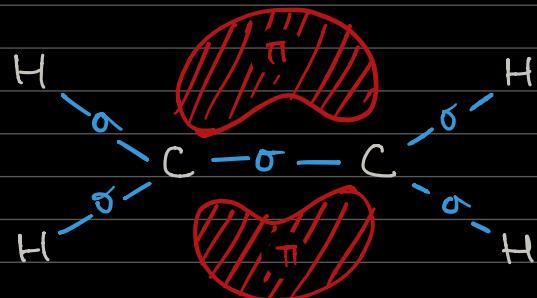
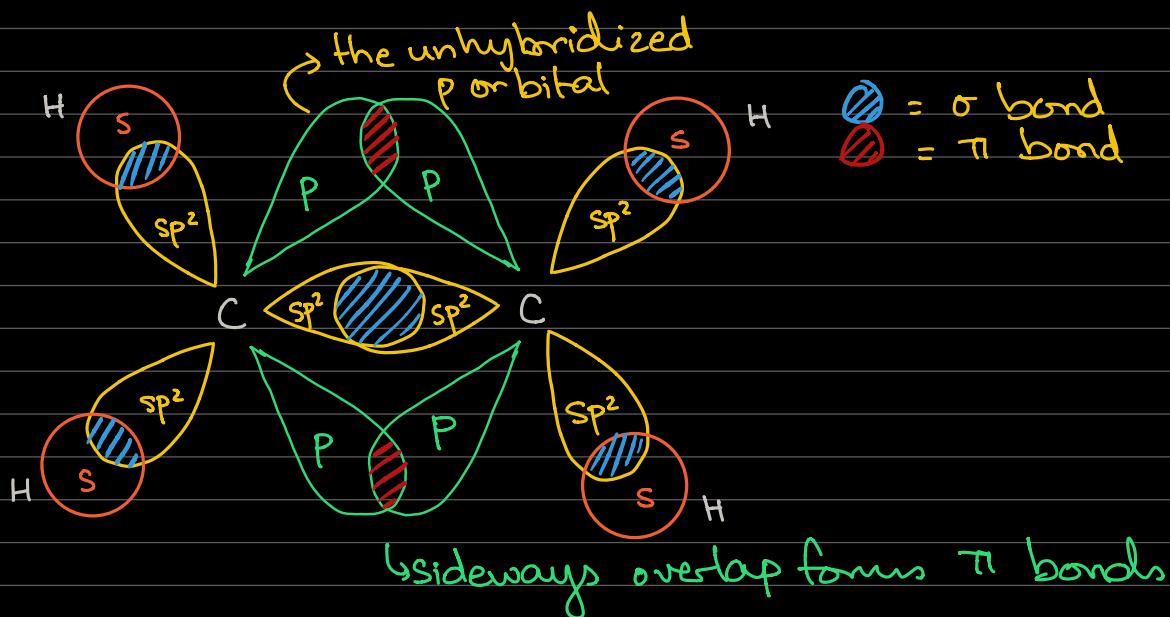
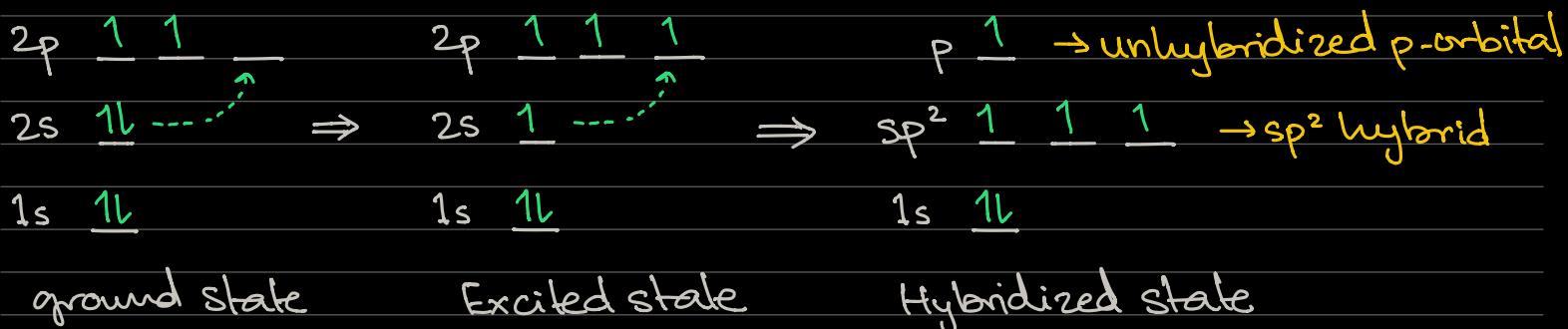


ALKENES : ORGANIC CHEMISTRY

- Alkenes are hydrocarbons that contain a C=C bond
 - They are unsaturated
 - The carbon and the hydrogen atoms lie in the same plane, with the H-C-H and C-C-H bond angles being 120°
 - Alkenes are trigonal planar around the carbon atoms
 - The C=C bond is made up of sigma (σ) and a pi (π) bond
 - The double bonded carbon atoms are sp^2 hybridized



- The π bond is created by the sideways overlap of unhybridized p-orbitals.
↳ This is important because it leads to the "rigidity" of the C=C
 - Rotation of the two halves of the double bond, with respect to each other, does not take place unless enough energy is provided to break the π bond

- The presence of a π bond confers two special characteristics on the structure and the reactivity of the alkene:
 - i) Hindered rotation, which leads to cis-trans isomerism
 - ii) It creates a region of high electron density above and below the π bond which makes alkenes very reactive towards electrophiles.

↳ This is what makes alkenes more reactive than alkanes

Strength of the C=C

- In a C=C, the σ bond is stronger than the π bond and it is the π bond that is broken during addition reactions.

REACTIONS

PREPARATION REACTIONS

1. Cracking : kerosene + naphtha fractions can undergo cracking to form alkenes (thermal + catalytic cracking)

2. Dehydration of Alcohols

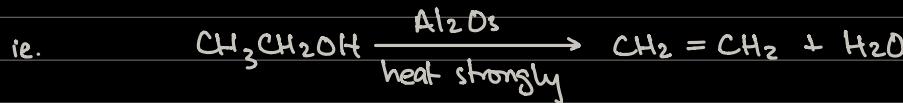
Alcohols can be dehydrated (elimination of H₂O) to form the corresponding alkene

i) Dehydrating using conc. H₂SO₄ (a drying agent)



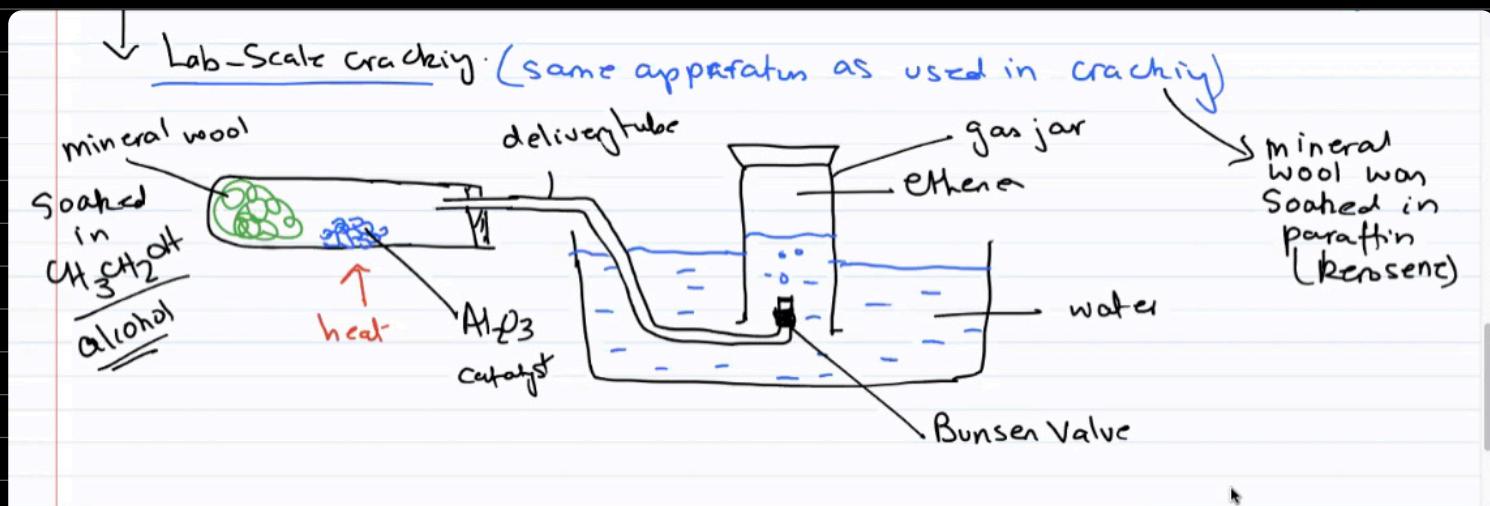
→ Industrial method

ii) By passing the heated vapour of the alcohol over a hot catalyst
 ↳ Al₂O₃, porous pot, or SiO₂



