14 An introduction to organic chemistry

Organic chemistry involves the study of a large class of chemical compounds containing carbon. This topic introduces naming conventions, organic reaction terminology and structures of organic molecules.

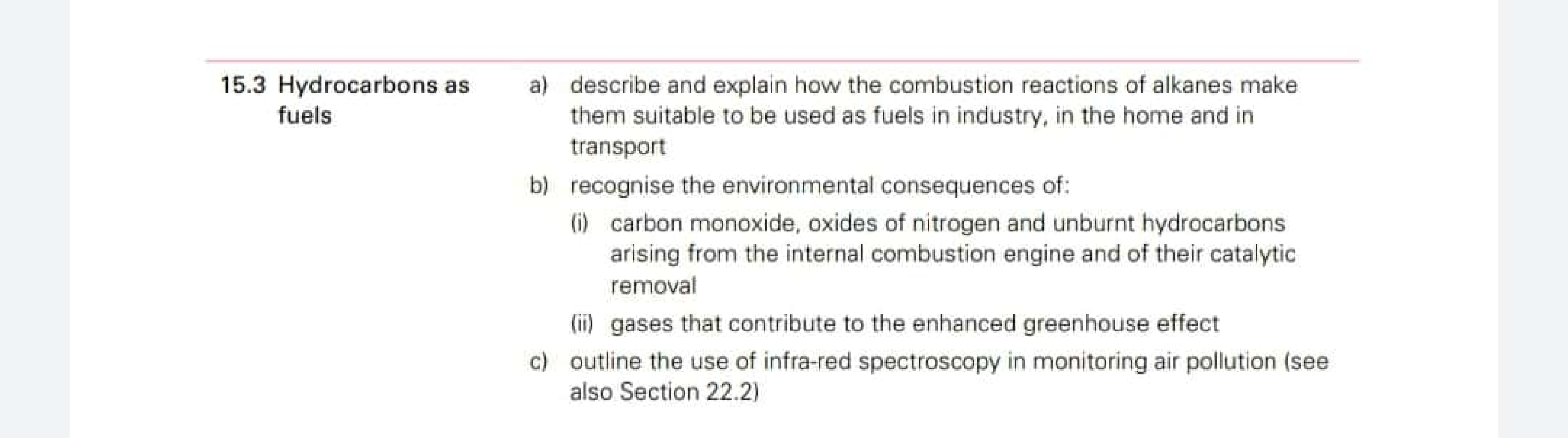
	Learning outcomes Candidates should be able to:
14.1 Formulae, functional groups and the naming of organic compounds	a) interpret and use the general, structural, displayed and skeletal formulae of the following classes of compound: (i) alkanes, alkenes **and arenes** (ii) halogenoalkanes **and halogenoarenes** (iii) alcohols (including primary, secondary and tertiary) **and phenols** (iv) aldehydes and ketones (v) carboxylic acids, esters **and acyl chlorides** (vi) amines (primary only), nitriles**, amides and amino acids** (Candidates are expected to recognise the shape of the benzene ring when it is present in organic compounds. Knowledge of benzene or its compounds is *not* required for AS Level.) b) understand and use systematic nomenclature of simple aliphatic organic molecules with functional groups detailed in 14.1(a), up to six carbon atoms (six plus six for esters and amides, straight chains only) **c) understand and use systematic nomenclature of simple aromatic molecules with one benzene ring and one or more simple substituents, for example 3-nitrobenzoic acid, 2,4,6-tribromophenol** d) deduce the possible isomers for an organic molecule of known molecular formula e) deduce the molecular formula of a compound, given its structural, displayed or skeletal formula
14.2 Characteristic organic reactions	a) interpret and use the following terminology associated with types of organic reactions: (i) functional group (ii) homolytic and heterolytic fission (iii) free radical, initiation, propagation, termination (iv) nucleophile, electrophile (v) addition, substitution, elimination, hydrolysis, condensation (vi) oxidation and reduction (in equations for organic redox reactions, the symbols [O] and [H] are acceptable for oxidising and reducing agents)

14.3 **Shapes of organic molecules; σ and π bonds**	a)	(i) describe and explain the shape of, and bond angles in, the ethane, ethene **and benzene** molecules in terms of σ and π bonds (ii) predict the shapes of, and bond angles in, other related molecules
14.4 **Isomerism: structural and stereoisomerism**	a)	describe structural isomerism and its division into chain, positional and functional group isomerism
	b)	describe stereoisomerism and its division into geometrical (cis-trans) and optical isomerism (use of E, Z nomenclature is acceptable but is *not* required)
	c)	describe geometrical (cis-trans) isomerism in alkenes, and explain its origin in terms of restricted rotation due to the presence of π bonds
	d)	explain what is meant by a chiral centre and that such a centre normally gives rise to optical isomerism (Candidates should appreciate that compounds can contain more than one chiral centre, but knowledge of meso compounds, or nomenclature such as *diastereoisomers* is *not* required.)
	e)	identify chiral centres and geometrical (cis-trans) isomerism in a molecule of given structural formula

15 Hydrocarbons

Compounds containing only carbon and hydrogen are called hydrocarbons. This class of compound can be subdivided into alkanes, alkenes and arenes.

	Learning outcomes Candidates should be able to:
15.1 Alkanes	a) understand the general unreactivity of alkanes, including towards polar reagents b) describe the chemistry of alkanes as exemplified by the following reactions of ethane: (i) combustion (ii) substitution by chlorine and by bromine c) describe the mechanism of free-radical substitution at methyl groups with particular reference to the initiation, propagation and termination reactions d) explain the use of crude oil as a source of both aliphatic and aromatic hydrocarbons e) suggest how cracking can be used to obtain more useful alkanes and alkenes of lower M_r from larger hydrocarbon molecules
15.2 Alkenes	a) describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene and propene (including the Markovnikov addition of asymmetric electrophiles to alkenes using propene as an example): (i) addition of hydrogen, steam, hydrogen halides and halogens (ii) oxidation by cold, dilute, acidified manganate(VII) ions to form the diol (iii) oxidation by hot, concentrated, acidified manganate(VII) ions leading to the rupture of the carbon–carbon double bond in order to determine the position of alkene linkages in larger molecules (iv) polymerisation (see also Section 21) b) describe the mechanism of electrophilic addition in alkenes, including using bromine/ethene and hydrogen bromide/propene as examples c) describe and explain the inductive effects of alkyl groups on the stability of cations formed during electrophilic addition d) describe the characteristics of addition polymerisation as exemplified by poly(ethene) and PVC e) deduce the repeat unit of an addition polymer obtained from a given monomer f) identify the monomer(s) present in a given section of an addition polymer molecule g) recognise the difficulty of the disposal of poly(alkene)s, i.e. non-biodegradability and harmful combustion products

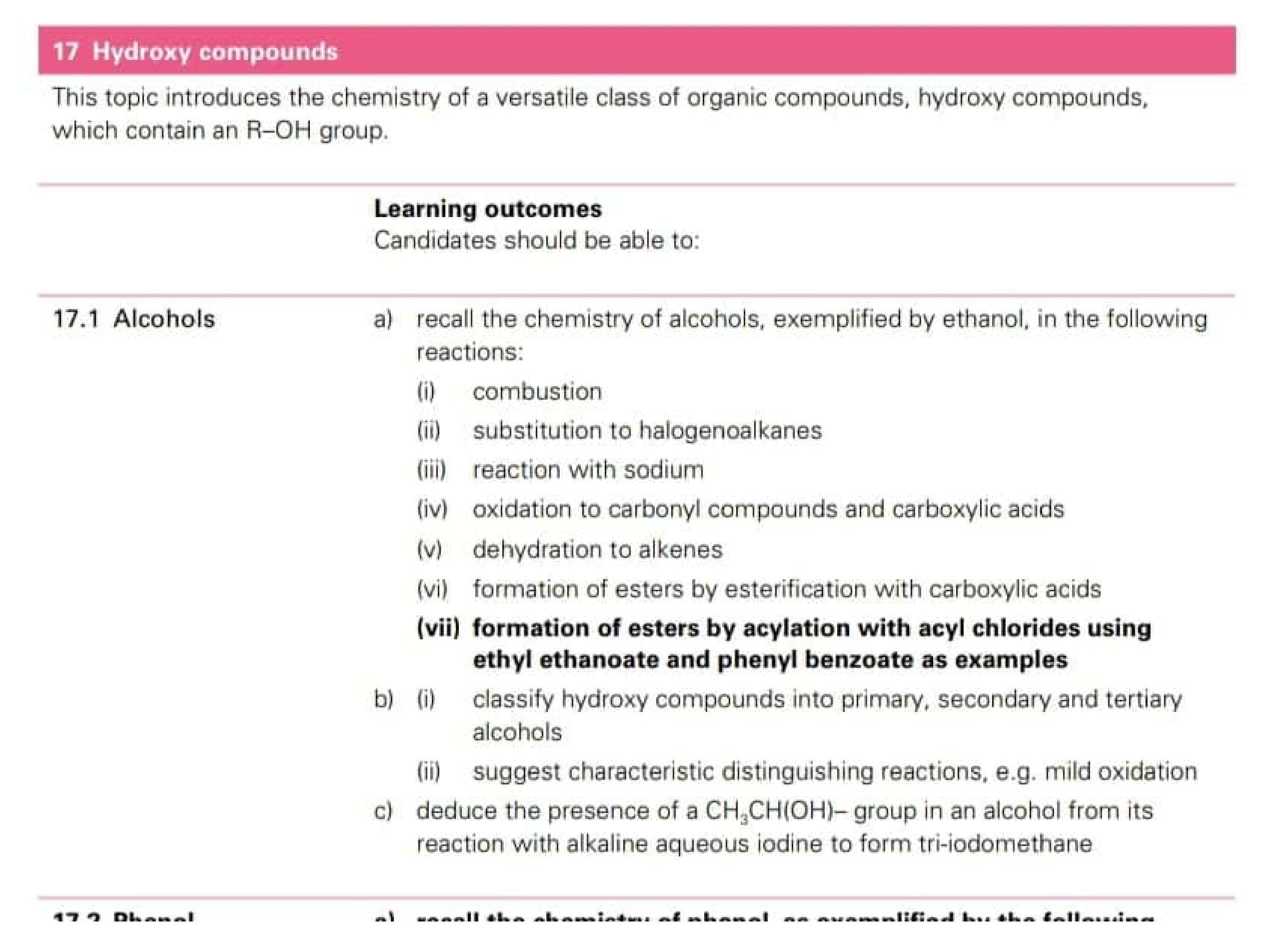


15.3 Hydrocarbons as fuels	a) describe and explain how the combustion reactions of alkanes make them suitable to be used as fuels in industry, in the home and in transport b) recognise the environmental consequences of: (i) carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine and of their catalytic removal (ii) gases that contribute to the enhanced greenhouse effect c) outline the use of infra-red spectroscopy in monitoring air pollution (see also Section 22.2)

16 Halogen derivatives

The inclusion of a halogen atom within an organic molecule affects its reactivity. The reactions of halogenoalkanes are very important in organic chemistry.

	Learning outcomes Candidates should be able to:
16.1 Halogenoalkanes	a) recall the chemistry of halogenoalkanes as exemplified by: (i) the following nucleophilic substitution reactions of bromoethane: hydrolysis, formation of nitriles, formation of primary amines by reaction with ammonia (ii) the elimination of hydrogen bromide from 2-bromopropane b) describe the S_N1 and S_N2 mechanisms of nucleophilic substitution in halogenoalkanes including the inductive effects of alkyl groups (see Section 15.2(c)) c) recall that primary halogenoalkanes tend to react via the S_N2 mechanism; tertiary halogenoalkanes via the S_N1 mechanism; and secondary halogenoalkanes by a mixture of the two, depending on structure
16.2 Relative strength of the C–Hal bond	a) interpret the different reactivities of halogenoalkanes (with particular reference to hydrolysis and to the relative strengths of the C–Hal bonds) b) explain the uses of fluoroalkanes and fluorohalogenoalkanes in terms of their relative chemical inertness c) recognise the concern about the effect of chlorofluoroalkanes on the ozone layer



17 Hydroxy compounds

This topic introduces the chemistry of a versatile class of organic compounds, hydroxy compounds, which contain an R–OH group.

Learning outcomes
Candidates should be able to:

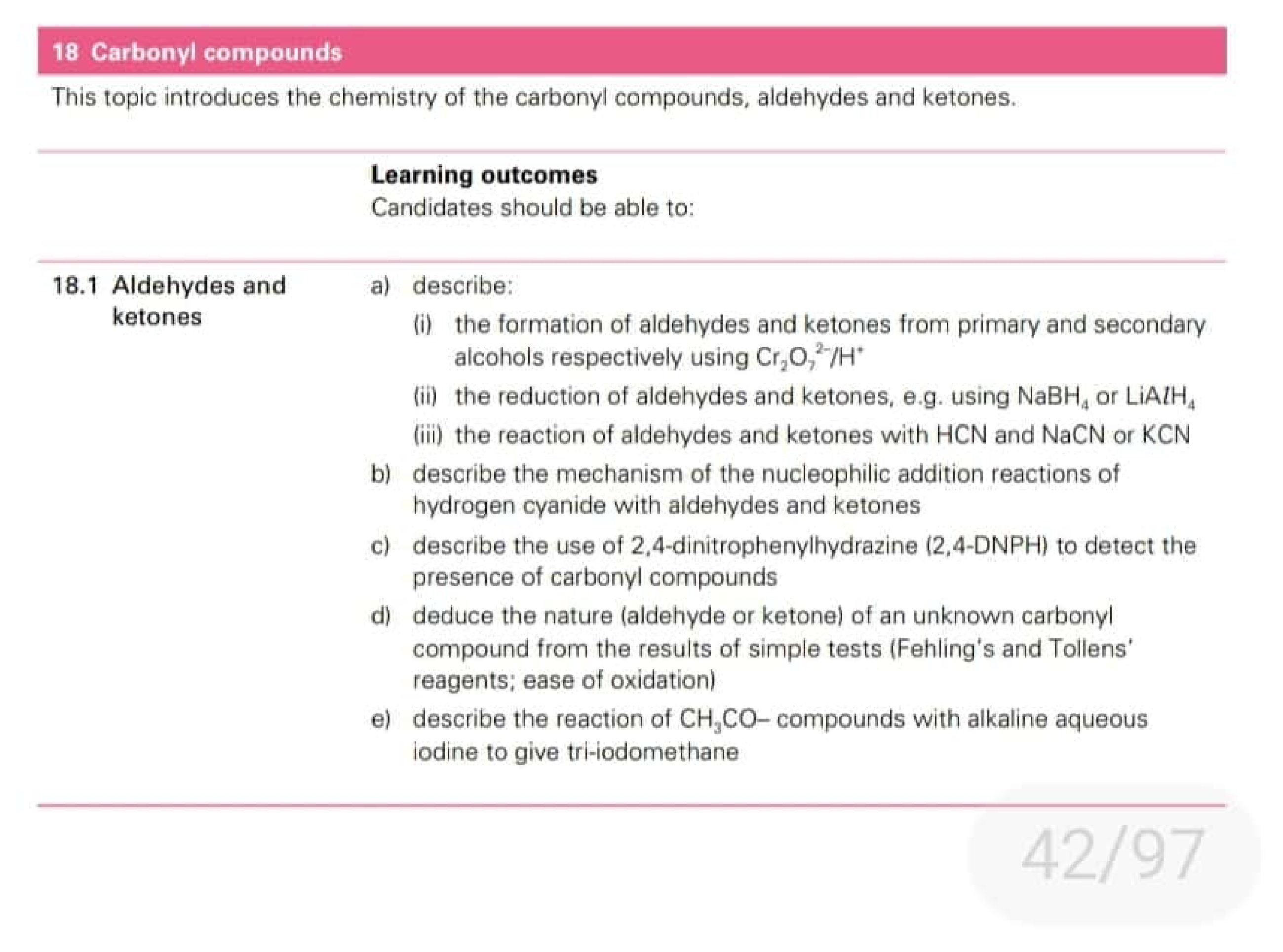
17.1 Alcohols

a) recall the chemistry of alcohols, exemplified by ethanol, in the following reactions:
  - (i) combustion
  - (ii) substitution to halogenoalkanes
  - (iii) reaction with sodium
  - (iv) oxidation to carbonyl compounds and carboxylic acids
  - (v) dehydration to alkenes
  - (vi) formation of esters by esterification with carboxylic acids
  - **(vii) formation of esters by acylation with acyl chlorides using ethyl ethanoate and phenyl benzoate as examples**

b) (i) classify hydroxy compounds into primary, secondary and tertiary alcohols
  - (ii) suggest characteristic distinguishing reactions, e.g. mild oxidation

c) deduce the presence of a $CH_3CH(OH)-$ group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane

17.2 Phenol a) **recall the chemistry of phenol, as exemplified by the following**



18 Carbonyl compounds

This topic introduces the chemistry of the carbonyl compounds, aldehydes and ketones.

	Learning outcomes Candidates should be able to:
18.1 Aldehydes and ketones	a) describe: (i) the formation of aldehydes and ketones from primary and secondary alcohols respectively using $Cr_2O_7^{2-}/H^+$ (ii) the reduction of aldehydes and ketones, e.g. using $NaBH_4$ or $LiAlH_4$ (iii) the reaction of aldehydes and ketones with HCN and NaCN or KCN b) describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones c) describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) to detect the presence of carbonyl compounds d) deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (Fehling's and Tollens' reagents; ease of oxidation) e) describe the reaction of CH_3CO- compounds with alkaline aqueous iodine to give tri-iodomethane

19 Carboxylic acids and derivatives

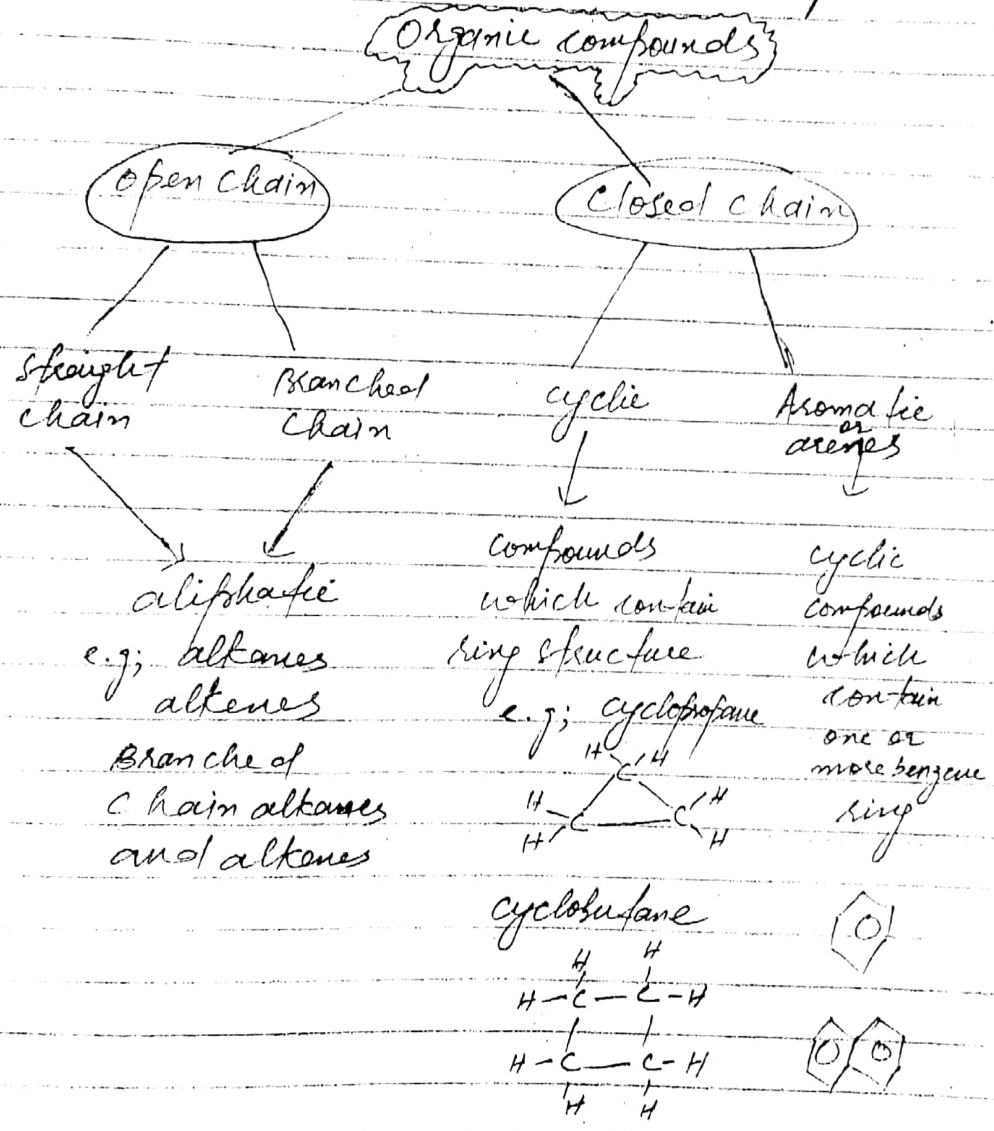
This topic introduces the chemistry of carboxylic acids and their derivatives.

	Learning outcomes Candidates should be able to:
19.1 Carboxylic acids	a) describe the formation of carboxylic acids from alcohols, aldehydes and nitriles b) describe the reactions of carboxylic acids in the formation of: (i) salts, by the use of reactive metals, alkalis or carbonates (ii) alkyl esters (iii) alcohols, by the use of $LiAlH_4$ **(iv) acyl chlorides** **c) recognise that some carboxylic acids can be further oxidised:** **(i) the oxidation of methanoic acid, HCO_2H, with Fehling's and Tollens' reagents** **(ii) the oxidation of ethanedioic acid, HO_2CCO_2H, with warm, acidified manganate(VII)** **d) explain the relative acidities of carboxylic acids, phenols and alcohols** **e) use the concept of electronegativity to explain the acidities of chlorine-substituted ethanoic acids**
19.2 Acyl chlorides	**a) describe the hydrolysis of acyl chlorides** **b) describe the reactions of acyl chlorides with alcohols, phenols, ammonia and primary amines** **c) explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides including the condensation (addition-elimination) mechanism for the hydrolysis of acyl chlorides**
19.3 Esters	a) describe the acid and base hydrolysis of esters b) state the major commercial uses of esters, e.g. solvents, perfumes, flavourings

Organic Chemistry

Organic chemistry is a branch of chemistry which deals with the study of carbon compounds excluding oxides of carbon, carbonates and hydrogen carbonates

Classification of organic compounds



Organic compounds

Open Chain

Closed chain

Straight chain

Branched Chain

cyclic

Aromatic or arenes

aliphatic
e.g; alkanes
alkenes
Branched Chain alkanes and alkenes

compounds which contain ring structure
e.g; cyclopropane
cyclobutane

cyclic compounds which contain one or more benzene ring

Representation of organic molecules

Molecular formula:- The formula which shows us the actual numbers of each type of atoms in a molecule. e.g;

Butane C_4H_{10}
Butene C_4H_8
Pentane C_5H_{12}

Structural formula:- This tells us about the atoms bonded to each carbon atom in the molecule.

the structural formula of Butane is $H_3C\,CH_2\,CH_2\,CH_3$

of Propene $H_3C\,CH=CH_2$

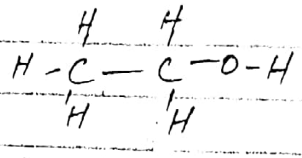
of But-2-ene $H_3C\,CH=CH\,CH_3$

of Butan-2-ol $H_3C\,CH_2\,CH_2\,CH_2OH$

Displayed formula:- The formula which shows all the bonds present in a molecule.

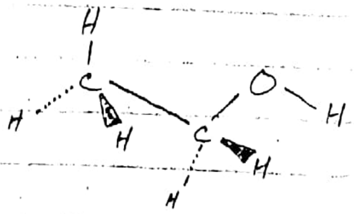
For example ethanol

2-dimensional

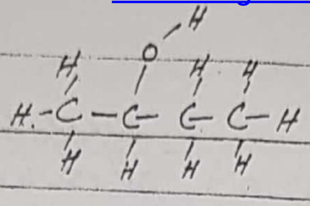


$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H$$

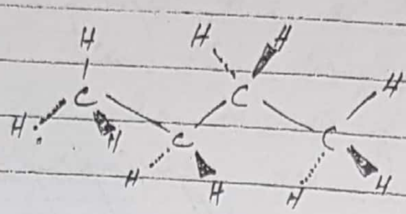
Displayed formula may be 3-dimensional



Butan-2-ol



2-dimensional



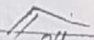
3-dimensional

Skeletal formula: Skeletal formula is also a type of displayed formula in which the symbols for carbon and hydrogen atoms are removed, as well the carbon to hydrogen bonds. The carbon to carbon bonds are left to place.

