AS ORGANIC CHEMISTRY NOTES

by

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"Nothing is Particularly Difficult if you Break it Down into Small Jobs"
"A little more Persistence, a little more Effort, and you might not be the Hopeless Failure you think you are, Genius and Failure don't happen overnight"

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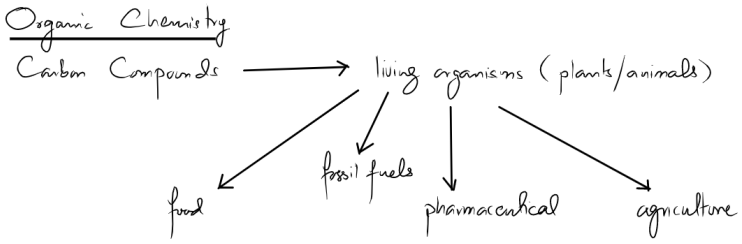


Formulas

1- **Molecular formula**

total no of atoms of elements in a compound

$C_4H_8O_2$, $C_6H_{12}O_6$ no information about structure

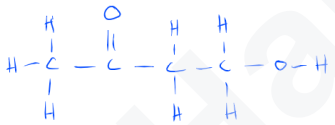
2- **Structural formula**

provides information about the structure

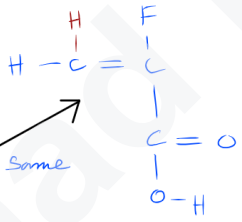
(a) **full-displayed formula**

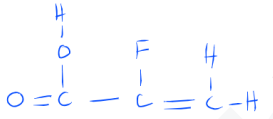
every single atom/bond is shown

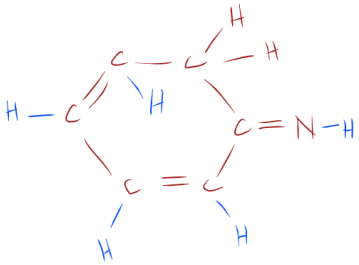
C – 4 bonds
N – 3 bonds
O – 2 bonds
H – 1 bond
halogens – 1 bond.



* not the actual shape

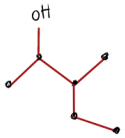


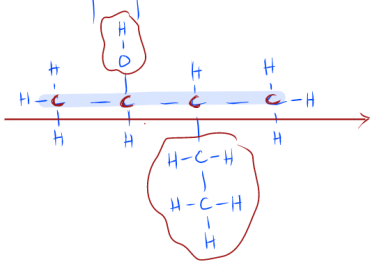




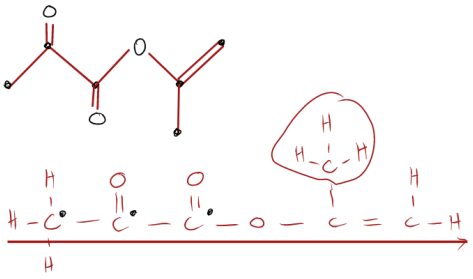
(b) condensed structural formula

running out of space

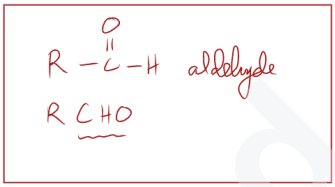




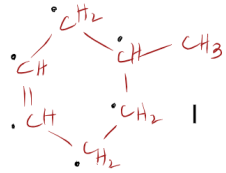
$CH_3\ CH(OH)\ CH(CH_2CH_3)\ CH_3$



$CH_3\ CO\ COO\ C(CH_3)=CH_2$

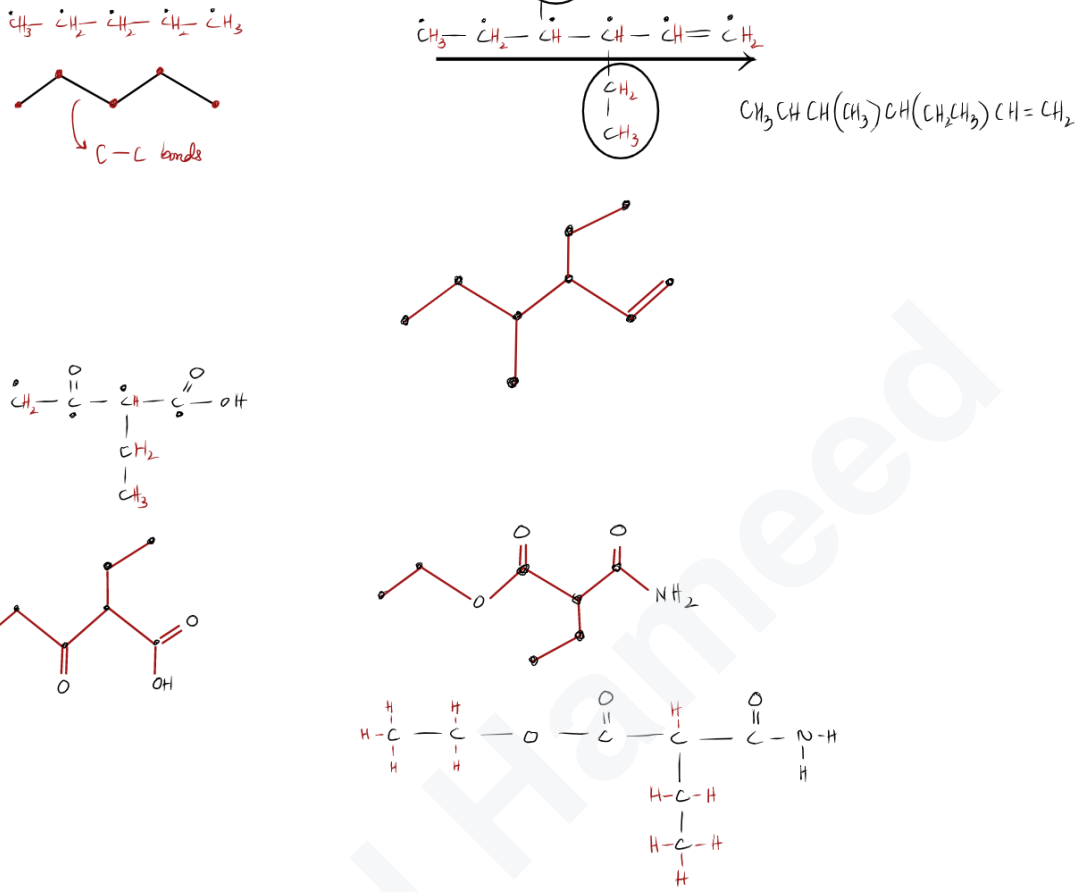


displayed + condensed



(c) skeletal formula

only C-C bonds shown and any functional group (no C/H atoms are shown)



Naming

Homologous Series family of organic molecules having

1. similar chemical properties
2. show trends in physical properties
   - molecule size increases
     - MP/BP higher
     - more viscousity
     - less flammability

   bigger molecule / more e^- / stronger Temporary / induced dipoles
   more van der waals forces

3. same functional group
   - group of atoms/structure that determines chemical properties

$CH_2 = CH - CH_2 - CH_3$ ← all reactions

instantaneous - induced dipole

4. same general formula
   only applicable for simple molecules
   C_nH_{2n} $CH_3 - CH = CH_2$ C_3H_6 general formula ✓

$CH_2 = CH - CH_2 - CH = CH - CH_3$ C_6H_{10} general formula does not work

5. Success members differ by CH_2

CH_4 C_2H_6 C_3H_8 C_4H_{10} (CH_2 CH_2 CH_2)

Prefix = number of carbon atoms

meth, eth, prop, but, pent, hex, hept, oct, non, dec
1C 2C 3C 4C 5C 6C 7C 8C 9C 10C

Suffix

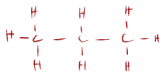
↳ homologous series

1- Alkane	-ane	saturated hydrocarbon	
2- Alkene	-ene	unsaturated hydrocarbon	C = C
3- Alcohol	-ol	-OH hydroxy group (hydroxyl)	
4- Carboxylic acid	-oic acid	$-C(=O)-OH$	
5- Carbonyl compounds			
(a) Aldehyde	-al	$-C(=O)-H$	at the end of the carbon chain
(b) ketone	-one	$-C(=O)-$	in the middle of the carbon chain
6- Nitriles	-nitrile	$-C \equiv N$	at the end of a Carbon chain
7- Amines	-amine	$-NH_2$	

