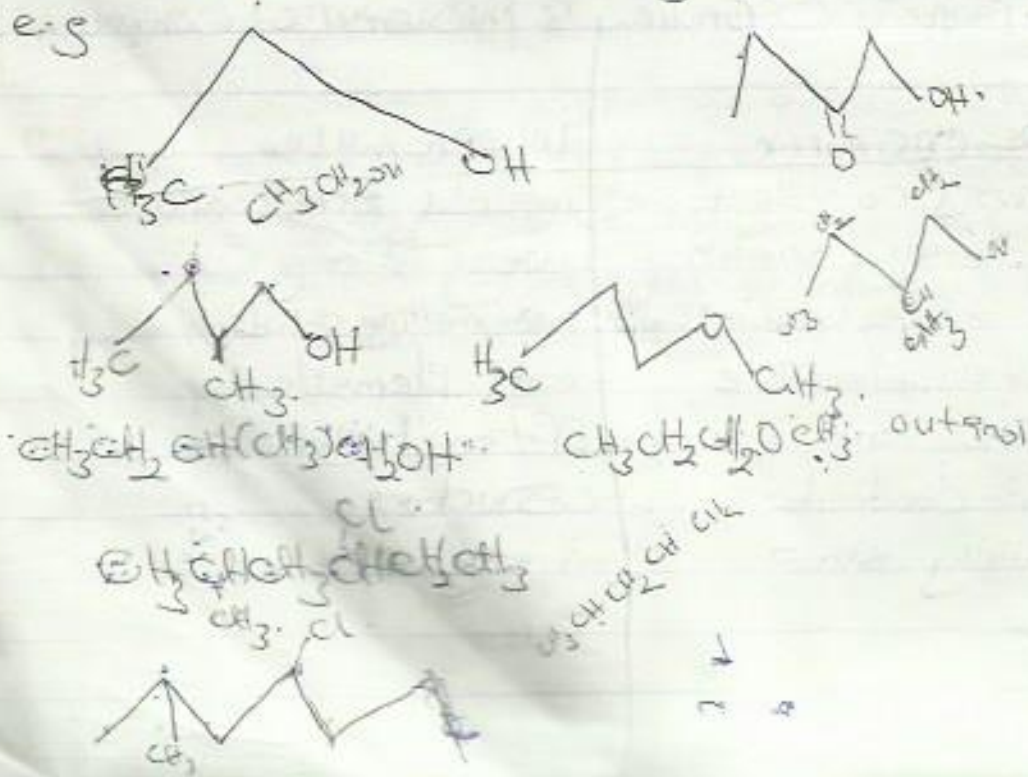
## STRUCTURES OF ORGANIC SUBSTANCE

An expanded structural formula shows all reactos present in a molecule and  $\pm$  bonds that connect them together - e.g. ethanol  $C_2H_5OH$



A condensed structural formula shows  $\pm$  arrangement of atom showing each carbon atom and it attached hydrogen atom as a group.  $CH_3-CH_2-OH$

A stick formula is a short-hand method and showing large & complex molecule easily. In this formula,  $\pm$  non-terminal carbon atom are displayed as joint and  $\pm$  non-terminal hydrogen are deleted.



All covalent compounds are not soluble in H<sub>2</sub>O  
Alkyl

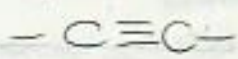
Alkene

Alkyl (R) (double bond)



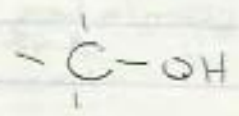
Alkyne

triple bond btw 2 carbon atoms

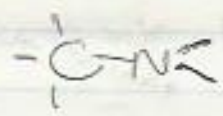


Alcohol

alcohol



Amine

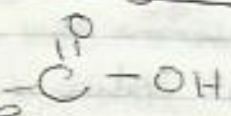


Ether

Oxygen is btw two carbon atoms



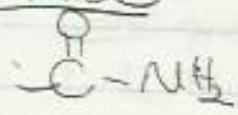
Carboxyl acid



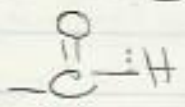
ester



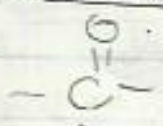
amide



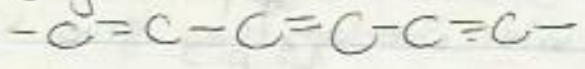
Aldehyde



Ketone



Conjugated double bond



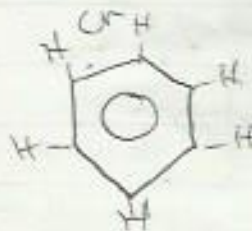
3 conjugated double bonds + additional rxn.

12-7A

aromatic compound  
Cyclic conjugated double bond.



not undergo additional rxn via substitution  
 double bond not as stable possible if can be changed  
 along 3 unshared double bond at 90 deg



r

rule 4 aromatic compound = Antar.

to Huckel's rule.

ring of 4n+2 pi electrons form a ring

Carbon can readily carbamate it because they possess

hybrid orbital.

hybrid orbital - region in space where probability of finding electron is high (s orbital, p, d, f)

hybrid orbital - orbital raised on a same energy level merge  
 2 orbitals come from high energy orbital 2 become

ground state - is an excited state but may stay element that mix

hybrid orbital - are more energetic than ordinary orbital

& can easily overcome the repulsive force.

3 types of sp<sup>3</sup> sp<sup>2</sup> sp

hybrid orbitals in organic chem

sp when

horizontal

angle btw 2 hybrid orbitals - 180° & it's linear

then 3 s orbital overlap they give sigma bond horizontal

2s " " overlap hybrid orbitals give 2 horizontal

when 2 hybrid orbitals overlap they give 2 sigma bond

hetero Allelopathy (killing of plants)  
 common to both in outside  
 $\downarrow$   $\downarrow$  molecular mass  $\downarrow$   $\downarrow$  solubility

$\pi$  bond - when 2 p orbitals overlap vertically they give  $\pi$  bond  
 when

- 1  $sp^3$   $109^\circ$  tetrahedral common in alkanes
- 2  $sp^2$   $120^\circ$  trigonal planar alkenes
- 3  $sp$   $180^\circ$  linear alkynes

degree of overlap -

$\downarrow$  higher  $\downarrow$  strength  $\downarrow$  stronger  $\downarrow$  bond.  
 bond strength -  $\downarrow$  more  $\downarrow$  bond b/w 2 carbon atoms  $\downarrow$  stronger  
 it b/w  $C \equiv C$  stronger than  $C=C$  than  $C-C$ .

length - triple bond is shorter than double. single is  $\downarrow$  longest.

2  $\pi$  single bond all 2  $\pi$  must envelope all.

strength comes from contraction  $\&$  contraction  $\downarrow$  short  $\downarrow$  length.

$sp^2$  is more electronegative than  $sp^3$ .  
 $sp^2$  " " " "  $sp$ .

$sp^2$  is more electronegative single is most reactive

double bond is more reactive than single bond.

$\downarrow$  more hybrid,  $\pi$  orbital  $\downarrow$  more difficult to release electron.

bond strength  
 bond length  
 electronegativity



Homologous Series

Alkene  $C_nH_{2n}$   $sp^2$  functional group Single bond



hybrid orbital is more energetic than d parent orbital.

Alkene - double bond  
 isolated <sup>when 2 double bonds are separated by more than one single bond.</sup>  
 conjugated <sup>when 2 double bonds are separated by 1 single bond.</sup>  
 cumulated <sup>when 2 double bonds are not separated by any single bond.</sup>

Alkyne - <sup>sp<sup>3</sup>-sp<sup>2</sup></sup> carbonyl 2 alcohols

Alkane C - C

Alkene C = C

Alkyne C ≡ C

Alcohol - OH

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

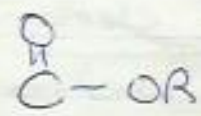
Alcaneone -  $\begin{array}{c} \text{O} \\ || \\ \text{---C---} \\ | \\ \text{O} \end{array} \text{---R}$

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

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

Alcaneamide - C-NH<sub>2</sub>

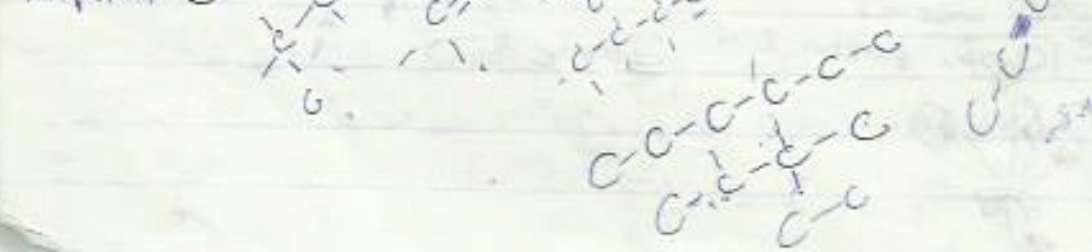
Carbonyl compounds



Aromatic / Alicyclic

All these type can exist as cyclic or

acyclic form.





↓ type of hybrid orbital

determine ↓

↓ shorter ↓ ring ↓ less stable ↓ Compound is.  
" longer " " " more " " " " " "

### Homologous series

passes ↓ same preparatory process.

Boiling increases with molecular formula.

density ↓ solubility decreases

functional <sup>group?</sup> substituent that is common to a set of compounds.  
↑ stability ↓ density & vice versa.

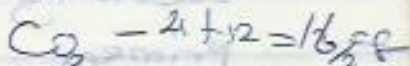
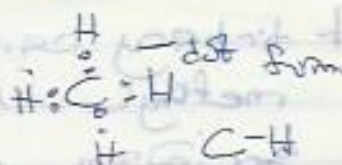
Alkane - carbon single bond. C-C

ways of writing  
hydrocarbon structure

Lewis structure

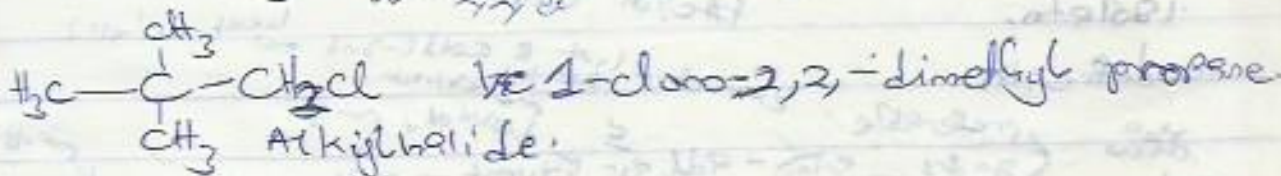
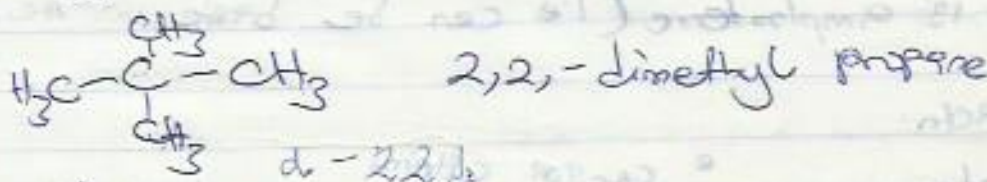
kekule "

condensed " -CH<sub>2</sub>CH<sub>3</sub>.

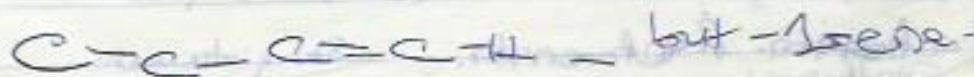
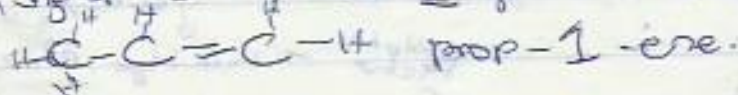


stereo.

Alkyl: Alkane deficient of 1 hydrogen.