- This method can also be used for lab-scale cracking (and hence requires largely the same apparatus, with a few exceptions)

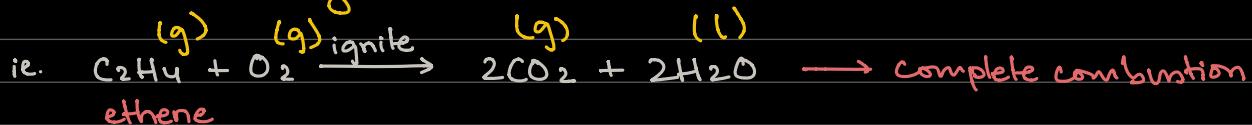
↳ the mineral wool is now soaked in the relevant alcohol instead of the kerosene / paraffin used in cracking



COMBUSTION REACTIONS

- Alkenes undergo complete combustion to form CO_2 and water (theoretically)
- but alkenes usually burn with a smoky / sooty flame (practically) due to some incomplete combustion

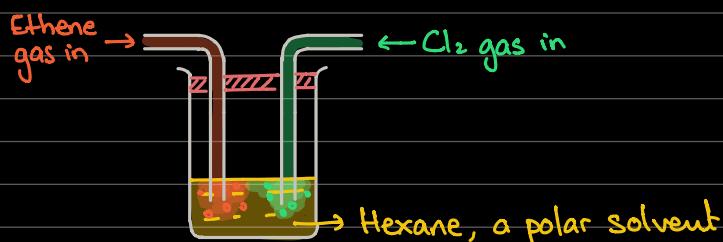
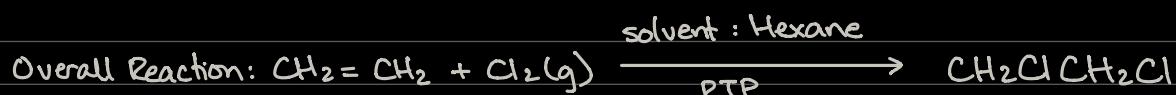
↳ This distinguishes alkanes from alkenes



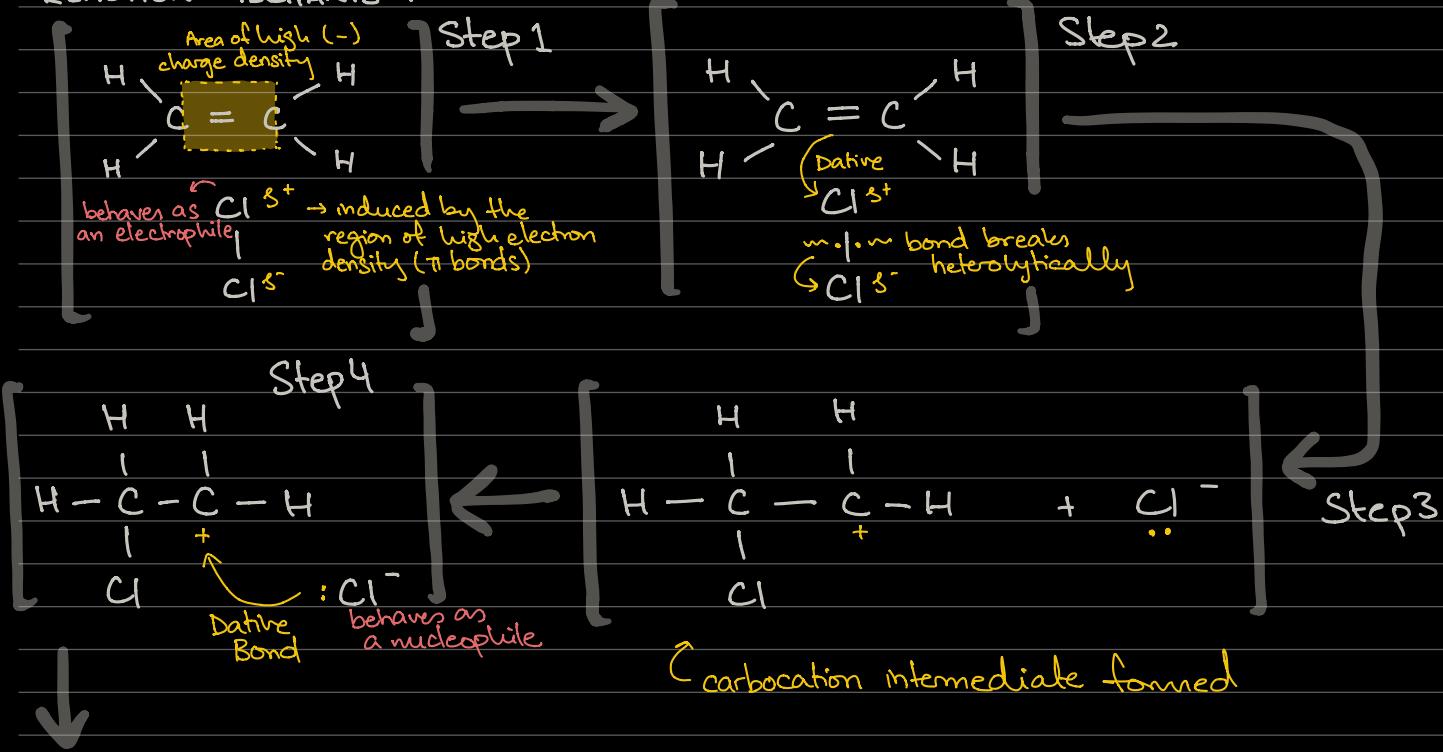
ELECTROPHILIC ADDITION

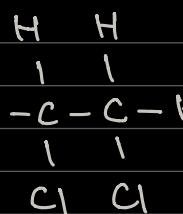
a) Addition of Halogens

- Electrophilic addition of halogen results in the formation of halogenoalkanes / alkyl halides
- i.e. Addition to ethene



REACTION MECHANISM





Step 5

→ Electrophilic addition
is complete

Mechanism Description :

Note: When asked to describe a reaction mechanism in the exam, describe it using equations and not sentences

- The π bond of ethene is an electron-rich area, and it induces a dipole in an approaching chlorine molecule by repelling the electrons in the Cl-Cl bond
- The π electrons re-arrange to form a dative covalent bond from one of the carbon atoms of ethene, to the nearest (Cl^{3+}) chlorine
- The Cl-Cl bond breaks heterolytically to form a chloride ion and a carbocation is formed
- Carbocations have a full positive charge on the carbon. They are very reactive and will react immediately with nucleophiles (ie. Cl^-)
- Hence, the Cl^- ion forms a dative bond with the carbocation, forming the product 1, 2 - dichloroethane

Note: It's called electrophilic addition because the first step in the reaction involves a reaction with an electrophile (Cl^{3+})

REACTION OF ETHENE WITH BROMINE

(Also electrophilic addition)

TWO CASES :

1. Ethene + Br_2 (l) in hexane (non-polar solvent)
2. Ethene + Br_2 (aq) → Bromine water test → test for unsaturation

Note: Br_2 (l) → Dark Brown

Br_2 (aq) → lighter red-brown / orange

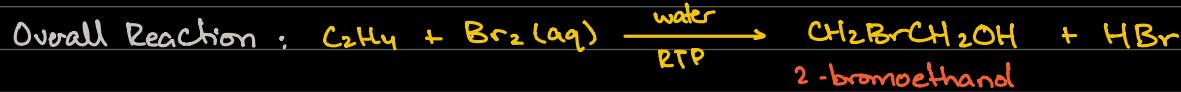
Observation → red-brown Br_2 is decolorised when reacted with alkenes