Prefix #C — an/en — Suffix homologous

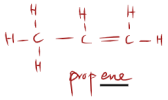
an/en → saturated or unsaturated

Alkanes

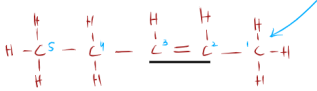


prop ane

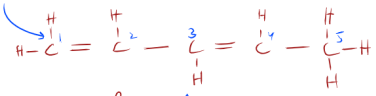
Alkenes



prop ene



pent - 2 - ene



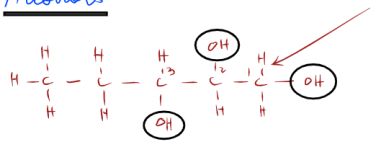
pent - 1,3 - di ene

↳ position of c=c

number (smaller number should be given to higher precedence group)

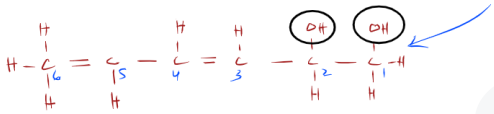
1. carboxylic acid
2. nitrile
3. aldehyd
4. ketones
5. alcohols (hydroxy)
6. amines (amino)

Alcohols



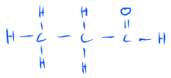
pent an - 1,2,3 - tri ol

↳ saturated carbon chain.



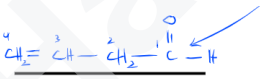
hex - 3,5 - dien - 1,2 - diol

Aldehyde - al



propan - 1 - al ≅ propanal

↳ unnecessary to write 1

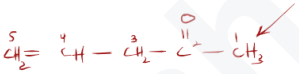


but - 3 - en (-1-) al

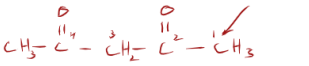
Ketones

middle of the chain

- one

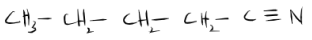


pent - 4 - en - 2 - one

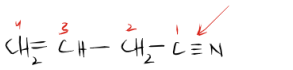


pent an - 2,4 - di one

Nitriles -C≡N

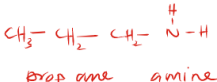


pent ane nitrile



but - 3 - ene nitrile

Ammines

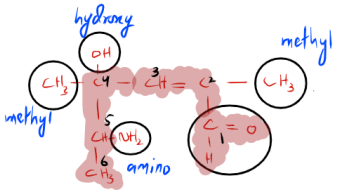


prop ane amine

branched molecules and multiple functional groups

number, number ⟶ comma

number – letter ⟶ dash



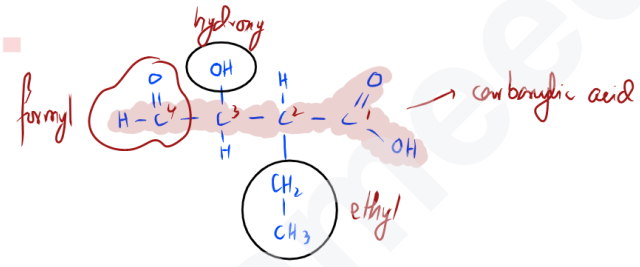
5-amino-4-hydroxy-2,4-dimethyl hex-2-en al

position - branches alphabetically.

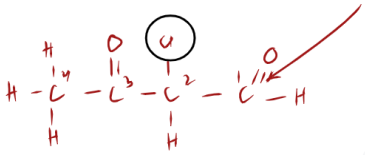
main chain
longest possible / continuous carbon atom chain
- suffix functional group
- max C=C, C≡C
- maximum groups attached to it

number
(smaller number should be given to higher precedence group)

1- carboxylic acid
2- nitrile (cyano)
3- aldehyd (formyl)
4- ketones (oxo)
5- alcohols (hydroxy)
6- amines (amino)



2-ethyl-3-formyl-3-hydroxy propanoic acid



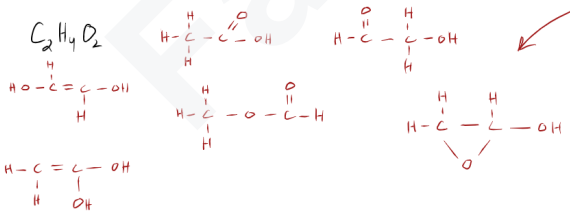
halogen branches chloro, bromo, iodo

Carbon branches alkyl, methyl etc

2-chloro but-an-3-one-1-al

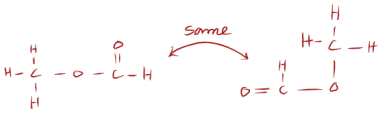
Isomers

$C_2H_4O_2$



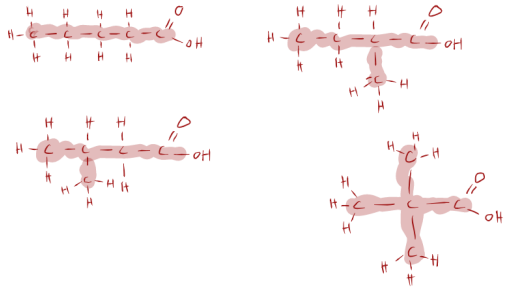
Structural Isomers

molecules having same molecular formula and different structural formulas

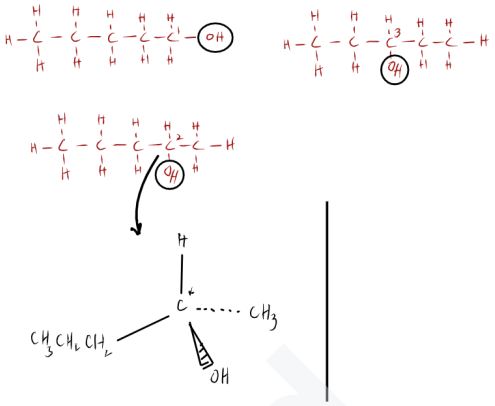


Types of Structural Isomers

(a) chain Isomer

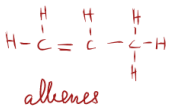


(b) Positional Isomers

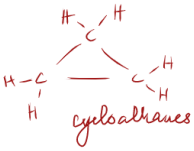


3- functional group isomer

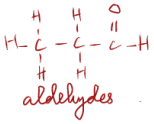
change the functional group



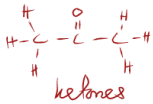
alkenes



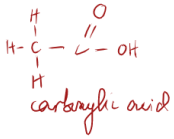
cycloalkanes



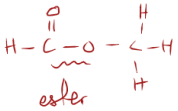
aldehydes



ketones



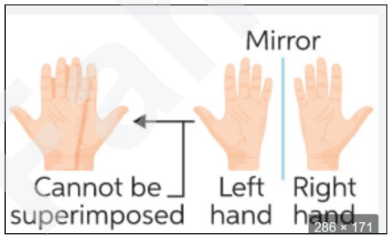
carboxylic acid



ester

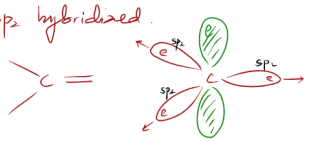
Stereo Isomer

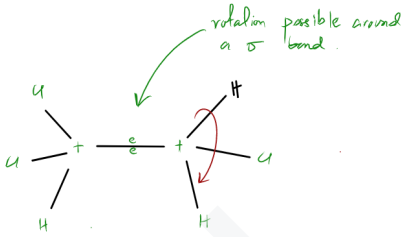
molecules having same molecular formula, same structural formula but different 3 dimensional geometry (shape is different).