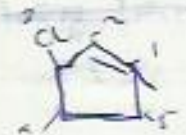
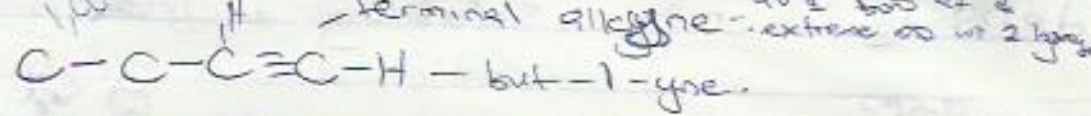
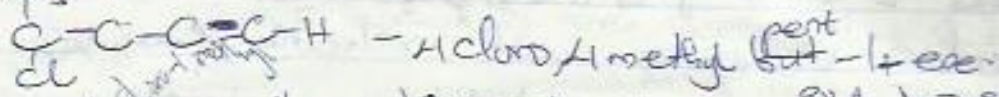
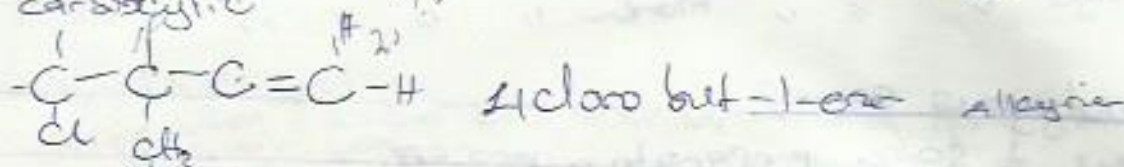


\* take ↓ longest chain as ↓ parent name.



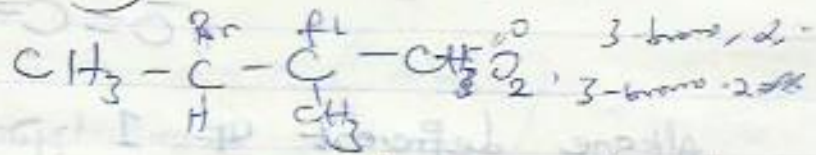
negative inductive effect -

carboxylic acid - most acidic in nature



3-chloro cyclopentene / 3-chloro cyclopent-1-ene

tert tertiary carbon - not no hydrogen attached 3 if methyl  
 secondary " 1 " " " " "  
 primary " 2 " " " " "



Alcohol is amphoteric (ie can be basic or acidic)

extractn.

isolate.

FACTOR OTHER

modification

polar - preferable - extract - hot & cold (dist. ext) heat all 2  
 medium polar - benzene chloroform - solvent - solk 21 rights - solvent  
 non - " - phyto. solvent screening - use amp filter.

crude extract

thin layer chromatography  
 (dist. line & general control)

fractionation: fractionation

Stinglobe gets

pathogen-disease causing organism.

### terrestrial agents

extract & potency of the extracts can be increased - extract can also be synthesized after extraction.

extracts from one made up of mixture of extract called crude extracts.

### Isolation of organic compounds cold/hot ex

How to extract compounds

prepare of sample - by <sup>sun</sup> air dry <sup>sun</sup> air drying is more advised

Grind of sample

cold/hot extraction -

selective/succession

1 cold extract - <sup>10</sup> <sup>20-4</sup> <sup>10</sup> <sup>20-4</sup> stir then filter & decant & solution - filter & solution

use <sup>normal</sup> extract <sup>ethere,</sup> <sup>petroleum ethyl,</sup> <sup>tetrahydro</sup>  
ethere <sup>use w/ & thermally</sup> <sup>stable</sup> <sup>compounds</sup>

or <sup>high</sup> evaporation: free of extract <sup>air</sup> <sup>or</sup> <sup>compound</sup>  
ring at low temp & high pressure.

If solvent is or target start at

pp 2p  
102  
22

solvent use & extract -

non-polar comp ↓ at see extract from non-polar soln

Condition 2 sol consider when choosing an extract.  
ease of soln of compounds

2<sup>nd</sup> stage " free & extract from compounds,

Andry

resorb your extract in a medium polar solvent (ie benzene,  
S & leave # 24-48 hrs.

Andry & free & material polar solvent  
then soak in a polar solvent - (H<sub>2</sub>O, methanol, ethanol, ?)  
concentrate using rotary  
evaporation

3 Identify <sup>no of</sup> <sup>in a</sup> <sup>compound</sup> <sup>extracted</sup>  
paper / thin layer chromatographic / precasted / plate / laboratory prepared plate  
silica gel / ~~alumina~~ alumina - IS use & cover a glass fitted  
& allowed to solidify.  
↓ appearance of ↓ spot on ↓ plane is called chromatograph.

RF <sup>use & identify</sup> Value = d distance moved by

to thin layer chromatography ↓ is ↓ process use & identify  
compounds present in an extract!

out of a small extract, a small quantity of extract is poured on a prepared plate. a solvent used is used to run a plate & a solvent went on a plate (function of their molecular weight) & after leave spots on a plate (d no)

## Method of separating & isolate.

### Column chromatography

### Preparing thin layer chromatography

column chromatography - dissolve a extract in a solvent column & it will form zones. we use UV light & it will show a no of compound present & showing spots. a no of spot is a no of compound present. If a no is has pure it is seen on TLC if it shows ~~more than~~ 2 colour it shows that it is pure if it is more than 2 " " " " " " " " impure.

When there is a much different b.p. & value of compounds use column chromatography & if its not much use a preparatory thin layer. The extracts are non-volatile essential oils - compounds which possess extracts from plants

Aromatherapy - allows extraction from plant hydrodistillation - make use of diaphragm apparatus  
Steam distillation - is carried out  
Microaqueous extraction process  
Supercritical fluid extracts

body humidity 1st factor of body temperature (100-300mK) range.

H<sub>2</sub>O is denser than vapour.

simultaneous distillation extract.

Soccol Soxhlet extractor - hot extraction  
no odour is soluble in H<sub>2</sub>O but they are soluble in ethanol  
hydrodistillation  
if odour is not vol'd

Supercritical fluid extraction - than when extract cannot be dissolved  
best technical method extract of odour

### BASIC REACTION OF SATURATED AND UNSATURATED H-C

Alkene

Saturated H-C atoms are unreactive - are called alkane  
bonded atom possess of some or very small diff in electronegativity

radical, electron deficient are called electrophile - they don't  
react with nucleophile  
nucleophile: rich in electrons, negatively charged, very reactive  
electrophile: electron deficient, positively charged, very reactive

### Types of Reagent

FREE RADICALS - they are neutral atom or group of atoms which possess an unpaired electron. They are highly reactive because of unstable electron configuration.  
e.g. Cl<sup>•</sup>, CH<sub>3</sub><sup>•</sup>, C<sub>2</sub>H<sub>5</sub><sup>•</sup>, H<sup>•</sup>, C<sup>•</sup>, H<sup>•</sup>, H<sup>•</sup>

2) ELECTROPHILES  $\rightarrow$  means electron lovers. They are electron deficient species who will attack an electron rich center in chemical rxn. e.g.  $\overset{\delta+}{C}H_3Cl$  electrophiles may be the charge ion i.e.  $H^+$ ,  $NO_2^+$ ,  $CH_3^+$ ,  $RN_2^+$ ,  $BF_3$  or they may be molecules w/ an incomplete outermost shell of electrons e.g.  $BF_3$ ,  $AlCl_3$ ,  $FeBr_3$ .

A Lewis Acid is therefore an electrophile b/c it is an electron deficient species. and in any chemical rxn it will seek an electron rich site on a basic species. i.e. Lewis acid are proton donor & electron acceptor.

3) NUCLEOPHILES  $\rightarrow$  are electron lovers. They are electron rich species who attack electron deficient center in a chemical reaction.  $\therefore$  Lewis base is a nucleophile b/c it is an electron donor i.e. a species who donate electron & accept proton. nucleophiles may be negatively charged ion  $OH^-$ ,  $CN^-$ ,  $OR^-$ ,  $Cl^-$  or they may be neutral molecule w/ lone pair of electrons.

many organic molecules are polar. The partial charges present in a molecule make a group electrophile or nucleophile b/c a compound dissociates while some molecules are polar e.g.  $H_3C^{\delta+}-Cl^{\delta-}$  charges difference also makes them either as electrophile or nucleophilic.



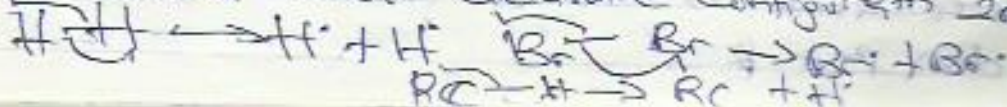
In chemical rxn,  $\delta$  electrostatic interaction can attract the +ve charge & -ve charge this makes nucleophile to always react w/ electrophile. Nucleophile i.e. electron rich as an unshared pair of electron acting as a reactive site seeking a +vely charged or electron deficient site in electrophiles.

### BOND FISSIONS / CLEAVAGES

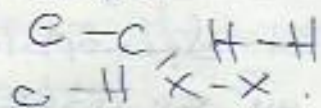
Organic Compounds are made up of co-valent bond, organic rxn involve bond breakage &  $\downarrow$  process of breaking  $\downarrow$  is bond is called bond fission / BOND CLEAVAGES. There are 2 type of co-valent bond fission - Homolytic and Heterolytic bond fission.

**HOMOLYTIC**  $\div$  occur in bonded atoms who are  $\downarrow$  same or minor variation in electronegativity. In this process each of  $\downarrow$  2 bonding electrons goes  $\div$  one ( $\downarrow$ ) of  $\downarrow$  bonded atoms.  $A \cdot B \rightarrow A \cdot + B \cdot$

A half ( $\div$ ) curved arrow is used  $\div$  indicate  $\downarrow$  movement of a single electron.  $A \cdot$  &  $B \cdot$  are free radicals & they possess an unpaired electron. They are very reactive as they always try  $\div$  attain  $\div$  octet electronic configuration  $\div$  rxn.



Hence homolytic bond fission occur in non-polar or slightly polar bonds.



## HOMOLYTIC & HETEROLYTIC BOND FISSIONS

### CONDITIONS THAT FAVOUR HOMOLYTIC BOND FISSION

- 1) The use of non-polar solvent
- 2) presence of free radical initiator, e.g. peroxide molecules  $\text{H}_2\text{O}_2$
- 3) High temperature
- 4) The presence of sunlight or UV light
- 5) " " " resonance or inductive effect that stabilizes a free radical.

HETEROLYTIC BOND FISSION / CLEAVAGES -! occur in bonded atom who are vary in electronegativity.

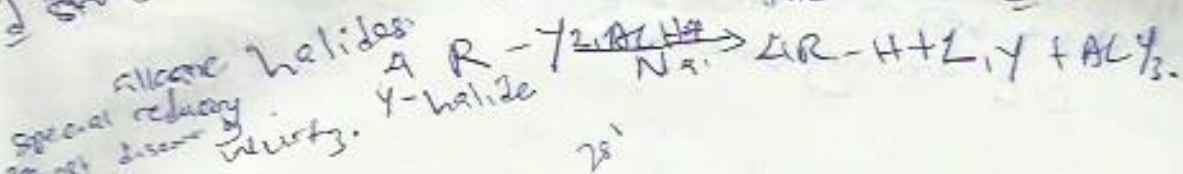
In dis fission, both of a shared electron go to just one (1) of a bonded atom (more electronegative atom). To produce  $\overset{\ominus}{\text{C}}$  &  $\overset{\oplus}{\text{X}}$  ion (carbanion & cation) as produced.

Thus, dis bond breaking occur in polar bond, when X is highly electronegative atom or group of atom.



