

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
- b describe the mechanism of electrophilic addition in alkenes, 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 ☐

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15.2 Alkenes

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-

ALKENES

Alkenes contain a C=C double bond. Another way of saying this is that the functional group present in alkenes is C=C.

Noncyclic alkenes containing just one C=C all have the same empirical formula: CH₂ and a general formula C_nH_{2n}

This has two fewer hydrogen atoms than the alkane with the same number of C atoms.

Alkenes are **unsaturated hydrocarbons** – they can still have hydrogen or halogen atoms added to their formula.

1

Name	Molecular formula	Empirical formula	Structural formula	
			Condensed	Full
ethene	C ₂ H ₄	CH ₂	CH ₂ =CH ₂	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C} = \text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$
prop-1-ene	C ₃ H ₆	CH ₂	CH ₂ =CHCH ₃	$\begin{array}{c} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{H} \\ & & \\ & & \text{H} \end{array}$
but-1-ene	C ₄ H ₈	CH ₂	CH ₂ =CHCH ₂ CH ₃	$\begin{array}{c} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{C}-\text{H} \\ & & & \\ & & \text{H} & \text{H} \end{array}$
pent-1-ene	C ₅ H ₁₀	CH ₂	CH ₂ =CHCH ₂ CH ₂ CH ₃	$\begin{array}{c} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ & & & & \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & \\ & & \text{H} & \text{H} & \text{H} \end{array}$

2

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Carbon atoms with a double bond are surrounded by 3 groups of electrons.

The three bonds form a flat trigonal plane with a bond angle of 120° .

The alkenes, like alkanes, are non-polar molecules with only van der Waals' forces between them.

This means that they are volatile, with the first four members being gases at room temperature. Owing to their non-polar nature, they are also insoluble in water.

3

REACTIVITY OF ALKENES

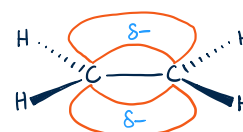
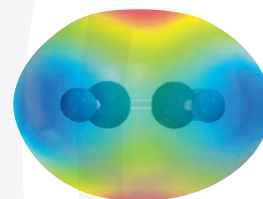
Alkenes are more reactive than alkanes.

The double bond in alkenes is made of a strong sigma bond and a weak pi bond.

In order to attain more stability the pi bond tends to get replaced by two stable sigma bonds. **Thus alkenes undergo addition reactions.**

Due to the presence of the double bond there is a layer of negative charge above and below the carbon atoms and hence alkenes are susceptible to electrophilic attack.

Thus the majority of the reactions of alkenes are **electrophilic addition reactions**.



4

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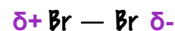
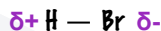
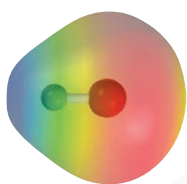
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ELECTROPHILES

An electrophile is a reagent (a positively charged ion or the positive end of a dipole)

that is attracted to regions of high electron density and accepts a pair of electrons to form a covalent bond.

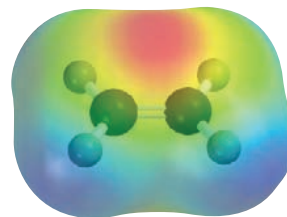
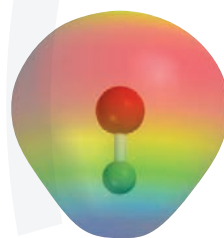
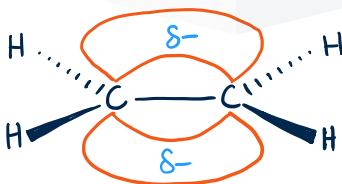
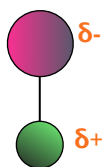


5

ELECTROPHILIC ATTACK

The C=C contains four electrons and is thus a region of very high electron density.

Electrophiles will be attracted to the electron density in the double bond.



6

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ELECTROPHILIC ADDITION OF HBr

The hydrogen halides HCl, HBr and HI all react with alkenes to give halogenoalkanes.

For example HBr with ethene gives 1-bromoethane.