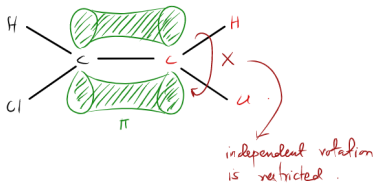


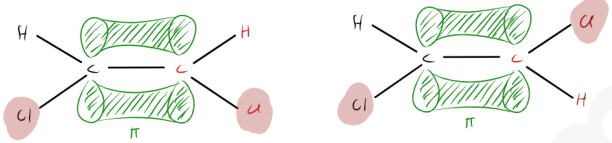
1- Geometric Isomer

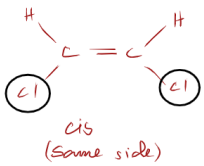
- C=C must be present, each C in C=C must be bonded to two different groups.

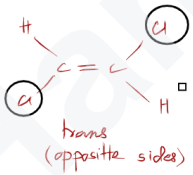






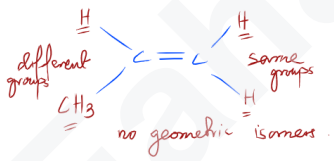




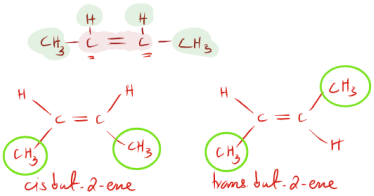


Examples

(a) $CH_3-CH=CH_2$ propene

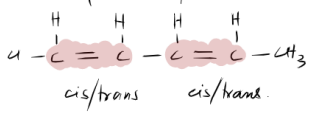


(b) but-2-ene

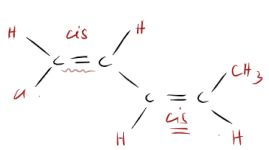


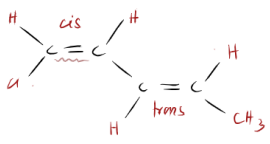
Unsymmetric molecules

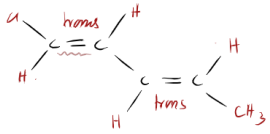
multiple cis / trans

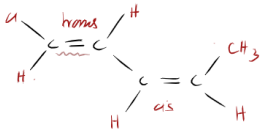


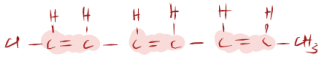
same if molecule is symmetric	cis	cis
	cis	trans
	trans	cis
	trans	trans











8

cis	cis	cis
cis	cis	trans
cis	trans	cis
cis	trans	trans
trans	cis	cis
trans	cis	trans
trans	trans	cis
trans	trans	trans

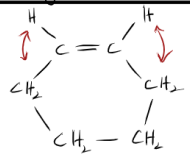
same if molecule is symmetric

number of geometric isomers

2^n

n is number of C=C that make cis / trans isomers in unsymmetric molecules (also add chiral centers)

Can't form geometric isomers in cyclic structures.



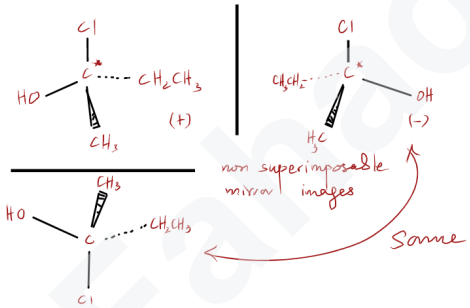
can't make trans version as cyclic structure needs to be broken

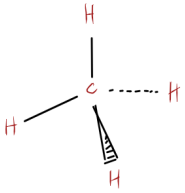
2 - Optical Isomers

Enantiomers, mixture of enantiomers → racemic mixture.

chiral center needed

C atom that is making 4 single bonds with 4 different groups.
- tetrahedral, 109.5° bond angles, sp^3 hybridized.





Enantiomers have almost identical physical / chemical properties
- Shape specific functionality varies a lot
  e.g biology / enzyme

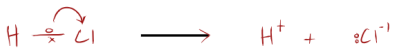
differentiate between Enantiomers

both enantiomers rotate plane polarized monochromatic light in opposite directions, clockwise (+) and anticlockwise (−)

homolytic bond fission – bond breaks equally

free radicals formed

heterolytic bond fission bond breaks unequally



Curly Arrows represent movements of e⁻

half-arrow movement of 1e

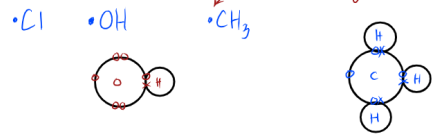
full arrow movement of 2e

Free Radical

a specie (atom or molecule) with unpaired e⁻

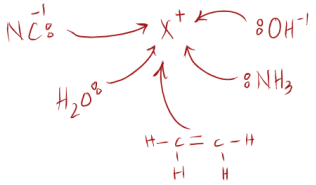
very reactive

single dot: unpaired e⁻



Nucleophile (attracted to +ve charge)

specie which can donate a pair of e⁻ and is attracted to +ve charge



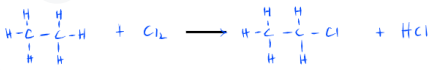
Electrophile

specie which can accept a pair of e⁻ and is attracted to –ve charge

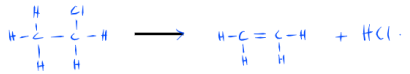
Types of Reactions

(a) Addition

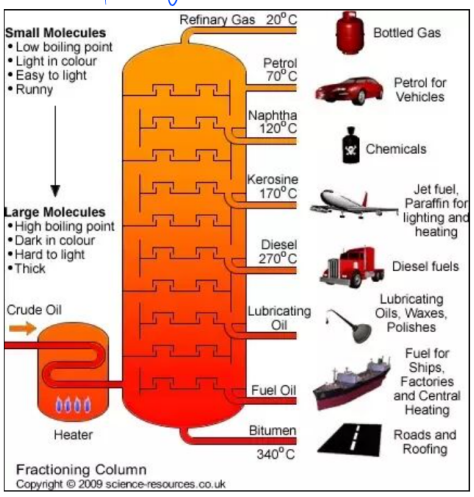
(b) Substitution



(c) Elimination

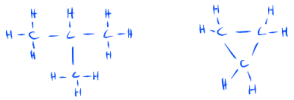


Source of Organic Compound ⟶ Fossil fuel



Alkanes — saturated hydrocarbons

C_nH_{2n+2}



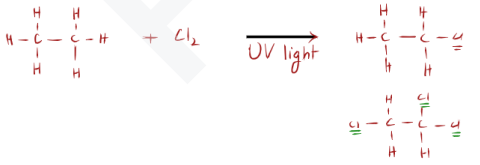
Physical Properties

- nonpolar, van der waals (weak)
- not soluble in water

when size of molecule increases
- more van der waals
- higher MP, BP
- more viscous
- less flammable

Free radical substitution

halogenation / chlorination / bromination (for I_2 reaction is very slow, F_2 reaction is very uncontrolled)

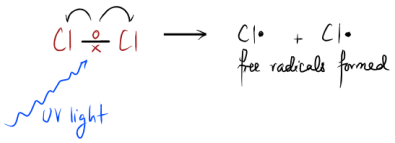


many random substitution products

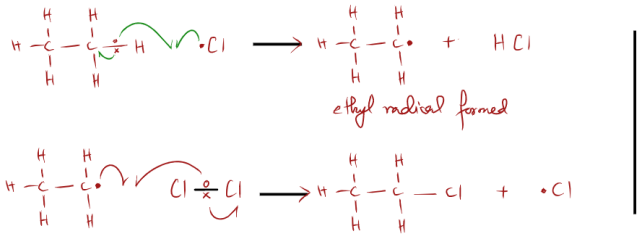
reaction can happen with any alkyl chain

Mechanism

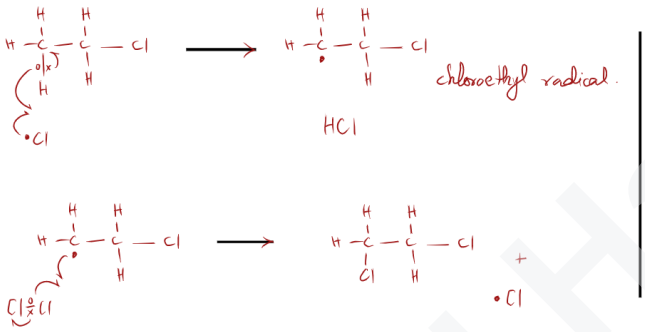
step 1 Initiation : free radicals formed, homolytic bond fission because of UV light



step 2 Propagation : total no. of free radicals remain constant.