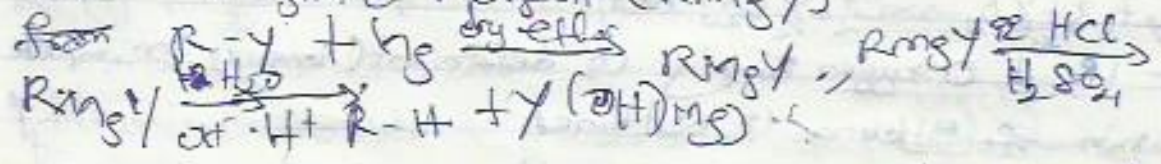
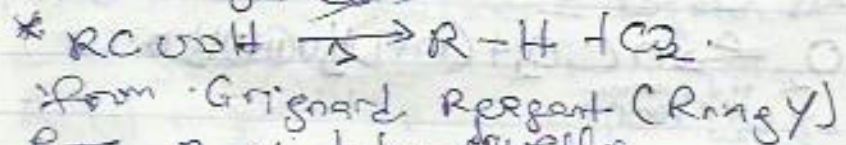
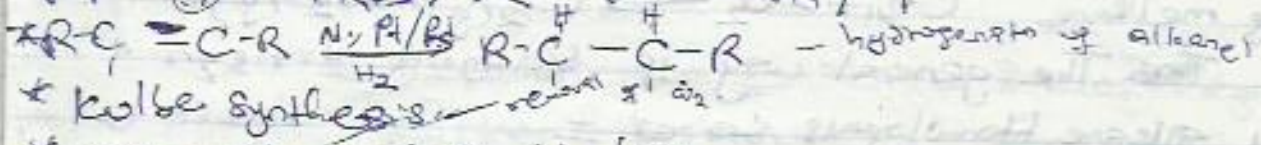
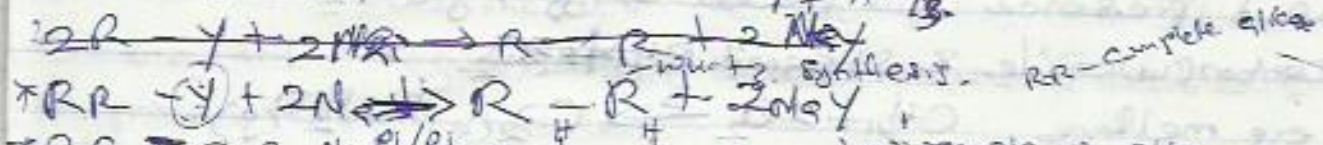
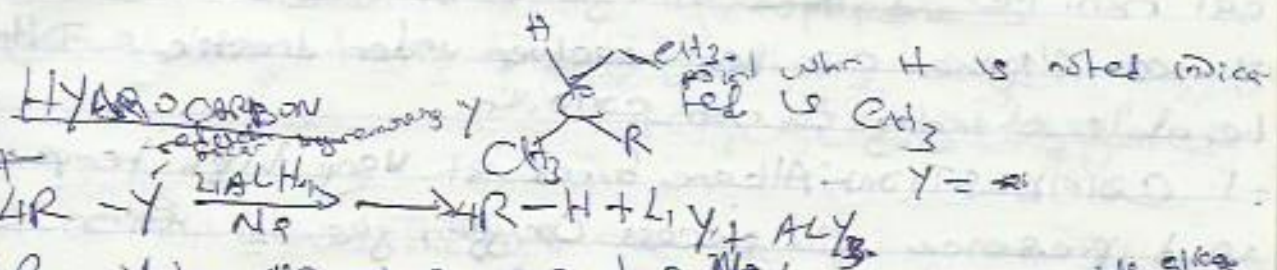
A  $\curvearrowright$  full curved arrow is used to indicate a movement of an electron pair.

Stronger bond & less reactive due to the strength of bond



CONDITION THAT FAVOUR HETEROLYTIC BOND

- 1) the use of polar solvent
- 2) presence of resonance or inductive effect that stabilizes charged species.



Production of Alkane halides (Y).

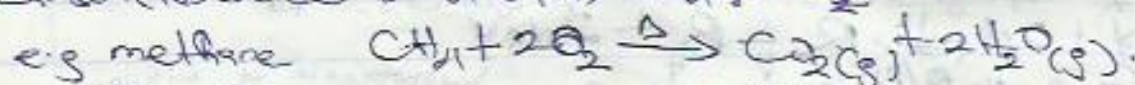
Addition of any highly electronegative atom - reduction tetavalent  $\rightarrow$  trivalent

sigma bond are strong & break.  
C-C are very unreactive.

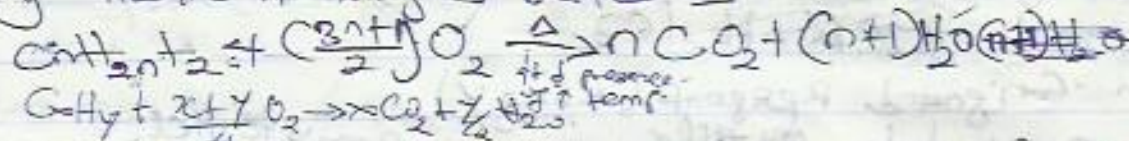
## REACTIONS OF ALKANES

Alkanes are very unreactive due to the presence of sigma bonds which is very strong & break during chemical rxn. The C-C sigma stronger & bond, & slower & rate of rxn. Alkanes can be reactive under drastic conditions while changing the rxn conditions.

-1 COMBUSTION: Alkanes burn at very high temp in the presence of excess oxygen gas & form carbon dioxide & steam.



The general way of balancing the eqn of any alkane homologous series =

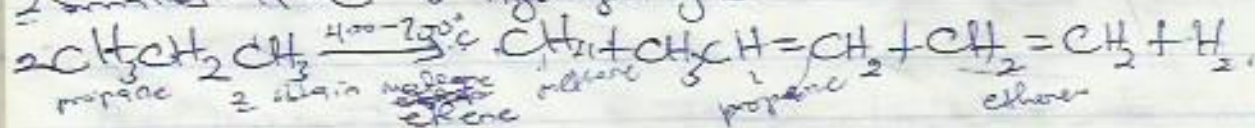


NOTE - If the oxygen supply is deficient (small), incomplete combustion of alkanes is obtained.

Hence - formation of carbon monoxide or coal.

use in petroleum industries

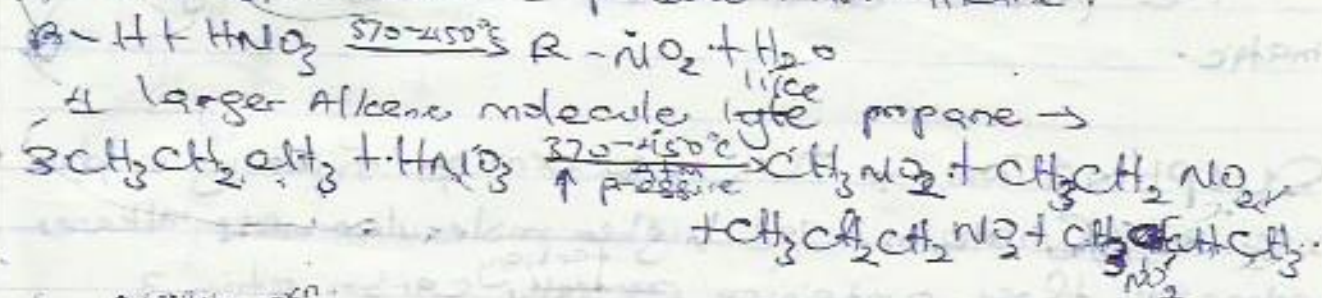
PYROLYSIS / CRACKING - This involves burning of alkanes in the absence of oxygen at high temp like 400-700°C leading to cleavage/breaking of bonds of alkanes to smaller H-C & hydrogen gas.



pyrolysis - 370-450  
 nitration - 370-450

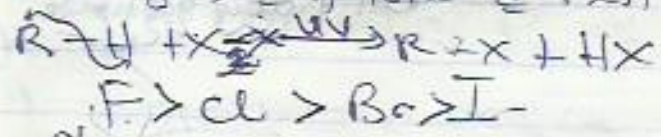
of hydrogen/water in presence of catalyst  
 rxn at higher temp

**NITRATION** : Alkene undergo nitration rxn using trioxocarbon nitrate,  $\text{O}_3$  acid in liquid state at high temp of about 370-450°C & produce nitro-alkane.



**HALOGENATION** : This is also substitution rxn. It involves alkene and halogen in presence of UV or visible light to produce alkene halide.

This rxn is depending on UV light & electronegativity power of halogens. i.e. higher the electronegativity of halogen, the faster the rxn rate.



Fluorine should not be used because of its highly electronegative & rxn is highly explosive.

**NOTE** : rxn mechanism describe the actual sequence of bond breakage & bond formation during the course of a rxn. the mechanism of dis rxn always bring free radical

$$R-H + X_2 \xrightarrow{UV} R-X + HX$$

**5) ΔHYDROGENATION** : This rxn involve the removal of hydrogen atom from alkenes in presence of oxidizing agent such as chromine(VI) oxide or Manganese(IV) oxide

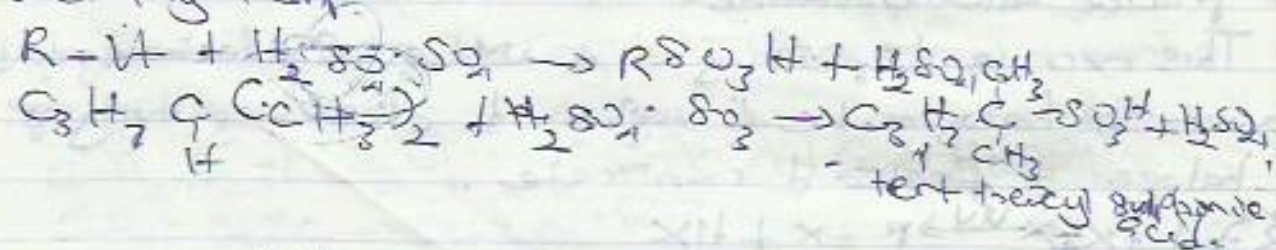
dehydrogenation - removal of hydrogen in presence of oxidizing agent

obtain 1-heptene  
toluene  
methylbenzene

on alumina at high temp of 450-500°C  
 $\text{CH}_3(\text{CH}_2)_5\text{CH}_3 \xrightarrow[\text{Alumina}]{\text{CrO}_2 \text{ or } \text{V}_2\text{O}_5, 450-500^\circ\text{C}}$   $\text{C}_6\text{H}_6 + \text{CH}_4$

The product obtain in this rxn is always aromatic.

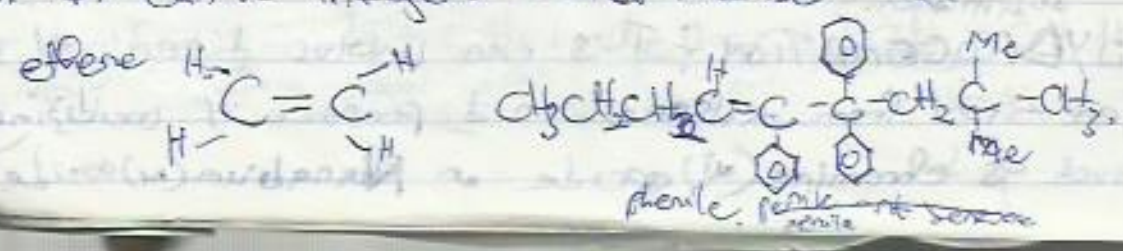
**SULPHURATION** → This is a rxn of fuming sulphuric acid (Cholium) and higher molecular mass alkanes especially those containing tertiary carbon atom produce sulphuric acid - concentrated sulphuric acid does not react appreciably with alkanes at ordinary temp.



### ALKENE

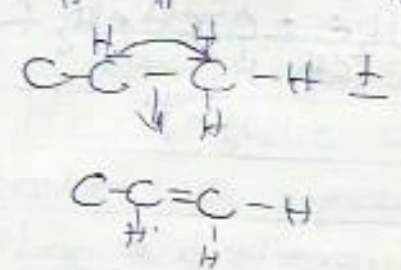
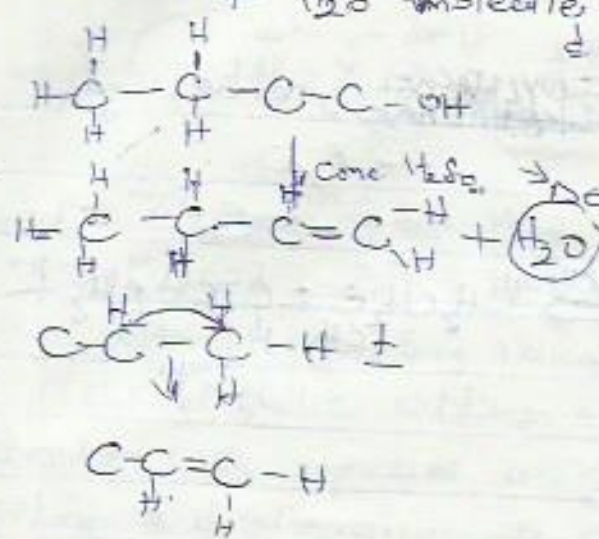
C=C - have pi bond in addition to their sigma bond. Alkene are unsaturated class of present of pi bond (pi bond) C=C. This unsaturated carbon atoms are sp<sup>2</sup> hybridized & are bonded to each other by a sigma bond and a pi bond.