The overall equation is:

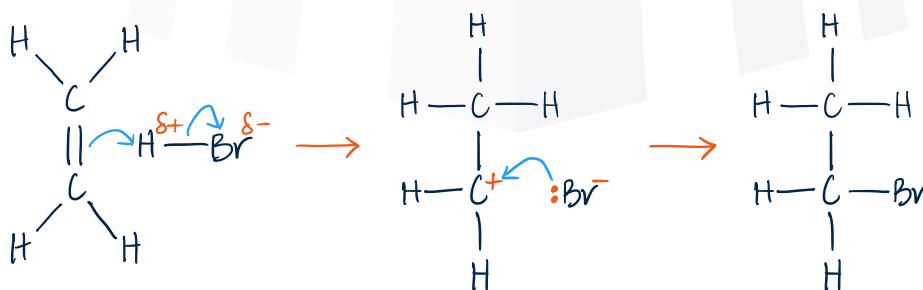


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ELECTROPHILIC ADDITION OF HBr

H-Br is polar, with the H δ^+ and the Br δ^- .

The H is thus attracted to the high electron density in the C=C.

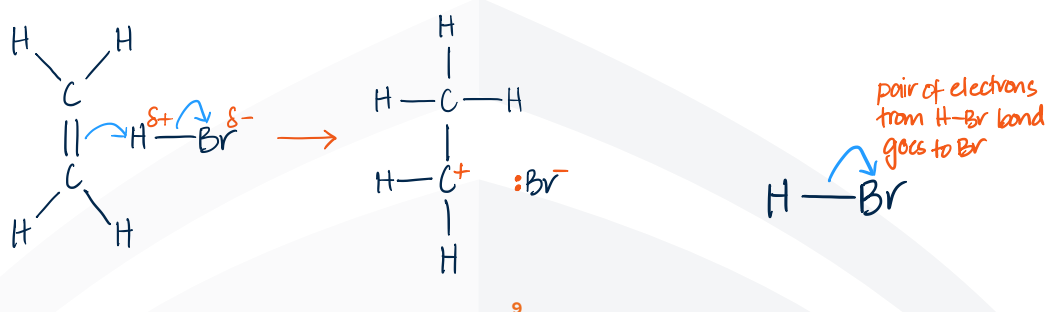


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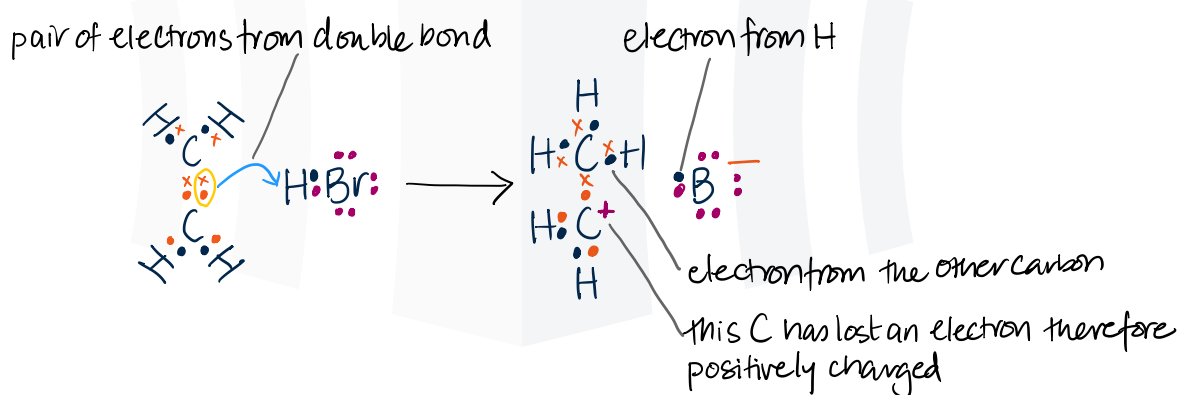
ELECTROPHILIC ADDITION: STEP 1

In the first stage, a pair of electrons is donated from the C=C to form a bond between one C and the H of the H-Br.

At the same time the H-Br bond breaks (heterolytic fission), and the pair of electrons from the bond goes to the Br.



ELECTROPHILIC ADDITION: STEP 1

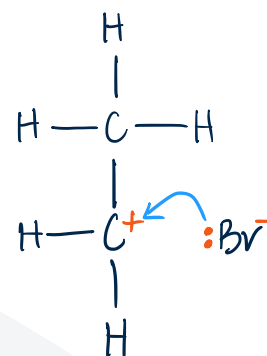


ELECTROPHILIC ADDITION: INTERMEDIATE

The other carbon has lost an electron (this electron is now in the C–H bond) and thus this carbon atom has a positive charge.