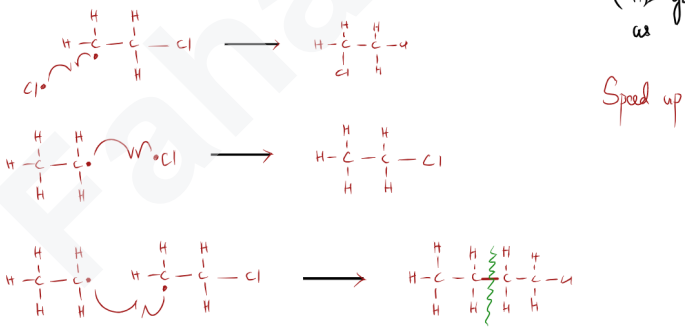


Propagation



Propagation

step 3 termination two free radicals join
no more free radicals → reaction stops

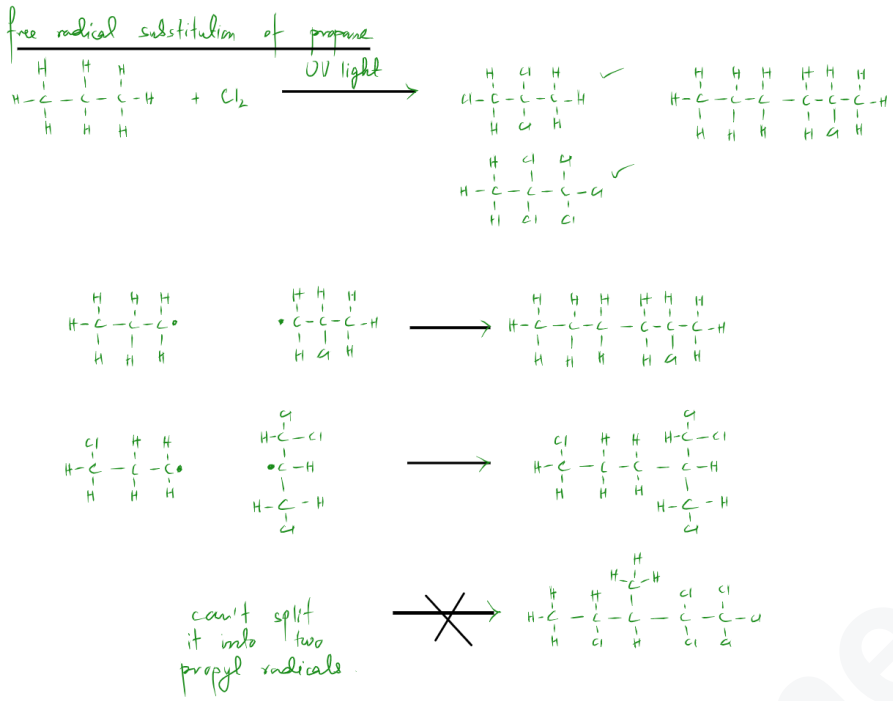


(H_2 gas molecules are never produced as there are no H• radicals)

Speed up free radical : higher concentration of free radicals

$Pb(CH_3)_4$ tetramethyl lead(IV)

↳ $\cdot CH_3$



All Hydrocarbons (& most organic compounds) & combustion

C_3H_6 (g) + $\frac{9}{2}$ O_2 (g) → 3 CO_2 (g) + 3 H_2O (l)

"excess"

complete combustion

In incomplete combustion

C (soot) and CO are produced

CO: deadly poisonous gas, causes choking. combines irreversibly with haemoglobin

Cracking of long Chain Hydrocarbons

fossil fuel → large molecules (Not Useful)

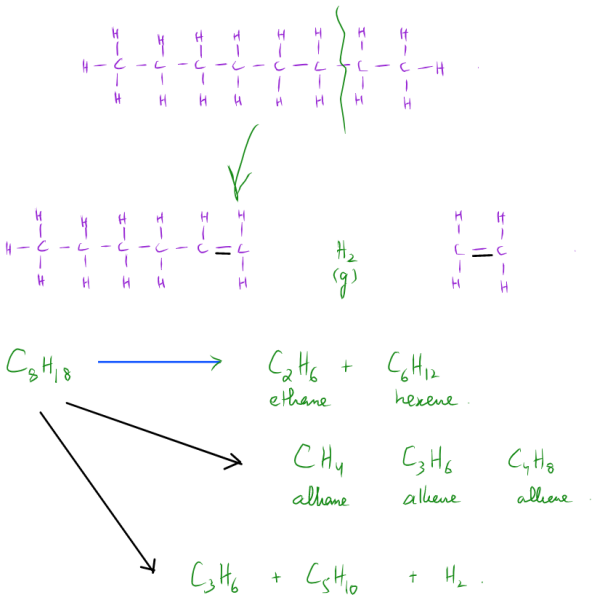
high MP/BP, more van der waals. solid, semi-solid, wax. very viscous less flammable.

catalytic cracking. T > 450°C

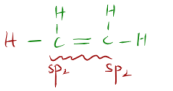
catalyst: Al_2O_3 / SiO_2 pumice / zeolite

→ small molecules (alkanes / alkenes) + Hydrogen gas

× low MP/BP less van der waals
× less viscous
× very flammable



Alkenes C_nH_{2n}

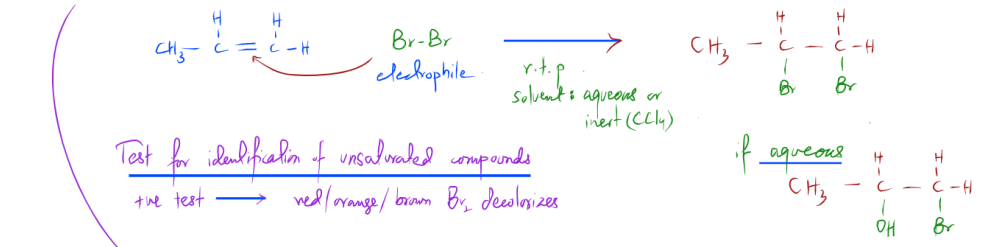


high charge density π e⁻ cloud

electrophiles
+ve ions, δ+ charge, electron deficient

Electrophilic Addition Reactions

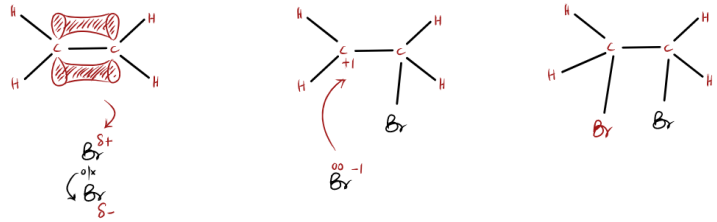
1- Bromination Reaction

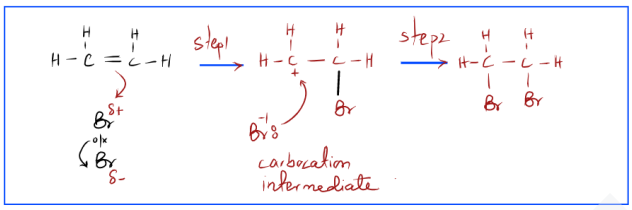


Test for identification of unsaturated compounds

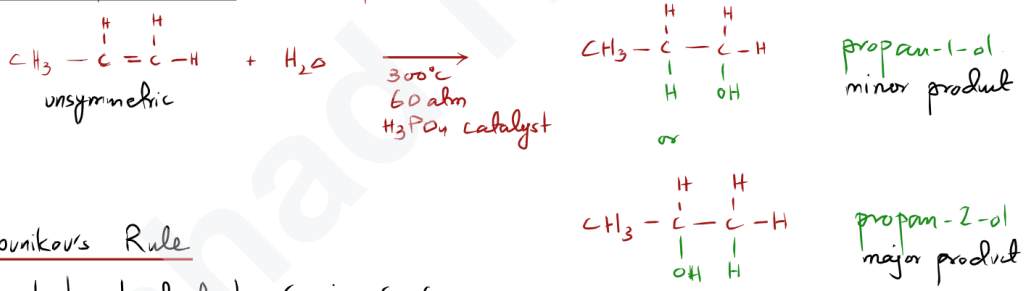
+ve test → red/orange/brown Br_2 decolorizes