1. ETHENE + Br_2 in HEXANE

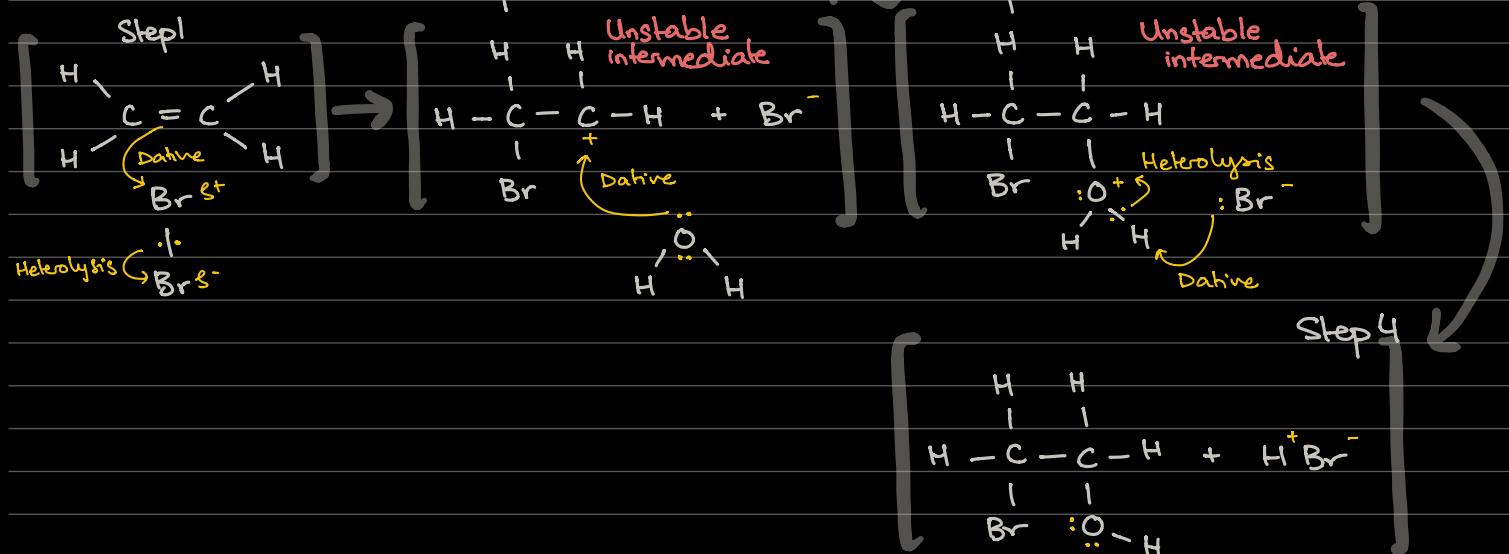
Overall Reaction : $\text{C}_2\text{H}_4 + \text{Br}_2 \rightarrow \text{CH}_2\text{BrCH}_2\text{Br}$

REACTION MECHANISM : Same as the chlorine one above

2. ETHENE + Br₂ (aq) → Bromine water test



MECHANISM :

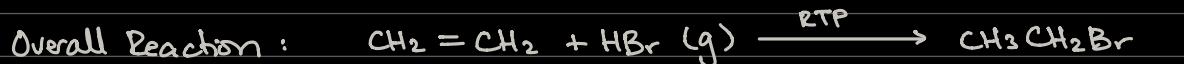
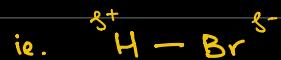


- Water is a nucleophile and is in excess

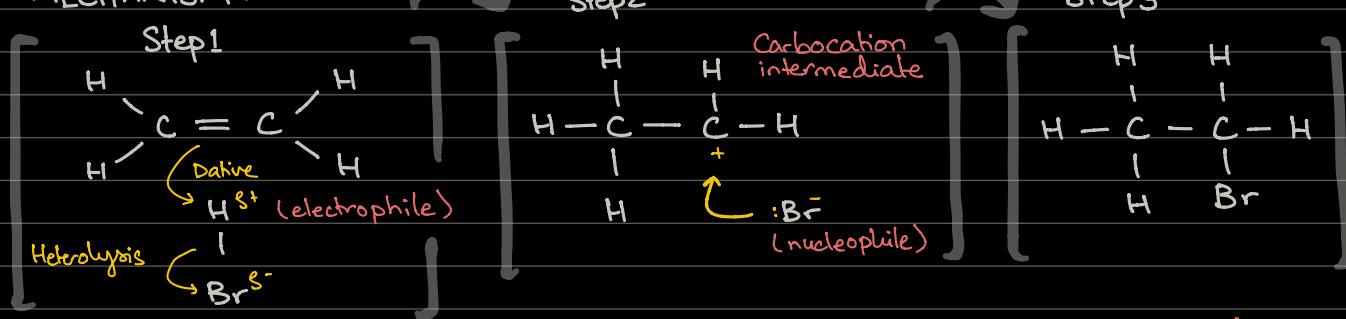
- Since water is in excess, so it attacks the carbocation
- The Br⁻ ion makes a dative bond with the H of water
- The O-H breaks heterolytically
- Both the electrons in the $\text{O}-\text{H}$ bond move to the oxygen
- and HBr is formed

b) Addition of Hydrogen Halides (gaseous)

- Hydrogen halides are polar molecules, hence they react very readily with alkenes (dipole doesn't need to be induced, it's already present)



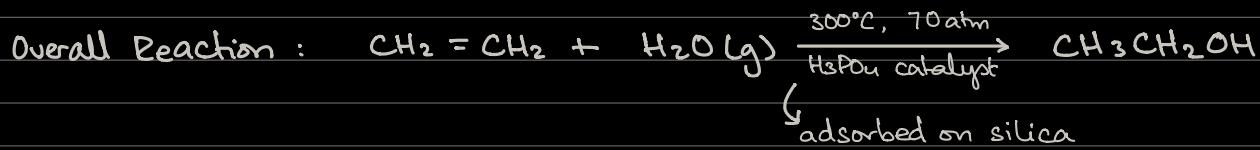
MECHANISM :



Note: The alkene is bubbled directly into HBr in ethanoic acid OR a concentrated solution of the hydrogen halide

c) Addition of steam (to form alcohols)