General molecular formula of Alkene = C<sub>n</sub>H<sub>2n</sub> where 'n' can be integers. Smallest member is ethene.

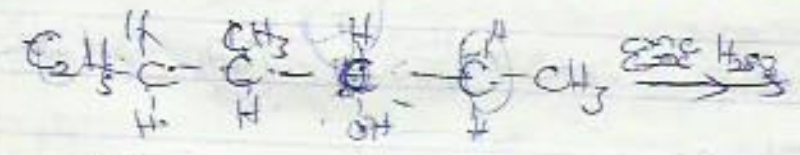


PREPARATION OF ALKENE. Dehydration of alcohol.

1) Removal of  $H_2O$  molecule from alcohol & form alkene in presence of hydroxy catalyst.



For secondary & tertiary alcohol, we have mixture of Alkene as products, and their relative proportion depend on stability of individual alkene obtained.

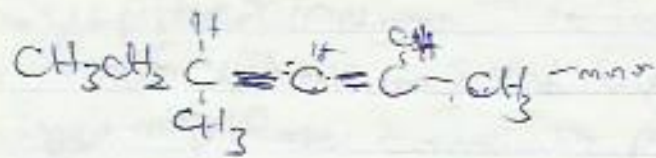
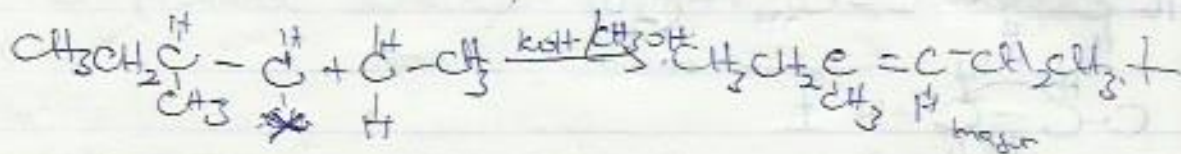


- 1)  $\text{C}_2\text{H}_5-\text{CH}_2-\text{C}(\text{CH}_3)=\text{C}-\text{CH}_2-\text{CH}_3$
- 2)  $\text{C}_2\text{H}_5-\text{CH}_2-\text{C}(\text{CH}_3)=\text{C}=\text{C}-\text{CH}_3$

1 is a major product because it has more H atom on  $\alpha$  carbon.  
 The rate of dehydration is determined by stability of alcohol.  
 $3^\circ \text{OH} > 2^\circ \text{OH} > 1^\circ \text{OH}$

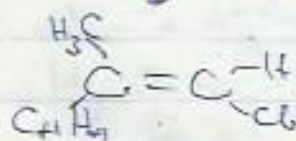
2) known if a comp is major or minor & no. of Hydrogen or  
 is class 2

2) Dehydrohalogenation of ~~ALKYL HALIDE~~ <sup>ALKENYL HALIDE</sup> removal of  
 hydrogen halide.



Reduction of Alkyl halides

1)  $\text{AlH}_3 / \text{NaBH}_4$



1-chloro-2-methylhex-1-ene.

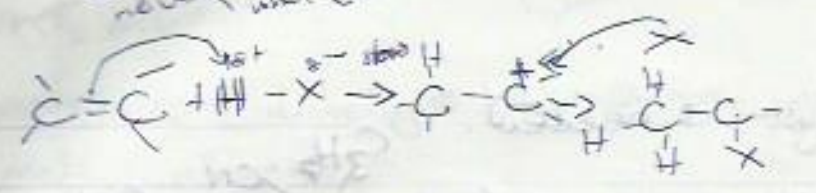
### REACTIONS OF ALKENES

Alkenes are very reactive b/cos of presence of pi-electron in carbon-carbon double bond. The main rxns. alkenes undergo are:

ADDITION REACTIONS. <sup>Substituted is seen converted 2.</sup> This rxn may be electrophilic, nucleophilic or free radical addition reaction. However a typical rxn of alkene are always electrophilic addition rxn b/c of presence of pi-electron which always make alkene a nucleophile i.e. electron rich species.



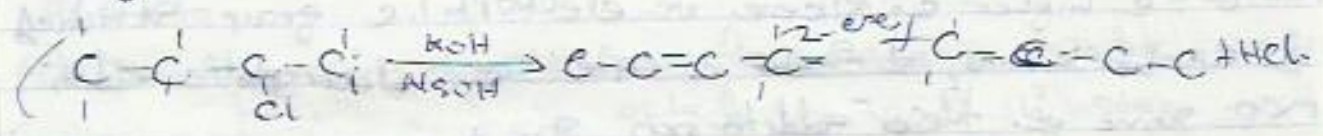
electronic ally adding rxo. electrophilic -1/2 charge on carbonion  
 nucleophile " more electro-



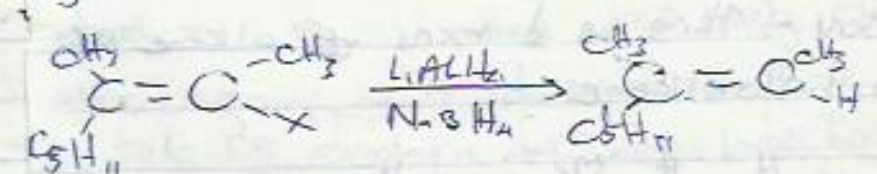
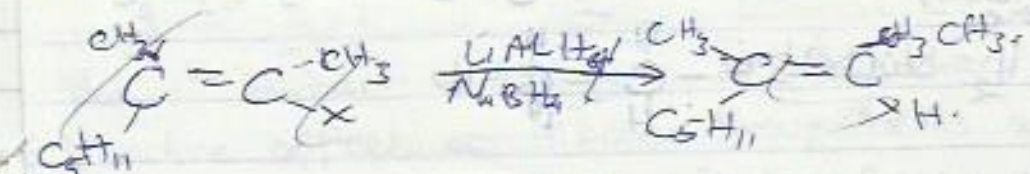
= pre electron makes H  $\delta^+$  & stabilized but H has been needed in 1<sup>st</sup> second order, 2<sup>nd</sup> is deficient of electron  
 when a bond is breaking faster than when a bond is forming

Nucleophilic addition + carbocation occur when an electron rich species or group is attached to a alkene leading to the formation of negatively charged carbon (carbanion) (Carbanion carbide ion). e.g.  $\text{C}=\text{C} + \text{CN}^- \rightarrow \text{C}^{\ominus}-\text{C}$   
 n/s kola.

dehydration of alcohol  
 dehydration of alcohol

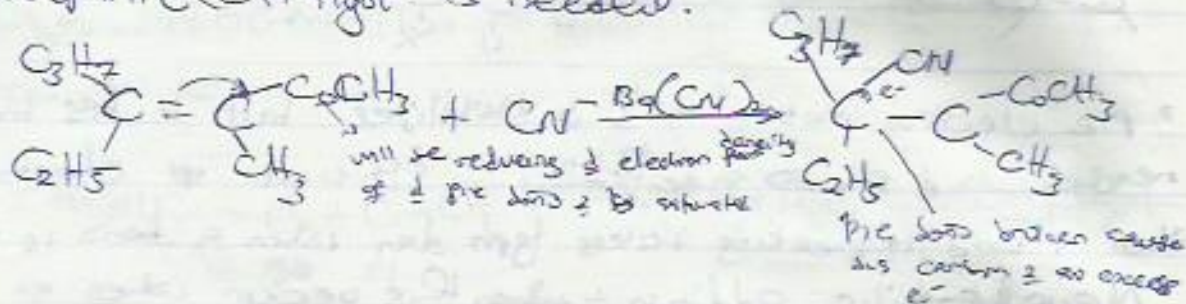


Reduction of ALKENYL HALIDE

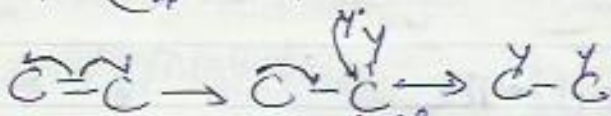
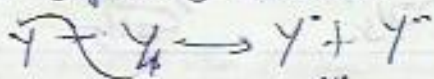


nucleophilic site will supply the  $e^-$   $\rightarrow$  alcohol  $\rightarrow$  can increase  $\rightarrow$   $e^-$

Nucleophilic (catalyst is needed).

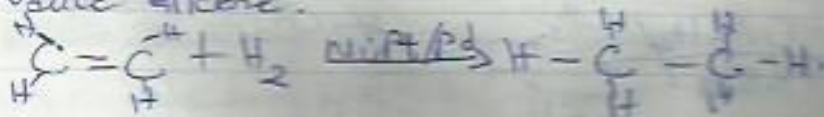


FREE RADICAL ADDITION RXN: This involves addition or combination of two or more atoms or groups of atoms which possess unpaired electrons

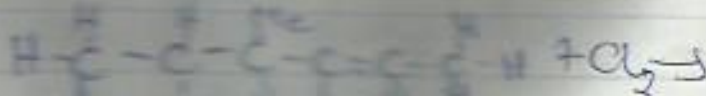
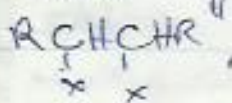
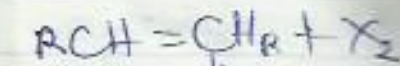


NOTE:  $\delta$  higher  $\delta$  in alkene or electrophilic group attached to carbon atoms,  $\delta$  faster  $\delta$  rate of electrophilic addition rxn. same of these addition rxn may

1) HYDROGENATION: This involves addition of  $\text{H}_2$  molecule to an alkene in the presence of hydrogenating catalyst (nickel, platinum, palladium) to produce alkane.



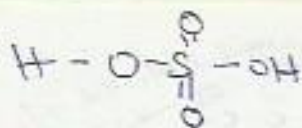
2) HALOGENATION RXN: This is a rxn of alkene with halogen halide to form haloalkane



1,2-dichloro-2,3-dimethylbutane

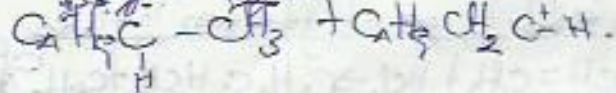
3) Hydrat...  
3  
#  
para  
nucleo  
note  
8/5  
el C  
The  
Induct  
electro  
Alkene  
effect  
the  
C $^+$   
 $\delta$  first





more stable than 2<sup>nd</sup> C<sup>+</sup> (product) w/ only 1 alkyl group attached to it.

Hence the <sup>1<sup>st</sup></sup> product is the major product.

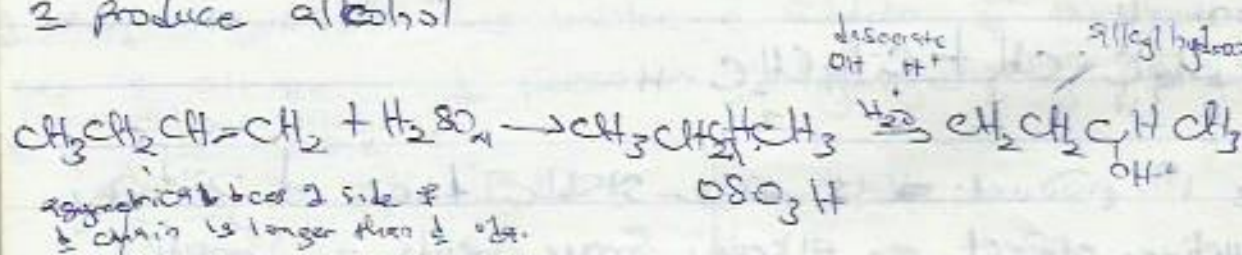


This

This is also supported by Markovnikov's rule. The rule says when a molecule HX/AB is added to an unsymmetrical alkene, hydrogen (or H<sup>+</sup>) which is part of the proton or electrophile is added or attaches to itself to the unsaturated carbon atom which carries a larger no. of hydrogen atoms.