Electrophilic Addition Mechanism



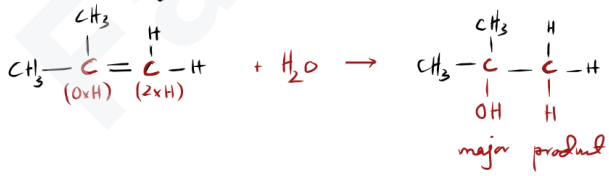


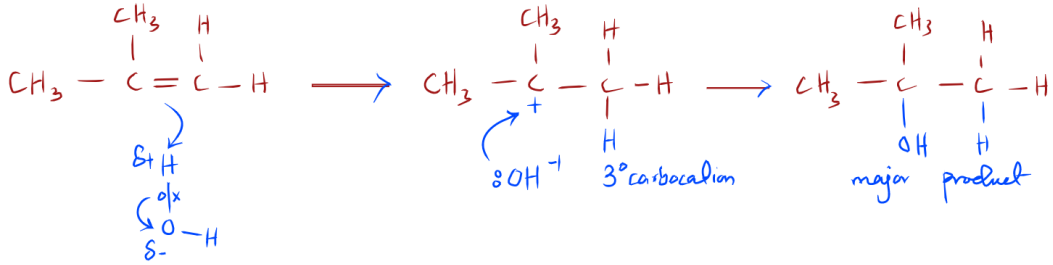
2. Hydration of alkenes (electrophilic addition)

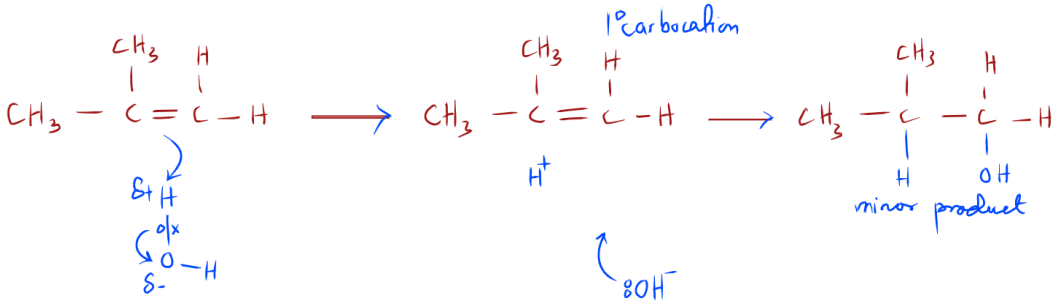


Markovnikov's Rule

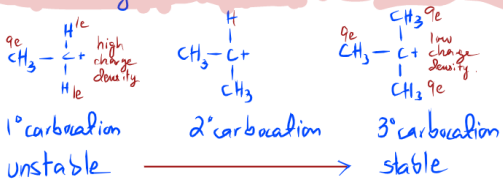
H likes to be bonded to C in C=C which is already bonded to more H-atoms



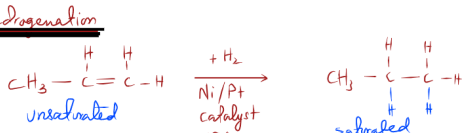


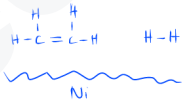


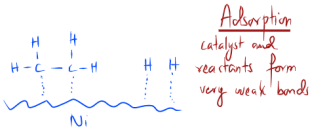
carbocations with more alkyl chains which are e⁻ donating are more stable, as they have lower charge density.

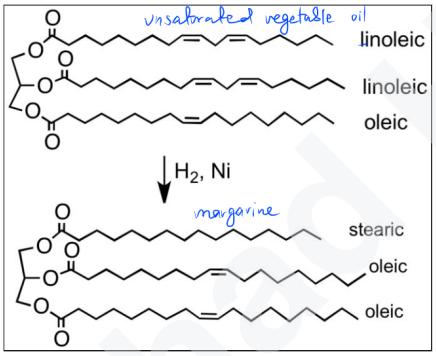


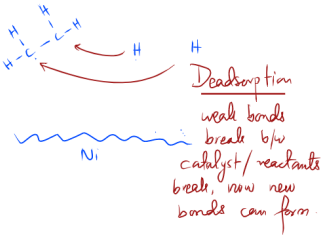
3 - Hydrogenation



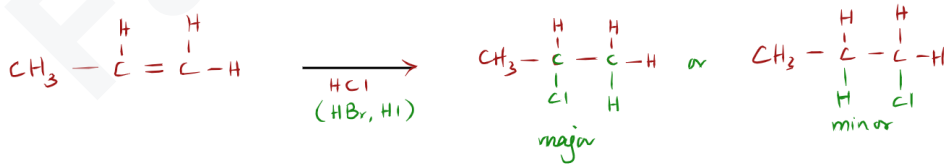


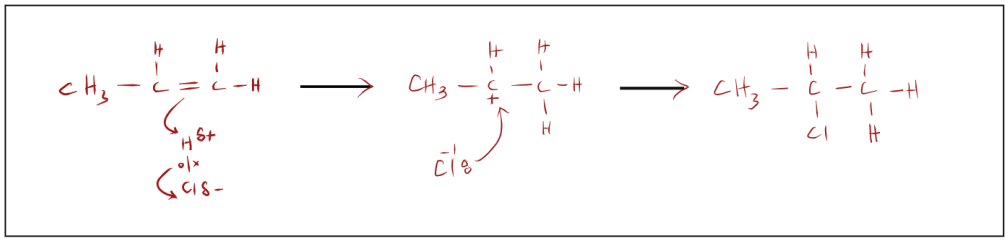






4 - Hydrogen Halides (Electrophilic Addition)





Oxidation of Alkenes

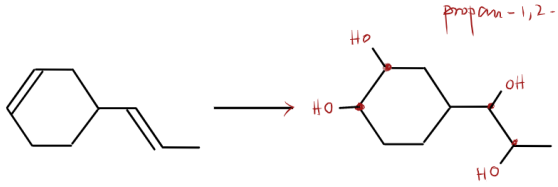
1- Mild Oxidation

cold/dilute $KMnO_4$

$CH_3-CH=CH-H + [O] \longrightarrow CH_3-CH(OH)-CH(OH)-H + H_2O$

diols formed

propan-1,2-diol



2- Strong Oxidation

hot, concentrated, acidified $KMnO_4$ (potassium manganate VII)

*double bond breaks completely.

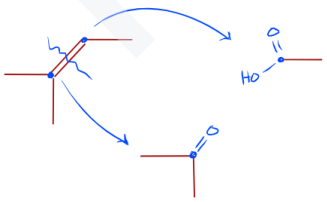
1- $=CH_2 \longrightarrow CO_2 + H_2O$

2- $=CHR \longrightarrow O=CHR \longrightarrow O=C(R)OH$ (aldehyde → carboxylic acid)

3- $=CR_2 \longrightarrow O=CR_2$ (ketone)

$CH_3-CH_2-CH_2-C(CH_3)=CH-H \longrightarrow =CH-H \longrightarrow CO_2 + H_2O$

$CH_3-CH_2-CH_2-C(CH_3)= \longrightarrow CH_3-CH_2-CH_2-C(CH_3)=O$ ketone



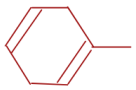
Assignment draw products for both mild and strong oxidation

1- 2, 3 di methyl pent-2-ene

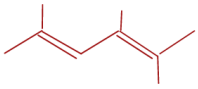
2 2 methyl but-1-ene

3.