For example

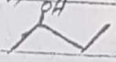
Skeletal formula of butane

propene

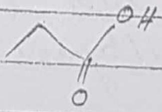


or

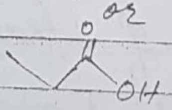
Butan-2-ol



Propanoic acid

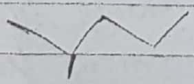


or



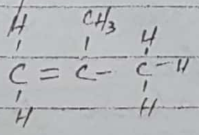
Ethene

2-methyl Pentane



or

2-methyl propene



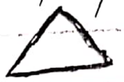
Benzene

cyclohexane

cyclopentane

cyclobutane

cyclopropane



Functional groups and naming of organic compounds

Functional group:- An atom or group of atoms which give characteristic properties to an organic compound is called functional group.

Double or triple covalent bonds are also the examples of functional group and are named as alkenes and alkynes respectively.

Naming of Straight Chain and Branched Chain alkanes

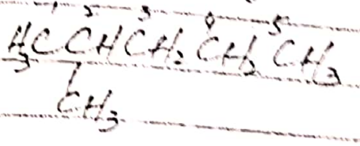
According to IUPAC following rules should be followed while naming branched chain alkanes

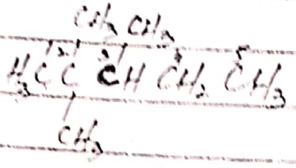
⇒ Select the longest chain of carbon atoms as parent chain

⇒ Number the parent chain from the side where the branch is neares

⇒ If the number of branches are 2 or more than 2, and are of the same type then use the prefix di, tri or tetra before the name of the branch.

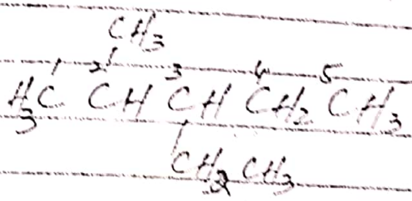
⇒ If the branches are different then they will be named using alphabetical orders e.g: ethyl will be named before methyl.


$\overset{1}{H_3C}\underset{CH_3}{\overset{2}{CH}}\overset{3}{CH_2}\overset{4}{CH_2}\overset{5}{CH_3}$

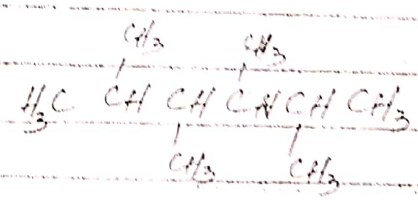

$H_3C\underset{CH_3}{\overset{CH_3}{C}}\overset{CH_3}{CH}CH_2CH_3$

2-methyl pentane
not 4-methyl pentane

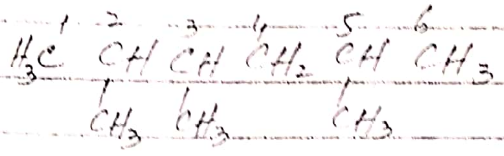
2,2,3-trimethyl pentane


$\overset{1}{H_3C}\overset{CH_3}{\overset{2}{CH}}\underset{CH_2CH_3}{\overset{3}{CH}}\overset{4}{CH_2}\overset{5}{CH_3}$

3-ethyl-2-methyl pentane


$H_3C\overset{CH_3}{CH}\underset{CH_3}{CH}\overset{CH_3}{CH}\underset{CH_3}{CH}CH_3$

2,3,4,5-tetramethylhexane


$\overset{1}{H_3C}\underset{CH_3}{\overset{2}{CH}}\underset{CH_3}{\overset{3}{CH}}\overset{4}{CH_2}\underset{CH_3}{\overset{5}{CH}}\overset{6}{CH_3}$

2,3,5-trimethyl hexane

IUPAC naming of alkenes

⇒ Selet the longest chain of carbon atoms which must contain double covalent bond as parent chain

⇒ Number the parent chain starting from the side where double bond is nearer.

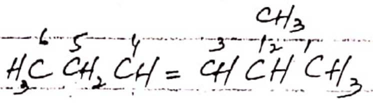
e.g.;

$H_2\overset{1}{C}=\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_3$ But-1-ene

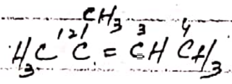
$H_3\overset{1}{C}\overset{2}{C}H=\overset{3}{C}H\overset{4}{C}H_3$ But-2-ene

⇒ If double bond is equally far from both sides, then preference will be given to the side where branch is nearer.

e.g.;



$H_3\overset{6}{C}\overset{5}{C}H_2\overset{4}{C}H=\overset{3}{C}H\overset{2}{\overset{CH_3}{C}}H\overset{1}{C}H_3$ 2-methyl hex-3-ene

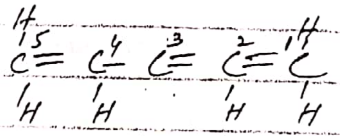


$H_3\overset{1}{C}\overset{2}{\overset{CH_3}{C}}=\overset{3}{C}H\overset{4}{C}H_3$ 2-methyl but-2-ene

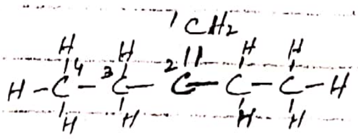
⇒ alkenes having two or more than two double covalent bonds are named by using the suffix "di" for two, "tri" for three and "tetra" for four

$H_2\overset{1}{C}=\overset{2}{C}H\overset{3}{C}H=\overset{4}{C}H_2$

Buta-1,3-diene



Penta-1,3,5-triene



↑ Branch

2-ethyl But-1-ene

Naming of halogen alkanes

halogen alkanes are obtained by replacing one hydrogen atom of alkane with a halogen atom.

=> Their general formula is $C_nH_{2n+1}X$ where X represents halogen atom.

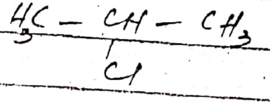
=> Halogen alkanes are named by selecting the longest chain containing halogen atom.

=> Numbering is started from the side where halogen is nearer

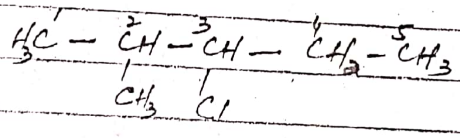
=> Chloro, Bromo, iodo is used to name chlorine, Bromine and iodine respectively

H_3C-CH_2-Cl Chloroethane

$H_3C-CH_2-CH_2-Cl$ 1-chloro propane

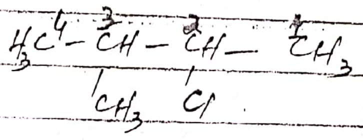


$H_3C-CH(Cl)-CH_3$ 2-chloro propane



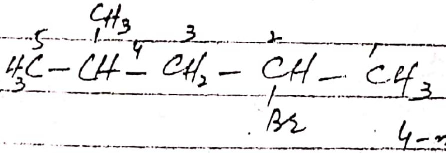
$H_3\overset{1}{C}-\overset{2}{C}H(CH_3)-\overset{3}{C}H(Cl)-\overset{4}{C}H_2-\overset{5}{C}H_3$

2-methyl-3-chloro pentane

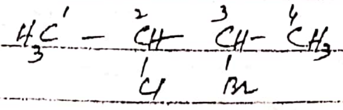


$H_3\overset{4}{C}-\overset{3}{C}H(CH_3)-\overset{2}{C}H(Cl)-\overset{1}{C}H_3$

3-methyl-2-chloro butane



$H_3\overset{5}{C}-\overset{4}{C}H(CH_3)-\overset{3}{C}H_2-\overset{2}{C}H(Br)-\overset{1}{C}H_3$ 4-methyl-2-bromopentane



$H_3\overset{1}{C}-\overset{2}{C}H(Cl)-\overset{3}{C}H(Br)-\overset{4}{C}H_3$ 3-bromo-2-chloro butane

Classification of halogen alkanes

(i) **Primary halogen alkanes:-** If the carbon atom bonded with halogen atom is directly bonded with one carbon atom or no carbon atom or If halogen bearing carbon atom which is also called α- carbon (alpha carbon) is bonded with minimum 2- hydrogen atoms, this is called primary halogen alkane.

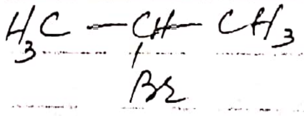
H_3C-CH_2-Cl

$H_3C-CH_2-CH_2-Cl$

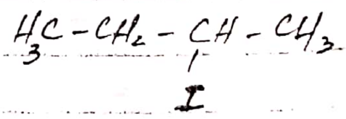
H_3C-Cl

Primary halogen alkane

(ii) **Secondary halogen alkanes:-** Halogen alkanes in which alpha carbon atom is bonded with two carbon atoms directly or bonded with one hydrogen atom are called secondary halogen alkanes.

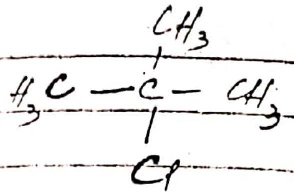


$H_3C-\underset{Br}{\underset{|}{CH}}-CH_3$

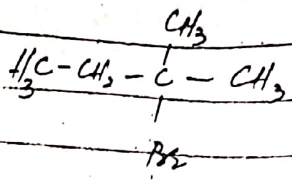


$H_3C-CH_2-\underset{I}{\underset{|}{CH}}-CH_3$

Tertiary halogen alkanes:- Halogen alkanes in which α- carbon is bonded with three other carbon atoms or α- carbon does not contain any hydrogen atom.



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{C}}-CH_3$$



$$H_3C-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}-CH_3$$

Ethers :- Ethers are the class of organic compounds in which two alkyl groups are bonded with one oxygen atom.

General representation R-O-R
R- alkyl group

$CH_3CH_2OCH_3$

$H_3COC_2H_5$

$C_3H_7OC_2H_5$.

Note :- Naming of ether is not required as it is not a part of syllabus, only its identification is required.

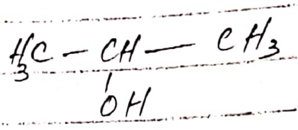
Alcohols or alkanols

Alcohols are obtained by replacing one hydrogen of an alkane by "OH" group.
Their general formula is $C_nH_{2n+1}OH$
They are named by suffixing "ol" after replacing "e" of alkanes.

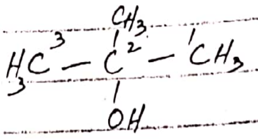
naming of alcohols

CH_3-CH_2-OH ethanol

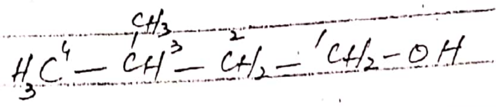
$H_3C-CH_2-CH_2-OH$ Propan-1-ol



$H_3C-\underset{\overset{|}{OH}}{CH}-CH_3$ propan-2-ol



$H_3\overset{3}{C}-\underset{\overset{|}{OH}}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}-\overset{1}{C}H_3$ 2-methyl propan-2-ol



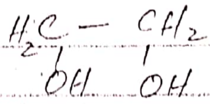
$H_3\overset{4}{C}-\overset{\overset{CH_3}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}H_2-OH$

3-methyl butan-2-ol

Naming of polyhydroxy alcohols

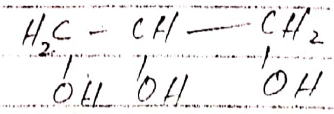
Alcohols containing more than one hydroxyl group "OH" are called polyhydroxy alcohols.

e.g;



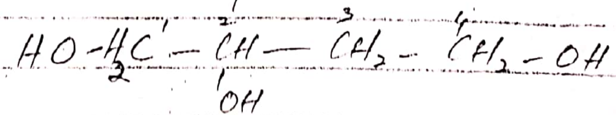
$\underset{\overset{|}{OH}}{H_2C}-\underset{\overset{|}{OH}}{CH_2}$

ethan-1,2-diol



$\underset{\overset{|}{OH}}{H_2C}-\underset{\overset{|}{OH}}{CH}-\underset{\overset{|}{OH}}{CH_2}$

propan-1,2,3-triol



$HO-H_2\overset{1}{C}-\underset{\overset{|}{OH}}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_2-OH$

Butan-1,2,4-triol

Classification of alcohols

Primary alcohols:- Alcohols in which α- carbon atom is directly bonded with one carbon atom or with minimum 2- hydrogen atoms are called primary alcohols.

H_3C-OH

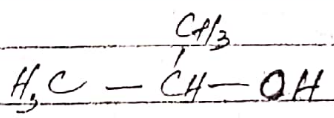
H_3C-CH_2-OH

$H_3C-CH_2-CH_2-OH$

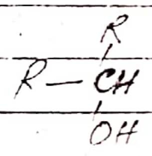
$R-OH$

$R-CH_2-OH$

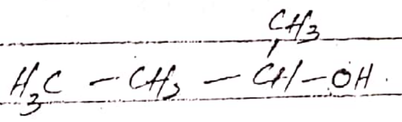
Secondary alcohols:- Alcohols in which α-carbon atom is directly bonded two carbon atoms or with one hydrogen atom is called secondary alcohol.



$H_3C-\overset{CH_3}{\overset{|}{C}H}-OH$

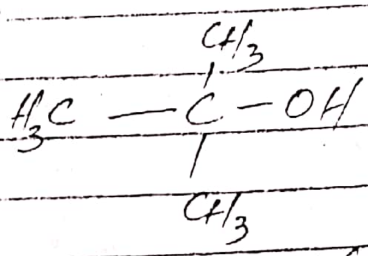


$R-\overset{R}{\overset{|}{\underset{OH}{\underset{|}{CH}}}}$

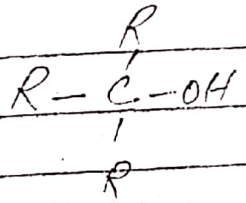


$H_3C-CH_2-\overset{CH_3}{\overset{|}{C}H}-OH$

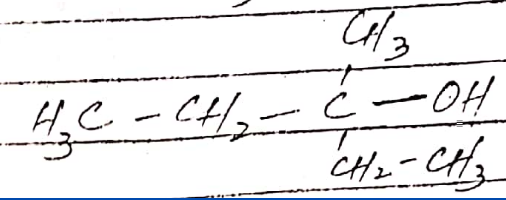
tertiary alcohols:- Alcohols in which α- carbon atom is directly bonded with three other carbon atoms or not bonded with any hydrogen atom.



$H_3C-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH$



$R-\overset{R}{\overset{|}{\underset{R}{\underset{|}{C}}}}-OH$



$H_3C-CH_2-\overset{CH_3}{\overset{|}{\underset{CH_2-CH_3}{\underset{|}{C}}}}-OH$

Amines

Amines are the derivatives of ammonia. They are formed when one or more hydrogen atoms of ammonia are replaced by alkyl groups.

They are named by suffixing amine with alkyl

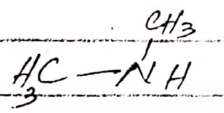
For example, CH_3NH_2 methylamine
$H_3C\ CH_2\ NH_2$ ethyl amine
$H_3C\ CH_2\ CH_2\ NH_2$ propylamine

Classification of amines

Primary amines:- Amines which are obtained by replacing one hydrogen atom of ammonia with an alkyl group

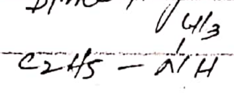
H_3C-NH_2
$H_3C-CH_2-NH_2$

Secondary amines:- Amines which are obtained by replacing two hydrogen atoms of ammonia with two alkyl groups.



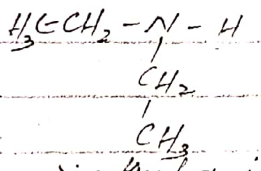
$H_3C-\overset{CH_3}{N}H$

Dimethylamine



$C_2H_5-\overset{CH_3}{N}H$

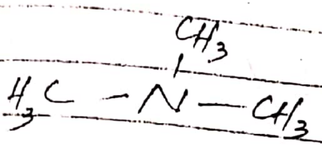
methylethylamine



$H_3C-CH_2-\underset{CH_2-CH_3}{N}-H$

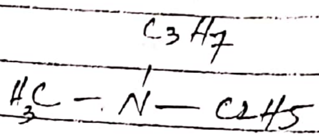
Diethylamine

Testiary amines:- Amines which are obtained by replacing all three hydrogen atoms of ammonia.



$H_3C-\overset{CH_3}{\overset{|}{N}}-CH_3$

Trimethylamine

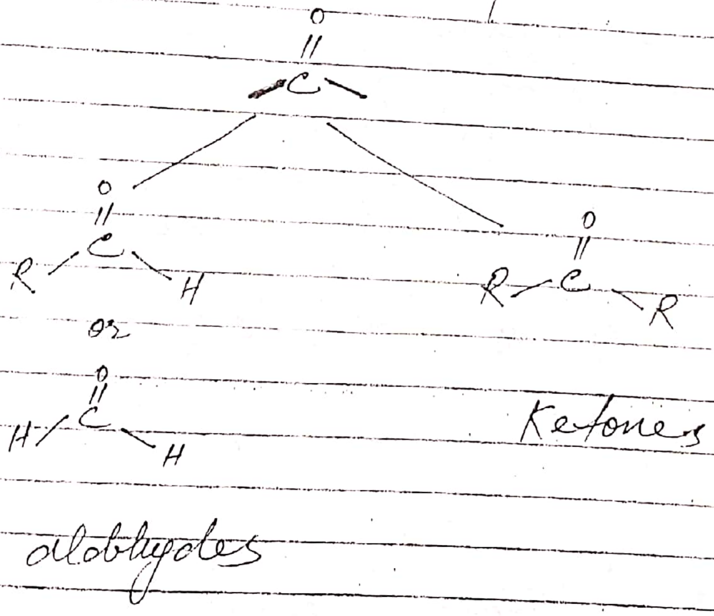


$H_3C-\overset{C_3H_7}{\overset{|}{N}}-C_2H_5$

Propyl ethyl methyl amine

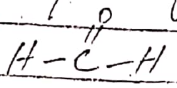
Naming of compounds containing Carbonyl ($-\overset{O}{\overset{||}{C}}-$) group

Carbonyl group ($-\overset{O}{\overset{||}{C}}-$) is a type of functional group which gives two different types of organic compounds

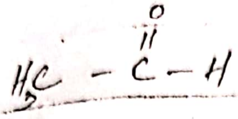


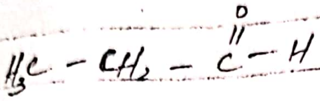
Naming of aldehydes: They are named by suffixing "al" after replacing "e" of alkanes.

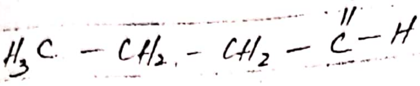
For example



$H-\overset{O}{\overset{||}{C}}-H$ methanal

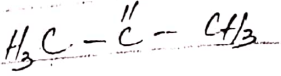

$H_3C-\overset{O}{\overset{\|}{C}}-H$ ethanal

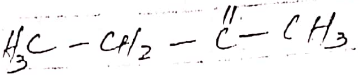

$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-H$ Propanal


$H_3C-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$ Butanal

Naming of Ketones:- They are named by suffixing "One" after replacing "e" of alkanes.

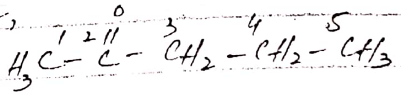
For example


$H_3C-\overset{O}{\overset{\|}{C}}-CH_3$ Propanone

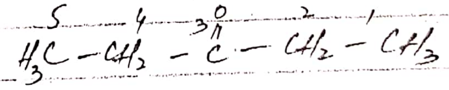

$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ Butanone

⇒ Ketones containing 5 or more than 5 carbon atoms are numbered from the side where the carbonyl carbon is nearer.

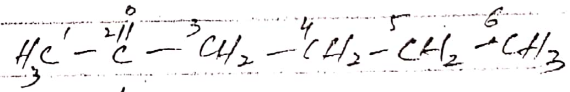
For example,


$H_3\overset{1}{C}-\overset{2}{\overset{O}{\overset{\|}{C}}}-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_3$

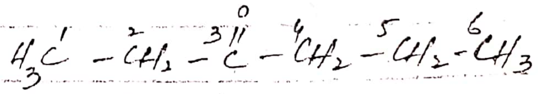
Pentan-2-one


$H_3\overset{5}{C}-\overset{4}{C}H_2-\overset{3}{\overset{O}{\overset{\|}{C}}}-\overset{2}{C}H_2-\overset{1}{C}H_3$

Pentan-3-one


$H_3\overset{1}{C}-\overset{2}{\overset{O}{\overset{\|}{C}}}-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$

Hexan-2-one


$H_3\overset{1}{C}-\overset{2}{C}H_2-\overset{3}{\overset{O}{\overset{\|}{C}}}-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$

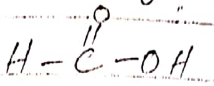
Hexan-3-one

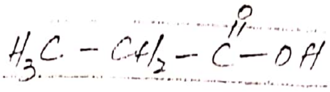
Carboxylic acids

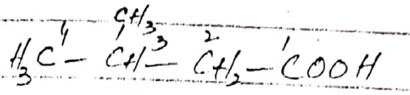
Organic compounds which contain carboxylic acid group $(-\overset{O}{\overset{\|}{C}}-OH)$ as functional group are called carboxylic acids. Carboxylic acid group is made up of two functional group, one carbonyl group $(-\overset{O}{\overset{\|}{C}}-)$ and hydroxyl group $(-OH)$

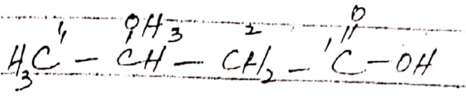
⇒ They are named by suffixing "oic acid" after replacing "e" of alkanes.

⇒ Their general formula is $C_nH_{2n+1}COOH$


$H-\overset{O}{\overset{\|}{C}}-OH$ methanoic acid

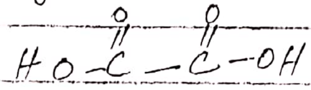

$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-OH$ Propanoic acid

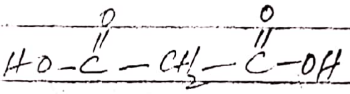

$\overset{4}{H_3C}-\overset{CH_3}{\overset{|}{\overset{3}{CH}}}-\overset{2}{CH_2}-\overset{1}{C}OOH$ 3-methyl butanoic acid

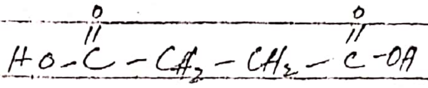

$\overset{4}{H_3C}-\overset{OH}{\overset{|}{\overset{3}{CH}}}-\overset{2}{CH_2}-\overset{O}{\overset{\|}{\overset{1}{C}}}-OH$ 3-hydroxy butanoic acid

Dicarboxylic acids

Organic compounds containing two carboxylic acid groups are called dicarboxylic acids

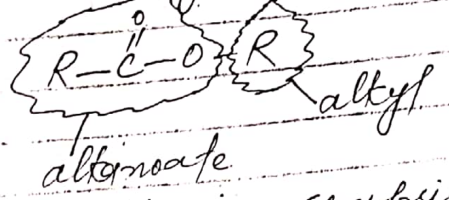

$HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH$ Ethandioic acid


$HO-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$ Propan dioic acid


$HO-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$ Butan dioic acid

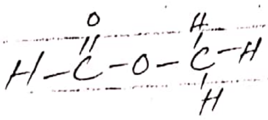
Derivatives of Carboxylic acids

(i) **Esters**:- Esters are the derivatives of carboxylic acids and alcohols. Esters are generally represented as

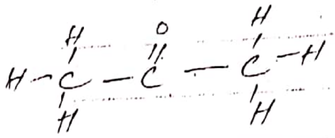


$R-\overset{O}{\overset{\|}{C}}-O-R$

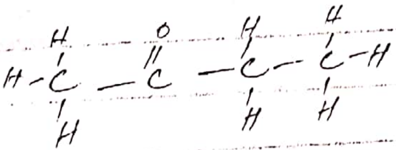
Name of ester is comprised of two parts, one part is derived from alkyl and other part from alkanoate



$H-\overset{O}{\overset{\|}{C}}-O-\underset{H}{\overset{H}{C}}-H$ methyl methanoate

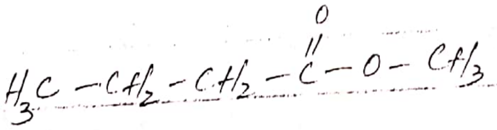


$H-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{H}{C}}-H$ methyl ethanoate

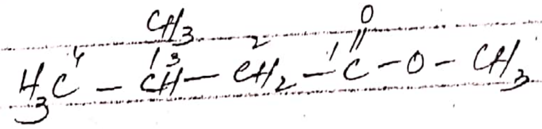


$H-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$ ethyl ethanoate

Isomers



$H_3C-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_3$ methyl butanoate



$H_3\overset{4}{C}-\overset{CH_3}{\overset{|}{\overset{3}{CH}}}-\overset{2}{CH_2}-\overset{O}{\overset{\|}{\overset{1}{C}}}-O-CH_3$ methyl-2-methyl propanoate

(ii) Acyl Chlorides or acid Chlorides

Organic compounds which are obtained when "OH" of Carboxylic acid is replaced by chlorine atom.