The intermediate formed is called a carbocation (a positively charged organic ion with a positive charge on C).

The Br atom has gained an electron from the H–Br bond and is therefore a negatively charged bromide ion.

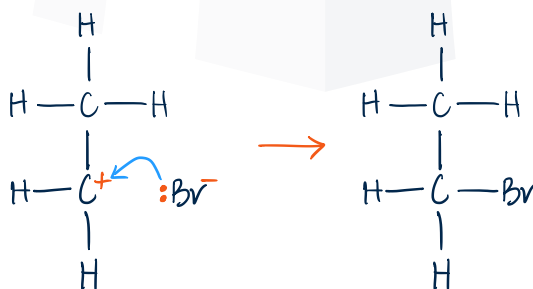


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ELECTROPHILIC ADDITION: STEP 2

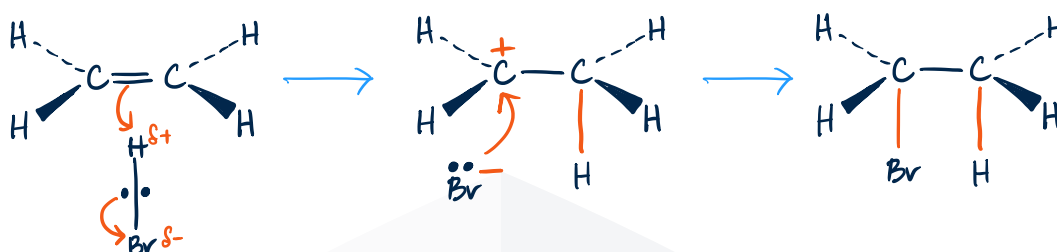
In the second stage the Br[−] ion is attracted to the C⁺ and donates a pair of electrons to form a bond.

The electrons in the final compound are also shown below.



12

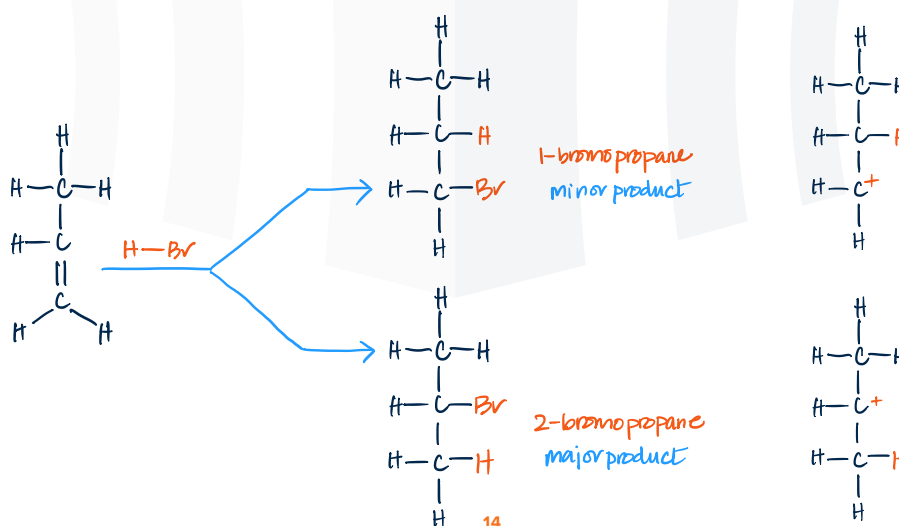
ELECTROPHILIC ADDITION OF HBr



13

REACTION OF HBr WITH PROPENE

When HBr adds to propene, two products are possible:

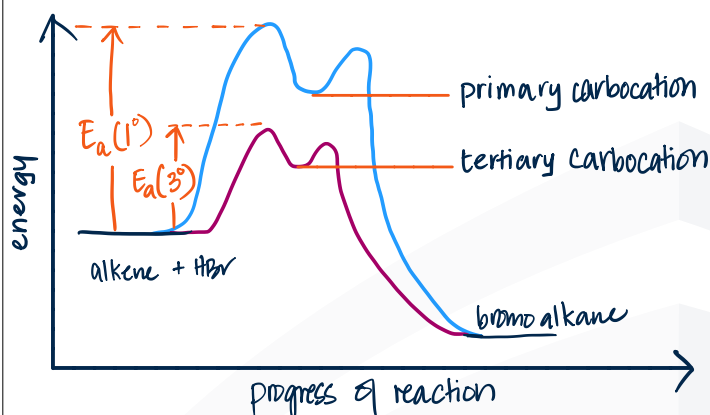


14

REACTION OF HBr WITH PROPENE

This is because when the electrophile $\text{H}^{\delta+}$ attacks the double bond either a secondary or a primary carbocation ion can form.