4-



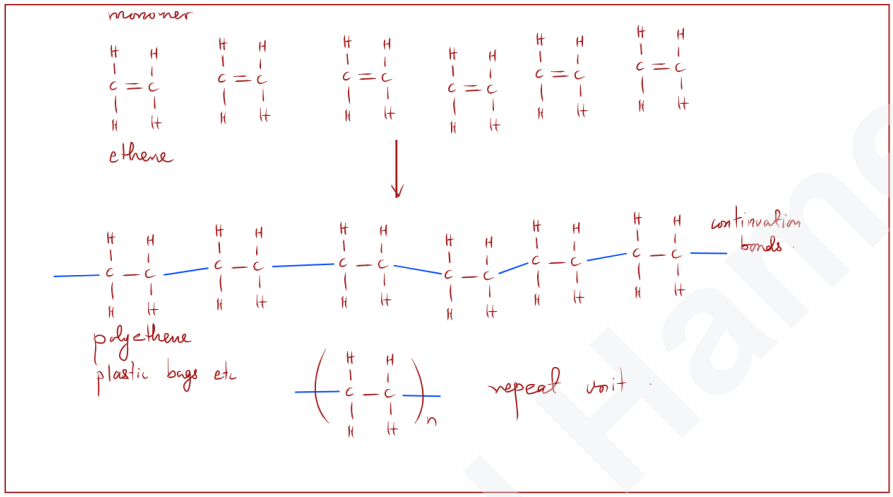
5.



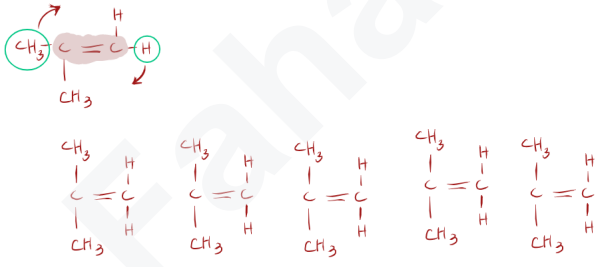
6 pent-1,3-diene

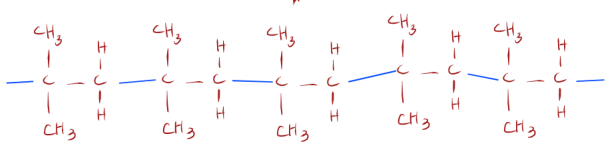
Alkenes - Addition Polymers

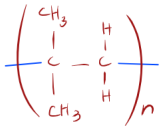
a very large macromolecule formed when hundreds of monomers join together



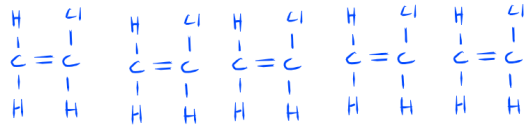
2 methyl propene



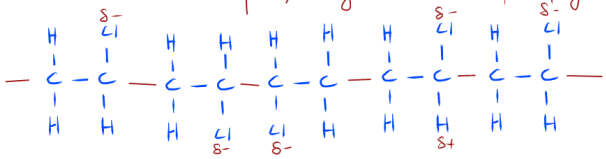




PVC Polyvinyl chloride, pipes, tiles, doors, windows



dipoles, stronger attraction b/w polymer chains



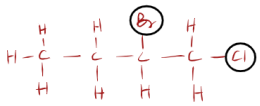
PTFE Teflon

no dipoles, less intermolecular
non stick in cooking.
C-F strong, heat resistant.

* Addition Polymers

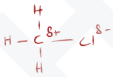
non biodegradable - C-C bonds are strong and unreactive/ non polar

Halogenoalkanes



* higher (slightly) melting and boiling points

polar molecules



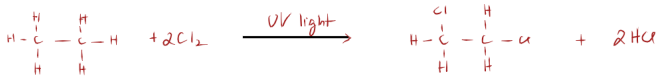
strength of dipoles decreases down the group, electronegativity of halogen decreases

(bigger molecules have more van der waals)

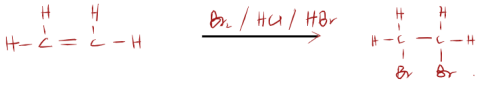
* Very slightly soluble in water

Formation of halogenoalkanes

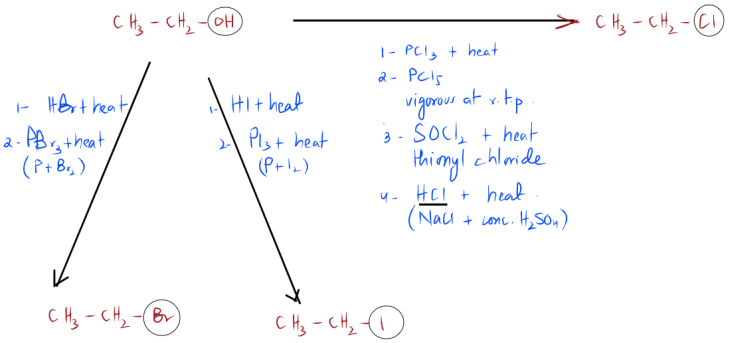
1- Free Radical Substitution (see alkanes)

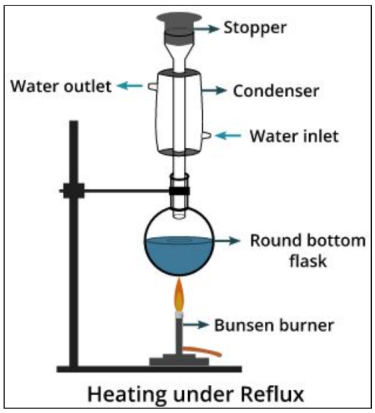


2. Electrophilic Addition of Alkenes (see alkenes)



3 - Alcohols (nucleophilic substitution)

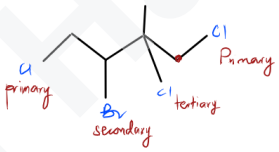




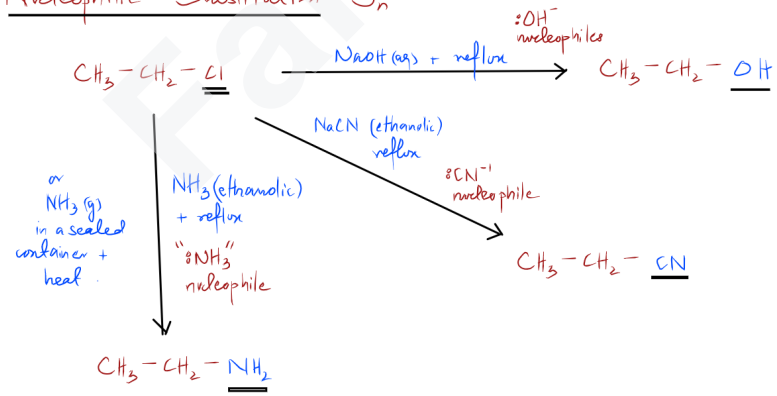
Primary halogenoalkane R — C*H2 — Cl

Secondary halogenoalkane R — C*H(R) — Cl

Tertiary halogenoalkane R — C*(R)2 — Cl



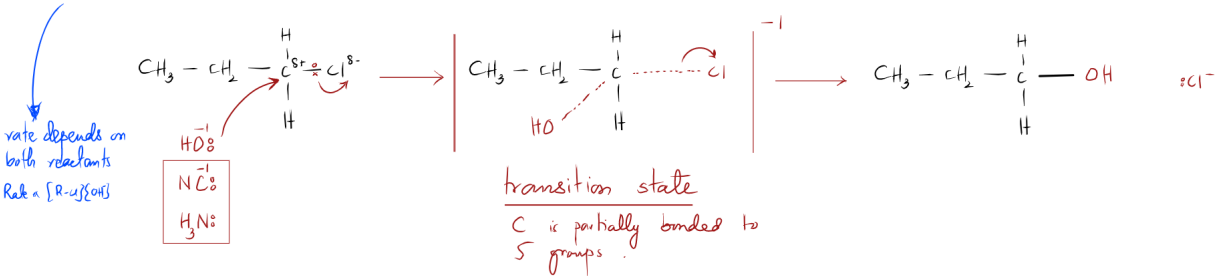
Nucleophilic Substitution S_n



nucleophile

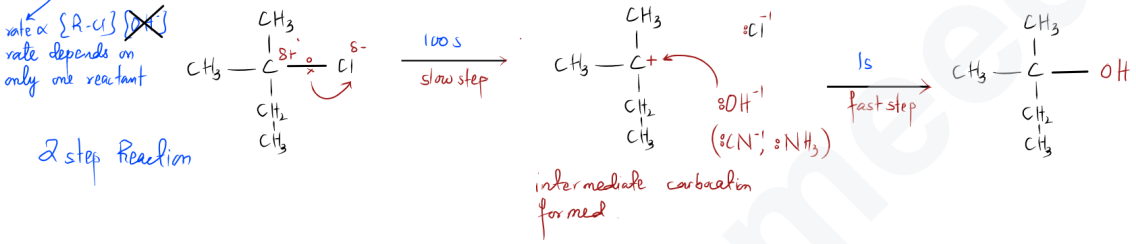
specie which is attracted to +ve charge, donates a pair of electrons