↳ aka. Hydration

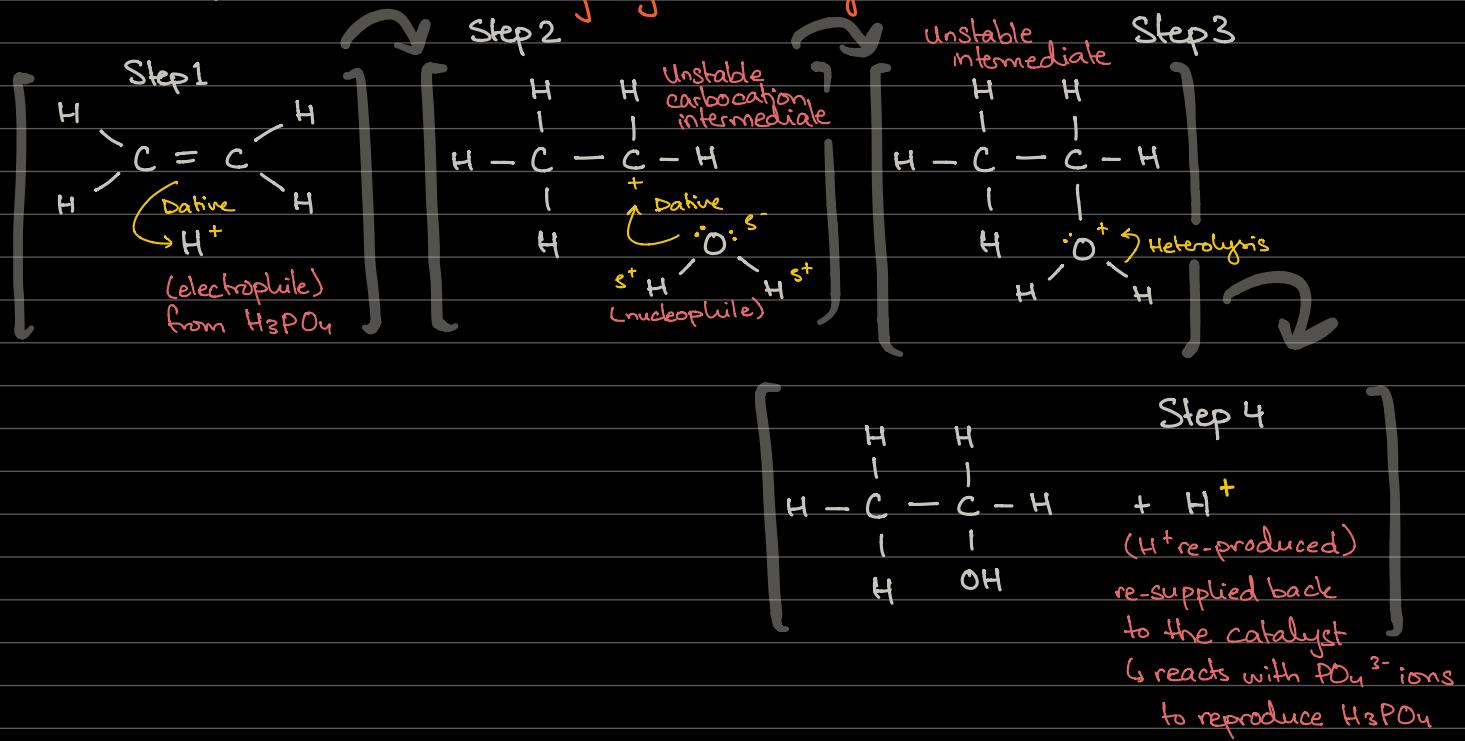


- Adsorption means to attach loosely

- Done to increase the surface area of the catalyst

Note: The electrophile in this reaction is the H^+ ion, supplied mainly by the catalyst

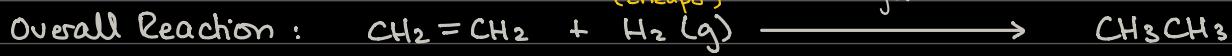
MECHANISM



d) Catalytic Addition of H_2 gas (to form alkanes)

↳ aka Hydrogenation

preferred in industrial reactions ↳ powdered / finely divided
 (cheaper) Ni catalyst at 140°C



[or Palladium catalyst ethane
 [or Platinum catalyst
 ↳ At RTP

Note: These catalysts work

by adsorption, increase reactive

surface area → increases rate of reaction

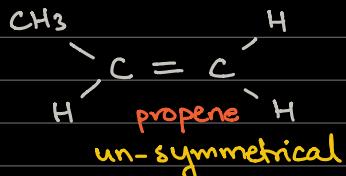
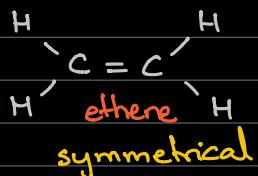
↳ facilitates bond-breaking and bond-making

Commercial importance of Hydrogenation :

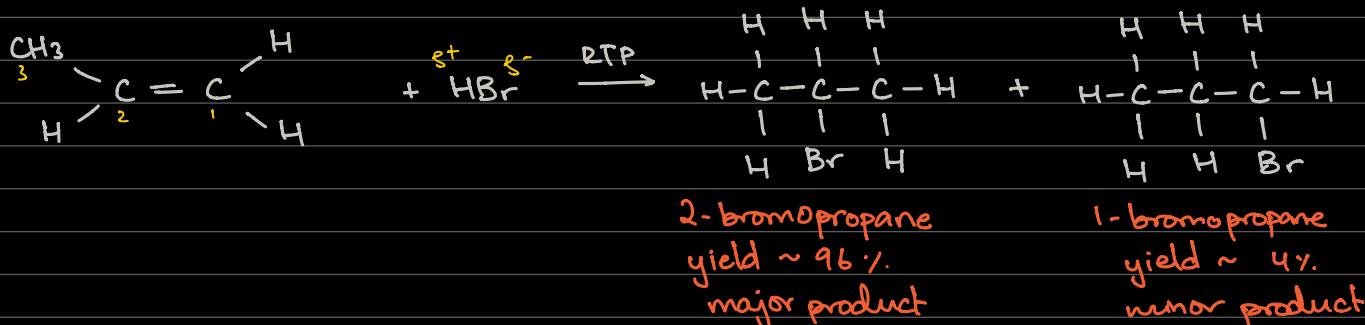
a) Manufacture of margarine



ELECTROPHILIC ADDITION TO NON-SYMMETRICAL ALKENES

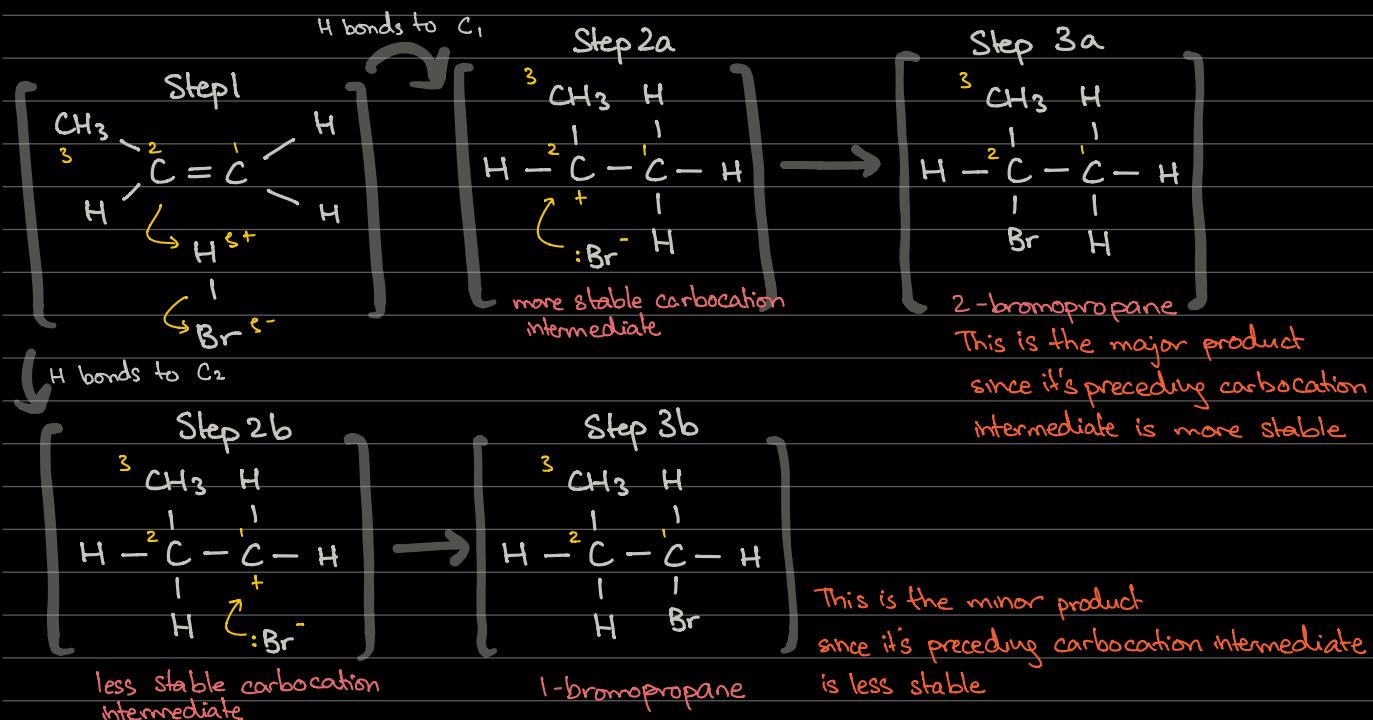


a) Addition of Hydrogen Halides



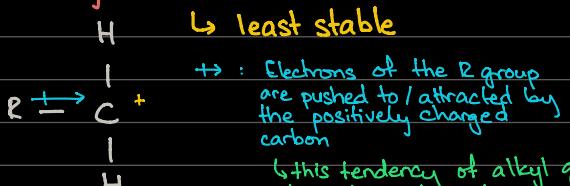
- The product formed depends on which C atom of the double bond form a bond with the electrophile first

MECHANISM:



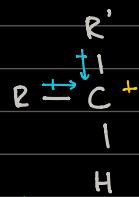
Types and stability of carbocations:

1. Primary (1°) carbocation



↳ this tendency of alkyl groups to push electron density away is called the Positive Inductive Effect (+I)

2. Secondary (2°) carbocation



- carbon⁺ is directly bonded to one other 'R' group or carbons

- C⁺ is directly bonded to two other 'R' groups / two other carbons

3. Tertiary (3°) carbocation

↳ most stable



- C⁺ is bonded directly to three other carbons / alkyl groups

what determines the stability?