The major product that forms depends on the stability of the intermediate carbocation.

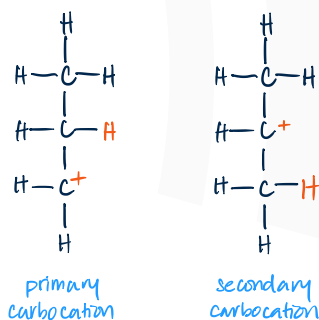


An electrophile adds on to an unsymmetrical alkene so that the most stable carbocation forms as the intermediate.

15

REACTION OF HBr WITH PROPENE

The two possible carbocations that can be formed when propene reacts with $\text{H}-\text{Br}$ are:



The secondary carbocation is more stable than the primary carbocation.

This is due to the electron-releasing effect of alkyl groups.

There are two alkyl groups next to the positively charged C in the secondary carbocation but only one in the primary carbocation.

Two alkyl groups reduce the positive charge on the C more than one alkyl group and thus stabilise the ion more.

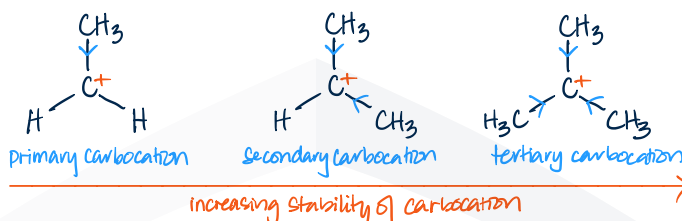
Since the secondary carbocation is more stable, it is more likely to be formed.

16

CARBOCATIONS

In general, the more alkyl groups there are attached to C^+ , the more stable the carbocation.

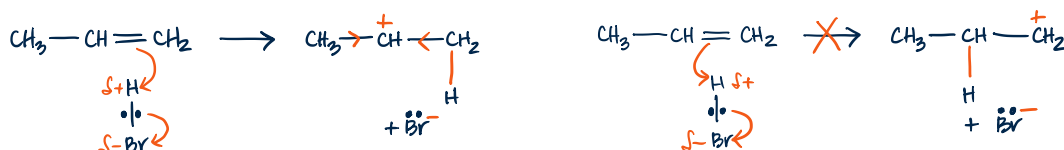
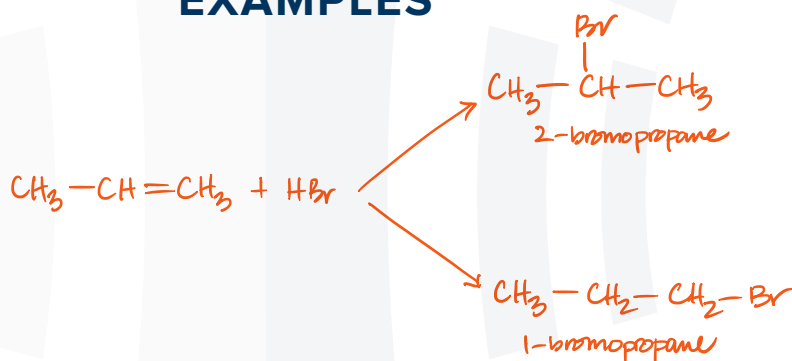
The electron-releasing effect is roughly independent of the size of the alkyl group, i.e. a methyl group donates approximately the same amount of electron density as an ethyl group.



Stability of carbocations is useful in determining the products of the reaction between unsymmetrical alkenes and halogen halides.