S_N2 Reaction Mechanism : Primary Halogenoalkanes

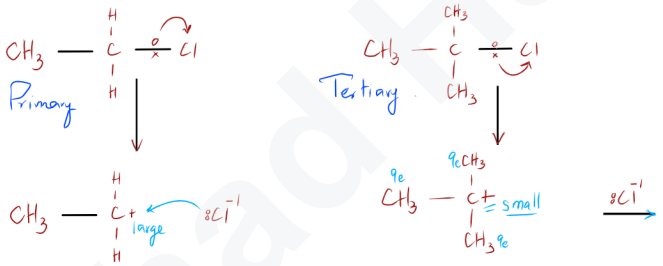


S_N2 : One Step Mechanism

S_N1 Reaction Mechanism : Tertiary Halogenoalkanes



Why do primary halogenalkanes undergo S_N2 and tertiary halogenoalkane undergo S_N1



Primary carbocations have less e⁻ donating alkyl chains, which increases charge density on carbocation making it very unstable, hence S_N2 mechanism

tertiary carbocations have more e⁻ donating alkyl chains, which decreases charge density on carbocation making it very stable, hence S_N1 mechanism

secondary : both S_N1 / S_N2 depends on conditions

Reactivity of Halogenalkanes

R – I > R – Br > R – Cl

very reactive

least reactive

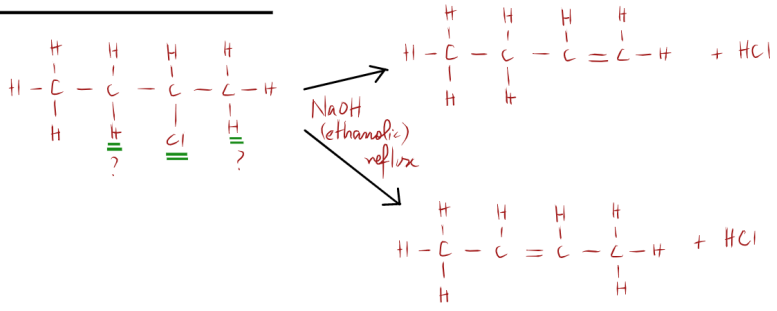
smaller atoms, make stronger bonds

shorter bond length

more orbital overlap

less shielded nuclei

Elimination Reactions



Identification of halogen in halogenalkane

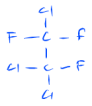
R – X ⇌ R^+ + X^-

X = Cl, Br, I

	Add aqueous $AgNO_3$	Dissolve in NH_3
Cl^-	AgCl(s) white ppt	dissolves in aqueous NH_3
Br^-	AgBr(s) cream ppt	dissolves in conc. NH_3
I^-	AgI(s) yellow ppt	does not dissolve

Uses of Halogenoalkanes

1- CFCs chlorofluorocarbons
inert solvents, volatile
- solvents, coolants, freons, anaesthetics, aerosols,



2. Fire Retardants - bromine related compounds

3- Polymers → PVC : Pipes, tiles,
Teflon PTFE : non stick in cooking utensils

harmful effect of CFC

destroy ozone free radicals in upper atmosphere / strong UV rays

Cl· radicals attack O_3 ozone

$Cl\cdot + O_3 \longrightarrow ClO\cdot + O_2$

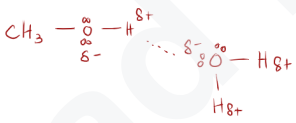
$ClO\cdot + O_3 \longrightarrow Cl\cdot + O_2 + O_2$

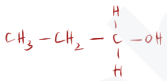
Ozone, reflects harmful UV rays.

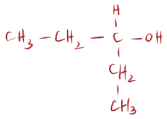
Alcohols

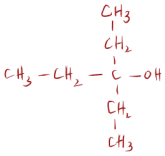
CH_3-CH_2-OH
hydroxy

1- high melting/boiling points
2. soluble in water
↳ form hydrogen bonds



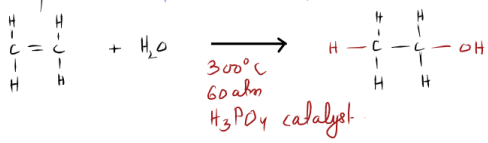
Primary Alcohol 

Secondary Alcohol 

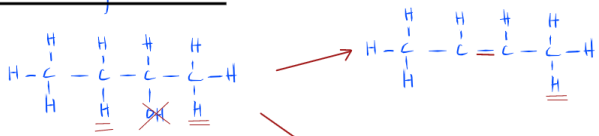
Tertiary Alcohol 

Formation of Alcohols

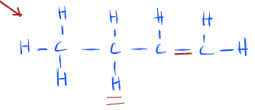
1. Hydration of alkenes (See Alkenes)



- Dehydration of Alkenes



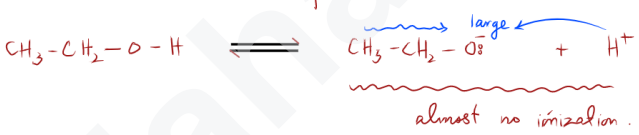
concentrated H_2SO_4 (dehydrating agent)
or
heat with Al_2O_3 / SiO_2 (pumice, zeolite)



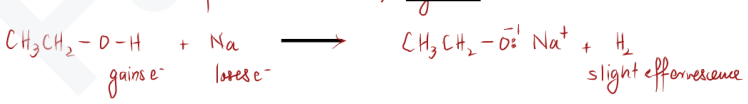
2. Sn Nucleophilic Substitution of halogenoalkanes (see Halogenoalkanes)

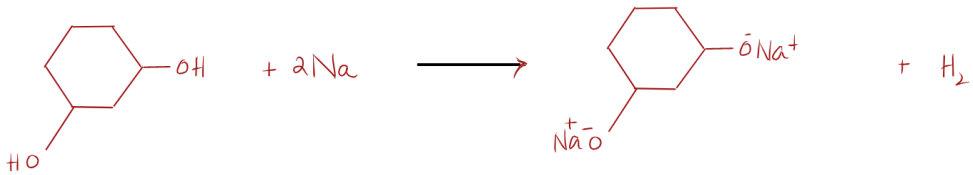
Alcohols are extremely weak acids (not acids, no acid-base reactions).

ionization is even weaker compared to H_2O



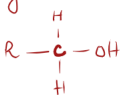
alcohols do react with Gp I reactive metals, very slow



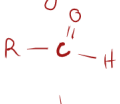


Oxidation of Alcohols

Primary Alcohols → aldehydes → carboxylic acids



1- $K_2Cr_2O_7 / H^+$ heat with reflux (orange to green)
2- $KMnO_4 / H^+$ heat with reflux (purple to colorless)



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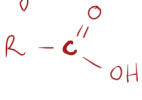


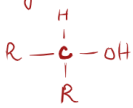
3- Tollens Reagent $[Ag(NH_3)_2]^+$ (mix $NH_{3(aq)} + AgNO_{3(aq)}$)
Silver mirror formed, black ppt
$Ag^+ + 1e \rightarrow Ag$

4- fehling Solution + heat
Cu^{2+} get reduced to a brick red ppt of Cu_2O

stopping reaction at aldehyde
- use distillation + heat instead of heat with reflux

aldehydes have a lower boiling point compared to alcohols, carboxylic acid so they will immediately evaporate once they are formed

Secondary Alcohols → Ketone (no further oxidation)