- In chemistry, having a lower charge density leads to higher stability
- Alkyl groups have a positive inductive effect on the ion, that is, they tend to push away their electron density toward the C⁺ atom, thereby spreading the charge more evenly throughout the ion, leading to the molecule being more stable
- Therefore, primary carbocations which only have one alkyl group have a more concentrated charge density and are hence less stable than tertiary carbocations which have three alkyl groups and thus thrice the positive inductive effect, more evenly distributed charge, hence, are more stable

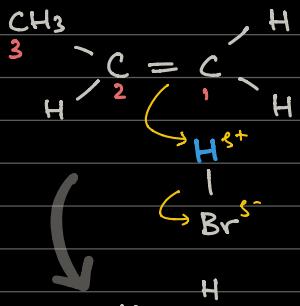
Teacher's Notes:

- Alkyl groups have electron pairs in the C-H bond
- In a carbocation, these electrons can be attracted towards the positive charge
- Electron density (of the R groups) "feeds" towards the positive charge, lowering the overall value of the positive charge and therefore, stabilizing the ion
- Alkyl groups "push" their electron density away from themselves, this is known as the positive inductive effect (+ I)
- The + I effect has the effect of reducing the size of the positive charge on the carbocation and stabilizes the ion
- Therefore, the + I effect of three alkyl groups (3° carbocation) is greater than the + I effect of two alkyl groups (2° carbocation), which in turn is greater than the + I effect of one alkyl group (1° carbocation)

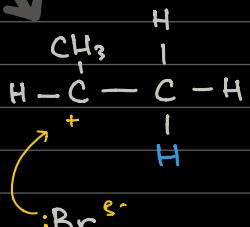
Markovnikov's Rule:

↳ relates to the addition reactions of unsymmetrical alkanes

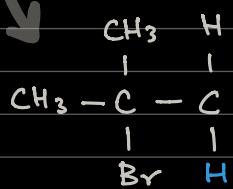
- The hydrogen of the H-X⁻ (or any other electrophile) will always add to the carbon of the C=C that already has more hydrogens bonded to it directly



C₂ has the most H atoms bonded to it directly



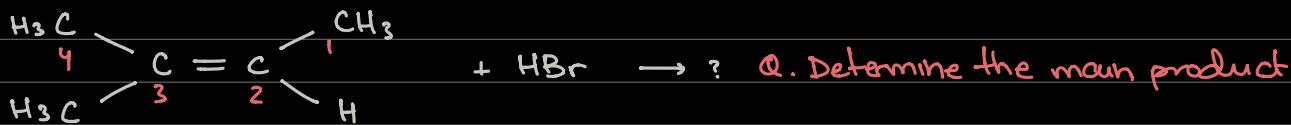
→ the more stable, secondary carbocation formed



2-bromo propane : The major product

Note: In paper 2 of CAIE exams, always explain formation of a major vs. minor product in terms of carbocation stability and the +I effect of the bonded alkyl groups

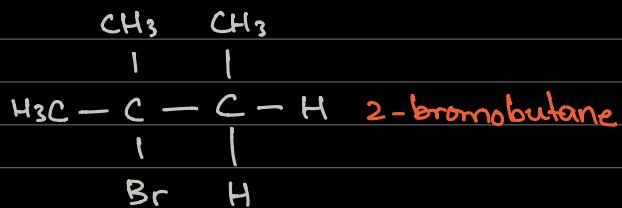
Example Q:



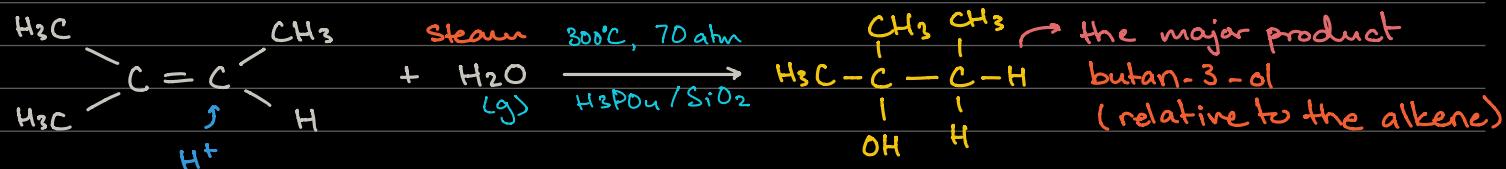
- H will be added to C₂. (Markonikov's Rule)



Hence, the final product is:

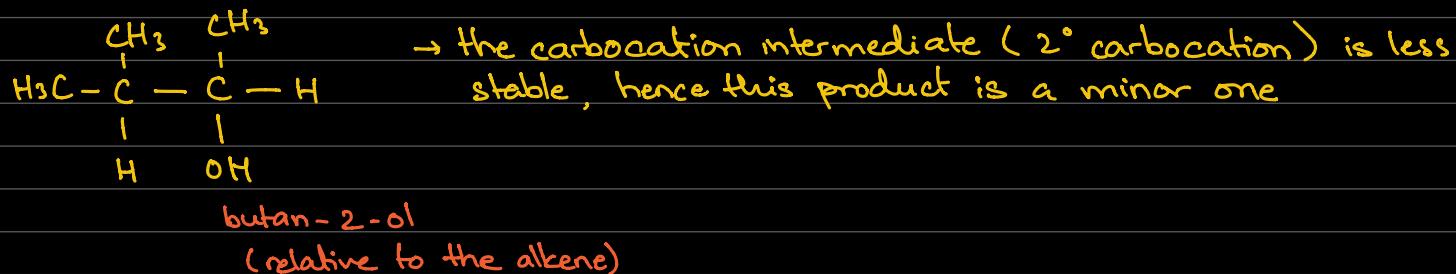


Example 2: Q. Determine the main product



Q. Determine the minor product.

Ans.



OXIDATION REACTIONS of alkenes

- Can be oxidised in two different ways.

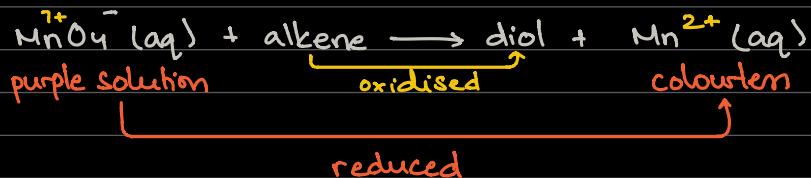
i) mild oxidation

ii) strong oxidation

a) MILD oxidation (diol produced)

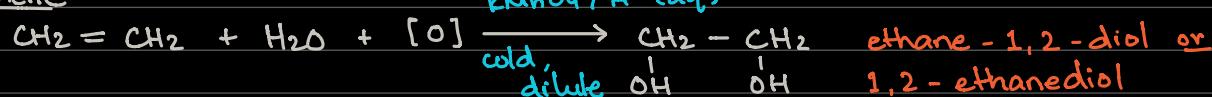
Reagents: cold KMnO_4 (purple), dilute acidified KMnO_4 (brown). $\text{H}^+(\text{aq})$ (cold dilute)

(oxidising agent)

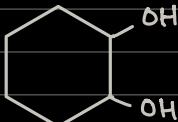
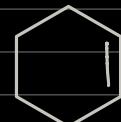