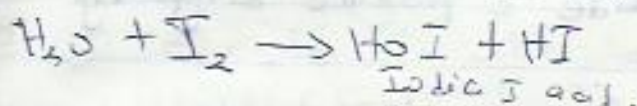
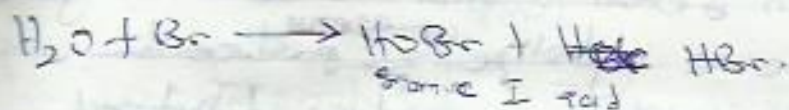
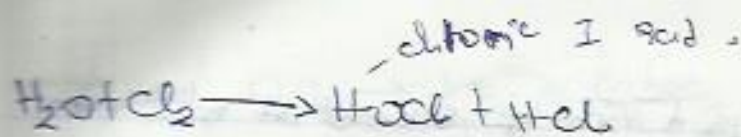
### ADDITION OF SULPHURIC ACID.

Alkene dissolve in concentrated sulphuric acid & form alkyl hydrogen sulphate. which are hydrolyzed by H<sub>2</sub>O & produce alcohol.

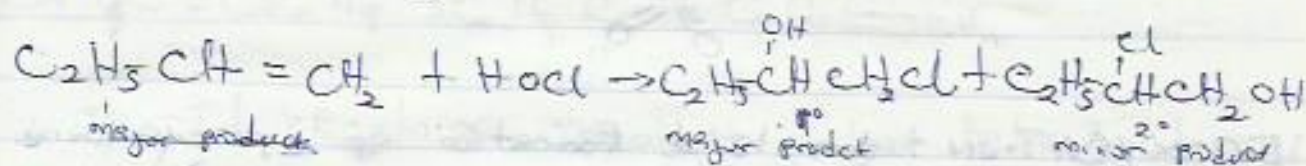


### ADDITION OF HALOGEN WATER (Cl<sub>2</sub>, Br<sub>2</sub>, Iodine water)

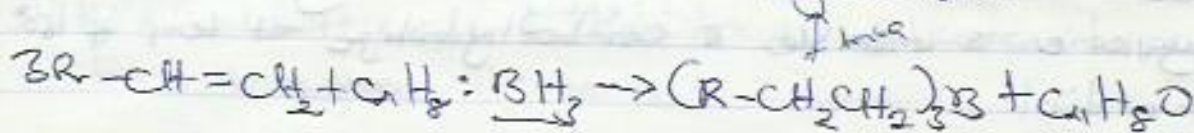
This involves addition of alkene w/ halogen H<sub>2</sub>O & form halohydrin also known as halohydrins.



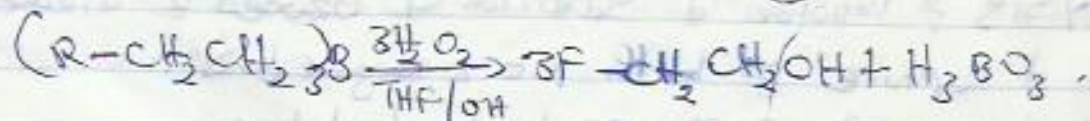
The halogen  $\text{H}_2\text{O}$  formed are called **HYPOHALOUS ACID**. These are added readily to alkene to produce halohydrin (haloalcohol)



**HYDROBORATION** = reaction of alkene w/ tetrahydrofuran (THF) to form tri-alkyl borane.

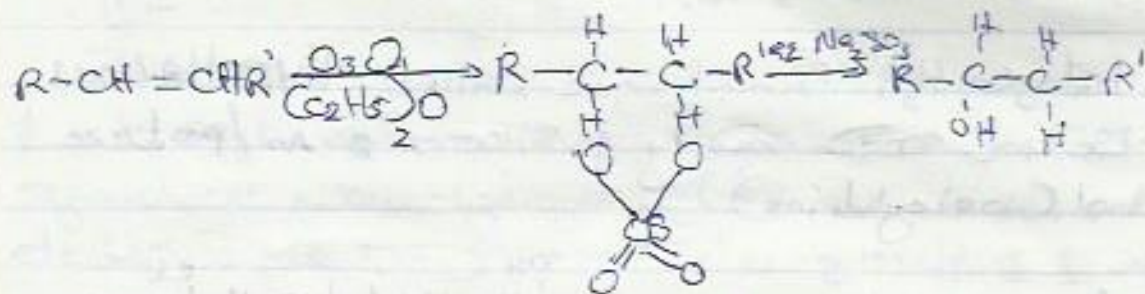


The tri-alkyl borane form can be oxidized in presence of Hydrogen peroxide in Tetrahydrofuran (THF) in basic medium to produce primary alcohol

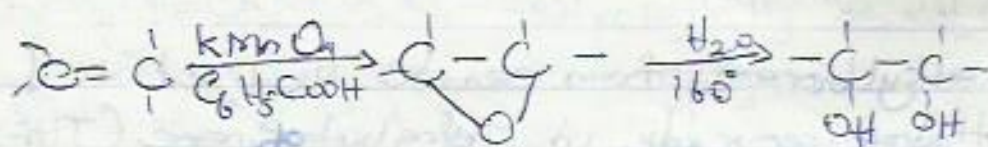


an di-ol

**HYDROXYLATION** - This is a rxn of alkene with ~~osmium~~ <sup>VIII</sup> osmium ~~oxide~~ <sup>oxide</sup> in ether solution to form a cyclic osmate ester which is hydrolyzed ~~with aqueous~~ <sup>with aqueous</sup> to produce diol. ~~But~~ <sup>But</sup> with ~~aqueous~~ sodium sulphide ~~it~~ <sup>it</sup> produces dihydroxyl compound.

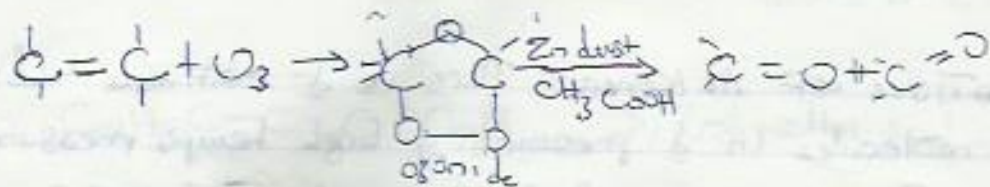


**EPHOXYDATION** - This is the formation of epoxyalkane from alkene. This involves a rxn of alkene with oxidizing agent like  $\text{KMnO}_4$ , peroxo-benzoic acid or hydrogen peroxide in ethanoic acid to produce epoxyalkane. epoxyalkane is unstable & can be easily hydrolyzed at temp of  $160^\circ$  to form diol.

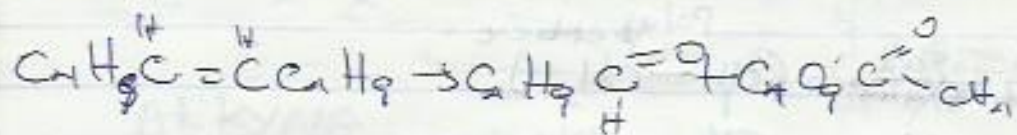


**OZONOLYSIS** - Involves the addition of ozonides to alkene. It involves the rupture of ~~the~~ pi & sigma bond. ~~the~~ ozonide is unstable & can easily be hydrolyzed.

00

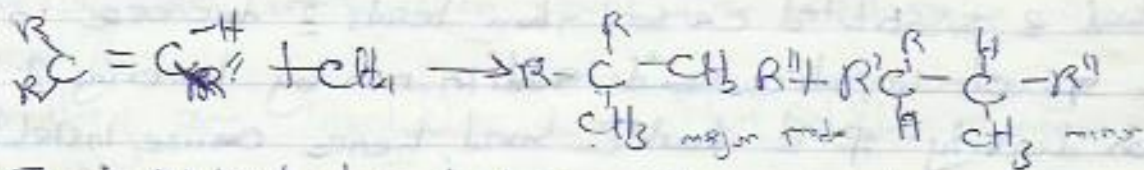


In ozonolysis - ozone reacts rapidly with alkene to form ozonide in which both pre & stigma bond are broken (broken down) since ozonide is unstable, it decomposes in the presence of zinc dust in ethanoic acid medium to produce alkenal or carboxylic acid.



NOTE - Identification of ozonolysis product helps to locate the position of a carbon-carbon double bond (C=C) in alkene molecules.

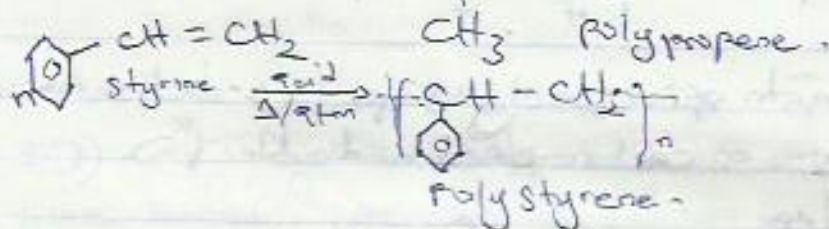
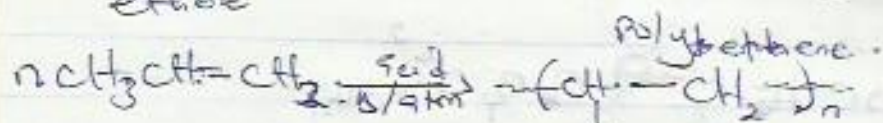
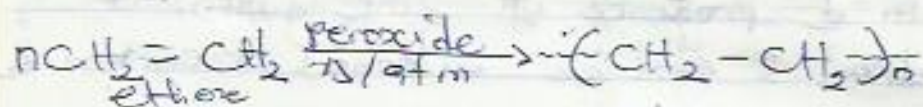
ALKYLATION: This is the addition of alkene to alkane to form a higher alkane.



NOTE: Alkylation takes place in the presence of acidic medium.

Alkylation

**POLYMERIZATIONS OF ALKENES:** This is a continuous addition of <sup>smaller</sup> alkene molecules in the presence of high temp, pressure & catalyst to form a long chain called polymer. e.g. polyethylene or polythene manufacture from ethene molecule by using peroxide catalyst at high temp & pressure where  $n = \text{integer}$

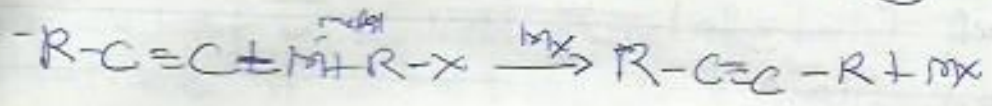
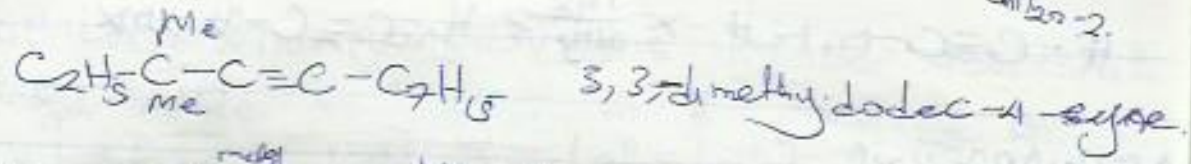


Alkene polymers are used as plastic materials, floor product & roofing sheet.

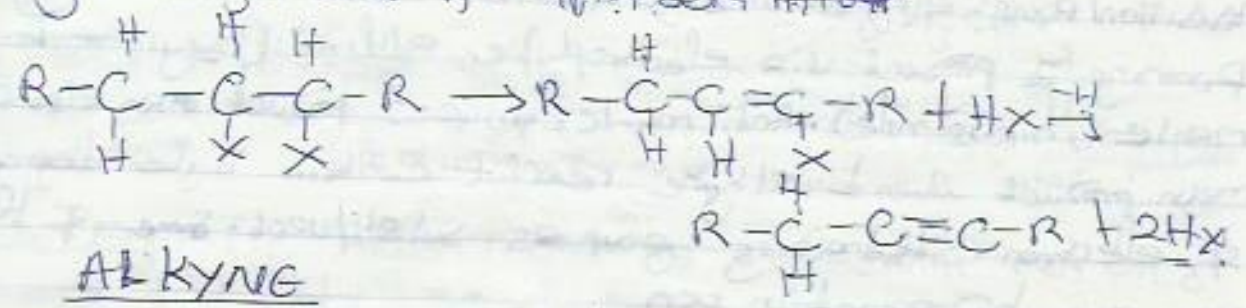
**NOTE:** Increase in the no. of electron withdrawing subs attached to substituted carbon atom leads to decrease in the rate of electrophilic addition rxn by lowering the electron density of the double bond, hence cause instability of the carbocation intermediate from the transition state i.e. the higher the stability of carbocation ion, the faster the rate of rxn.