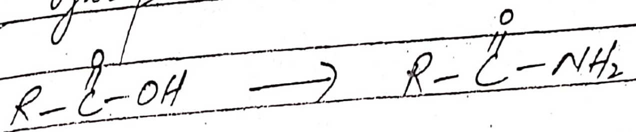
Acyl chlorides are named by suffixing "oyl chloride" after replacing "e" of alkanes.

For example $H-\overset{O}{\overset{\|}{C}}-Cl$ methanoyl chloride

$CH_3-\overset{O}{\overset{\|}{C}}-Cl$ ethanoyl chloride

$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-Cl$ propanoyl chloride

(iii) **Acid amides** :- Organic compounds which are obtained by replacing "OH" of Carboxylic acid with "NH₂" group are called acid amides.



$$R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2$$

Nitriles :- Organic compounds which contain cyanide (–CN) functional group are called nitriles.

Nitriles are generally represented as

$R-C\equiv N$

they are named by suffixing nitrile with the name of alkane

H_3C-CN ethane nitrile

H_3C-CH_2-CN propane nitrile

$H_3C-CH_2-CH_2-CN$ Butane nitrile

Isomerism

Compounds which have same molecular formula but different structures are called isomers and this phenomenon is called isomerism.

Types of isomers

Structural isomers

Compounds which have same molecular formula but different structural formula

Stereo isomers

Compounds which have same molecular and structural formula but different arrangement of atoms in space or different displayed formula

Types of structural isomers

(i) Chain isomers
(ii) Position isomers
(iii) Functional group isomers

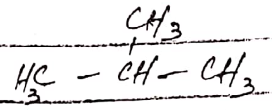
Chain isomers

Isomers which are different from each other due to the difference in chain length are called chain isomers.

For example

$H_3C-CH_2-CH_2-CH_3$

n- butane

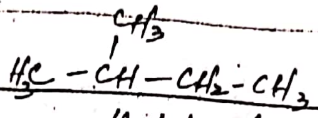


$H_3C-CH(CH_3)-CH_3$

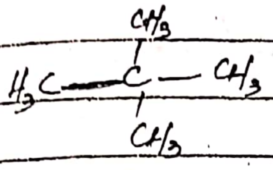
2-methyl propane

$H_3C-CH_2-CH_2-CH_2-CH_3$

n- Pentane


$H_3C-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3$

2- methyl butane


$H_3C-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

2,2 - dimethyl propane

(2) Position isomers

Types of isomers which differ from each other due to difference in the position of functional group.

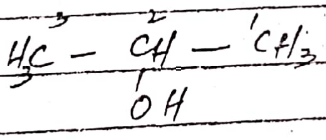
$CH_3-CH=CH-CH_3$

But-2-ene

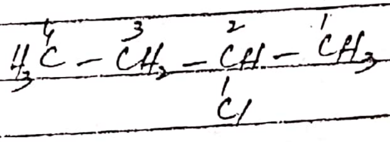
$H_2C=CH-CH_2-CH_3$

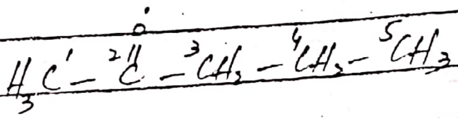
But-1-ene

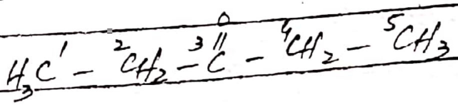
$H_3\overset{3}{C}-\overset{2}{CH_2}-\overset{1}{CH_2}-OH$ Propan-1-ol


$H_3\overset{3}{C}-\underset{OH}{\underset{|}{\overset{2}{CH}}}-\overset{1}{CH_3}$ Propan-2-ol

$H_3\overset{4}{C}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_2}-Cl$ 1- Chlorobutane


$H_3\overset{4}{C}-\overset{3}{CH_2}-\underset{Cl}{\underset{|}{\overset{2}{CH}}}-\overset{1}{CH_3}$ 2- Chloro butane


$H_3\overset{1}{C}-\overset{O}{\overset{\|}{\overset{2}{C}}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3}$ Pentan-2-one


$H_3\overset{1}{C}-\overset{2}{CH_2}-\overset{O}{\overset{\|}{\overset{3}{C}}}-\overset{4}{CH_2}-\overset{5}{CH_3}$ Pentan-3-one

(3) Functional group Isomers

Compounds which have same molecular formula but have different functional groups.

For example alcohols and ethers with same number of carbon atoms are isomers of each other.

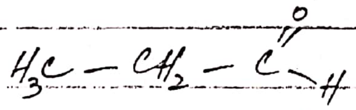
① H_3C-CH_2-OH ② $H_3C-O-CH_3$

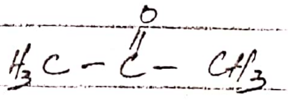
①. $H_3C-CH_2-CH_2-OH$ (2) $H_3C-CH_2-O-CH_3$

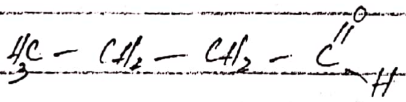
(1) $H_3C-CH_2-CH_2-CH_2-OH$ (2) $H_3C-O-CH_2-CH_2-CH_3$

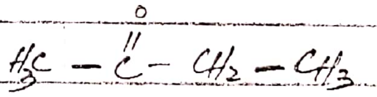
③ $H_3C-CH_2-O-CH_2-CH_3$

Aldehydes and Ketones with same number of carbon atoms are isomers of each other.

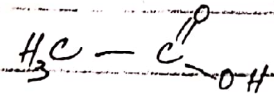
①

$H_3C-CH_2-C(=O)-H$

②

$H_3C-C(=O)-CH_3$

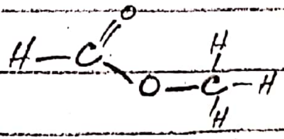
(1)

$H_3C-CH_2-CH_2-C(=O)-H$

(2)

$H_3C-C(=O)-CH_2-CH_3$

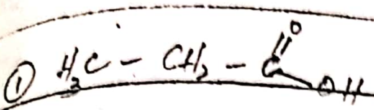
Carboxylic acids and esters with same number of carbon atoms are isomers of each other.


$H_3C-C(=O)-OH$

ethanoic acid

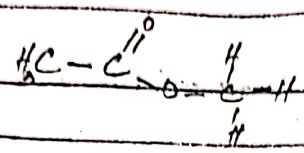

$H-C(=O)-O-CH_3$

methyl methanoate

① 

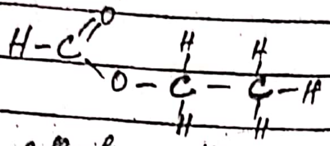
$H_3C-CH_2-C(=O)-OH$

Propanoic acid

(2) 

$H_3C-C(=O)-O-CH_3$

methyl ethanoate

(3) 

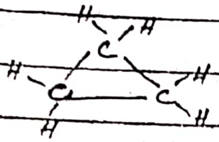
$H-C(=O)-O-CH_2-CH_3$

ethyl methanoate

$H_3C-CH=CH_2$

Propene

C_3H_6



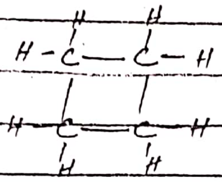
cyclopropane

(C_3H_6)

$H_3C-CH=CH-CH_3$

But-2-ene

(C_4H_8)



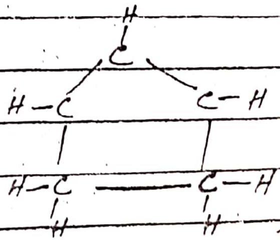
(C_4H_8)

cyclobutane

$H_3C-CH_2-CH_2-CH=CH_2$

Pent-1-ene

(C_5H_{10})



cyclopentane

(C_5H_{10})

Types of Stereoisomers

There are two types of stereoisomers
(i) Geometrical isomers or cis-trans isomers
(ii) Optical isomers

(i) Geometrical or cis-trans isomers

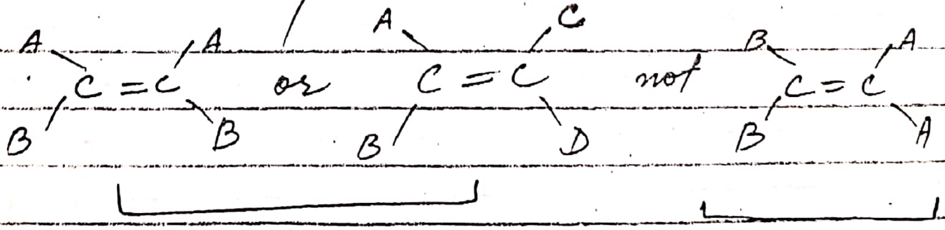
Compounds which are different from each other due to the difference in arrangement of atoms or group of atoms in space are called cis-trans or geometrical isomers.

⇒ Geometrical isomers arise due to the restricted **rotation** of double bond between carbon atoms (C=C)

Important features to show cis-trans isomerism

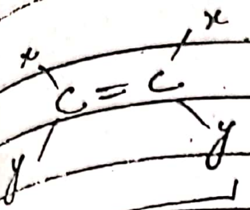
(1) Presence of double covalent bond between carbon atoms
(2) The two atoms or group of atoms attached to each carbon atom must be different.

For example

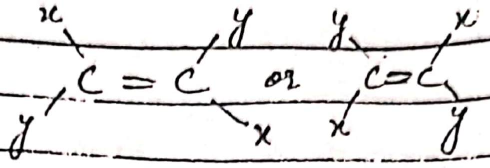


Can show cis-trans isomers

Cannot show cis-trans isomers

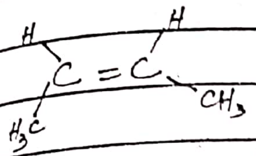


Similar groups at one side
cis - isomer

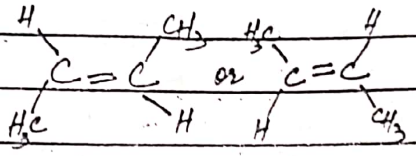


Similar groups at opposite side
Trans - isomers

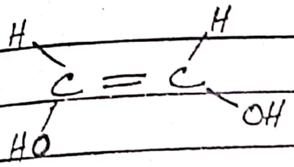
Examples of Geometrical isomers



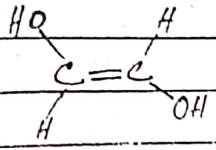
cis-2-butene



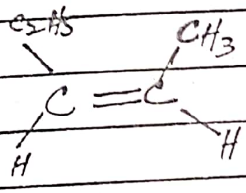
trans-2-butene



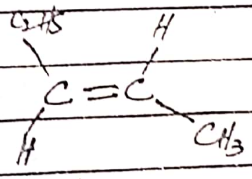
cis



trans

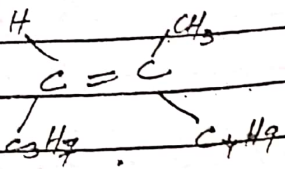


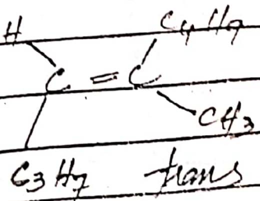
cis



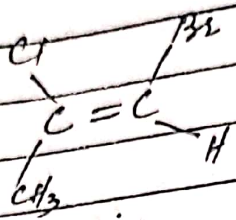
trans

Important:- If all four groups are different then cis isomers will be the one which has lighter groups (groups have lower Mr) at one side and heavier groups at same side.

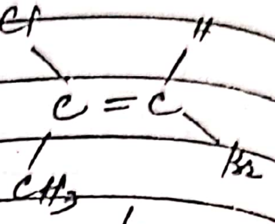




trans



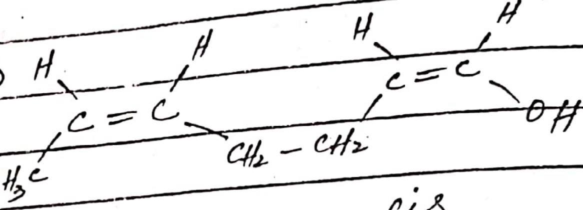
cis



trans

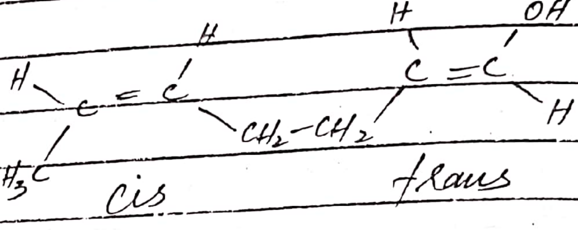
$H_3C-CH=CH-CH_2-CH_2-CH=CH.OH$ (4 Isomers)

(1)



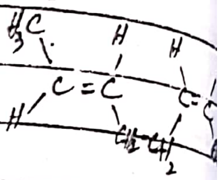
cis cis

(2)



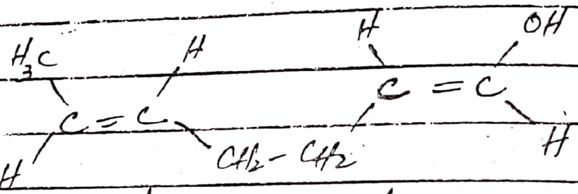
cis trans

(3)



trans - cis

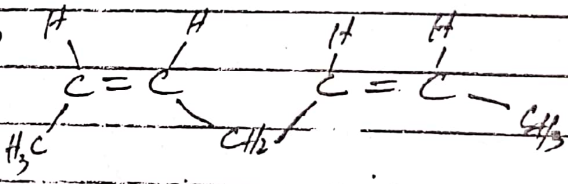
(4)



trans trans

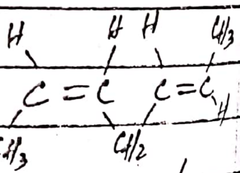
$H_3C-CH=CH-CH_2-CH=CHCH_3$ (only 3 isomers)

(1)



cis cis

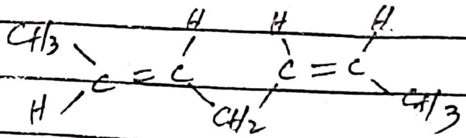
(2)



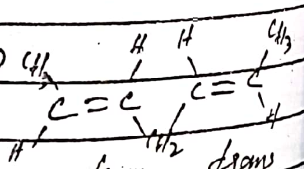
cis - trans

same

(3)



(4)



trans - trans

2 and 3 are same

(2) Optical Isomers

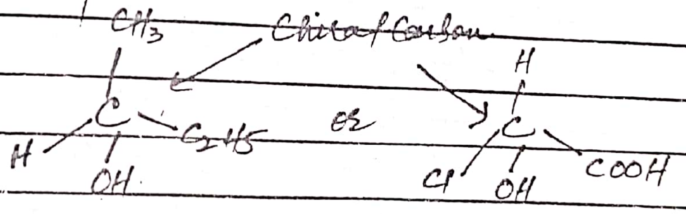
Compounds which have same molecular and structural formula but have spatial or 3D arrangement of atoms in space.

⇒ optical isomers rotate plane polarised light in different directions i.e., if one rotates towards right, other rotates towards left

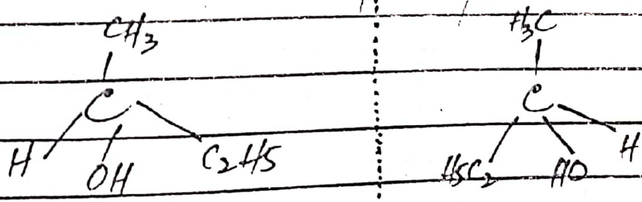
⇒ optical isomers have same physical and chemical properties but rotate plane polarised light differently.

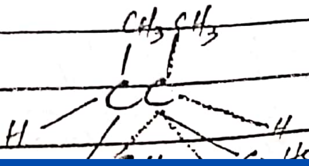
Conditions required to show optical isomerism

(i) Compounds which contain chiral carbon atom (carbon atom bonded with four different atoms or groups of atoms) show optical isomerism.



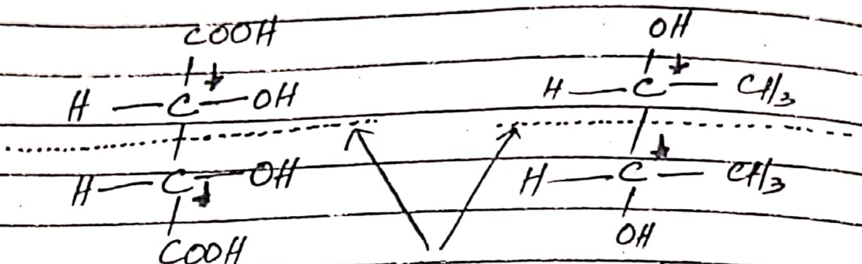
(ii) Compound and its mirror image are called isomers of each other if they are not superimposable





← non superimposable

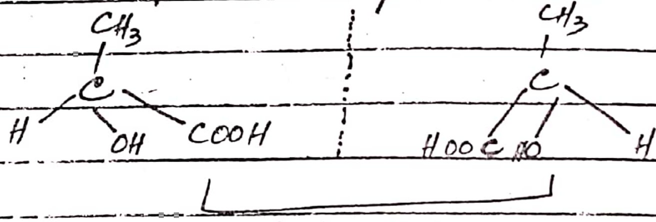
(3) There should not be any line of symmetry in the molecule i.e; molecule should be non symmetrical.



Line of symmetry

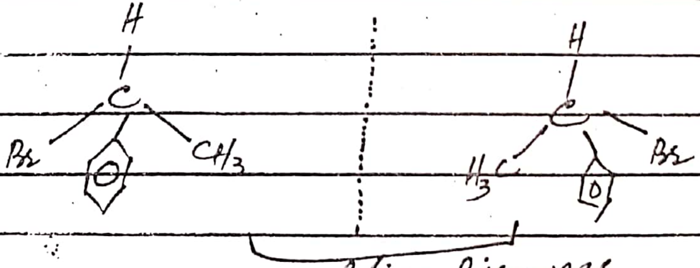
Both the molecules contain a chiral carbon atom but due to the line of symmetry, cannot show optical isomers rather just a Isomers.

Examples of optical isomers

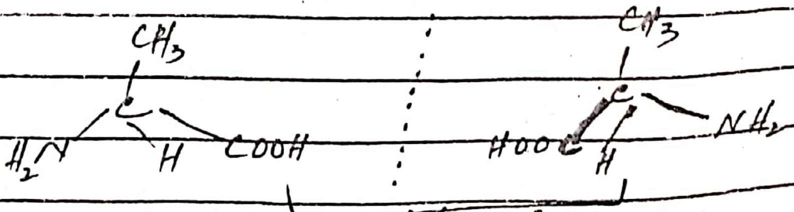


optical isomers

Optical isomers are also called enantiomers

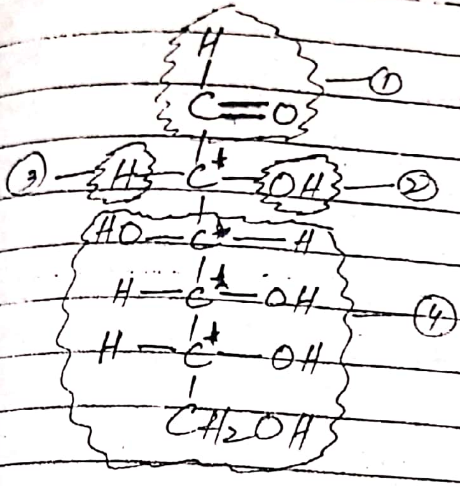


optical isomers

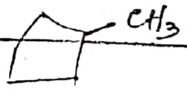


optical isomers

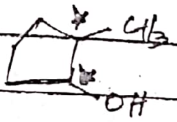
Identify the number of chiral Carbon in the given molecules

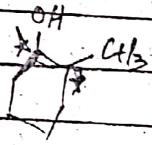


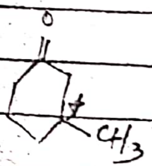
Four carbon atoms with sterie are chiral carbon atoms.

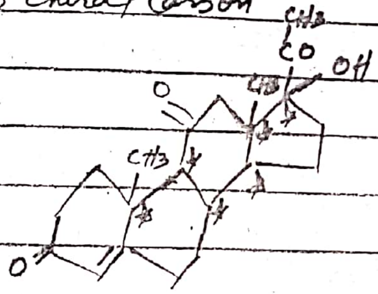


No chiral Carbon

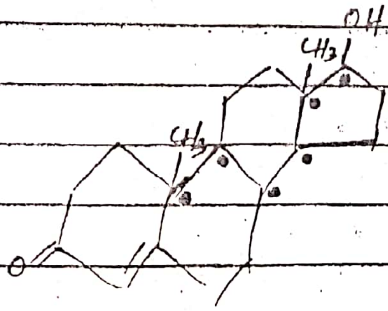




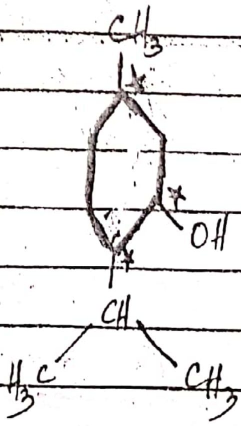




6 chiral carbon atoms



6 - chiral carbon



3 - Chiral Carbon atoms

Alkanes

Alkanes are the straight chain hydrocarbons with general formula C_nH_{2n+2} where n = number of carbon atoms. First four members of alkane family are gases.

Low reactivity of alkanes

Alkanes are also known as paraffins which means less reactive or little affinity. Alkanes do not react with acids, bases oxidising agent and other polar reagents due to the non polar nature of alkanes.

The non polar nature of alkanes is due to the non polar covalent bond between carbon atoms and very less polar covalent bond between carbon and hydrogen atoms which is due to the very less electronegativity difference between carbon and hydrogen.

Another reason of less reactivity of alkanes is due to the presence of strong σ-bonds (sigma bonds) which needs very high amount of energy to break.

Chemical properties of alkanes

(i) **Combustion reactions:-** Those reactions in which a substance burns in the presence of oxygen to produce heat are called combustion reactions.

Alkanes combust to give three different types of reactions.

Complete combustion (In excess of oxygen)

$CH_4 + O_2 \longrightarrow CO_2 + {}^{2}H_2O + Heat$

$C_8H_{18} \overset{12\frac{1}{2}}{+{}^{2}} O_2 \longrightarrow 8CO_2 + 9H_2O + Heat$
octane

Incomplete combustion (In limited oxygen)

$CH_4 + O_2 \longrightarrow CO_2 + CO + H_2O + Heat$

OR

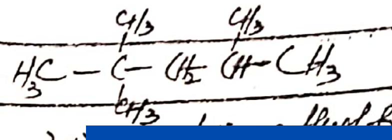
$CH_4 + O_2 \longrightarrow CO_2 + CO + \underset{\substack{(s)\\ \uparrow \\ soot}}{C} + H_2O + Heat$

Flames which produce carbon are called sooty flame or smoky flame.