Examples:

Ethene



Propene



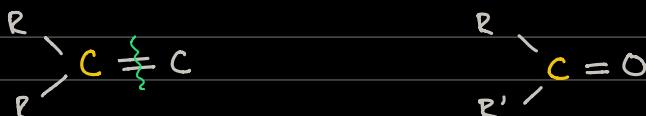
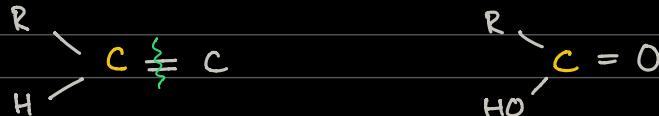
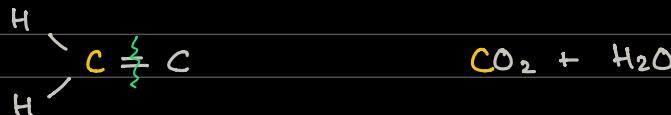
b) STRONG oxidation

Reagents: hot, concentrated, acidified KMnO_4

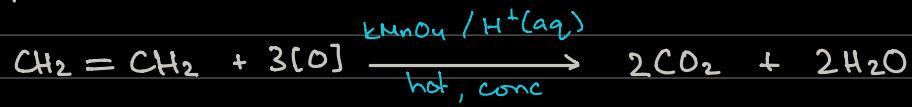
Observation : purple KMnO_4 is decolorised

- During oxidation, the double bond breaks, and the oxidation products are based on the groups attached to the double bonded carbon atoms

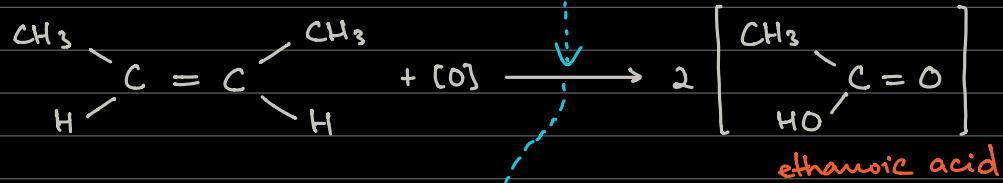
Groups Oxidation Products



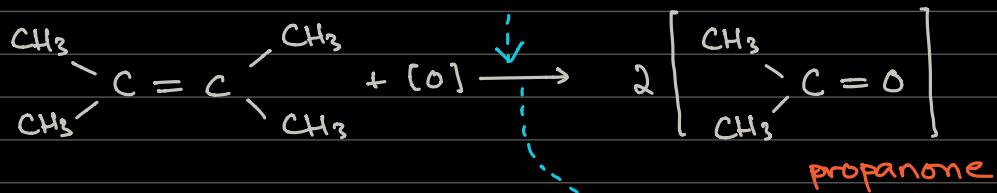
Example:



Example :



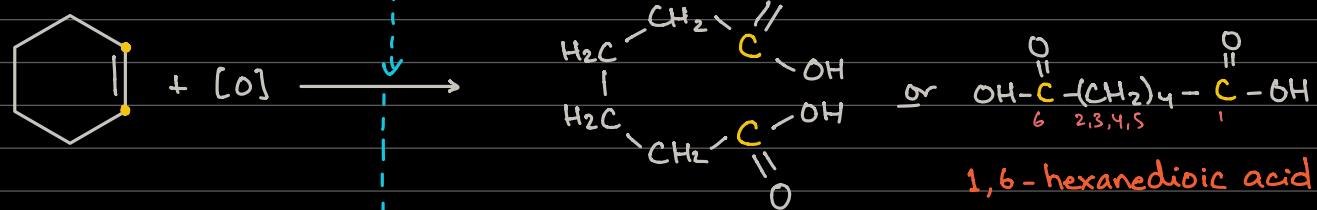
Example:



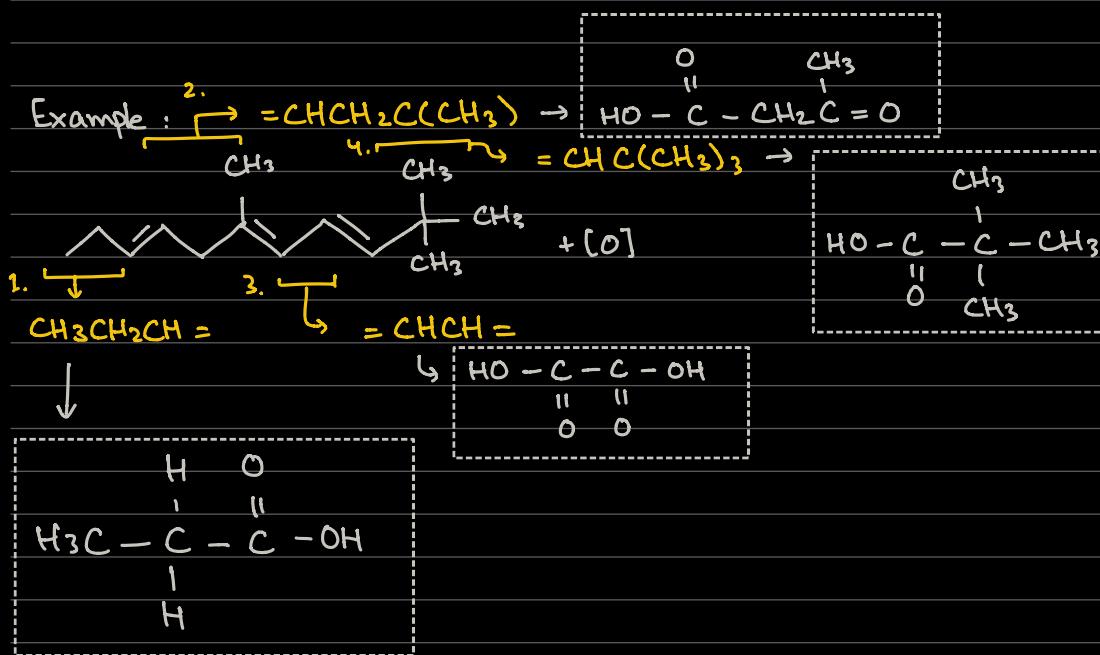
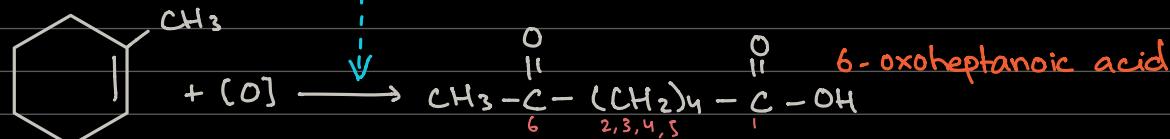
Example:



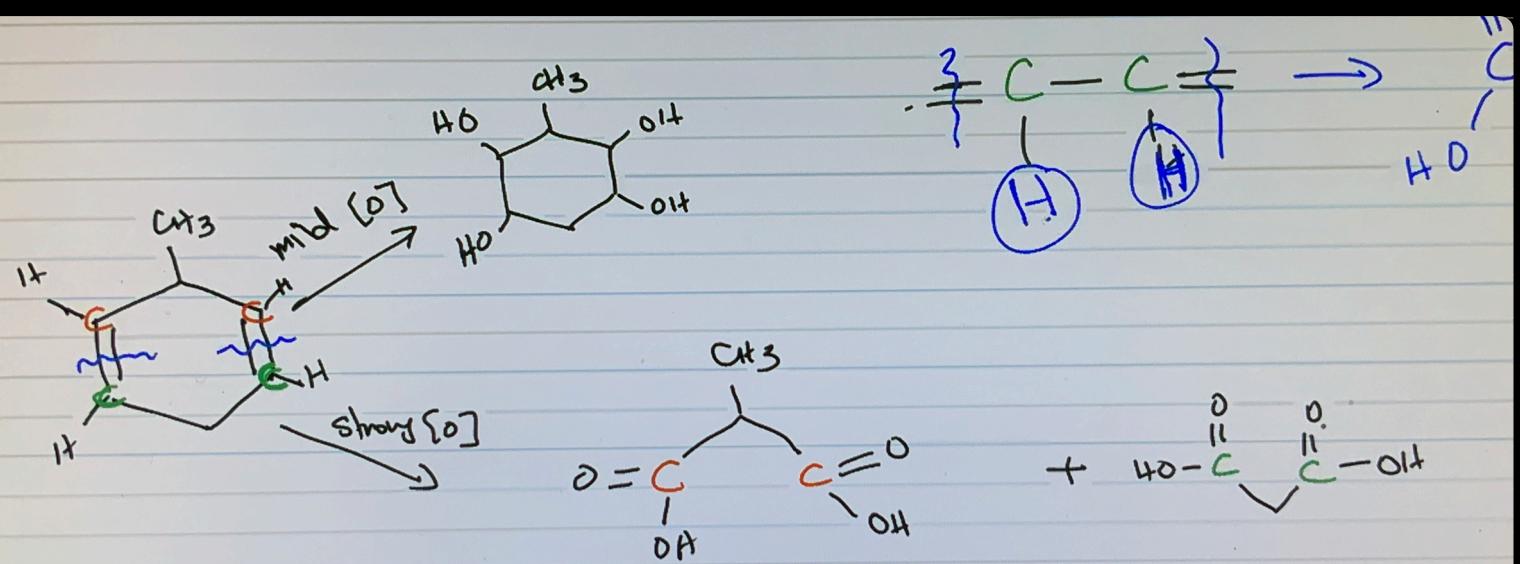
Example



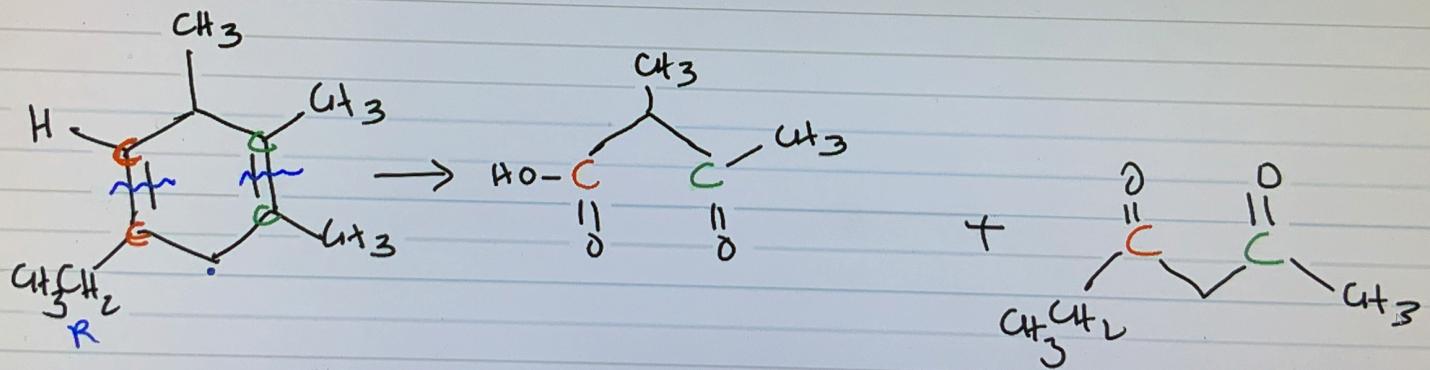
Example:



Example:



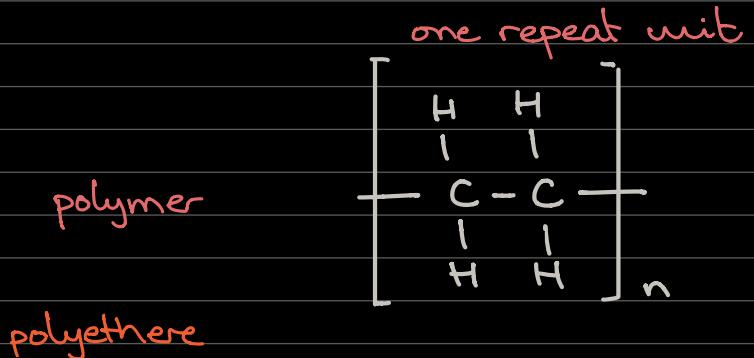
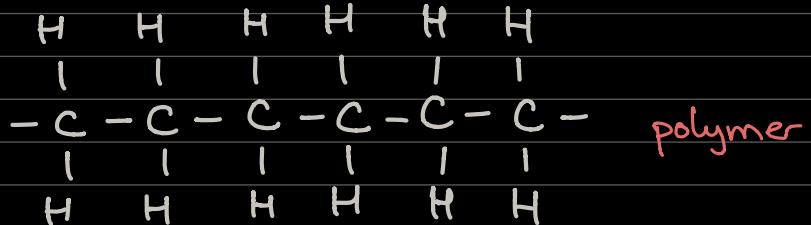
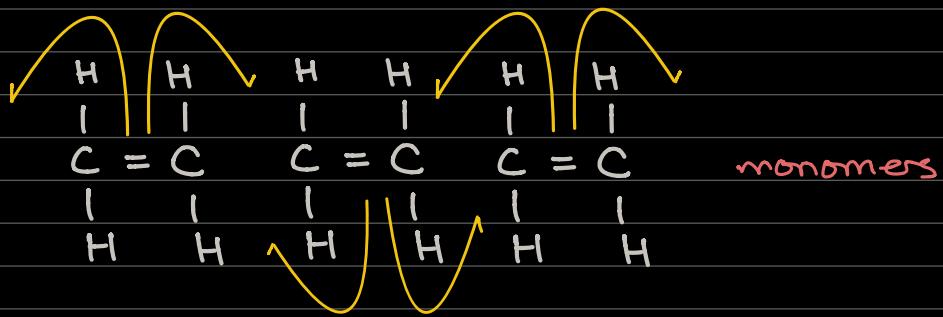
Example :



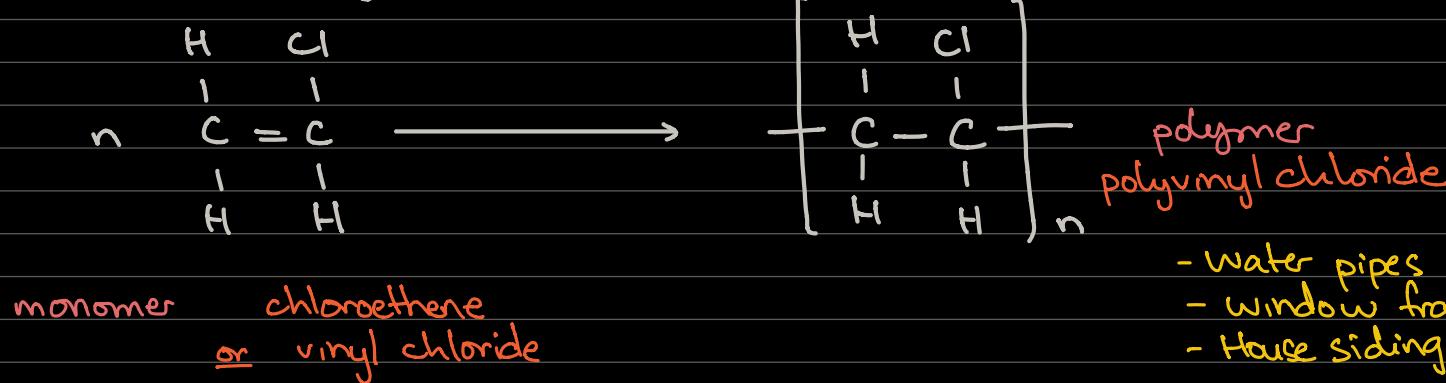
ADDITION POLYMERISATION

Polymers : very large molecules, consisting of many/several repeating units

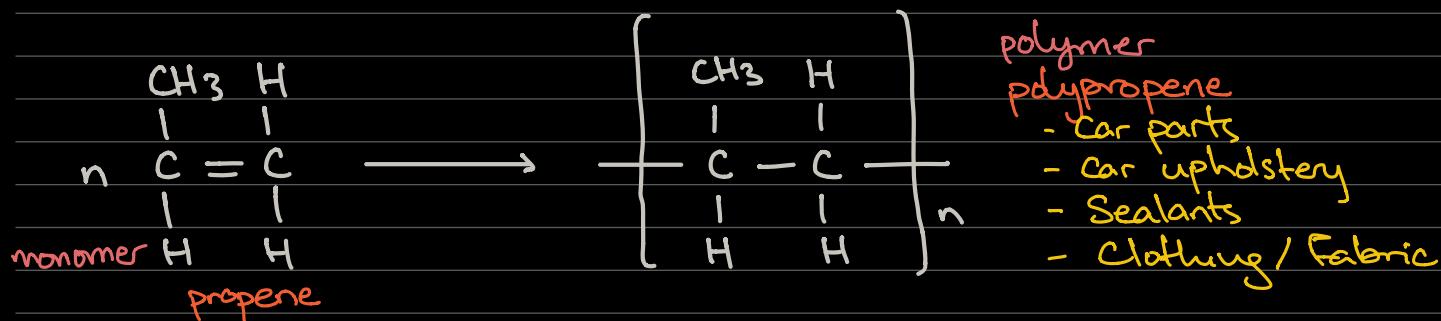
Monomer : Simple molecules that are joined together to make a polymer