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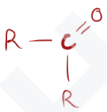
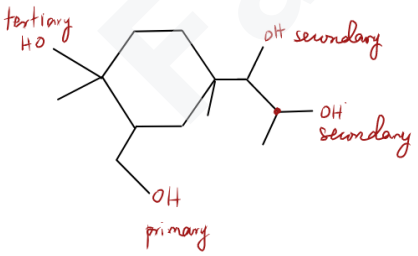
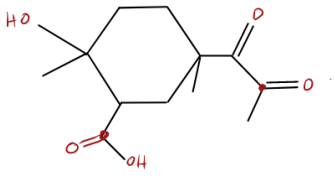


* Tertiary Alcohols are not oxidized

Examples: Oxidation of alcohols



$K_2Cr_2O_7 / H^+$, reflux



Reduction.

gain of H / loss of O

Carboxylic acid $\xrightarrow{LiAlH_4}$ aldehyde $\xrightarrow[\text{or } NaBH_4]{LiAlH_4}$ primary alcohol

$CH_3-C(=O)-OH \rightarrow CH_3-C(=O)-H \rightarrow CH_3-CH_2-OH$

$LiAlH_4$ Reducing Agent

Lithium Aluminium hydride

AlH_4^{-1} source of H^{-1} ions

Ketone $\xrightarrow{LiAlH_4 \text{ or } NaBH_4}$ secondary alcohol

$CH_3-C(=O)-CH_3 \rightarrow CH_3-CH(OH)-CH_3$

$R-C(=O)-R$ $\delta+$ carbon; $:H^{-1}$ nucleophiles

Uses of Alcohols

- Alcoholic Drinks.
- Industrial methylated spirits.
- Use of ethanol as a fuel.
- Ethanol as a solvent.
- Methanol as a fuel.
- Methanol as an industrial feedstock.

Aldehyde and Ketones

carbonyl compound $-C^{\delta+}(=O^{\delta-})-$

polar molecule

permanent dipole - permanent dipole attraction

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

Example

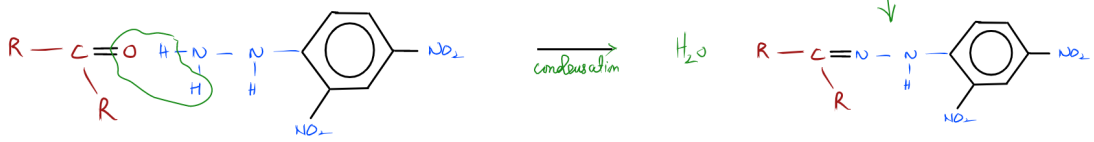
$CH_3-CH_2-C(=O)-H$ propanal

$CH_3-C(=O)-CH_2-CH_3$ butan-2-one

Identification of Carbonyl Compounds

add 2,4 – DNPH (2,4 – dinitrophenyl hydrazine) → Orange Precipitate

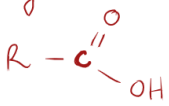
$H_2NNHC_6H_4(NO_2)_2$



How to differential between aldelyde/ ketone

aldelydes get oxidized , Ketones don't

aldelydes —"oxidation"→ carbonylic acids



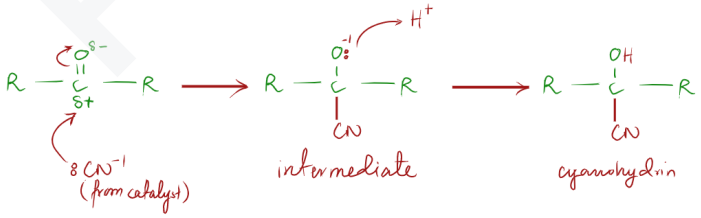
1- $K_2Cr_2O_7 / H^+$
heat with reflux
(orange to green)

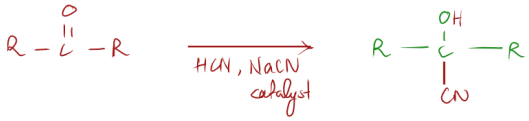
2- $KMnO_4 / H^+$
heat with reflux
(purple to colorless)

3- Tollens Reagent
$[Ag(NH_3)_2]^+$ (mix $NH_{(aq)} + AgNO_{3(aq)}$)
Silver mirror formed, black ppt
$Ag^+ + 1e \rightarrow Ag$

4- fehling Solution + heat
Cu^{2+} get reduced to
a brick red ppt of Cu_2O

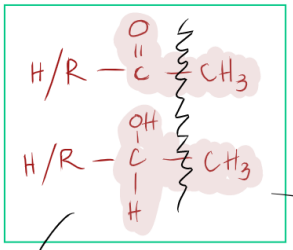
Carbonyl Compounds, nucleophilic addition (mechanism, 2 step reaction)





Iodoform Test ($NaOH_{(aq)} + I_2$)

identifies a specific structure



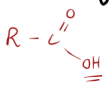
not carboxylic acid or esters
R represents an alkyl chain

CHI_3
triiodomethane
yellow ppt

$R/H-C(=O)-O^-Na^+$

alkaline condition.
$RCOOH \longrightarrow RCOO^-Na^+$
further acidification can form RCOOH

Carboxylic Acids



hydrogen bonds
high melting / boiling points
very soluble in water

Weak acids pH = 3 - 7
partially dissociate and produce fewer H^+ ions

Acid + Metal → Salt + H_2

$RCOOH + Na \longrightarrow RCOO^-Na^+ + \frac{1}{2}H_2$

Redox Reaction
Na loses e^-, H^+ gains e^-

Acid + Metaloxide/hydroxide → Salt + H_2O

$RCOOH + NaOH \longrightarrow RCOO^-Na^+ + H_2O$

Acid + Metal Carbonate ⟶ Salt + H_2O + CO_2

$RCOOH$ + Na ⟶ $RCOO^-Na^+$ + H_2O + CO_2

Acid + NH_3 ⟶ Ammonium Salt

$RCOOH$ + Na ⟶ $RCOO^-NH_4^+$

ESTERFICATION

Formation of Esters

$R-\overset{\overset{O}{\|}}{C}-OH$ + $H-O-R$

condensation ↓ conc. H_2SO_4 catalyst, heat with reflux

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

Hydrolysis of esters

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

dil. NaOH (aq) or dil. H_2SO_4 (aq), reflux ↓ hydrolysis

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

In alkaline hydrolysis acid reacts with alkali

$RCOO^-Na^+$

Naming of Esters

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

4C butanoate / 1C methyl

Hydrolysis of Nitriles

$R-C\equiv N$ $\xrightarrow{+H_2O}$ $R-\overset{\overset{O}{\|}}{C}-OH$ + NH_4^+

dilute H_2SO_4 reflux

or

dilute NaOH reflux

In alkaline conditions

$RCOO^-Na^+$

add acid H^+

$RCOOH$

Infrared Spectroscopy

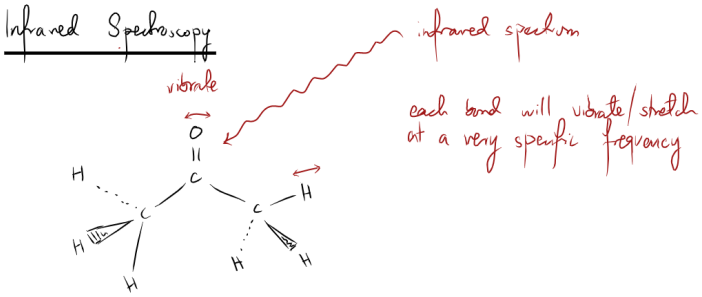


Table 4.2 $1/\lambda \propto$ frequency

bond	functional group containing the bond	characteristic infrared absorption range (in wavenumbers)/cm^{-1}
C–O	hydroxy, ester	1040–1300
C=C	aromatic compound, alkene	1500–1680
C=O	amide carbonyl, carboxyl ester	1640–1690 1670–1740 1710–1750
C≡N	nitrile	2200–2250
C–H	alkane	2850–3100
N–H	amine, amide	3300–3500
O–H	carboxyl hydroxy alcohol	2500–3000 3200–3650

40 Which diagram shows the infrared spectrum of a compound that contains both a C=O and an O–H group?