Combustion of high octane and low octane

Branched chain alkanes burn slowly in internal combustion engine as compared to straight chain alkanes, so branched chain alkanes undergo complete combustion and are better fuel, because they do not cause any knocking in engine

$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3 + O_2 \longrightarrow CO_2 + H_2O + Heat$
n-octane (low octane)



$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-CH_3 + O_2 \longrightarrow CO_2 + H_2O + Heat$

2, thyl Pentane (High-octane)

(2) **Cracking**:- cracking is a process by which long chain hydrocarbons are converted to small chain hydrocarbons by heating them to high temperature.

Purpose of cracking is to convert less useful hydrocarbons to more useful hydrocarbons.

Conditions for cracking:

High temperature i-e; 400°c to 500°c
High pressure i-e; 10 atm
Absence of oxygen
Presence of catalyst i-e; mixture of Al_2O_3 and SiO_2
or Porcelain chips

Examples of cracking

A compound when cracked gives variety of products depends upon conditions of temperature and pressure. e.g;

$$C_8H_{18} \xrightarrow{\text{cracking}} H_3C(CH_2)_4CH_3 + H_2C=CH_2$$

Hexane ethene

OR

$$C_8H_{18} \longrightarrow 2\ CH_3CH_2CH=CH_2 + H_2$$

Butene

OR

$$C_8H_{18} \longrightarrow H_3C(CH_2)_3CH_3 + H_3C-CH=CH_2$$

Pentane Propene

Similarly

$$C_{17}H_{36} \longrightarrow C_8H_{18} + C_3H_6 + 3C_2H_4$$

octane propene ethene

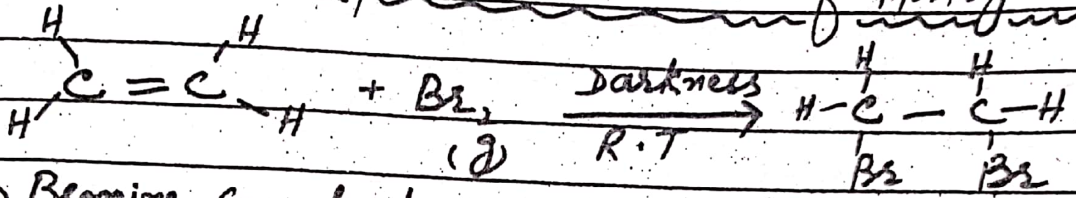
Chemical Properties of alkenes

Electrophilic addition reactions

Electrophile
Electrophi — phile
↓ Electron — ↓ Loving

Those reactions in which an electrophile (Positively charged substance) attacks over the π electrons and form a new bond after breaking the π bond is called Electrophilic addition reactions

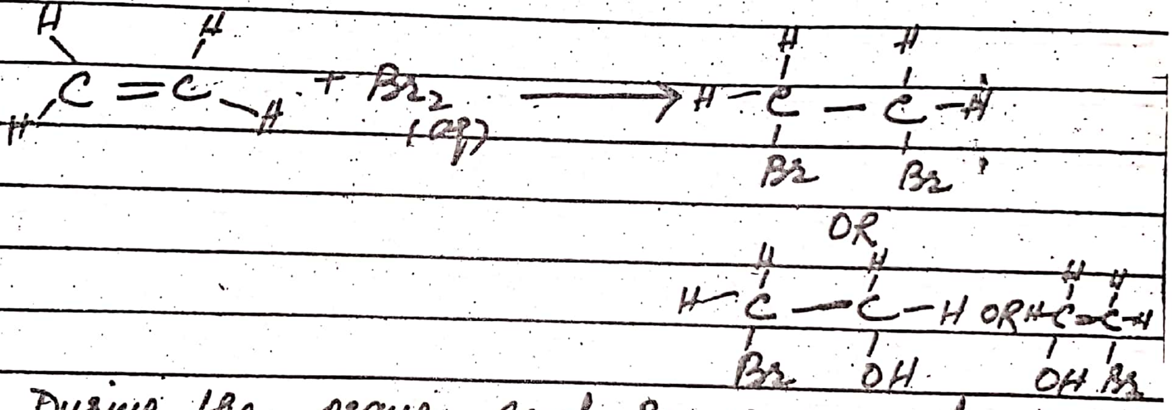
(1) Electrophilic addition of Halogens



$$H_2C=CH_2 + Br_{2(g)} \xrightarrow[R.T]{Darkness} H-\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-H$$

⇒ Bromine can also be used with CCl_4 solvent.

With aqueous Bromine



$$H_2C=CH_2 + Br_{2(aq)} \longrightarrow H-\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-H$$

OR

$$H-\underset{Br}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H \text{ OR } H-\underset{OH}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-H$$

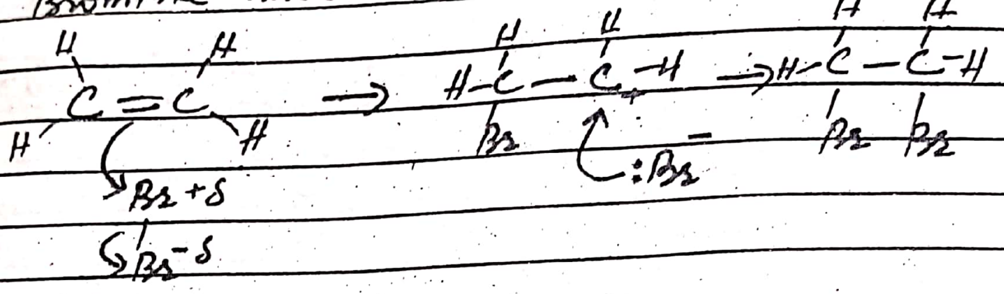
During the, orange red Bromine water $Br_{2(aq)}$ turns colourless.

Chlorine and Iodine also react in a similar way but with Cl_2 reaction is very fast because it is more reactive than Br_2. Reaction with I_2 is very slow.

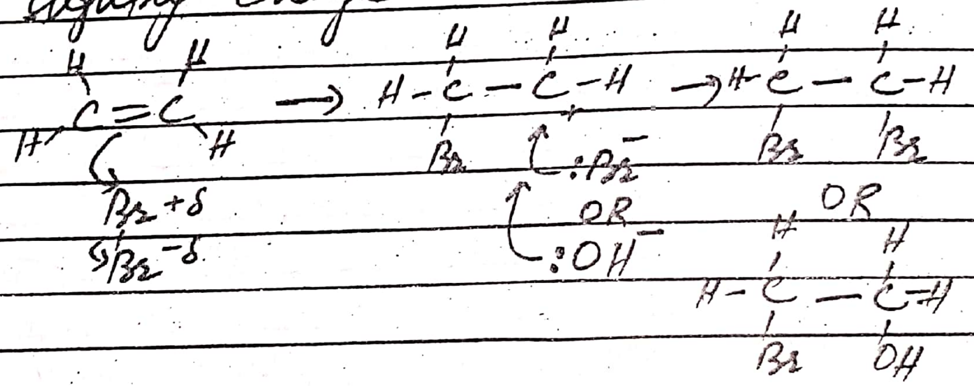
Mechanism of Electrophilic addition

Bromine is a non polar molecule, so as

molecules are polarised due to the repulsion between the π electrons of ethene and electron pair between the Bromine atoms, as a result pair of electrons is shifted towards the Bromine which is further from the π electrons, which ultimately leads to the heterolytic fission of Bromine molecules.



with aq Bromine situation may slightly change.

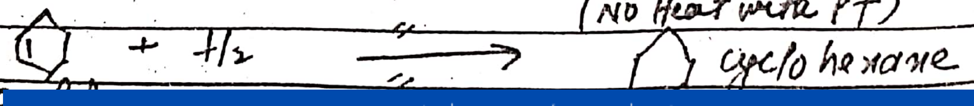


Electrophilic addition of H_2

Electrophilic addition of H_2 takes place in the presence of Ni or Pt catalyst and at a temp of 140–200°C.

$H_2C = CH_2 + H_2 \xrightarrow[140-200°C]{Ni\ or\ Pt} H_3C - CH_3$
(No Heat with Pt)

$CH_3CH = CHCH_3 + H_2 \xrightarrow[140-200°C]{Ni\ or\ Pt} CH_3CH_2CH_2CH_3$
(No Heat with Pt)



Electrophilic addition of halogen acid to unsymmetrical alkenes

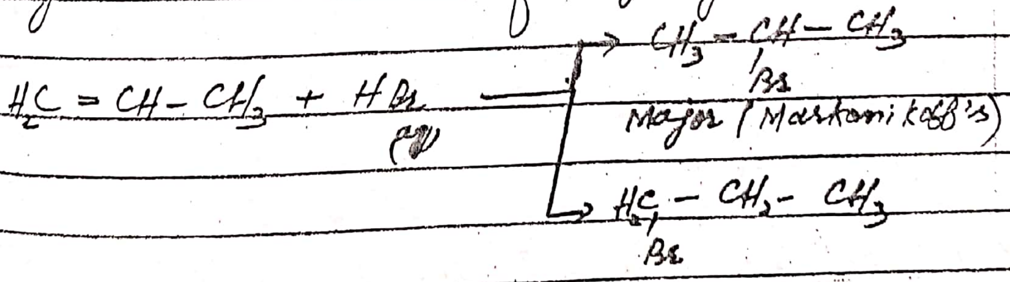
$H_2C = CH_2$
$H_3C-CH=CH-CH_3$ } symmetrical alkenes

$H_3C-CH=CH_2$ unsymmetrical alkene

Addition of halogen acid or any other acid to an unsymmetrical alkenes takes place according to Markonikoff's rule.

Markonikoff's rule

According to Markonikoff's rule, addition of halogen acid or any other polar compounds which contains hydrogen takes place in a way that the negative part is bonded to that carbon of alkene which contains lesser number of hydrogen atom or hydrogen is bonded to that carbon atom which is bonded with greater number of hydrogen atoms.



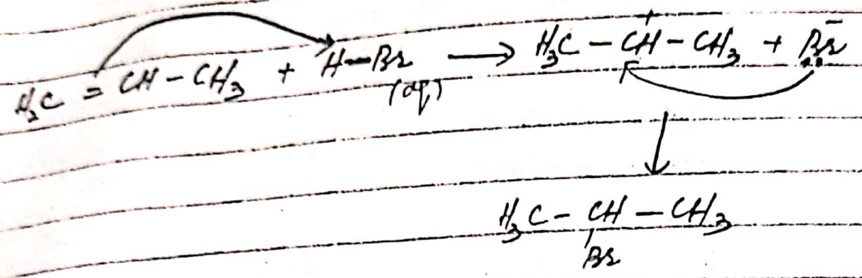
$H_2C=CH-CH_3 + HBr_{(g)} \rightarrow CH_3-\underset{Br}{CH}-CH_3$

Major (Markonikoff's)

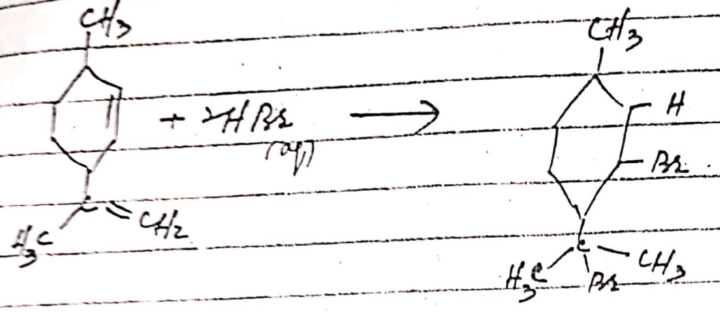
$\rightarrow \underset{Br}{H_2C}-CH_2-CH_3$

Minor (Anti-markonikoff's product)

Mechanism



$H_2C=CH-CH_3 + H-Br_{(aq)} \rightarrow H_3C-\overset{+}{C}H-CH_3 + Br^- \rightarrow H_3C-CH(Br)-CH_3$

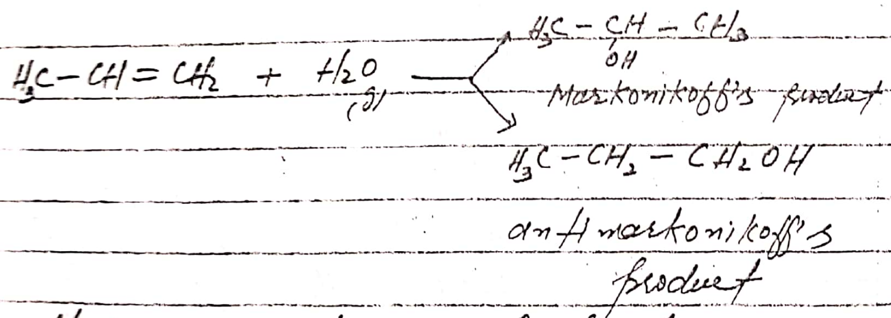


$+ HBr_{(aq)} \rightarrow$

Electrophilic addition of Steam
OR
Hydration of alkenes

$H_2C=CH_2 + H_2O_{(g)} \xrightarrow[350°C/70atm]{H_3PO_4} H_3C-CH_2OH$

ethanol



$H_3C-CH=CH_2 + H_2O_{(g)} \rightarrow$

$H_3C-CH(OH)-CH_3$

Markonikoff's product

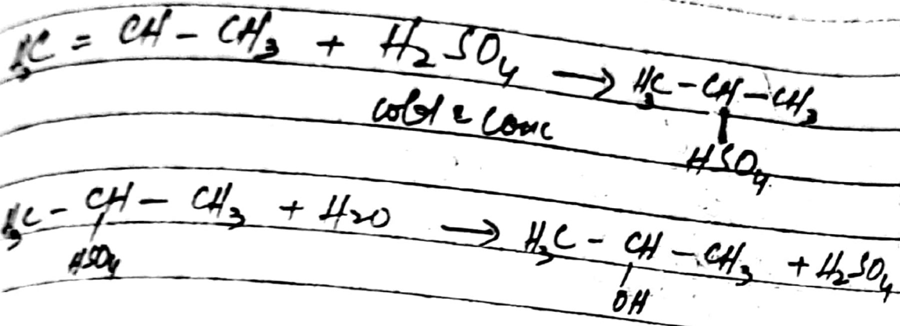
$H_3C-CH_2-CH_2OH$

anti markonikoff's product

alkenes can also be hydrated using concentrated sulphuric acid

(37)

Hydration of alkenes with conc H_2SO_4



$$H_2C=CH-CH_3 + H_2SO_4 \xrightarrow[\text{cold \& conc}]{} H_3C-\underset{HSO_4}{\underset{|}{CH}}-CH_3$$

$$H_3C-\underset{HSO_4}{\underset{|}{CH}}-CH_3 + H_2O \rightarrow H_3C-\underset{OH}{\underset{|}{CH}}-CH_3 + H_2SO_4$$

Classification of carbocations

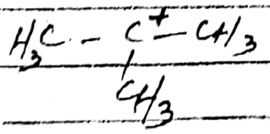
Primary carbocations :- The carbocations in which positively charged carbon atom is bonded with only one alkyl group are called primary carbocation e.g;

$H_3C-\overset{+}{C}H_2$ and $H_3C-CH_2-\overset{+}{C}H_2$

Secondary carbocations :- The carbocations in which positively charged carbon atoms is directly bonded with two alkyl groups e.g.

$H_3C-\overset{+}{C}H-C_2H_5$ and $H_3C-\overset{+}{C}H-CH_3$

(iii) **tertiary carbocations** :- The carbocations in which positively charged carbon atom is directly bonded with three alkyl groups e.g;



$$H_3C-\underset{CH_3}{\underset{|}{\overset{+}{C}}}-CH_3$$

Order of stability of carbocation and their reactivity

Tertiary carbocation > Secondary > Primary

Tertiary carbocations are most stable because of the presence of 3 electron donating alkyl groups which push pair of electrons towards carbocation, thus decrease the magnitude of positive charge and keep positive charge available for a longer time for a nucleophile.

Markovnikoff's rule is also based on the same concept

Order of reactivity

Tertiary carbocation > Secondary > Primary

Oxidation reactions of alkenes

(1) Using cold and dilute Acidified $KMnO_4$

$$CH_2=CH_2 + [O] \xrightarrow{\text{cold and dil } KMnO_4} \underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}}$$

Ethan-1,2-diol

$$H_3C-CH=CH_2 + [O] \xrightarrow{\text{cold and dil } KMnO_4} H_3C-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$$

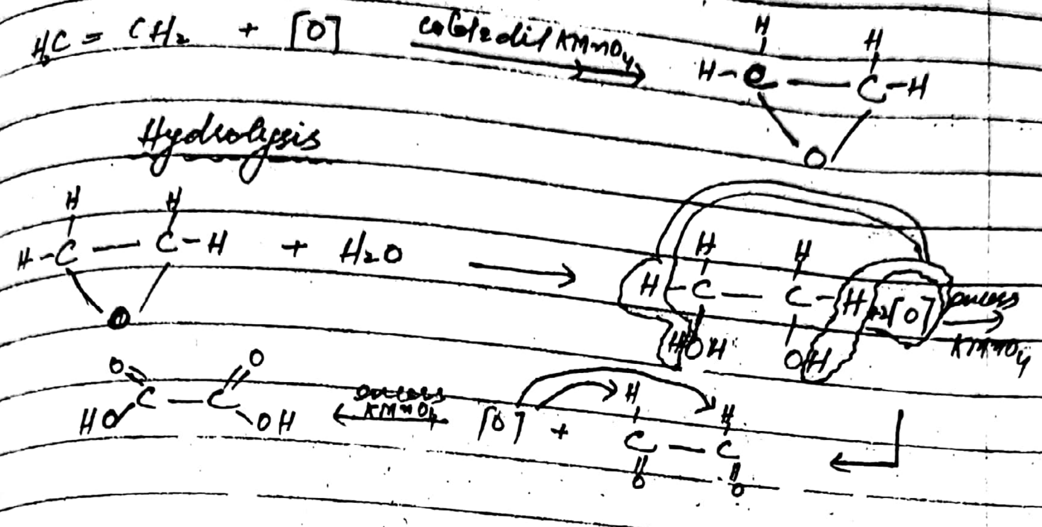
Propan-1,2-diol

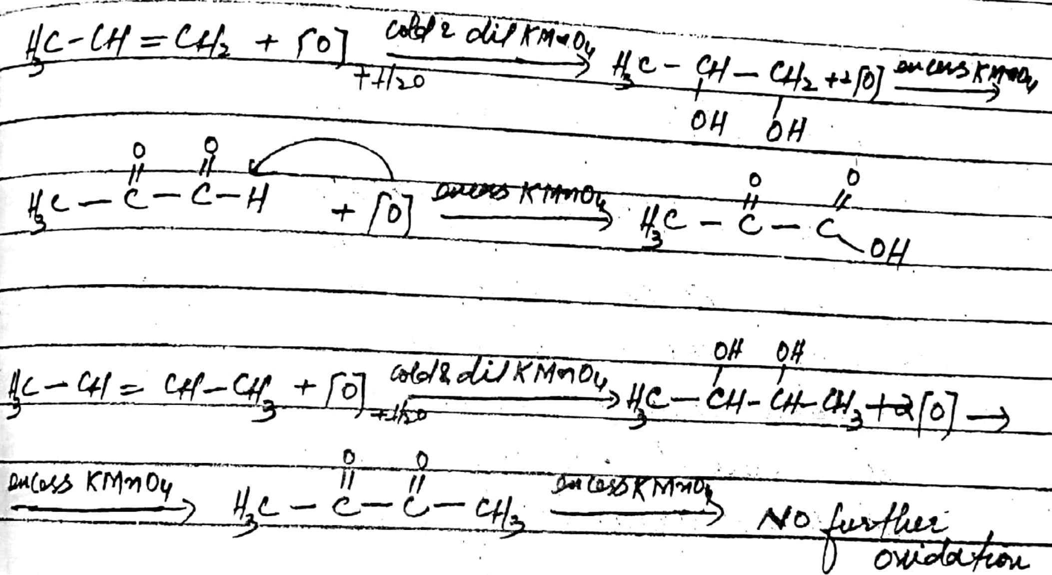
If excess of cold & dil $KMnO_4$

$$\underset{OH}{\underset{|}{H_2C}}-\underset{OH}{\underset{|}{CH_2}} + [O] \xrightarrow{\text{cold \& dil } KMnO_4} H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H + [O] \longrightarrow HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

(aldehyde) Dicarboxylic acid

Mechanism of reaction





$H_3C-CH=CH_2 + [O] \xrightarrow[+H_2O]{\text{cold \& dil } KMnO_4} H_3C-\underset{OH}{CH}-\underset{OH}{CH_2} + 2[O] \xrightarrow{\text{excess } KMnO_4}$

$H_3C-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H + [O] \xrightarrow{\text{excess } KMnO_4} H_3C-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH$

$H_3C-CH=CH-CH_3 + [O] \xrightarrow[+H_2O]{\text{cold \& dil } KMnO_4} H_3C-\overset{OH}{CH}-\overset{OH}{CH}-CH_3 + 2[O] \longrightarrow$

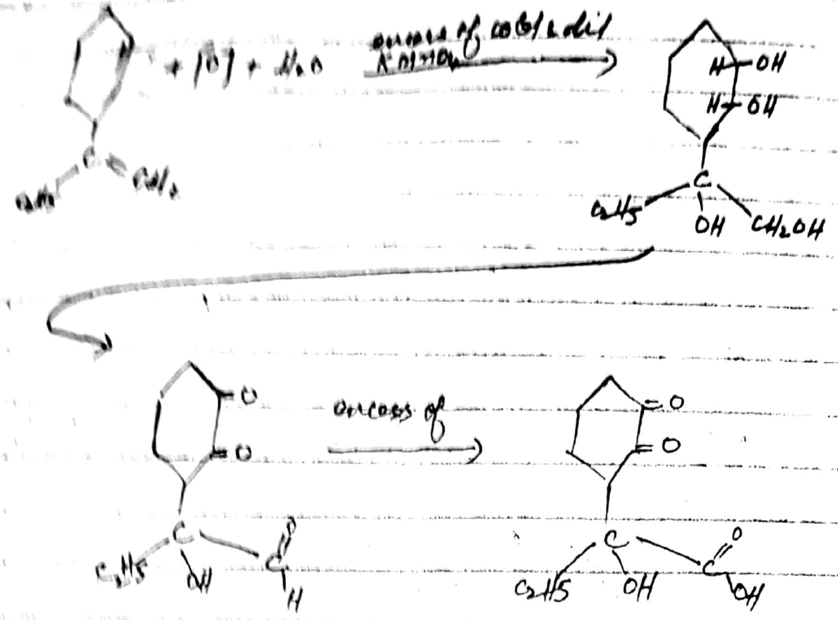
$\xrightarrow{\text{excess } KMnO_4} H_3C-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{excess } KMnO_4}$ No further oxidation

Ketone cannot be oxidised

Primary alcohols $\xrightarrow{\text{oxidised}}$ aldehyde

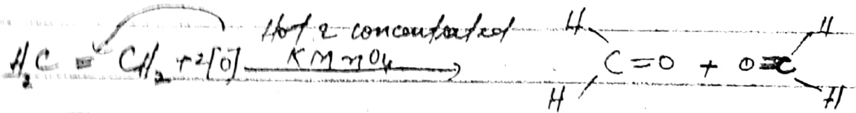
Secondary alcohols $\xrightarrow{\text{oxidised}}$ Ketone

tertiary alcohols $\xrightarrow{\text{oxidised}}$ No reaction

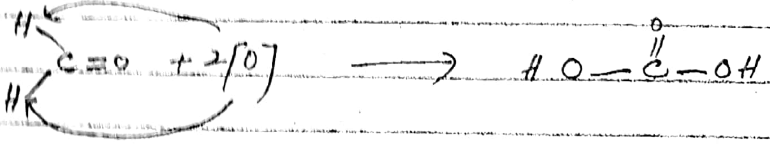


Oxidation of alkenes using hot and concentrated acidified $KMnO_4$

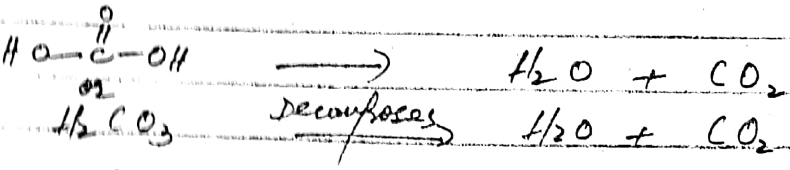
In the presence of hot and concentrated acidified $KMnO_4$ double bond between the carbon atoms breaks and both carbon atoms are bonded to oxygen atoms through double covalent bonds.