Alkyne  
~~Alkyne~~ - very reactive but it is much less reactive than alkene. In it being saturated, it breaks down 2 alkene. Note of reactivity of alkene is greater than alkyne. It has 2  $\pi$  bond in addition to  $\sigma$  bond. Cotten-2.



Dehydrohalogenation of ~~alkane~~ <sup>haloalkane</sup> alkane



ALKYNE

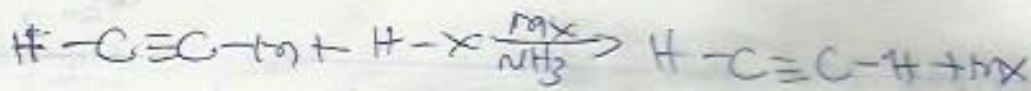
Alkyne also form homologous series of unsaturated hydrocarbon containing carbon-carbon <sup>triple bond</sup> ( $C \equiv C$ ). This  $C \equiv C$  is a functional group. It has a general molecular formula of Cotten-2. Triple bond contain 1  $\sigma$  bond & 2  $\pi$  bond. ethyne  $C_2H_2$  is a simplest alkyne family member.

Note: These hydrocarbons (unsaturated & saturated) show increase in boiling point with increasing molecular mass. It

→ They are insoluble in  $H_2O$  <sup>due to their low polarity</sup> but soluble in non-polar solvent.

PREPARATION OF ALKYNE.

ALKYLATION OF ALKYNE METALS (metallic acetylides)  
 Alkylates of alkyne metal with alkyl halide in presence of liquid ammonia with M-metal & X-halide.

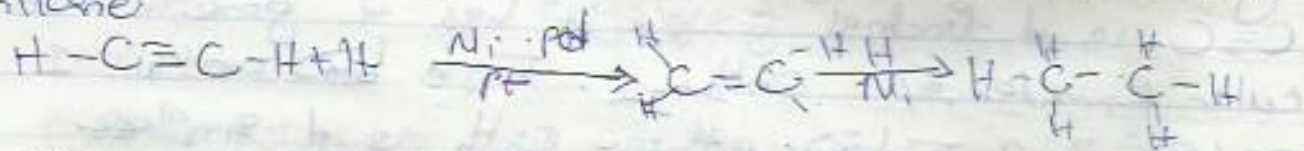


## DEHYDRATION

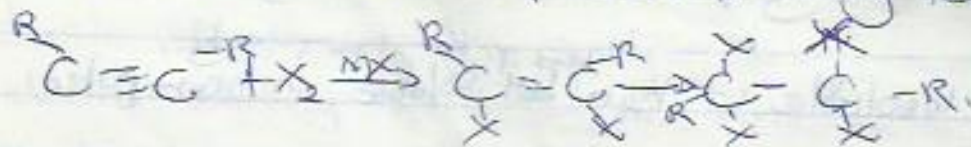
### REACTION OF ALKYNES

ADDITION RXN: Alkynes undergo addition reaction as alkene by forming 2 product via electrophilic addition. (they follow Markovnikov's rule). Anti-Markovnikov product can also form major product when alkyne reactant contain higher degree of electron withdrawing group as substituent. Some of these rxns are hydrogenation rxn.

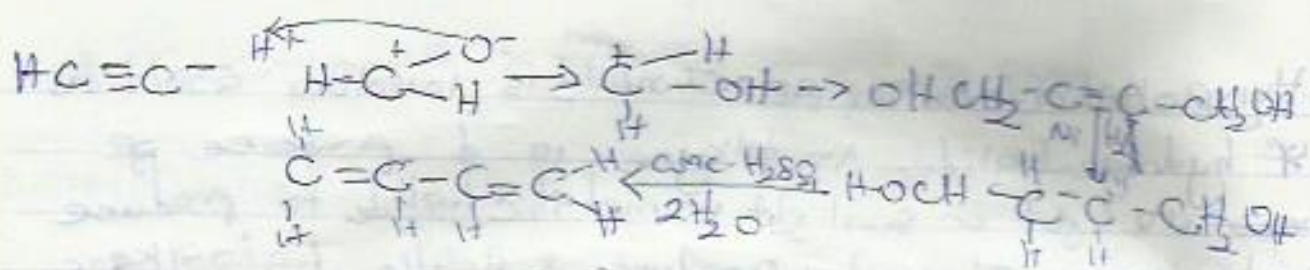
Alkyne react with hydrogen molecule in presence of hydrogenating catalyst 2 product alkene & final product alkane



HALOGENATION RXN: It undergoes halogenation rxn by reacting with halogen in presence of metallic halide 2 form di-haloalkene as initial product & finally tetra-haloalkane

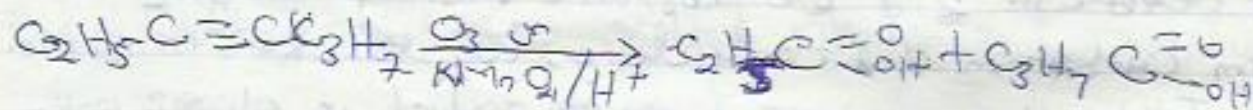
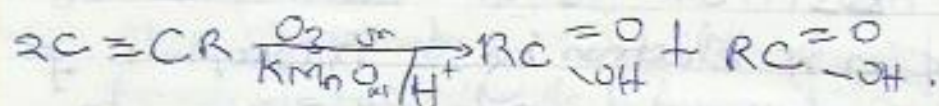




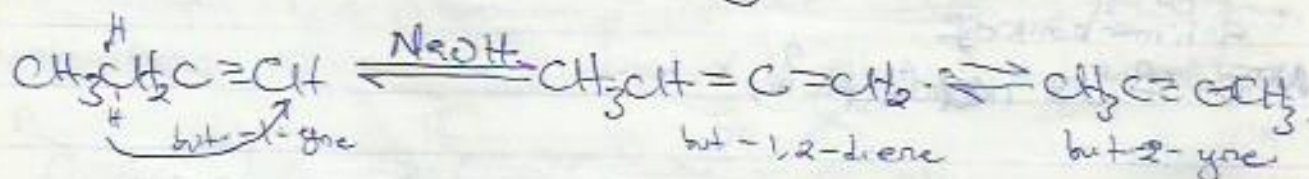


dis rxn increase d change d - rxn.

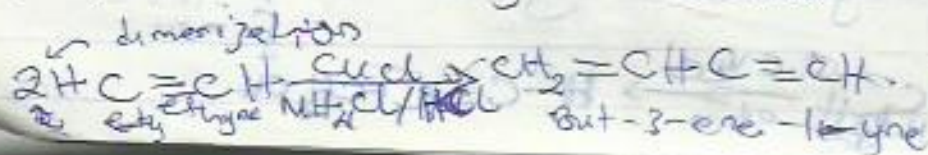
OXIDATION: Alkyne undergo oxidation rxn in d presence of strong oxidizing agent like ozone or  $\text{KMnO}_4$  in acidic medium to produce carboxylic acid.



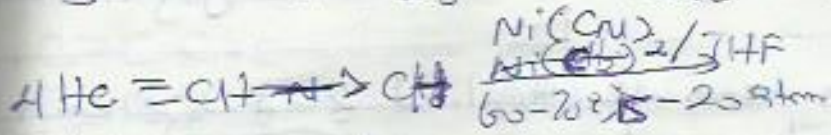
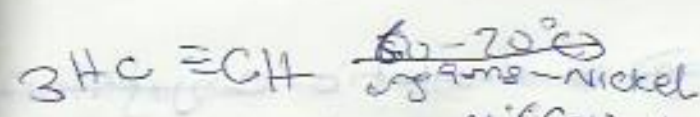
ISOMERIZATION RXN: dis rxn takes place in d presence of strong base when alkyne transform 2 alkene isomers or another isomer of alkyne



POLYMERIZATION RXN: Alkyne undergo polymerization rxn like alkenes in d presence of some specific catalyst & also form other organic molecules



31 d excit no  $\neq$  carbon excites



cyclooctatetraene

Tetramerization

Isolation

purification

Structural determination  $\neq$  IR, O.C.

Separation by filtration

### STRUCTURAL DETERMINATION OF ORGANIC COMPOUNDS

#### Spectroscopy Method

These are techniques which are considered as a key identification of a compound. Most modern spectroscopic methods are ultraviolet, visible light, <sup>spec</sup>UV/visible, Infrared (IR) spectroscopy, mass spec.

nuclear magnetic resonance.

UV/visible: This involves absorption of UV or visible radiations by a molecule which leads to transition among electronic energy levels of a molecule. Since this absorption brings about transition to electronic energy level of a molecule, hence this technique is also called **ELECTRONIC SPECTROSCOPY**.

All organic compounds absorb UV light. The strength of electronic spectroscopy lies in its ability to

↓ extent of multiple bond & aromatic conjugation within molecules

**Chromophores** - this term is applied to a system responsible for imparting colour to a compound. Chromophore is colour carrier e.g. in azobenzene ( $Ar-N=N-Ar$ ), aryl conjugated azo group is far clearly a principal chromophore. In nitro-compound, a yellow colour is carried by  $-NO_2$ . This term has been retained in an extended interpretation to include any functional group that absorbs electromagnetic radiation.

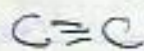
**Auxochrome** - this is term used to define a group that enhances the colour imparting properties of a chromophore, without being itself a chromophore.  $-OR$ ,  $-NH_2$ ,  $-NR_2$ , the effect of auxochrome is coupled with their ability to extend the conjugation of a chromophore by sharing a non-bonding electron. The UV visible spectroscopy is measured in wavelength & the unit is Nanometre. Compounds absorbing light of wavelength b/w 400 & 800nm (visible light) appear coloured to the human eye. It can be seen with human eye.

B/w 200 & 400nm, it is UV region.

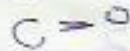
Chromophore  $\lambda_{max}(nm)$



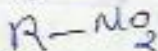
175



175, 175, 223



160, 185, 280



200, 274

$C \equiv N$	2100-2260
$C=C-C=C$	1640
$C=C-C=O$	1680, 1715
$C=C-C \equiv C$	2100, 2260,
$C \equiv C$	1840, 2040, 2250

For e.g. an isolated carbonyl group is in acetone absorbs UV light around 280nm.

### INFRA-RED SPECTROSCOPY (IR)

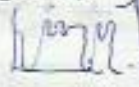
This depends on the vibration of atoms w.r.t. respect to each other in the molecule. When IR is passed through a sample of an organic compound, some of the frequencies are absorbed while others are transmitted and the bonds of the organic molecule without been absorbed. IR frequency range from  $1.2 \times 10^3$  to  $1.2 \times 10^{14} \text{ Hz}$ . The IR spectrum can then tell us whether any particular functional group or group is or are present in a molecule.

The atoms in organic molecules are dynamic & vibrate about their equilibrium positions. The frequency of vibration of a pair bonded atoms depends on their mass & the strength of bond that they form.  $\begin{matrix} O & - & H \\ & \parallel & \\ C & - & H \end{matrix}$

A particular type of bond b/w a certain pair of atom has a characteristic frequency of vibration. This vibrational occur at certain frequencies in the IR region of the electromagnetic spectrum.

When IR radiation of a particular frequency is

incident upon a molecule, energy is absorbed and the atoms in the molecule vibrate much more vigorously. Since frequency is directly proportional to wave no, the absorption is usually in wave no ( $\text{cm}^{-1}$ ). The wave no is a direct measure of frequency. I.R spectrum can be split into 4 regions of interpretation

WAVE NO ( $\text{cm}^{-1}$ )	INTERPRETATION
1500 - 1500 	This region is not easily seen. It consists of many diff complicated bands. It is called finger print region. This is not always used for identification.
1500 - 2000	Absorption by double bond ( $\text{C}=\text{C}$ , $\text{C}=\text{O}$ ).
2000 - 2500	Absorption by triple bond ( $\text{C}\equiv\text{C}$ , $\text{C}\equiv\text{N}$ ).
2500 - 4000	Absorption by single bond formed by hydrogen ( $\text{C}-\text{H}$ , $\text{O}-\text{H}$ , $\text{N}-\text{H}$ etc.).