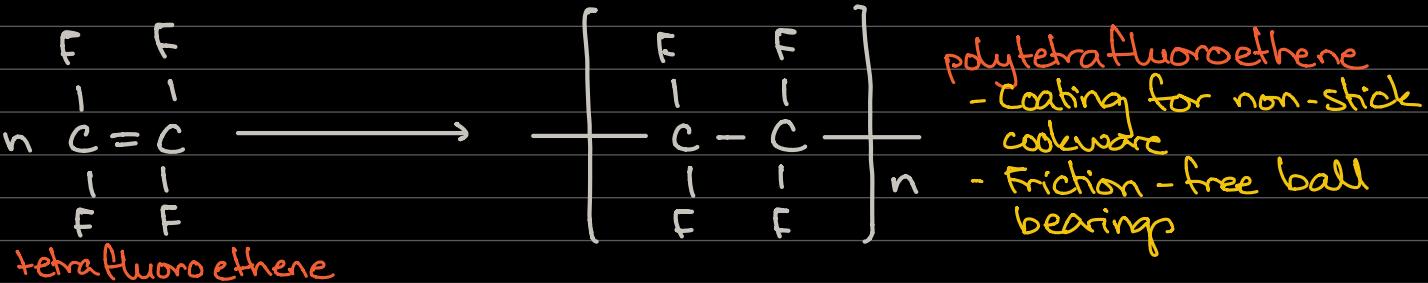
PVC - Polyvinyl chloride



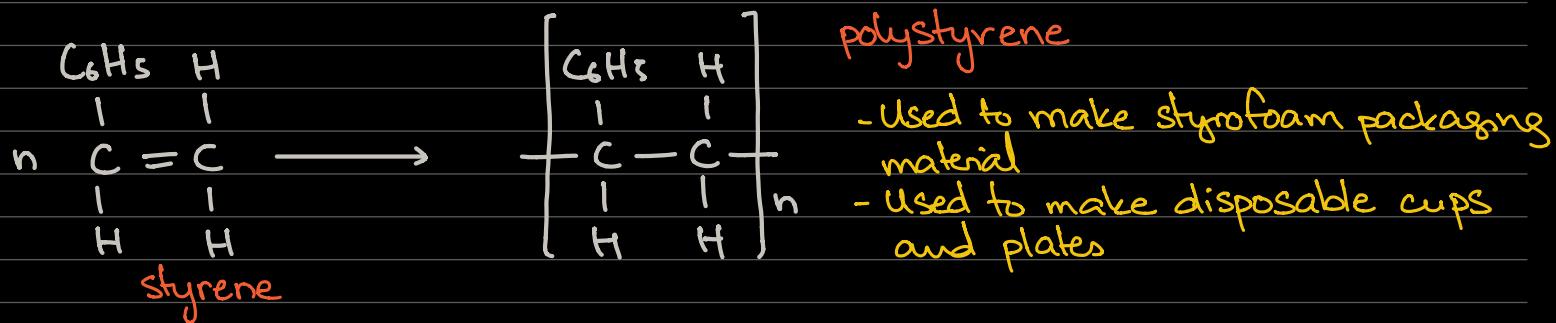
Polypropene



Teflon or PTFE (polytetrafluoroethylene)



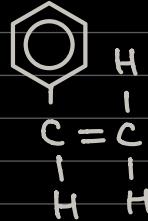
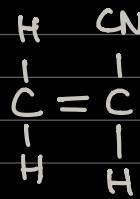
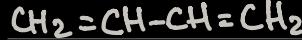
Polystyrene



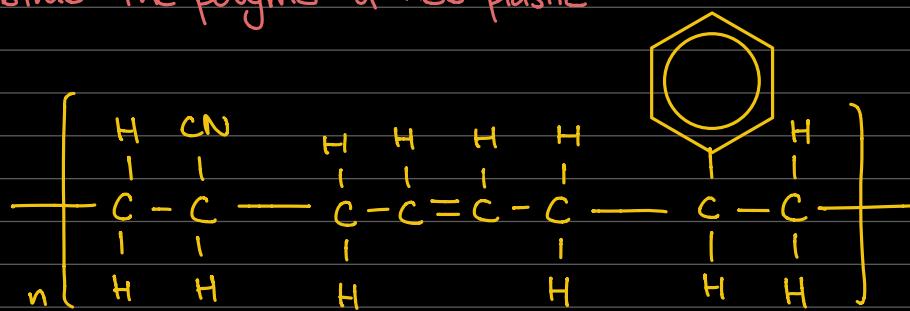
HW

ABS plastic \rightarrow polymer

monomers: Acrylonitrile \longrightarrow
 Butadiene
 Styrene



a) Construct the polymer of ABS plastic



b) With reference to the structure of the repeat unit, explain why ABS plastic is a durable, tough rigid polymer.

Ans. It is so because of the $\text{C}=\text{C}$ double bond which is resistant to rotation

Poly(ethene) and some other polymers

LDPE

low Density Poly Ethene

HDPE

High Density Poly Ethene

LDPE :



- ↳ • melts at $\sim 130^\circ\text{C}$
- tensile strength is low - can be pulled
- Very flexible
- plastic/garbage bags etc.

density : $\frac{\text{mass}}{\text{volume}}$

Low Density : 1. Low mass \rightarrow less repeat units

OR

Different case,
doesn't apply to
above example

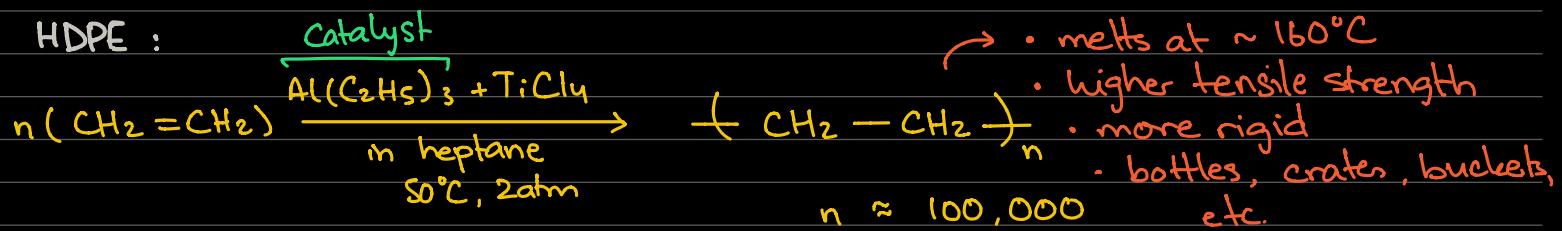
2. High volume

↳ increase number of hydrocarbon branches
on polymeric chain

↳ chains cannot pack close together

↳ resulting in a higher volume and hence
a lower density

HDPE :



Catalyst : "Ziegler - Natta Catalyst"
triethylaluminium plus titanium (IV) chloride

High Density = 1. High mass \rightarrow more repeat units

OR

2. Low volume \rightarrow due to close packing of the polymeric
chains as they have no / few
branches

SUMMARY OF REACTIONS OF ALKENES