$$H_2C = CH_2 + 2[O] \xrightarrow[KMnO_4]{\text{Hot \& concentrated}} H_2C=O + O=CH_2$$



$$H_2C=O + 2[O] \longrightarrow HO-\overset{O}{\overset{\parallel}{C}}-OH$$



$$HO-\overset{O}{\overset{\parallel}{C}}-OH \longrightarrow H_2O + CO_2$$

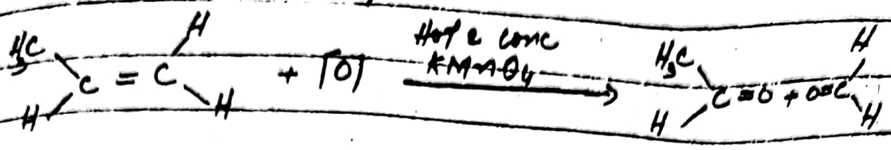
or

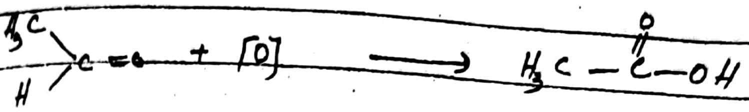
$$H_2CO_3 \xrightarrow{\text{Decomposes}} H_2O + CO_2$$

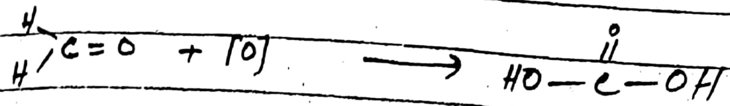
Carbonic acid

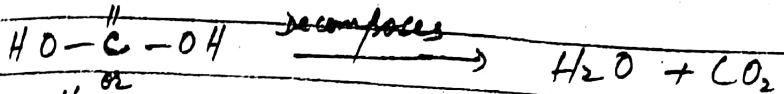
(41)

oxidation of propene







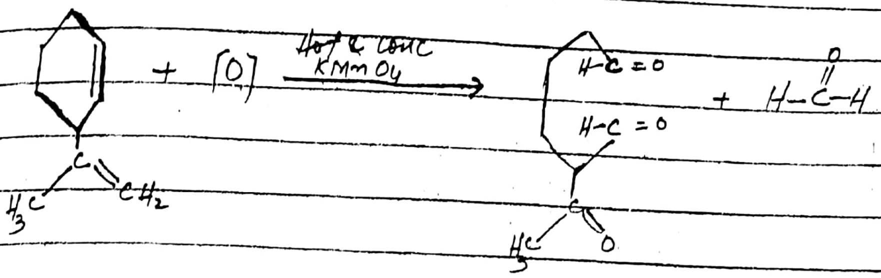


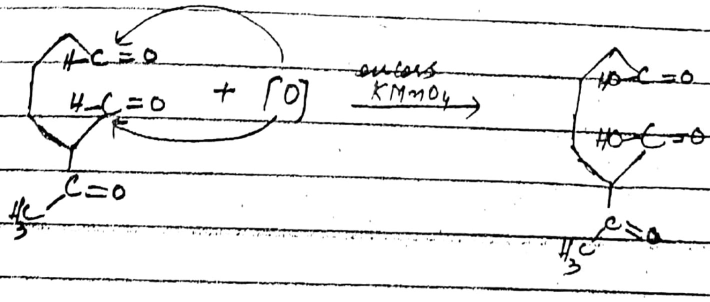
$$HO-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{\text{decomposes}} H_2O + CO_2$$

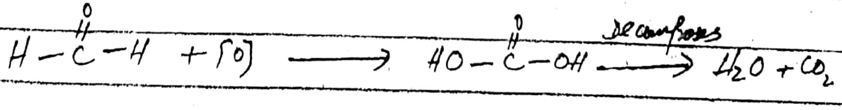
or

H_2CO_3

carbonic acid







$$H-\overset{\overset{O}{\|}}{C}-H + [O] \longrightarrow HO-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{\text{decomposes}} H_2O + CO_2$$

Polymerisation

When large number of small molecules combine to form a big molecule, this big molecule is called polymer and this phenomenon is called polymerisation

monomers :- Small molecules are called monomers.

Types of polymers

There are two types of polymers

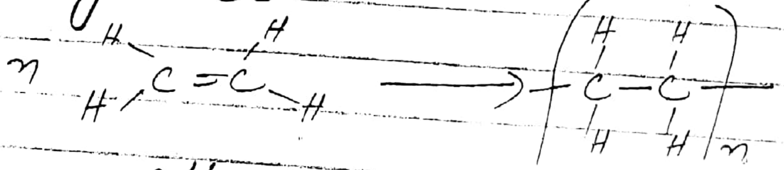
① Addition polymers
(ii) Condensation polymers

Addition polymers

In addition polymers, no by product is formed.

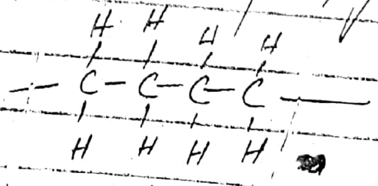
Examples of addition polymers

Polyethene



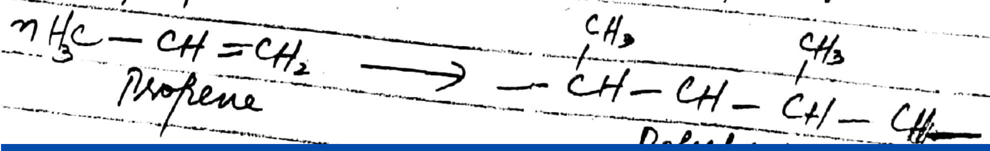
ethene
(monomers)

Polyethene
one repeating unit



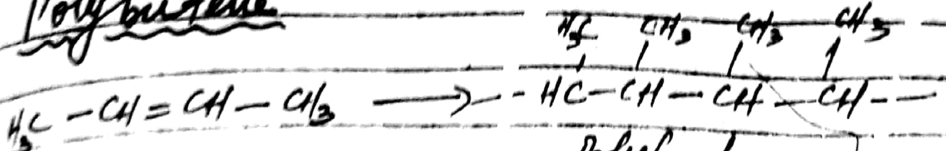
Polyethene
two repeating units

Polypropene



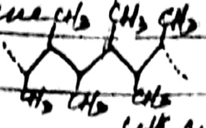
$nH_3C-CH=CH_2 \longrightarrow -CH(CH_3)-CH-CH(CH_3)-CH-$

Polybutene

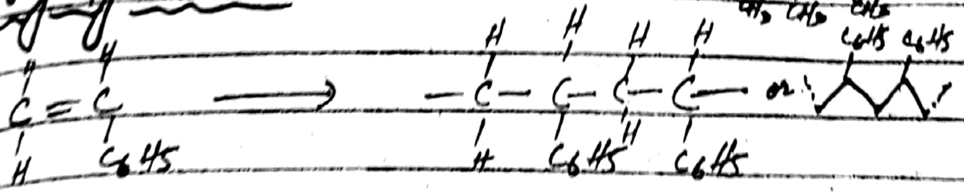


$$H_3C-CH=CH-CH_3 \longrightarrow --\overset{H_3C}{\overset{|}{HC}}-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}--$$

Polybutene



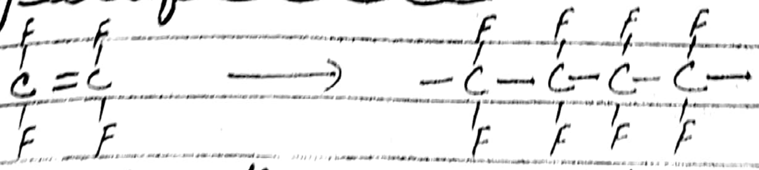
Polystyrene



$$\overset{H}{\underset{H}{C}}=\overset{H}{\underset{C_6H_5}{C}} \longrightarrow -\overset{H}{\underset{H}{C}}-\overset{H}{\underset{C_6H_5}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{C_6H_5}{C}}- \text{ or}$$

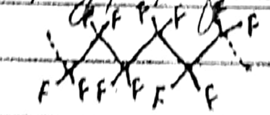
styrene polystyrene

Polytetrafluoroethene

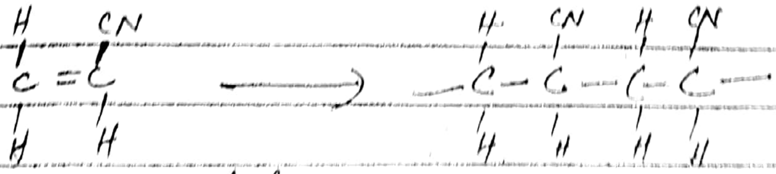


$$\overset{F}{\underset{F}{C}}=\overset{F}{\underset{F}{C}} \longrightarrow -\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-$$

tetrafluoroethene Polytetrafluoroethene



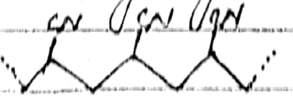
Polyacrylonitrile



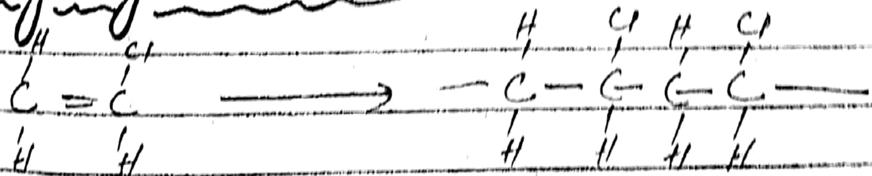
$$\overset{H}{\underset{H}{C}}=\overset{CN}{\underset{H}{C}} \longrightarrow -\overset{H}{\underset{H}{C}}-\overset{CN}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{CN}{\underset{H}{C}}-$$

Propenenitrile
or
acrylonitrile

Polyacrylonitrile



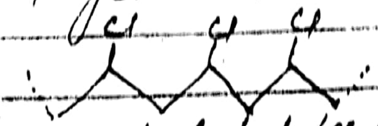
Polyvinylchloride



$$\overset{H}{\underset{H}{C}}=\overset{Cl}{\underset{H}{C}} \longrightarrow -\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-$$

vinyl chloride
or
Chloroethene

Polyvinyl chloride
or
Polychloroethene



skeletal formula

Advantages of addition polymers
OR
Plastics

They are light weight, easy to clean, are available in variety of colours, transparent, highly malleable and are resistant to corrosion.

Disadvantages

Being non biodegradable plastics (addition polymers) are the major cause of increasing litter, block drains and sewers.
They need more lanfil site to dump.
On burning they release pollutant gases e.g; HCN fumes are released by PVC (polyvinyl chloride) plastics.

Halogen derivatives

there are two types of halogen derivatives
(i) Halogenalkanes $Br-CH_2-CH_2-Cl$
(ii) Halogen arenes

Halogen alkanes

Halogen alkanes are the alkanes which have one or more hydrogen atoms replaced by halogen atoms.
the general formula for halogenalkanes which contain only one halogen atom is $C_nH_{2n+1}X$ where X is F, Cl, Br or I

Reactivity of halogenalkanes

Most of the chemical reactions of halogen alkanes involve the breaking of carbon - halogen. Therefore the reactivity of halogenalkanes depends upon the bond energy of carbon-halogen bond, bond polarity of carbon-halogen bond and stability of carbocation.

(i) Bond energy of Carbon-halogen bond

Weaker the Carbon-halogen bond, higher will be its reactivity.
Following is the order of Bond energy

$C-F > C-Cl > C-Br > C-I$

So the order of reactivity of halogenalkanes

$R-I > R-Br > R-Cl > R-F$

(ii) Bond polarity

Bond polarity depends upon the difference of electronegativity between bonded atoms. Following is the order of the bond polarity of C–X bond.

$$C-F > C-Cl > C-Br > C-I$$

(iii) Stability of Carbocation

Higher the stability of carbocation, more will be the reactivity. The order of the stability of carbocation is given below

tertiary carbocation > secondary > Primary

The reactivity of halogenalkanes is mainly controlled by the strength of carbon – halogen bond. Stronger the bond lesser will be the reactivity. Hence the order of reactivity is a follows.

$$R-I > R-Br > R-Cl > R-F$$

Chemical reactions of halogenalkanes

Nucleophilic substitution reactions

Nucleophile:- A substance which carry negative charge or contains a lone pair of electrons can behave as a nucleophile e.g; $\ddot{N}H_3$, $R\ddot{N}H_2$, $H_2\ddot{O}$; $C\bar{N}$, $O\bar{H}$, $\bar{Cl}$, $\bar{Br}$, $\bar{I}$, NO_2^{-1} etc

Examples of nucleophilic substitution reactions

$$R-X \quad + \quad :\bar{Nu} \longrightarrow R-Nu \quad + \quad \bar{X}$$

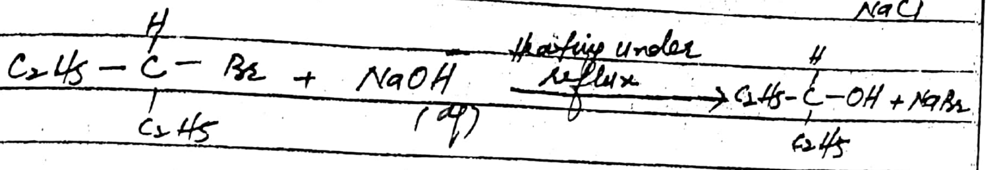
substrate — attacking nucleophile — Product — leaving nucleophile

(i) Hydrolysis of halogenalkanes

Halogenalkanes cannot be hydrolysed by water as they do not mix with water. They are hydrolysed by an aqueous solution of an alkali e.g; aq NaOH to produce an alcohol.

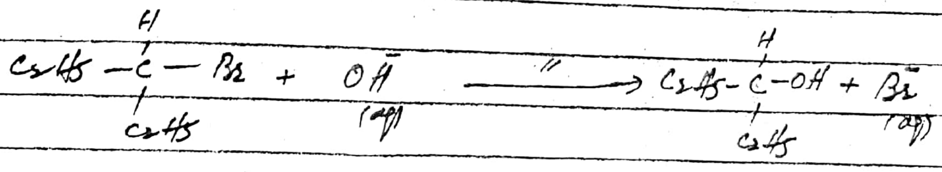
$$H_3C-CH_2-Cl + NaOH_{(aq)} \xrightarrow{\text{Heating under reflux}} H_3C-CH_2OH + \bar{Cl}$$

or NaCl

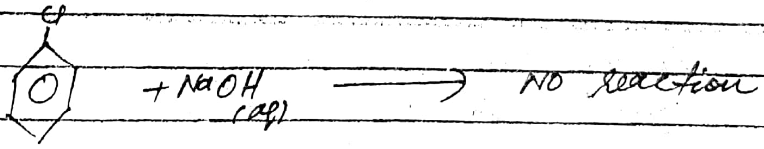


$$C_2H_5-\underset{C_2H_5}{\overset{H}{C}}-Br + NaOH_{(aq)} \xrightarrow{\text{heating under reflux}} C_2H_5-\underset{C_2H_5}{\overset{H}{C}}-OH + NaBr$$

or



$$C_2H_5-\underset{C_2H_5}{\overset{H}{C}}-Br + \bar{OH}_{(aq)} \xrightarrow{\text{"}} C_2H_5-\underset{C_2H_5}{\overset{H}{C}}-OH + \bar{Br}_{(aq)}$$



$+ NaOH_{(aq)} \longrightarrow$ No reaction

Determination of relative rate of hydrolysis of halogenalkanes

The extent of hydrolysis reaction can be measured by adding acidified aq $AgNO_3$ in the reaction mixture.

Chloroalkane produces white precipitate slowly

$$Ag^+_{(aq)} + Cl^-_{(aq)} \longrightarrow \underset{\text{white precipitates}}{AgCl_{(s)}}$$

Bromoalkanes produce creamy white ppt rapidly

$$Ag^+_{(aq)} + I^-_{(aq)} \longrightarrow \underset{\text{creamy ppt}}{AgI_{(s)}}$$

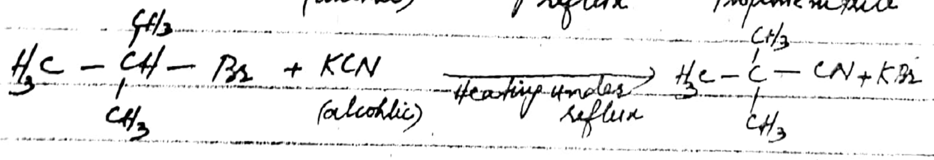
Iodoalkanes produce yellow precipitate more rapidly.

$$Ag^+_{(aq)} + I^-_{(aq)} \longrightarrow \underset{\text{yellow ppt}}{AgI_{(s)}}$$

(2) Formation of nitriles
OR
Substitution of cyanide ion CN^-

$$CH_3-CH_2-Cl + \underset{(\text{alcohlic})}{KCN} \xrightarrow[\text{reflux}]{\text{Heating under}} H_3C-CH_2-CN + KCl$$

Propane nitrile



$$H_3C-\overset{CH_3}{\underset{CH_3}{CH}}-Br + \underset{(\text{alcohlic})}{KCN} \xrightarrow[\text{reflux}]{\text{Heating under}} H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CN + KBr$$

2,2-dimethyl propane nitrile

Aqueous KCN is not used because water contains OH^- which will substitute halide ion and CN^- will not react in the presence of OH^-.

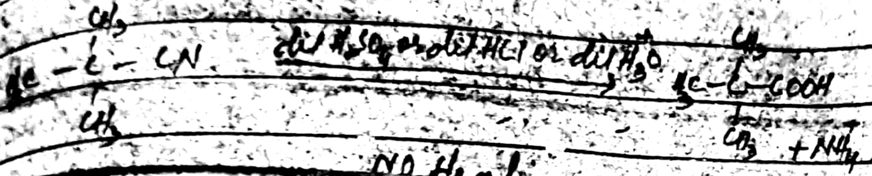
Hydrolysis of alkane nitriles

In the presence of dil acid, alkane nitrile is hydrolysed to carboxylic acid.

(5)

$$H_3C-CH_2-CN \xrightarrow{\text{dil } H_2SO_4 \text{ or dil } HCl} H_3C-CH_2-COOH + NH_4^+$$

No heating



$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CN \xrightarrow{\text{dil } H_2SO_4 \text{ or dil } HCl \text{ or dil } H_3O^+} H_3C-\underset{CH_3}{\overset{CH_3}{C}}-COOH + NH_4^+$$

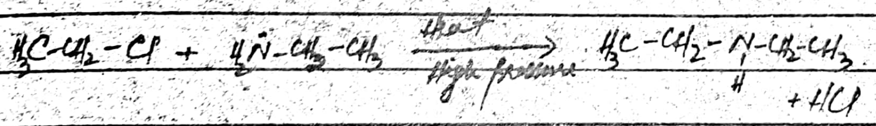
No heating

(3) Reaction with Ammonia :- Halogen alkanes produce primary amines on reacting with ethanolic solution of ammonia by heating under high pressure or with sealed vessel or tube because NH_3 is poisonous

$$H_3C-CH_2-Cl + \underset{\text{ethanolic}}{\ddot{N}H_3} \xrightarrow[\text{High pressure}]{\text{Heat}} CH_3-CH_2-NH_2 + HCl$$

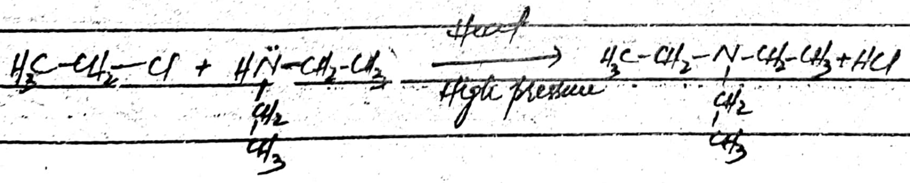
Primary amine

If excess of halogenalkanes is present, secondary, tertiary and quaternary amine are produced



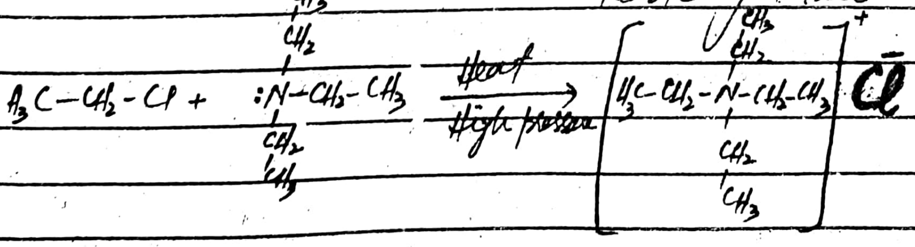
$$H_3C-CH_2-Cl + H_2\ddot{N}-CH_2-CH_3 \xrightarrow[\text{High pressure}]{\text{Heat}} H_3C-CH_2-\underset{H}{N}-CH_2-CH_3 + HCl$$

Secondary amine



$$H_3C-CH_2-Cl + H\underset{\underset{CH_3}{CH_2}}{\ddot{N}}-CH_2-CH_3 \xrightarrow[\text{High pressure}]{\text{Heat}} H_3C-CH_2-\underset{\underset{CH_3}{CH_2}}{N}-CH_2-CH_3 + HCl$$

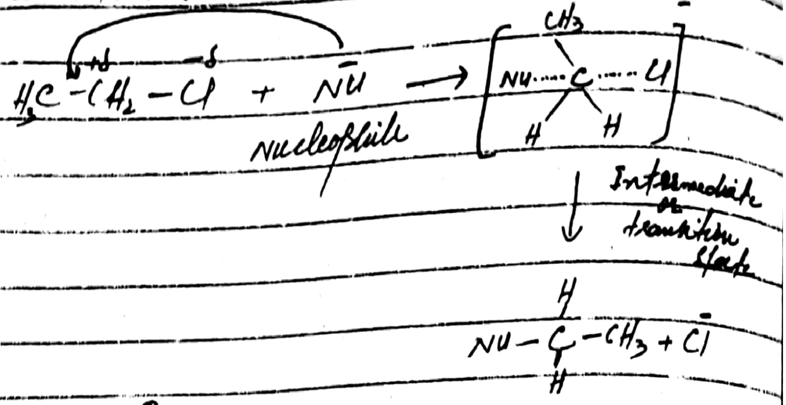
tertiary amine



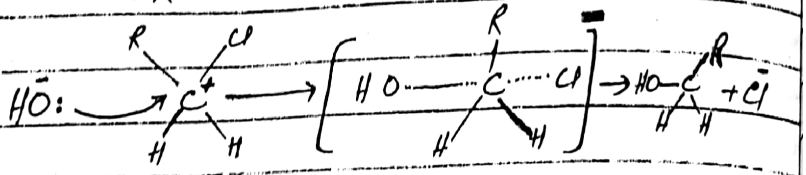
$$H_3C-CH_2-Cl + :\underset{\underset{CH_3}{CH_2}}{\overset{\overset{CH_3}{CH_2}}{N}}-CH_2-CH_3 \xrightarrow[\text{High pressure}]{\text{Heat}} \left[H_3C-CH_2-\underset{\underset{CH_3}{CH_2}}{\overset{\overset{CH_3}{CH_2}}{N}}-CH_2-CH_3\right]^+ \bar{Cl}$$

Mechanism of nucleophilic substitution reaction

SN₂ mechanism:- SN₂ stands for nucleophilic substitution bimolecular reaction.



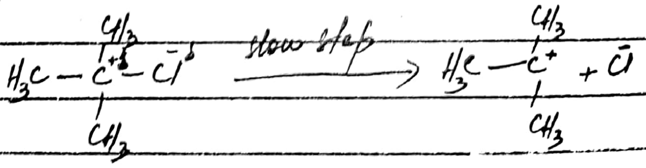
OR



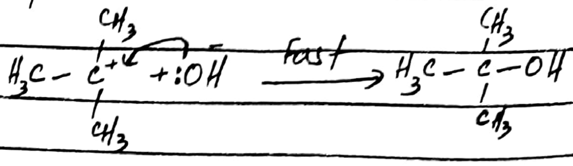
Intermediate or transition state

SN₁ mechanism:- SN₁ stands for nucleophilic substitution unimolecular.