The region above finger print region ( $1500\text{cm}^{-1}$  & above) are used for identification of functional group from their characteristic absorption wave no.



Group	Bond	Wave no.
Alkene	C=C	1610-1680
Aldehydes	C=O	1720-1740
Ketones	C=O	1705-1725
Acid & esters	C=O	1735-1750
Alkyne	C≡C	2070-2250
Nitriles	C≡N	2250-2280
Acid (hydrogen bonded)	O-H	2500-3300
Alkane, alkene, alkyne	C-H	2840-3095
Alcohol, phenol	O-H	3230-3670
Hydrogen bonded	N-H	<del>3350-3500</del>
Amines	N-H	3350-3500

200-1000  
1500-2000  
aldehyde - 1720-1740  
C≡N - 2250-2280  
OH - 3230-3670  
1500-2500

### MASS SPECTROSCOPY

mass spec (MS) is a technique which gives us information of molecular weight of molecule of organic comp by fragmentation of a compound.

### NMR Spectroscopy

This is nuclear magnetic resonance. It depends on the magnetic properties of the atomic nuclei in a molecule.

The 2 major types of NMR are proton NMR & carbon 13 (<sup>13</sup>C) NMR.

The proton NMR spec tells us the no. of hydrogen nuclei present in a molecule & gives information about their

Structural or chemical environment of  $\downarrow$  hydrogen. while  $^{13}\text{C}$  NMR spec gives us  $\downarrow$  no of carbon nuclei present in organic compound or molecule & provide information about structural environment of  $\downarrow$  carbon. Also

NMR also tells us correlation or interaction b/w H & C-nuclei.

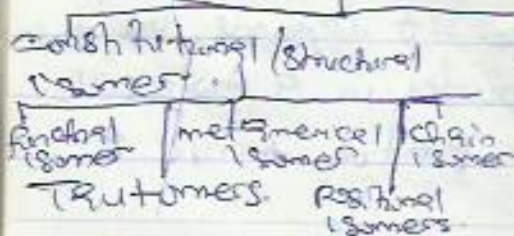
This spectroscopic method (UV, IR, MS, & ~~IR~~ <sup>NMR</sup>) provide additional information which offer easier & more precise analysis of  $\downarrow$  compound &  $\downarrow$  med.

or more substance.

STEREOCHEMISTRY = explain & arrangement of substituent (atoms or groups of atoms), chain branches etc about  $\downarrow$  carbon atom in space.

Isomers are non-identical molecules that possess same no of & kind of atom/molecules <sup>with</sup> & same molecular formula but diff structural formula. e.g.  $\text{C}_2\text{H}_6\text{O}$  or  $\text{C}_2\text{H}_5\text{OH}$

## STEREOCHEMISTRY



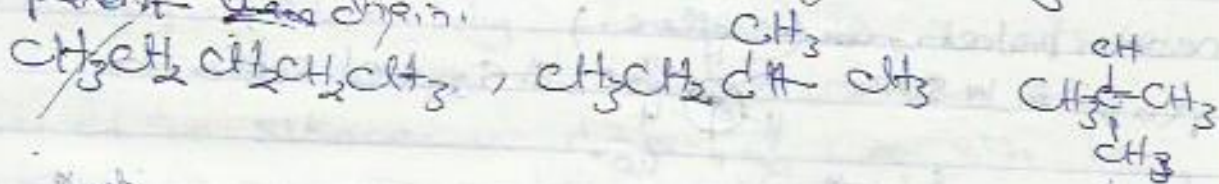
Stereoisomers -

- Conformational isomer.
- Configurational isomer.
- Optical isomers

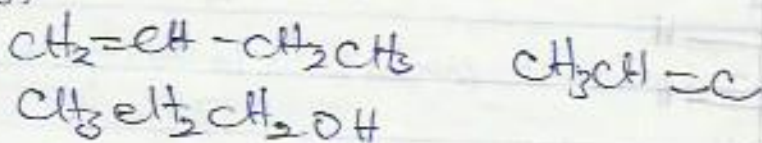
Functional isomer: diff. av. d. same molecular formula & diff. structural formula.  $C_3H_6O$ ,  $CH_3CH_2OH$  or  $CH_3COCH_3$  (2)  $C_3H_4O$ ,  $CH_3C(=O)CH_3$   $C_3H_4O$ ,  $CH_3C \equiv CH$ .  
 (1) ethyl methyl ketone.

METAMERICAL isomer (metamers): diff. isomer different arrangement of alkyl substituent e.g.  $CH_3OCH_2CH_2CH_2CH_3$   
 $CH_3COCH_2CH_2CH_3$  -  $CH_3COCH_2CH_2CH_3$

CHAIN isomer: differs in d. length of branching from parent chain.



POSITIONAL isomer: differ in d. position of (substituent functional group) i.e. d. substituent group are ~~not~~ in d. same position.



TAUTOMERS: d. represent product & reactant in equilibrium such that their is a rapid interconversion at room temperature.



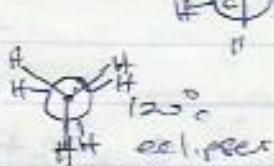
STAGGERED (isomers) differs in the way their atoms are arranged in space. i.e. the atoms are connected in a same way but differ in spatial arrangement in space.

CONFORMATIONAL ISOMERS: - by ~~resu~~ result from rotational about C-C single bond or as a result of ~~the~~ prime inversion. There is free rotation in a single bond. It can be observed using NEWMAN PROJECTION FORMULA. When the substituents are far away from each other it is called staggered conformation, and when they are close to each other it is called eclipsed conformation e.g.

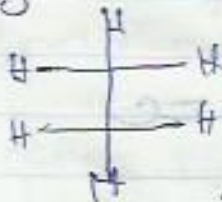
newman projections - resp (of ethane.)

ROTATION IN STAGGERED

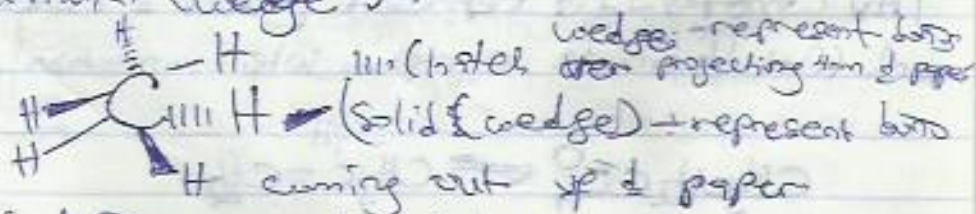
60° - staggered conformation



Fischer projection Formula (of ethane)



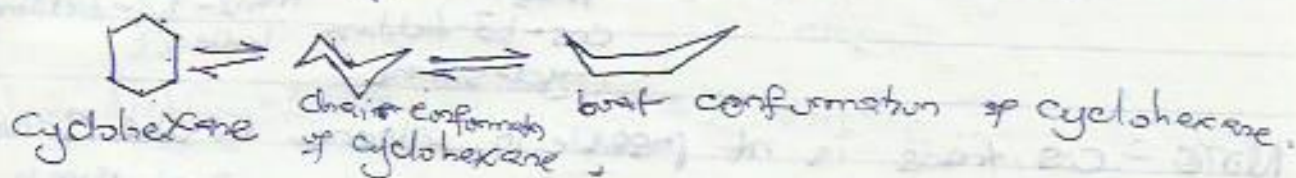
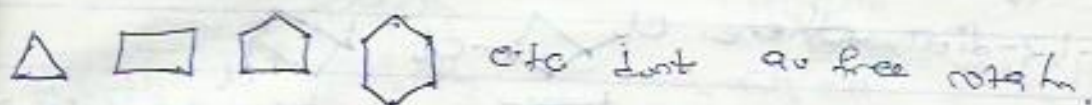
Perspective formula (wedge)



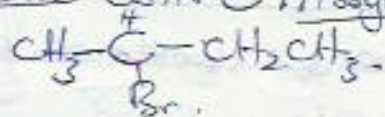
ordinary line = bonds on the plain of paper

Stereogenic  
asymmetric  
chirality

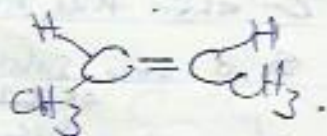
ROTATION IN CYCLOALKANES - there is no free rotation in cycloalkanes because of the rings / angle strength. with exception of hexane, heptane & above.



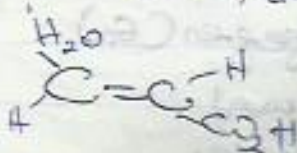
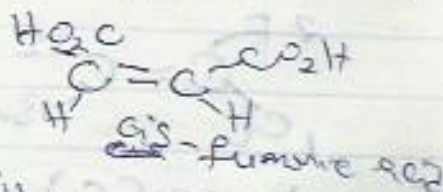
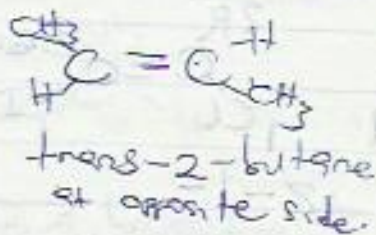
Configurational isomers do not inter-convert readily under normal conditions, therefore, they are stable & can be separated easily. It occurs in geometrical isomers (i.e. ~~cis-trans~~ cis-trans isomers) which are observed in alkenes or rings. It can also be observed in compounds containing ~~chirality~~ chirality centres / stereogenic centre / asymmetric centres.



e.g. geometrical / cis-trans isomers -  $\text{CH}_3\text{CH}=\text{CHCH}_3$

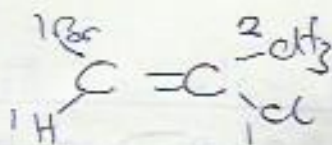


when u have similar <sup>chem</sup> isomers across d. carbon it is called cis-butane  
cis-2-butane

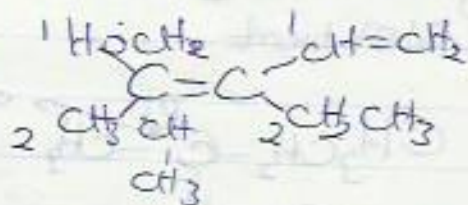
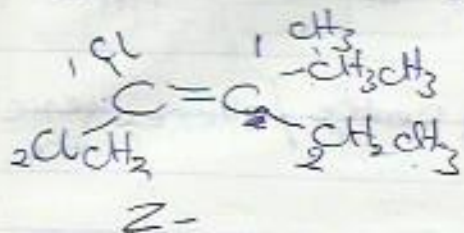




# Saytseff rule

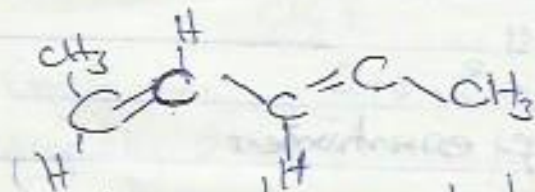


E - 1-bromo-2-chloro propene

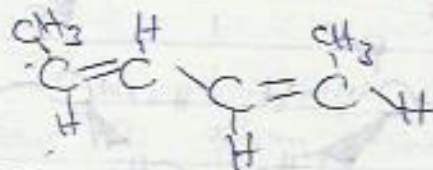


1,2-dichloro-3-ethyl-4-methyl-2-butene

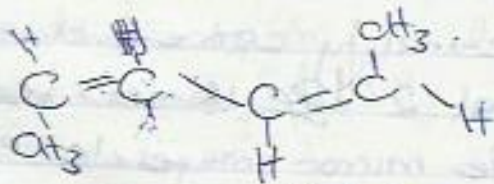
Many compounds have more than one double bond & each may have a potential of cis & trans isomerism. e.g. 2,4-hexadiene has 3 diff. configurations which are designated as trans-trans, cis-cis, & trans-cis.