Step 1



Step 2



Difference between SN_1 and SN_2 mechanism

SN_2	SN_1
Primary halogenalkanes undergo SN_2 mechanism	tertiary halogenalkanes undergo SN_1 mechanism
Reaction occurs in one step	Reaction occurs in two steps
Attack of attacking nucleophile and departure of leaving nucleophile takes place simultaneously	attacking of attacking nucleophile and departure of leaving nucleophile takes place in 2 steps.
Attacking nucleophile attacks from the opposite side of the leaving nucleophile	Attacking nucleophile may attack from either side
Inversion of configuration takes place	Retention of configuration may occur.
Two molecules are involved in a slow step which is a rate determining step.	One molecule is involved in slow step which is a rate determining step.
Reaction is 2nd order	Reaction is 1st order.

Why tertiary halogenalkanes undergo S_{N_1} mechanism while primary halogenalkanes undergo S_{N_2} mechanism

⇒ In S_{N_1} mechanism formation of carbocation is involved which is only possible if carbocation remain remains stable till the attack of attacking nucleophile, but primary carbocations formed by primary halogenalkanes is highly unstable and do not stay till the attack occurs.

⇒ Secondary carbocations and tertiary carbocations are stable enough that can stay till the attack of attacking nucleophile occurs, therefore they undergo S_{N_1} mechanism.

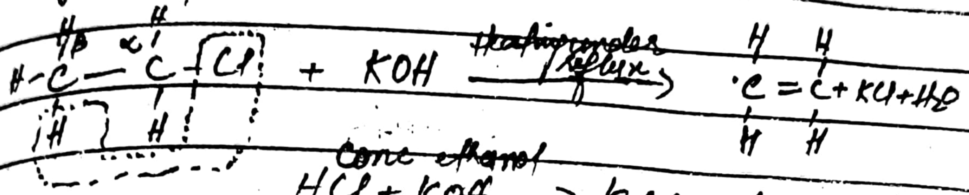
Tertiary halogen alkanes do not undergo S_{N_2} mechanism due to the presence of three bulky alkyl groups around alpha carbon atom which offer steric hinderance to the attacking nucleophile

⇒ Secondary halogenalkanes undergo both S_{N_1} and S_{N_2} mechanism.

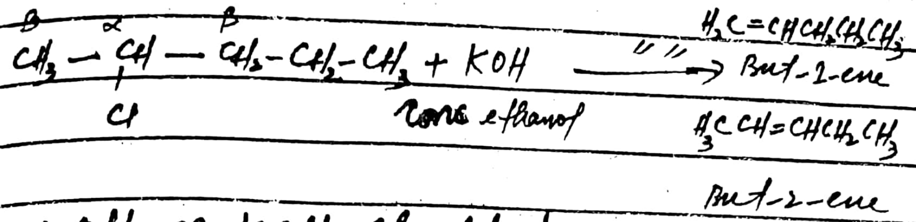
Elimination reactions of halogenalkanes

Those reactions which involve removal of atoms or group of atoms from two adjacent carbon atoms to form double covalent bond between carbon atoms is called elimination reaction.

Halogenalkanes undergo elimination reaction to form alkene in the presence of concentrated ethanolic KOH or NaOH and at high temperature.



$HCl + KOH \longrightarrow KCl + H_2O$



$$CH_3 - \underset{Cl}{CH} - CH_2 - CH_2 - CH_3 + KOH \xrightarrow[\text{conc ethanol}]{''\ ''} \begin{array}{l} H_2C=CHCH_2CH_2CH_3 \\ \text{But-1-ene} \\ H_3C\,CH=CHCH_2CH_3 \\ \text{But-2-ene} \end{array}$$

NaOH or KOH should be concentrated ethanolic

KCl + H_2O

Uses of halogenalkanes

⇒ CFCs (Chlorofluoro carbons) are used as refrigerants and aerosol propellents because of their inert, non flammable and non toxic nature.

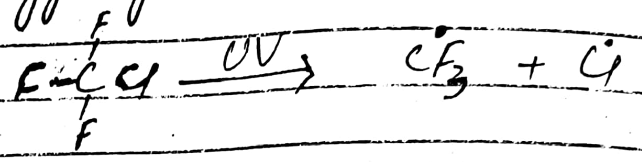
⇒ Trichloromethane and fluoroethane are used as anaesthesia to faint patients before surgery.

⇒ Fluoroalkanes are used as flame retardants.

⇒ Chloroalkanes and fluoroalkanes are used for making polymers which are used as plastics.

Harmful effects of CFCs in upper atmosphere

are inert so they reach into the stratosphere (in upper atmosphere) without being decomposed. In upper atmosphere, in the presence of UV rays, CFCs break their weakest bond i.e. the bond present between carbon and chlorine atom to release chlorine free radical ($\dot{Cl}$) which attacks ozone O_3 to convert it into Oxygen gas O_2.



$$F-\overset{F}{\underset{F}{C}}-Cl \xrightarrow{UV} \dot{C}F_3 + \dot{Cl}$$

$$\dot{Cl} + O_3 \longrightarrow ClO^{\cdot} + O_2$$

$$ClO^{\cdot} + O_3 \longrightarrow \dot{Cl} + 2O_2$$

or

$$ClO^{\cdot} + ClO^{\cdot} \longrightarrow 2\dot{Cl} + O_2$$

or

$$ClO^{\cdot} + O^{\cdot} \longrightarrow Cl^{\cdot} + O_2$$

Chlorine free radical behaves as catalyst

Ozone depletion potential

Ozone depletion potential of a CFCs depends upon the number of Chlorine atoms in CFCs. Greater the number of chlorine atoms, greater will be the ozone depletion potential of CFCs.

Hydroxy compounds

Organic compounds which contain "OH" functional group are called hydroxy compounds.

Types of hydroxy compounds

Alcohols

Aliphatic organic compounds containing 'OH' group are called alcohols

e.g. CH_3OH, CH_3CH_2OH

Phenols

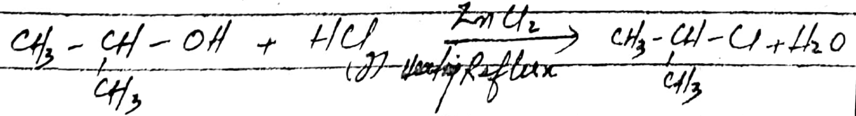
Aromatic organic compounds containing "OH" group are called phenols.

Chemical properties of alcohols

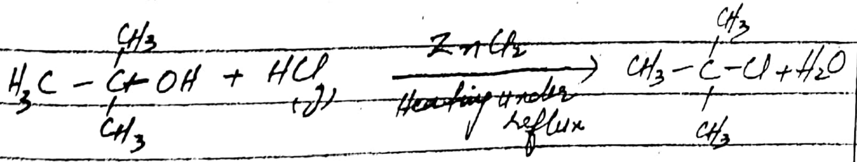
(1) Nucleophilic substitution reactions

In this substitution reaction, the –OH group in the alcohol is replaced by a halogen atom to produce halogenoalkanes

$$CH_3CH_2OH + HCl_{(l)} \xrightarrow[\text{Reflux}]{ZnCl_2} CH_3CH_2-Cl + H_2O$$



$$\underset{\displaystyle CH_3}{CH_3-\underset{|}{CH}-OH} + HCl_{(l)} \xrightarrow[\text{~~heating~~ Reflux}]{ZnCl_2} CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-Cl + H_2O$$



$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH + HCl_{(l)} \xrightarrow[\text{Heating under reflux}]{ZnCl_2} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Cl + H_2O$$

$$CH_3CH_2OH + HBr_{(l)} \longrightarrow CH_3CH_2Br + H_2O$$

(2)

$HCl_{(g)}$ and HBr are produced by reacting concentrated sulphuric acid with NaCl and with NaBr respectively.

$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

or

$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$

$2NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + HBr$

Formation of Halogenalkanes using PCl5, PCl3, PBr3, PI3 and SOCl2

$C_2H_5OH + PCl_5 \xrightarrow{\text{Room temperature}} C_2H_5Cl + \underset{\text{(g) Steamy fumes}}{HCl} + POCl_3$

Formation of steamy fumes is test for the identifications of alcohols.

$3C_2H_5OH + PCl_3 \xrightarrow{\text{Heating under reflux}} 3C_2H_5Cl + H_2PO_3$

$3C_2H_5OH + PBr_3 \xrightarrow{\text{Heating under reflux}} 3C_2H_5Br + H_3PO_3$

$3C_2H_5OH + PI_3 \xrightarrow{\text{" " "}} 3C_2H_5Br + H_3PO_3$

PBr_3 and PI_3 can be produced by warming red phosphorus with Br_2 and I_2 respectively.

$2P + 3Br_2 \xrightarrow{\text{Heat}} 2PBr_3$

$2P + 3I_2 \xrightarrow{\text{Heat}} 2PI_3$

$C_2H_5OH + SOCl_2 \longrightarrow C_2H_5Cl + \underset{(g)}{SO_2} + \underset{(g)}{HCl}$

(ii) Reaction with sodium metal

Alcohols are very weakly acidic that they cannot react with metal hydroxides and metal carbonates i.e. with bases but can only react with highly reactive metals e.g; Na or K to form salt and H_2.

$$2C_2H_5OH + 2Na \longrightarrow 2\underset{\substack{\uparrow \\ \text{Ionic part} \\ \text{of compound}}}{C_2H_5\bar{O}}Na^+ + H_2$$

$$2CH_3CH_2CH_2OH + 2K \longrightarrow 2CH_3CH_2CH_2\bar{O}K^+ + H_2$$

Charges must be shown

(iii) Oxidation of alcohols:

Primary alcohols $\xrightarrow{\text{oxidation}}$ Aldehydes $\xrightarrow{[O]}$ Carboxylic acid

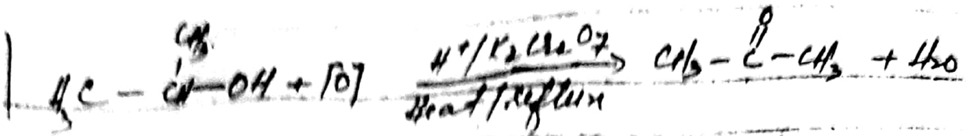
Secondary alcohols $\xrightarrow{\text{oxidation}}$ Ketones

Tertiary alcohols $\xrightarrow{\text{oxidation}}$ No oxidation under ordinary conditions

$$\underset{\text{Primary alcohols}}{H_3C-CH_2-OH} + [O] \xrightarrow[\text{Heating/reflux}]{H^+/K_2Cr_2O_7} H_3C-\overset{\overset{O}{\|}}{C}-H + [O]$$

$$\Big\downarrow H^+/K_2Cr_2O_7$$

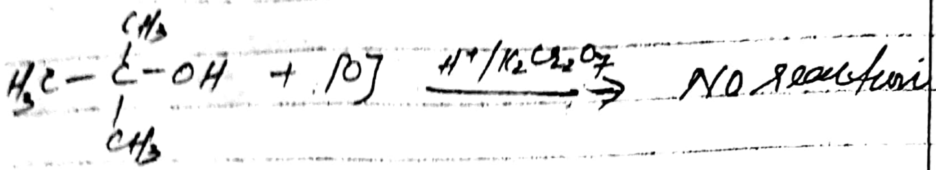
$$H_3C-\overset{\overset{O}{\|}}{C}-OH$$



$H_3C-\overset{CH_3}{CH}-OH + [O] \xrightarrow[Heat/reflux]{H^+/K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$

secondary alcohol

Ketone



$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH + [O] \xrightarrow{H^+/K_2Cr_2O_7}$ No reaction

tertiary alcohols

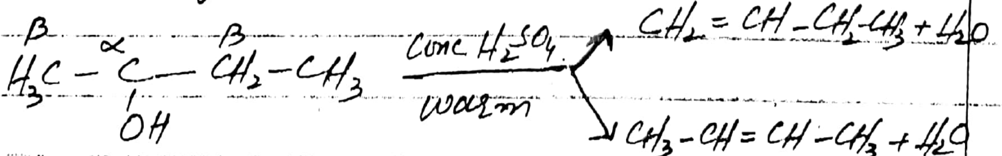
oxidation reaction can be used to distinguish primary, secondary and tertiary alcohols.

(iii) Dehydration or elimination reaction of alcohols

Alcohols on dehydration are converted to alkenes in the presence of concentrated Sulphuric acid at 170°C or in the presence of Al_2O_3 at 300°C

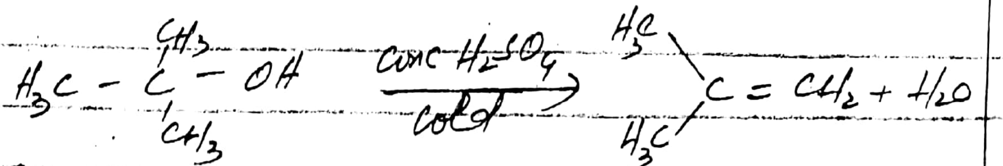
$CH_3-CH_2-OH \xrightarrow[170^\circ C]{conc\ H_2SO_4} H_2C=CH_2 + H_2O$

Primary alcohol



$\overset{\beta}{H_3C}-\underset{OH}{\overset{\alpha}{C}}-\overset{\beta}{CH_2}-CH_3 \xrightarrow[warm]{conc\ H_2SO_4}$ $CH_2=CH-CH_2-CH_3 + H_2O$; $CH_3-CH=CH-CH_3 + H_2O$

Secondary alcohol



$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[cold]{conc\ H_2SO_4} (H_3C)_2C=CH_2 + H_2O$

Formation of alkene can be tested by adding aq. Br_2

Dehydration reaction is a test to distinguish primary & secondary and tertiary alcohol due to difference in dehydrating temp with the concentrated sulphuric acid

(iv) Acylation reaction of alcohols

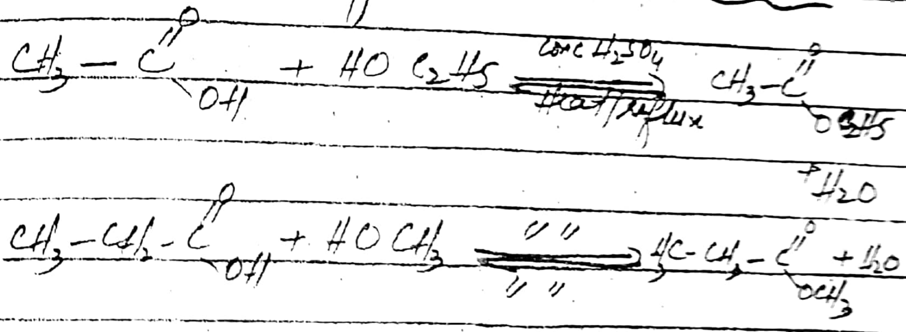
When hydrogen of an alcohol is replaced by an acyl group ($R-\overset{O}{\overset{\|}{C}}-$) is called acylation of alcohol.

There are two ways of acylation

(i) with carboxylic acids

(ii) with acyl chloride

Reaction with Carboxylic acid or Esterification reaction



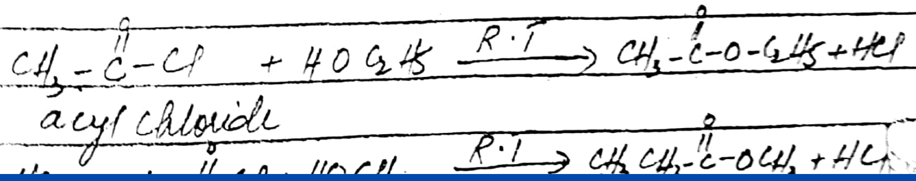
$$CH_3-\overset{O}{\overset{\|}{C}}-OH + HOC_2H_5 \underset{Heat/Reflux}{\overset{Conc\ H_2SO_4}{\rightleftharpoons}} CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H_2O$$

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + HOCH_3 \underset{''\ ''}{\overset{''\ ''}{\rightleftharpoons}} H_3C-CH_2-\overset{O}{\overset{\|}{C}}-OCH_3 + H_2O$$

Ester

Forward reaction is esterification reaction while backward reaction is hydrolysis.

Reaction with acyl Chloride

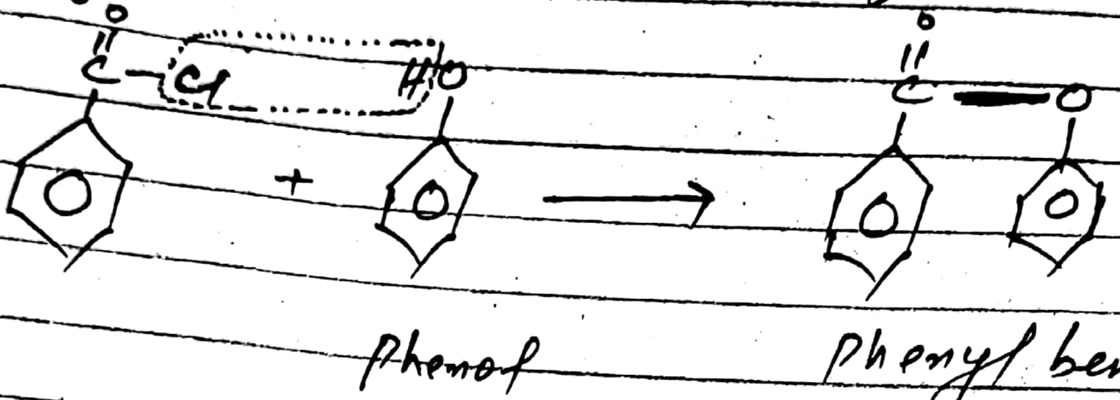


$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + HOC_2H_5 \xrightarrow{R.T} CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5 + HCl$$

acyl chloride

$$HOCH \xrightarrow{R.T} CH_3CH_2-\overset{O}{\overset{\|}{C}}-OCH_3 + HCl$$

Formation of phenyl benzoate is anot
example of formation of ester usi
acyl chlorides.



Acylation reaction with Carboxylic aci
is called esterification but not
with acyl chloride.

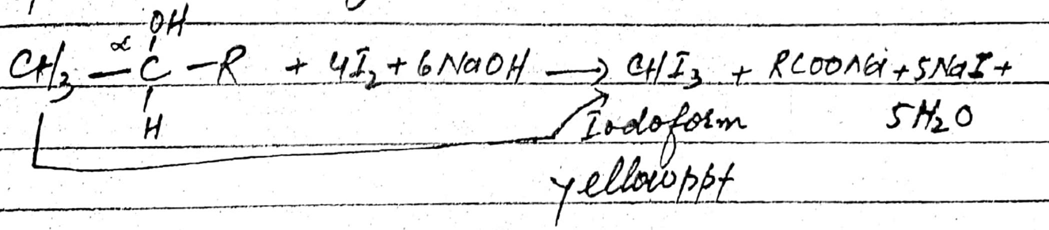
Hydroxy compounds

Reaction of alcohols with iodine in the presence of aq NaOH
OR
Iodoform test

⇒ All secondary alcohols $(R-\overset{OH}{\underset{H}{C}}-R)$ in which one of the R-group (alkyl group) is methyl, $-CH_3$ show positive iodoform test.

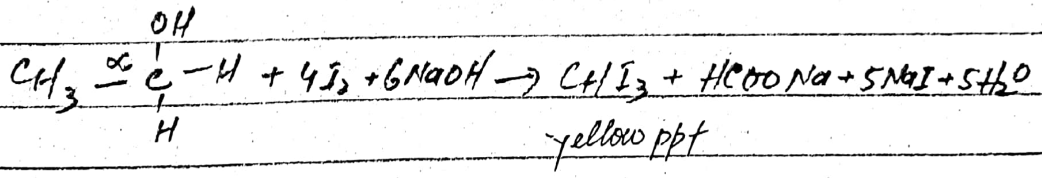
⇒ No tertiary alcohol $(R-\overset{OH}{\underset{R}{C}}-R)$ gives positive iodoform test due to the absence of $(-\overset{OH}{\underset{H}{C}}-)$ group

⇒ Except ethanol $(CH_3-\overset{OH}{\underset{H}{C}}-H)$ no other primary alcohol gives positive iodoform test because ethanol fulfils the requirement $(CH_3-\overset{OH}{\underset{H}{C}}-)$ for positive iodoform test.



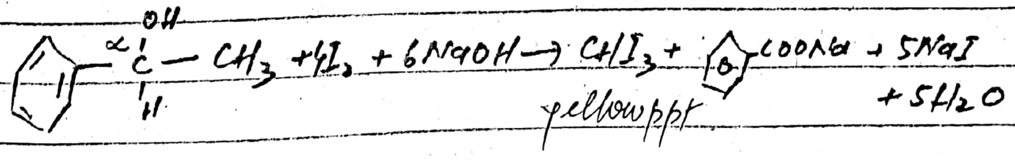
$$CH_3\overset{\alpha}{-}\overset{OH}{\underset{H}{C}}-R + 4I_2 + 6NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + RCOONa + 5NaI + 5H_2O$$

yellow ppt

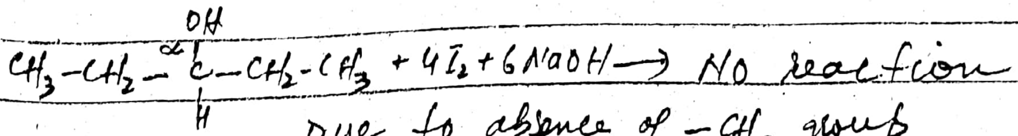


$$CH_3\overset{\alpha}{-}\overset{OH}{\underset{H}{C}}-H + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$$

yellow ppt



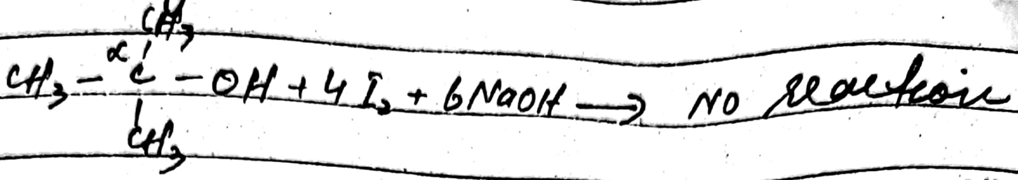
yellow ppt



$$CH_3-CH_2\overset{\alpha}{-}\overset{OH}{\underset{H}{C}}-CH_2-CH_3 + 4I_2 + 6NaOH \longrightarrow \text{No reaction}$$

Due to absence of $-CH_3$ group

directly bonded with α- Carbon atom

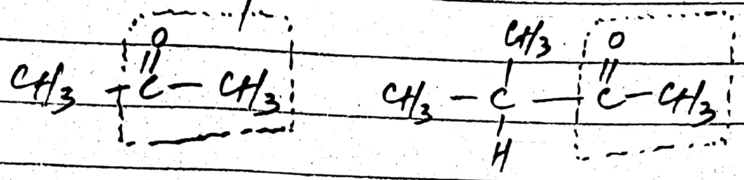


$$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{\alpha}{C}}}-OH + 4I_2 + 6NaOH \longrightarrow \text{No reaction}$$

Due to the absence of "H" with α- Carbon atom.

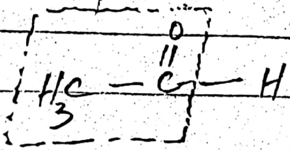
⇒ Aldehydes and ketones containing $CH_3-\overset{O}{\overset{\|}{C}}-$ group also give positive iodoform test.

For example,



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \qquad CH_3-\overset{CH_3}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

Propanone



$$H_3C-\overset{O}{\overset{\|}{C}}-H$$

ethanal

⇒ Ethanal is the only aldehyde which gives positive iodoform test.

Application of iodoform test

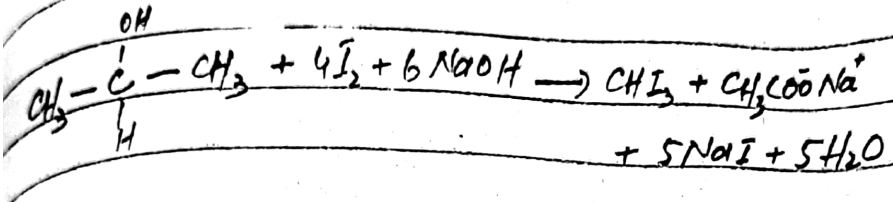
⇒ This test is used to distinguish a secondary alcohol from a tertiary alcohol

⇒ to distinguish ethanol from methanol

⇒ to distinguish ethanal from other aldehydes

⇒ to distinguish a ketone containing a methyl group from one which does not contain methyl group bonded with α- Carbon.

Mechanism of iodoform test

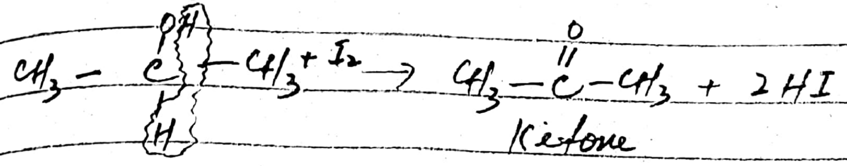


$$CH_3-\underset{H}{\overset{OH}{C}}-CH_3 + 4I_2 + 6NaOH \longrightarrow CHI_3 + CH_3CO\bar{O}Na^+ + 5NaI + 5H_2O$$

Mechanism

Step I

Alcohol is oxidised to aldehyde or ketone by I_2.

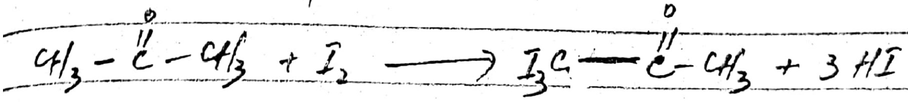


$$CH_3-\underset{H}{\overset{OH}{C}}-CH_3 + I_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 2HI$$

Ketone

Step II

Free radical substitution of I_2 over methyl group



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + I_2 \longrightarrow I_3C-\overset{O}{\overset{\|}{C}}-CH_3 + 3HI$$

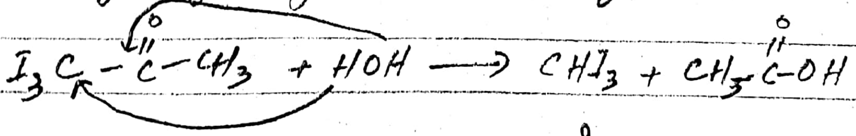
Step III

Neutralisation of HI by NaOH

$$5HI + 5NaOH \longrightarrow 5NaI + 5H_2O$$

Step IV

Hydrolysis of $I_3C-\overset{O}{\overset{\|}{C}}-CH_3$ by water



$$I_3C-\overset{O}{\overset{\|}{C}}-CH_3 + HOH \longrightarrow CHI_3 + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

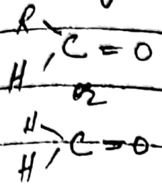
Step V Neutralization of $CH_3\overset{O}{\overset{\|}{C}}-OH$ by NaOH

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

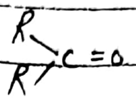
Chemistry of Carbonyl compounds

Types of Carbonyl compounds

aldehyde


$R(H)C=O$ or $H_2C=O$

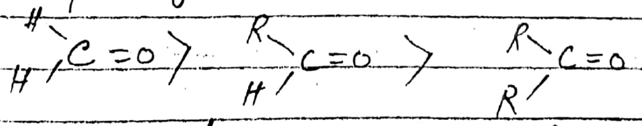
Ketones


$RR'C=O$

(i) Addition reactions of Carbonyl compounds

Carbonyl compounds undergo addition reactions due to the presence of double covalent bond between carbon and oxygen atom, but unlike alkenes they do not undergo electrophilic addition rather nucleophilic addition due to the presence of partial positively charged carbon atom bonded with oxygen atom.

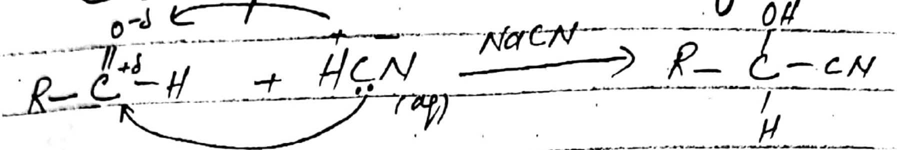
Nucleophilic addition becomes easier in those carbonyl compounds where carbonyl carbon is bonded with greater number of hydrogen atoms or with lesser number of alkyl groups e.g;


$H_2C=O > R(H)C=O > RR'C=O$

more reactive   less reactive

Presence of alkyl groups decrease the magnitude of positive charge ~~over~~ over carbonyl carbon as alkyl groups are electron donating and push pair of electrons towards carbonyl carbon atom, this decreases the positive charge over carbonyl carbon and makes the nucleophile's attack less easier.

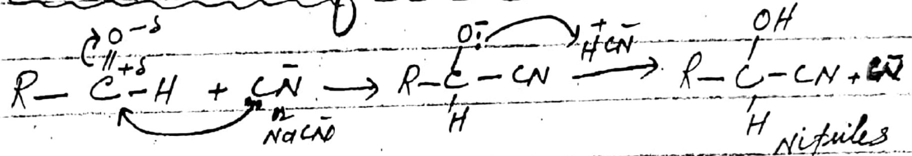
Nucleophilic addition of HCN



$$R-\overset{O^{-\delta}}{\overset{\|}{C^{+\delta}}}-H + HCN_{(aq)} \xrightarrow{NaCN} R-\overset{OH}{\underset{H}{C}}-CN$$

HCN is a weak acid therefore NaCN is used as catalyst to increase the concentration of $C\bar{N}$ and to speed up the process.

Mechanism of reaction

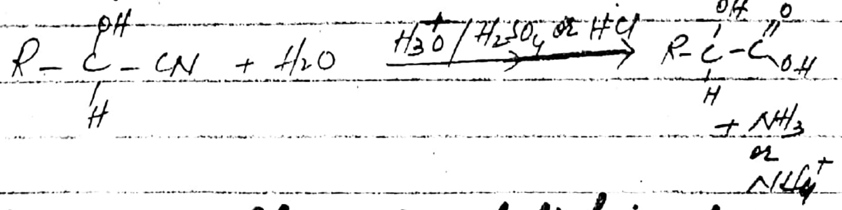


$$R-\overset{O^{-\delta}}{\overset{\|}{C^{+\delta}}}-H + \underset{NaC\bar{N}}{C\bar{N}} \longrightarrow R-\overset{O^{-}}{\underset{H}{C}}-CN \xrightarrow{H^{+}C\bar{N}} R-\overset{OH}{\underset{H}{C}}-CN + C\bar{N}$$

$$:C\bar{N} + Na^{+} \longrightarrow NaCN$$

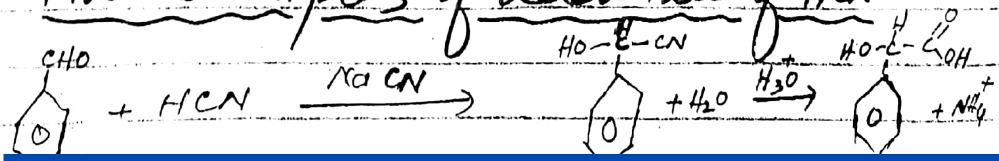
Hydrolysis of nitriles

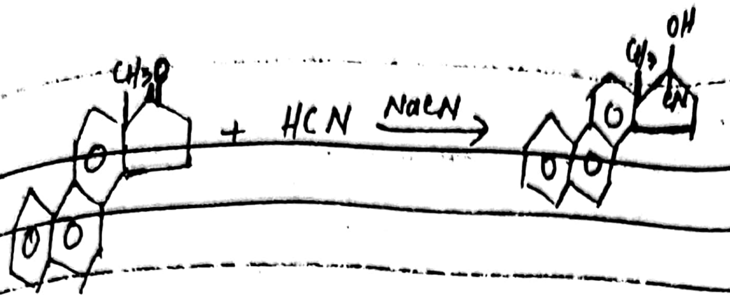
Nitrile can be hydrolysed by heating it in the presence of dil H_2SO_4 to give carbonylic acid.

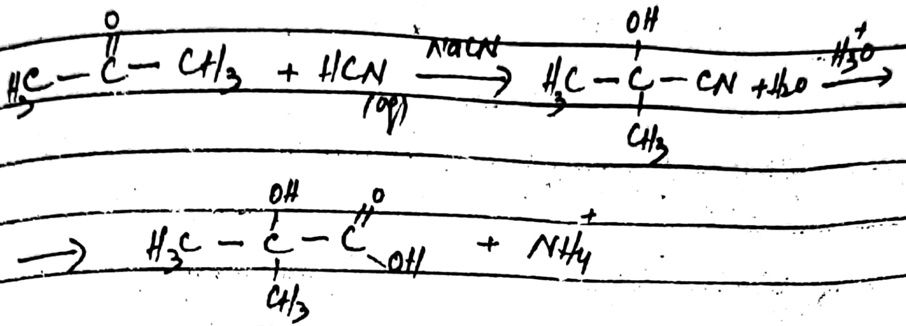


$$R-\overset{OH}{\underset{H}{C}}-CN + H_2O \xrightarrow{H_3O^{+}/H_2SO_4 \text{ or } HCl} R-\overset{OH}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH + NH_3 \text{ or } NH_4^{+}$$

More examples of addition of HCN





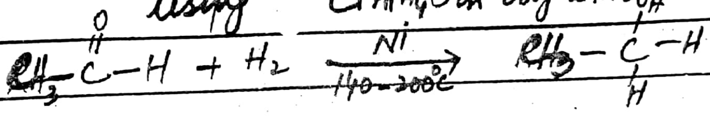


$$H_3C-\overset{O}{\overset{\|}{C}}-CH_3 + HCN_{(aq)} \xrightarrow{NaCN} H_3C-\underset{CH_3}{\overset{OH}{C}}-CN + H_2O \xrightarrow{H_3O^+}$$

$$\longrightarrow H_3C-\underset{CH_3}{\overset{OH}{C}}-\overset{O}{\overset{\|}{C}}-OH + NH_4^+$$

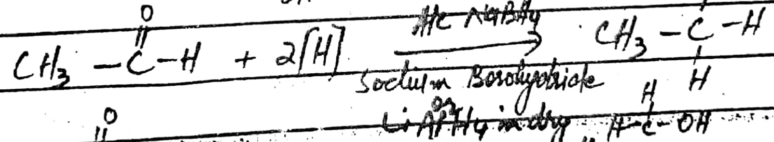
Reduction reactions

Aldehydes are reduced to primary alcohols while ketones are reduced to secondary alcohols in the presence of Alcohlic $NaBH_4$ or by treating directly with the hydrogen gas in the presence of nickel as Catalyst at a temperature of 140-200°C, OR by using $LiAlH_4$ in dry ether

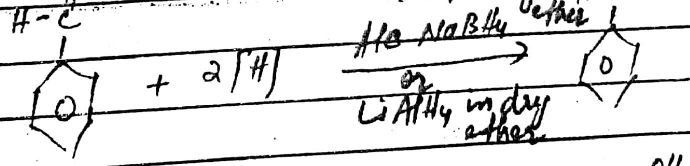


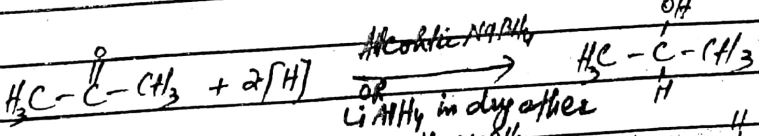
$$CH_3-\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow[140-200^\circ C]{Ni} CH_3-\underset{H}{\overset{OH}{C}}-H$$

OR

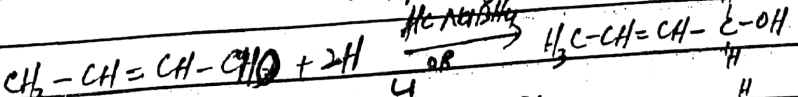


$$CH_3-\overset{O}{\overset{\|}{C}}-H + 2[H] \xrightarrow[\text{Sodium Borohydride or } LiAlH_4 \text{ in dry ether}]{\text{Alc } NaBH_4} CH_3-\underset{H}{\overset{OH}{C}}-H$$

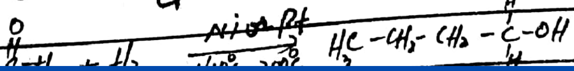




$$H_3C-\overset{O}{\overset{\|}{C}}-CH_3 + 2[H] \xrightarrow[\text{OR } LiAlH_4 \text{ in dry ether}]{\text{Alcohlic } NaBH_4} H_3C-\underset{H}{\overset{OH}{C}}-CH_3$$



$$CH_3-CH=CH-CHO + 2H \xrightarrow[\text{OR Li}]{\text{Alc } NaBH_4} H_3C-CH=CH-\underset{H}{\overset{H}{C}}-OH$$



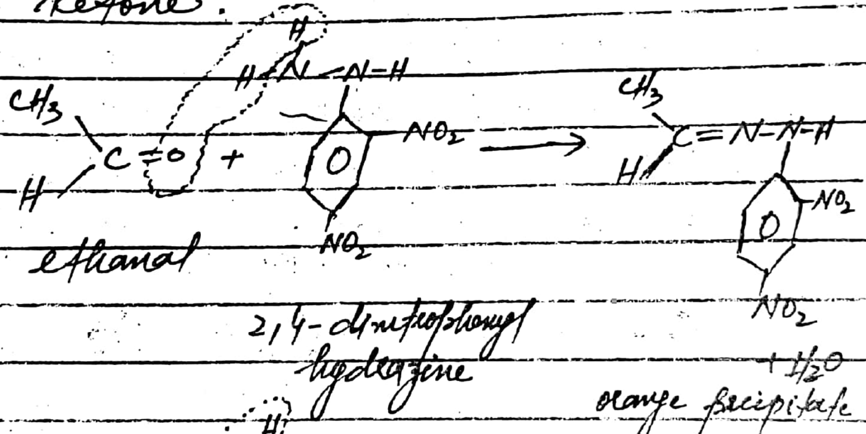
$$\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow[140-200^\circ]{\text{Ni or Pt}} H_3C-CH_2-CH_2-\underset{H}{\overset{H}{C}}-OH$$

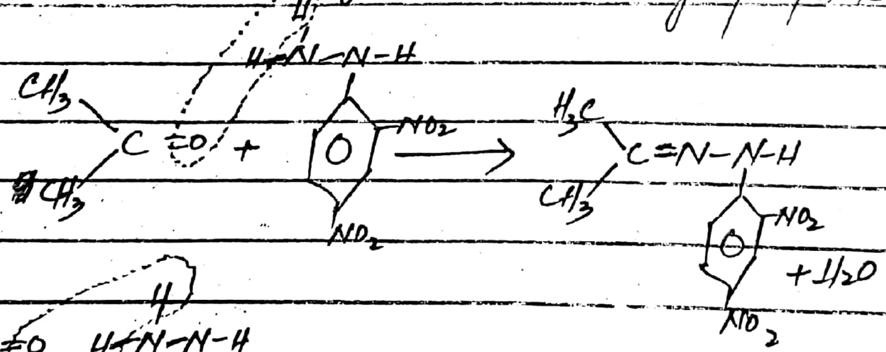
Alcoholic $NaBH_4$ can't reduce alkene but only carbonyl group ... but Hydrogen gas in the presence of nickel and high temperature can reduce both alkene and carbonyl group. Platinum catalyst alongwith H_2 can also reduce alkene and carbonyl group but at room temp because Pt is more powerful.

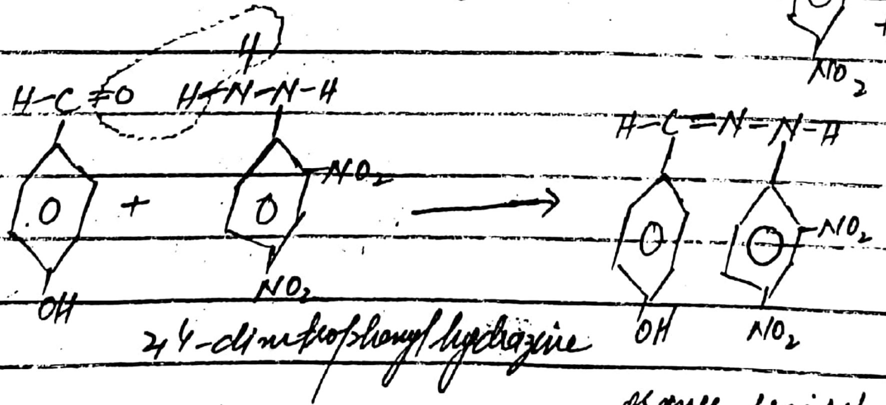
Reaction with 2,4-dinitrophenyl hydrazine (2,4 DNPH)

2,4-dinitrophenyl hydrazine reacts with aldehyde or ketone to give orange precipitate.

This is also a test to detect aldehyde or ketone.







oxidation reactions

Aldehydes can be oxidised to carboxylic acids while ketones cannot be oxidised. This difference helps distinguish between aldehydes and ketones

Oxidation by using Tollen's reagent
or
Silver mirror test
or
ammonical silver nitrate solution

When an ammonical solution of $AgNO_3$ is warmed with aldehyde, aldehyde is oxidised to carboxylic acid and a silver mirror is formed which is deposited on the test tube.

$$R-\overset{O}{\overset{\|}{C}}-H + 2[Ag(NH_3)_2]^{+}NO_3^{-} + NH_4OH \xrightarrow{warm}$$

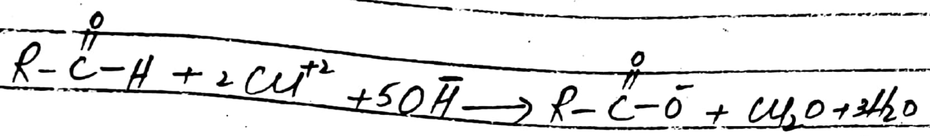
$$R-\overset{O}{\overset{\|}{C}}-\bar{O}NH_4^{+} + 3H_2O + 2Ag + NH_4NO_3$$

OR

$$R-\overset{O}{\overset{\|}{C}}-H + \text{Tollen's reagent} \xrightarrow{warm} R-\overset{O}{\overset{\|}{C}}-\bar{O} + \underset{\substack{\text{Silver}\\\text{mirror}\\\text{or}\\\text{Silvery}\\\text{precipitates}}}{Ag}$$

Oxidation by Fehling's Solution

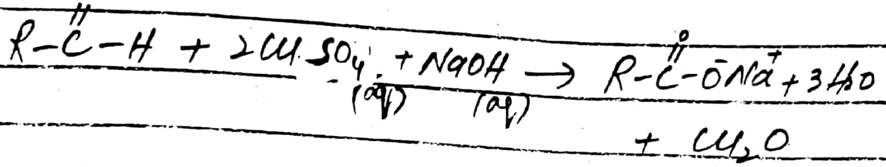
Fehling solution is an alkaline solution of copper(II) salt, which can also only oxidise aldehyde to carboxylic acid but ketone cannot be oxidised. On oxidation brick red precipitates are seen.



$$R-\overset{O}{\overset{\|}{C}}-H + 2Cu^{+2} + 5\bar{OH} \longrightarrow R-\overset{O}{\overset{\|}{C}}-\bar{O} + Cu_2O + 3H_2O$$

Brick red ppt

OR



$$R-\overset{O}{\overset{\|}{C}}-H + 2CuSO_{4(aq)} + NaOH_{(aq)} \longrightarrow R-\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{Na} + 3H_2O + Cu_2O$$

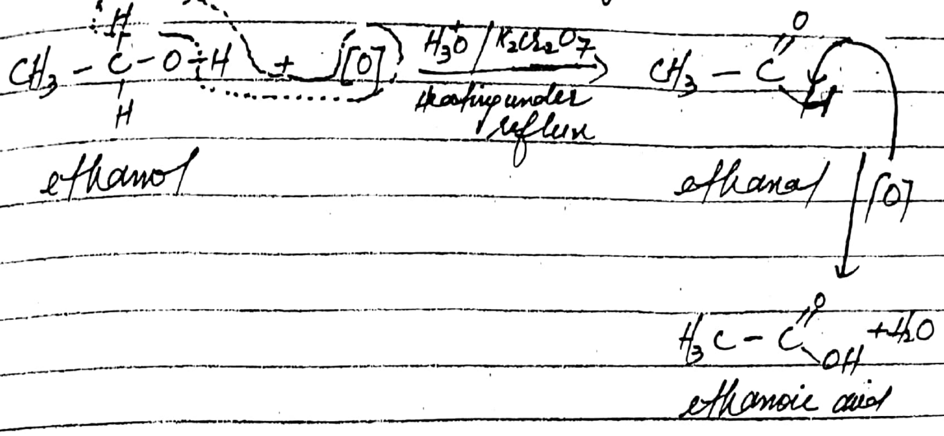
Brick red ppt

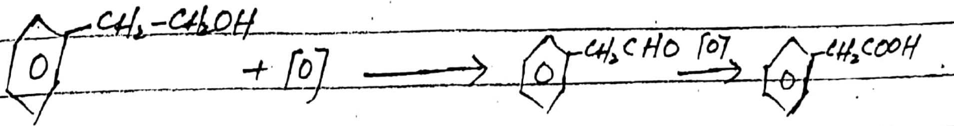
Carboxylic acids and their derivatives

Formation of carboxylic acid

(i) By the oxidation of Alcohols and aldehydes

Primary Alcohols on oxidation with acidified potassium dichromate (VI) by heating under reflux are converted to carboxylic acids



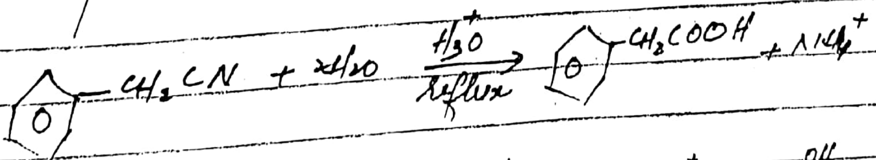


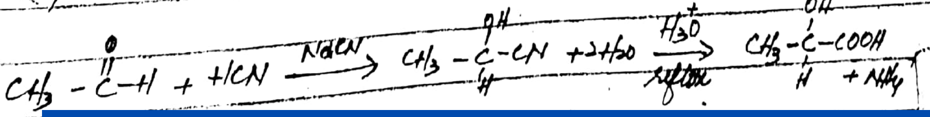
(ii) By the hydrolysis of nitriles

Nitriles are hydrolysed to carboxylic acids in the presence of dilute H_2SO_4 or dil HCl by heating the mixture under reflux.

$$CH_3-CH_2-CN + 2H_2O \xrightarrow[\text{reflux}]{H_3\overset{+}{O}} CH_3-CH_2-COOH + NH_4^+$$

propanenitrile





$$CH_3-\overset{O}{\overset{\|}{C}}-H + HCN \xrightarrow{NaCN} CH_3-\underset{H}{\overset{OH}{C}}-CN + 2H_2O \xrightarrow[\text{reflux}]{H_3\overset{+}{O}} CH_3-\underset{H}{\overset{OH}{C}}-COOH + NH_4^+$$

Chemical properties of Carboxylic acids

Carboxylic acids are ionised in water to produce H^+ but unlike mineral acids, they are weak acids and are partially ionised to produce lesser number of hydrogen ions.

$$CH_3COOH + H_2O \rightleftharpoons CH_3CO\bar{O} + H^+$$

(i) Reaction with metals

$$2CH_3COOH + 2Na \longrightarrow 2CH_3CO\bar{O}\overset{+}{Na} + H_2$$

$$2CH_3CH_2COOH + Mg \longrightarrow (CH_3CH_2CO\bar{O})_2\overset{+2}{Mg} + H_2$$

(ii) Reaction with Bases

$$2CH_3COOH + K_2CO_3 \longrightarrow 2CH_3CO\bar{O}\overset{+}{K} + H_2O + CO_2$$

$$CH_3COOH + KHCO_3 \longrightarrow CH_3CO\bar{O}\overset{+}{K} + H_2O + CO_2$$

$$2CH_3COOH + MgO \longrightarrow (CH_3CO\bar{O})_2\overset{+2}{Mg} + H_2O$$

$$CH_3COOH + NH_3 \longrightarrow CH_3CO\bar{O}NH_4^+$$

$$CH_3COOH + KOH \longrightarrow CH_3CO\bar{O}K^+ + H_2O$$

↑
Ionic Compound
charges must be present over ions

Reduction of Carboxylic acids:- Can be reduced by using $LiAlH_4$ in dry ether as reducing agent.

$$CH_3CH_2COOH \xrightarrow[\text{Dry ether}]{LiAlH_4} CH_3CH_2CH_2OH$$

Primary alcohol

(iii) Formation of acyl chloride

$CH_3-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \xrightarrow{\text{Room temp}} CH_3-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + H_2O$

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \xrightarrow{\text{Room temp}} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + H_2O$

$3CH_3-\overset{O}{\overset{\|}{C}}-OH + PCl_3 \xrightarrow[\text{Heating under reflux}]{} CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$

ethanoyl chloride

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + PCl_3 \xrightarrow[\text{reflux}]{\text{Heating under}} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$

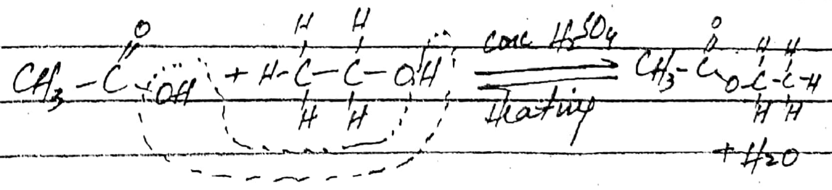
Propanoyl chloride

$CH_3-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \xrightarrow{R.T} CH_3-\overset{O}{\overset{\|}{C}}-Cl + SO_2 + HCl$

(iv) Formation of ester

(a) From alcohols

Carboxylic acids react with alcohols in the presence of concentrated sulphuric acid to give esters and water.



$$CH_3-\overset{O}{\overset{\|}{C}}-OH + H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH \xrightarrow[\text{Heating}]{\text{conc } H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H + H_2O$$

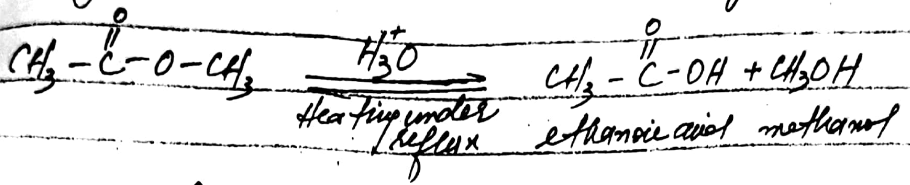
$$CH_3CH_2COOH + CH_3OH \xrightleftharpoons[\text{Heat}]{\text{Conc } H_2SO_4} CH_3CH_2COOCH_3 + H_2O$$

ester

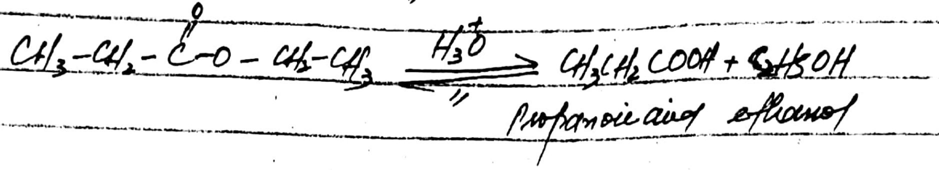
Chemical properties of esters.