trans-trans-2,4-hexadiene



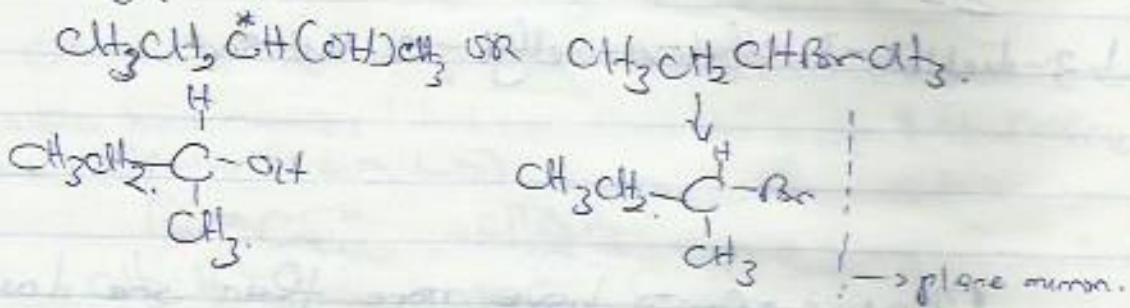
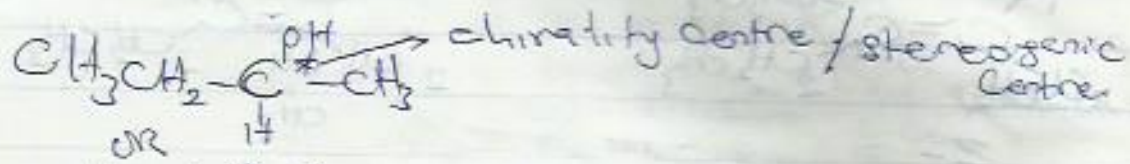
Trans-cis-2,4-hexadiene



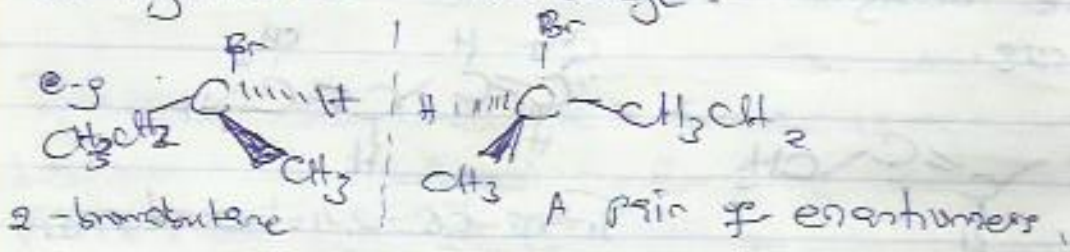
cis-cis-2,4-hexadiene

# OPTICAL ISOMERS.

Optical isomerism are experience in compound containing  
 chirality centre eg. A C bonded to different  
 group of substituent



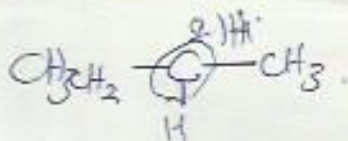
stereochemical representation using d. hatch wedge,  
 ordinary line or solid wedge.



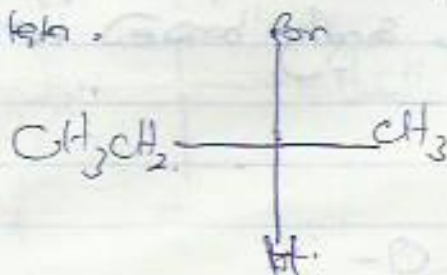
non-superimposable.

A compound with a chirality centre such as 2-bromobutane can exist in 2 diff isomer, because they are diff & non-superimposable mirror images, i.e. enantiomers  
 ENANTIOMERS are non-superimposable mirror images of one another.





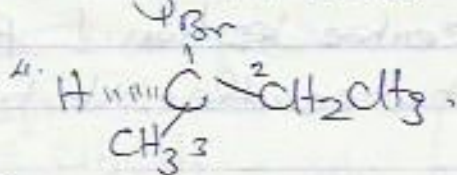
It can also be represented with Fischer projection representation.



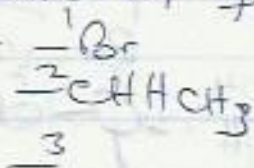
R, S Configuration with respects to optical isomerism

Cahn - Ingold - Prelog system.

Guide-line 1 - Rank the groups or atom that are bonded with the chirality center in an order of priority which depends on the atomic no. of the atoms that are directly attached to the chirality center.

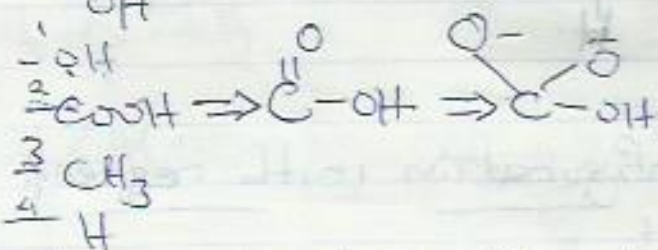
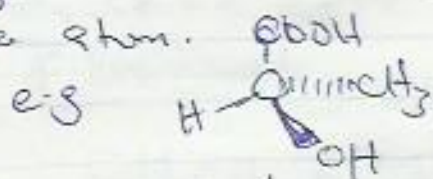


Guide-line no 2 → in case when 2 atoms are bonded directly to the chirality center or the same atomic no., then the atomic no. of next bonded atom will be considered.



G-3 → If an atom is doubly bonded to another atom, the priority system treats it as if it were

Single bonded to two of these atoms & if triply bonded, the system treat it as if it were singly bonded to 3 of these atoms.



G. 4.1 → orient the molecule so that the group or atom of lowest priority (4) is directed away from you then draw an imaginary arrow from the group of atom of highest priority (1) to the group of the next highest priority (2) and so on. If the arrow points in a clockwise direction the chirality centre has the R configuration but if counter clockwise then it has S-configuration.

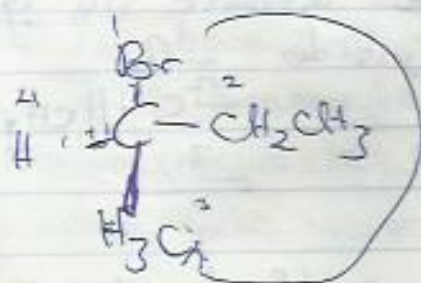
R - is a Greek word called RECTUS (which means

RIGHT)

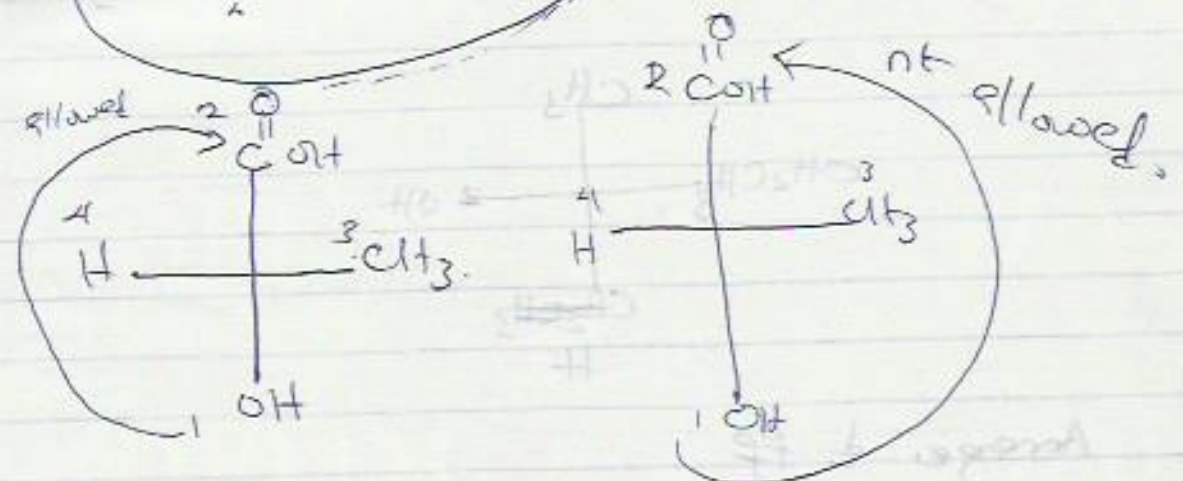
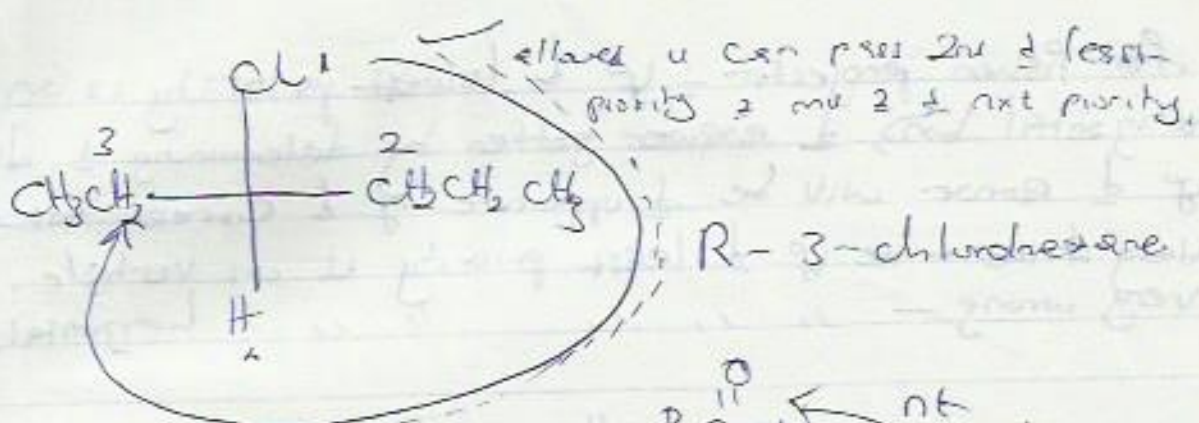
S - Sinister (which means left).



(S)-2-bromobutane

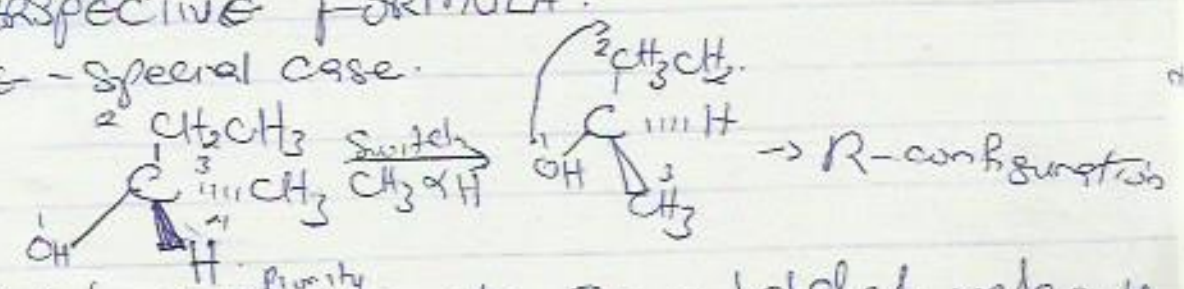


R-2-bromobutane



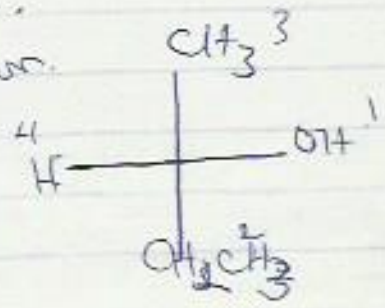
PERSPECTIVE FORMULA.

NOTE - special case.

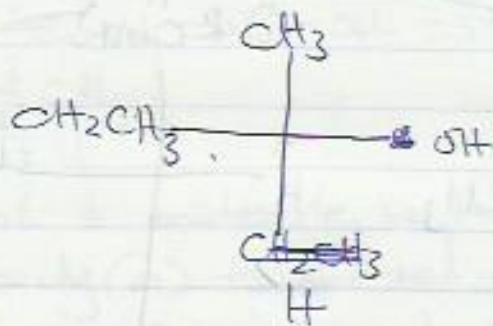


If a least priority atom is on a hatched wedge, you switch over.

Fischer projection.



For Fisher projector = if  $\downarrow$  lowest priority is on  
 horizontal bond,  $\downarrow$  answer gotten by determining  $\downarrow$  direction  
 of  $\downarrow$  error will be  $\downarrow$  opposite of  $\downarrow$  correct answer.  
 Very true - if  $\downarrow$  least priority is on vertical.  
 very wrong - " " " " " " " " horizontal.



Arrange  $\downarrow$  ff