(i) Hydrolysis of esters by acids

Esters on hydrolysis in the presence of acid and by heating under reflux to give alcohol and carboxylic acid.



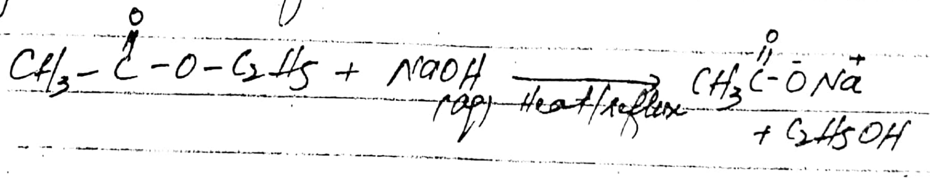
$$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3 \xrightarrow[\text{Heating under reflux}]{H_3O^+} \underset{\text{ethanoic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{methanol}}{CH_3OH}$$



$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 \underset{''}{\overset{H_3O^+}{\rightleftharpoons}} \underset{\text{Propanoic acid}}{CH_3CH_2COOH} + \underset{\text{ethanol}}{C_2H_5OH}$$

(ii) Base hydrolysis

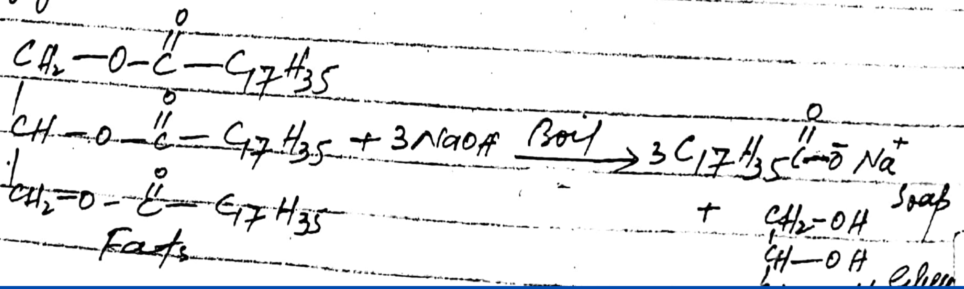
When esters are hydrolysed in the presence of alkali by heating under reflux, it gives salt of acid and alcohol.



$$CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5 + \underset{(aq)}{NaOH} \xrightarrow{\text{Heat/reflux}} CH_3\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{Na} + C_2H_5OH$$

Saponification of esters

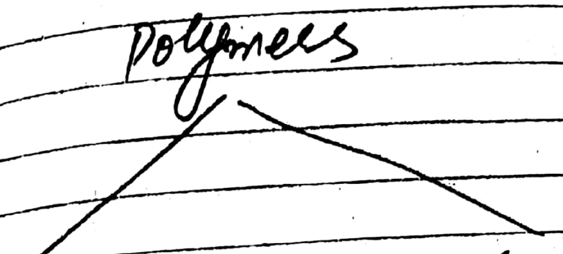
Fats and vegetable oil are also esters which on hydrolysis in the presence of aq NaOH or KOH to give soap and glycerol.



$$\underset{\text{Fats}}{\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \end{array}} + 3NaOH \xrightarrow{\text{Boil}} \underset{\text{Soap}}{3C_{17}H_{35}\overset{O}{\overset{\|}{C}}-\bar{O}\,\overset{+}{Na}} + \begin{array}{l} CH_2-OH \\ | \\ CH-OH \end{array} \text{Glyce}$$

uses of esters

- ⇒ Esters are used in flavouring juices and other foods due to their fruity smell.
- ⇒ as solvent in nail polish and varnish
- ⇒ are used for making soaps



Addition polymers	Condensation polymer
⇒ No by product is formed in the formation of addition polymers	By product is formed which is mostly water
⇒ only unsaturated organic compounds are involved	⇒ saturated and unsaturated both are involved

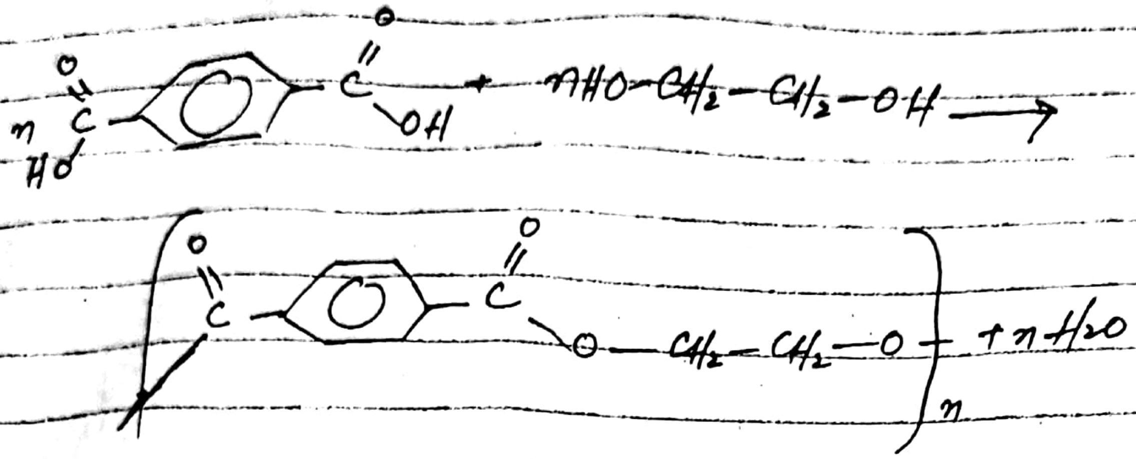
Examples of addition polymers

Examples of addition polymers have already been discussed in the topic of alkanes.

Examples of condensation polymers

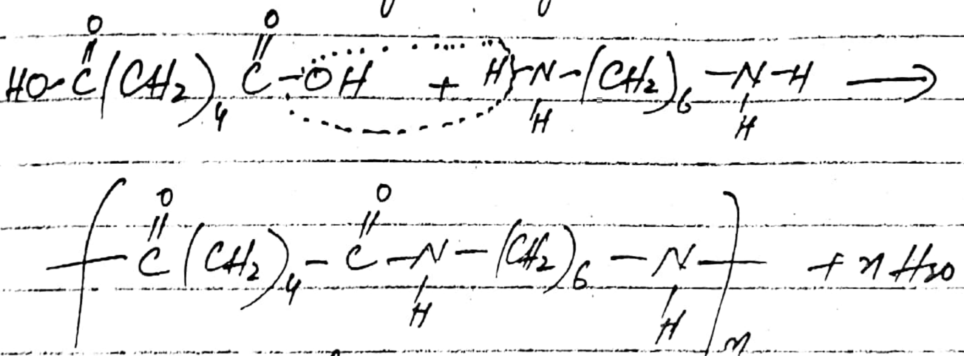
Polyesters:- Polyesters can be
by reacting dicarboxylic acids

with diol. e.g; Terylene



Terylene

Polyamides :- Polyamides are formed when dicarboxylic acid reacts with diammine e.g; Nylon 6,6



$$HO-\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-OH + H-\underset{H}{N}-(CH_2)_6-\underset{H}{N}-H \longrightarrow$$

$$\left[\overset{O}{\overset{\|}{C}}(CH_2)_4-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-(CH_2)_6-\underset{H}{N}\right]_n + nH_2O$$

nylon 6,6 (Polyamide)

Infra-red Spectroscopy

when infra red light (photons in the infra-red region of the spectrum) is passed through a sample of an organic compound, the vibrational energy of bonds is increased. Each type of vibration will absorb characteristic wavelengths of infra-red radiations. These are often expressed as the reciprocal of the wavelengths in a unit called wavenumbers (measured in cm^{-1}).

The frequency of vibration is determined by the stiffness of the bond and the masses of the atoms. The stiffness of a bond is closely related to its Bond energy.

A light atom attached by a strong bond e.g., O–H bond vibrates at a higher frequency, while a heavy atom attached by a weak bond e.g., C–I vibrates at a lower frequency.

Factors influencing vibrational frequency

(1) **Effect of bond**:- vibrational frequency increases as the number of bonds increases, for example $C\equiv C > C=C > C-C$ which from 2000–2300 cm^{-1}, 1500–1900 cm^{-1} and 800–1300 cm^{-1} for triple, double and single bond respectively.

(2) **Effect of mass**:- The vibrational frequency decreases as the mass of the system increases e.g., O–H has more vibrational frequency than O–D.

(3) Effect of bond strength or electronegativity

The vibrational frequency increases as the bond strength increases. For example, the vibrational frequency of C–H, N–H, O–H and F–H is expected to decrease due to the increase in mass but vibrational frequency of F–H > O–H > N–H > C–H due to increase in electronegativity from C to F.

Infra-red spectra of small molecules

A molecule absorbs in the infrared region only if the vibration causes a change in its dipole moment. The most common gases in the atmosphere N_2, O_2 and Ar, therefore do not absorb but CO_2 and water vapours do absorb.

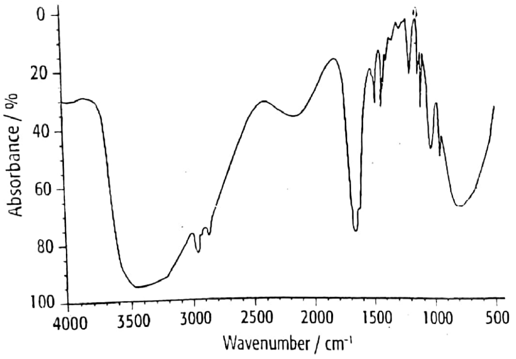
Infra-red spectra of larger molecules

If the molecule is fairly large, a particular bond may vibrate fairly independently of the rest of the molecule. this means that certain bonds show characteristic vibration frequencies, irrespective of where they are found. The actual frequency does vary slightly from one molecule to another, so the vibration bands are in a region of the infrared spectrum, rather that at a specific frequency. therefore we can identify the presence or absence of different functional groups from the absorption pattern on an infra-red spectrum.

Absorption frequencies of some common bonds and functional groups

Bond	Functional groups containing the bond	Absorption range (in wavenumbers)/cm^{-1}	Appearance of peak (*s* = strong, *w* = weak)
C–O	alcohols, ethers, esters	1040–1300	*s*
C=C	aromatic compounds, alkenes	1500–1680	*w* unless conjugated
C=O	amides ketones and aldehydes esters	1640–1690 1670–1740 1710–1750	*s* *s* *s*
C≡C	alkynes	2150–2250	*w* unless conjugated
C≡N	nitriles	2200–2250	*w*
C–H	alkanes, CH_2–H alkenes/arenes, =C–H	2850–2950 3000–3100	*s* *w*
N–H	amines, amides	3300–3500	*w*
O–H	carboxylic acids, RCO_2–H H-bonded alcohol, RO–H free alcohol, RO–H	2500–3000 3200–3600 3580–3650	*s* and very broad *s* *s* and sharp

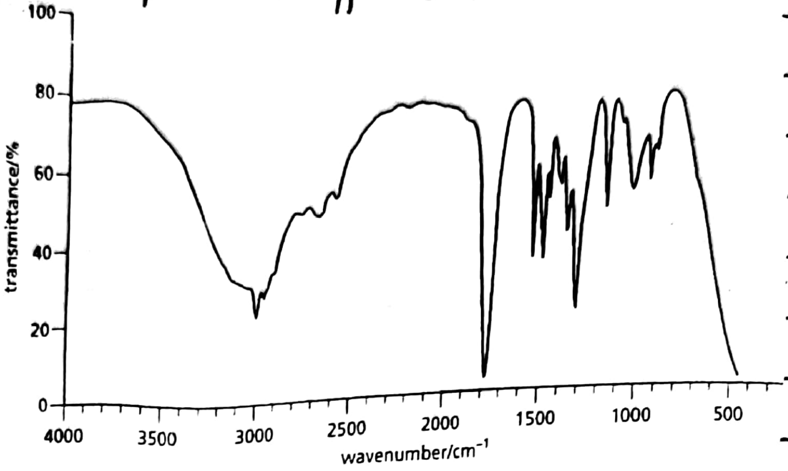
Infra red spectra of ethylamine ($CH_3CH_2NH_2$)



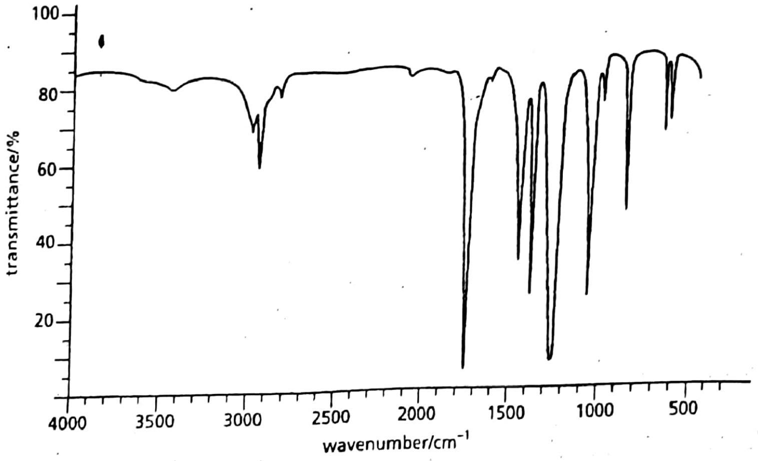
Peak from 3300 – 3500 cm^{-1} shows the presence

Infra red spectra of the two isomers of C_3H_6O

IR spectrum of T.

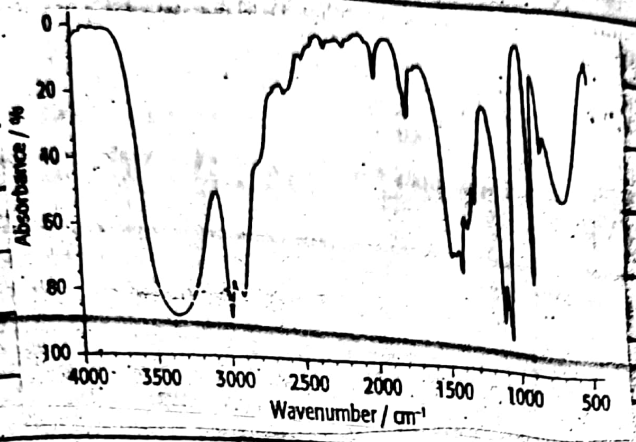


IR spectrum of U.



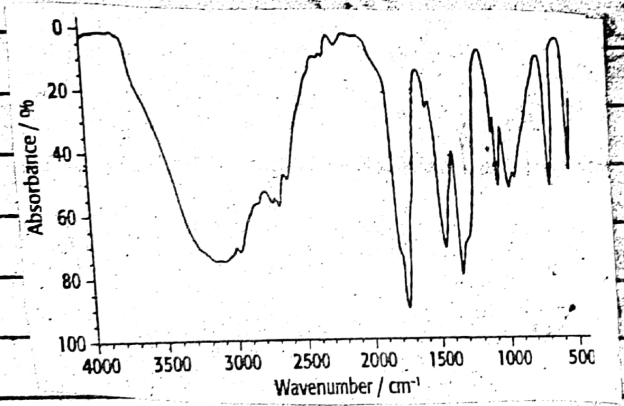
Both T and U show a C=O absorption in their spectrum at about 1700 cm^{-1} and C–O absorption at about 1250 cm^{-1}.
T shows a broad hydrogen bonded O–H band from 3300 to 2500 cm^{-1}, while U shows no O–H band at all.
So T is $CH_3CH_2CO_2H$ (propanoic acid) and U could be either the ester $CH_3CO_2CH_3$ (methyl ethanoate) or the ester $HCO_2CH_2CH_3$ (ethyl methanoate).

Infra-red spectrum of ethanol



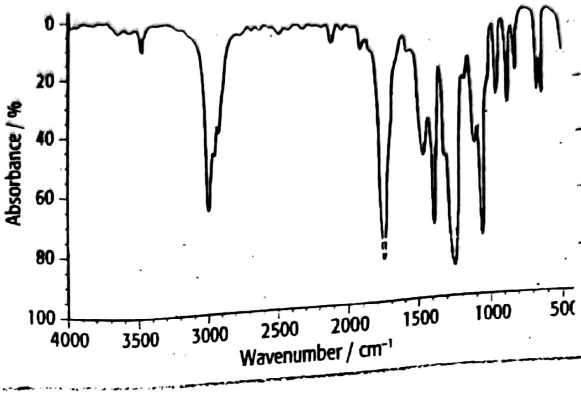
Strong band from 3200-3600 cm^{-1} arising from the O-H groups involved in hydrogen bonding in the alcohol.

Infra-red spectrum of ethanoic acid



Strong and very broad peak from 2500-3000 cm^{-1} shows the presence of O-H groups involved in hydrogen bonding in the carboxylic acid. Another strong peak at 1720 cm^{-1} shows the presence of C=O group in carboxylic acid.

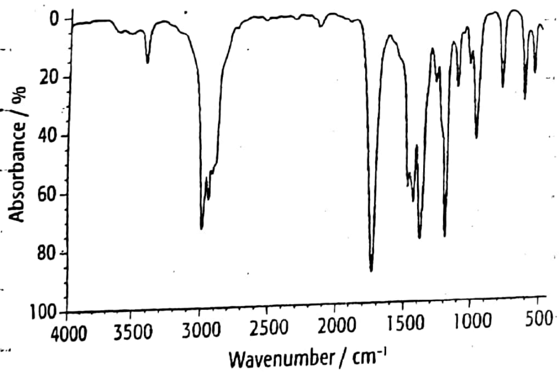
Infra-red spectrum of ethyl ethanoa



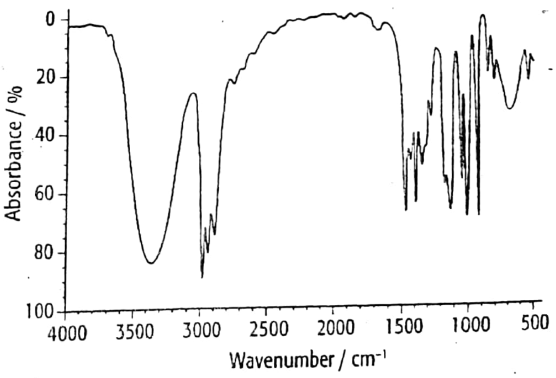
Strong peak at 1740 cm^{-1} shows the presence of $C=O$ group in ester. Another strong peak from 1040 to 1300cm shows the presence of $C-O$ in ester.

More examples

A



B

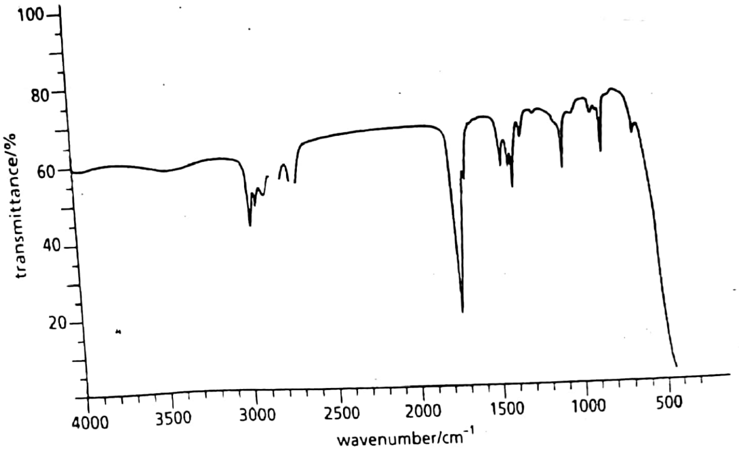


Whic one of the spectra is that of butanone and butan-2-ol? Spectra A shows a strong peak from 1670 to 1740 c shows the presence of $C=O$ in Ketone. Spectra B shows a strong and broad pea from 3200 to 3600 cm^{-1} shows the presence of O-H in alco 2-o

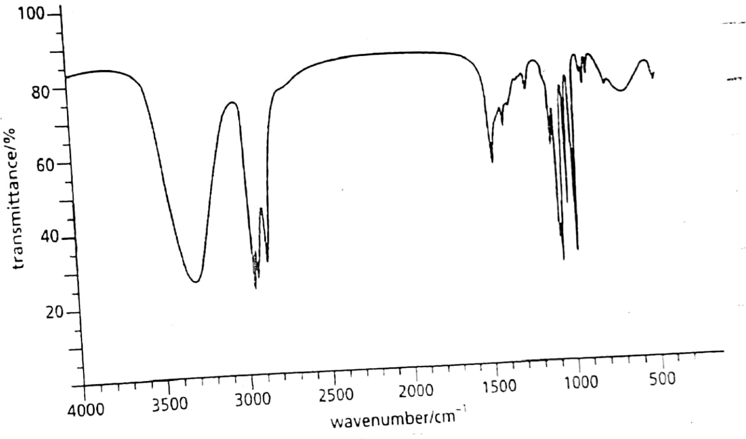
Solved example

Compound V (C_3H_6O) gives a silver mirror when warmed with Tollen's reagent. It can be converted to compound W by reagent X. Use the following spectras to identify the functional groups present in V and W.

IR spectrum of V.



IR spectrum of W.



Solution :- In spectra of V, there is a strong peak from 1670–1740 cm⁻¹ shows the presence of C=O in aldehyde. whereas a strong peak from 3200–3600 cm⁻¹ in the spectra of W shows the presence of O–H group in alcohol. No C=O peak at 1740 cm⁻¹ in the spectra of W confirms that W is not a carboxylic acid.