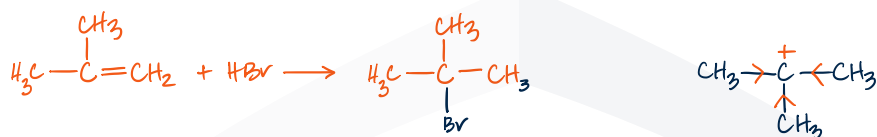
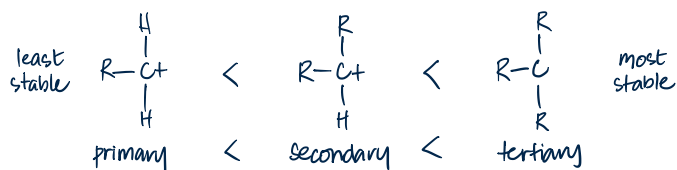
17

EXAMPLES



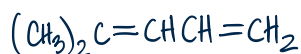
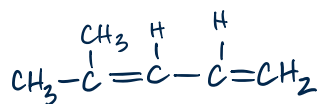
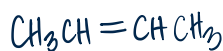
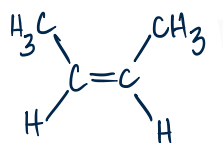
18

REACTION OF HBr WITH METHYLPROPENE



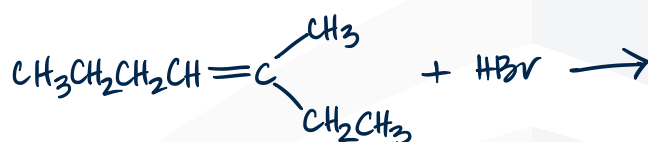
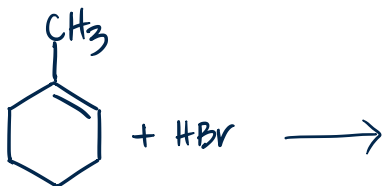
19

SKILL CHECK 1



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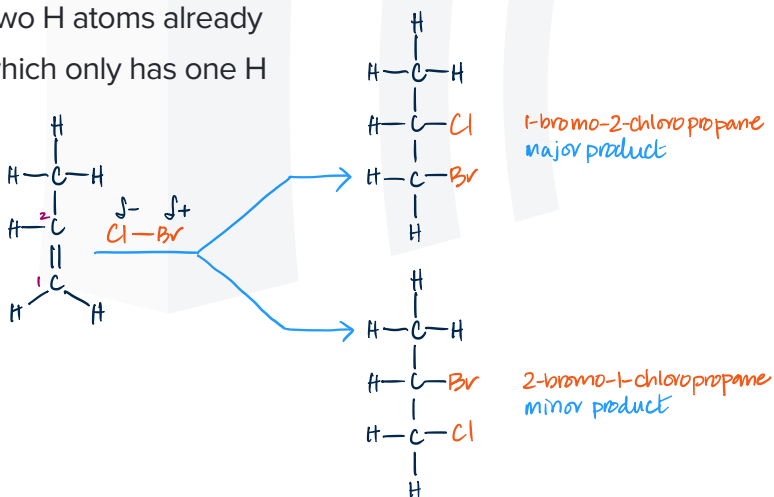
SKILL CHECK 2



21

PROPENE WITH BrCl

Br is less electronegative than Cl and becomes attached to C1, which has two H atoms already attached, rather than C2, which only has one H atom already attached.



22

ETHENE WITH BROMINE



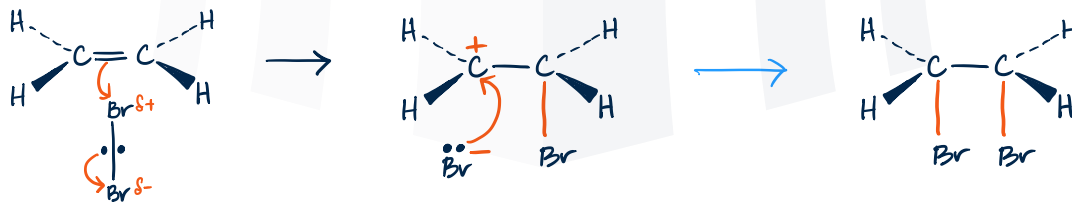
Although the bromine is not originally polar, as it approaches the high electron density in the $\text{C}=\text{C}$ it becomes polarised (there is an induced dipole).

The electrons are repelled in the Br_2 molecule so that the Br closest to the $\text{C}=\text{C}$ has a slight positive charge and the Br further away has a slight negative charge.



ALKENES WITH BROMINE

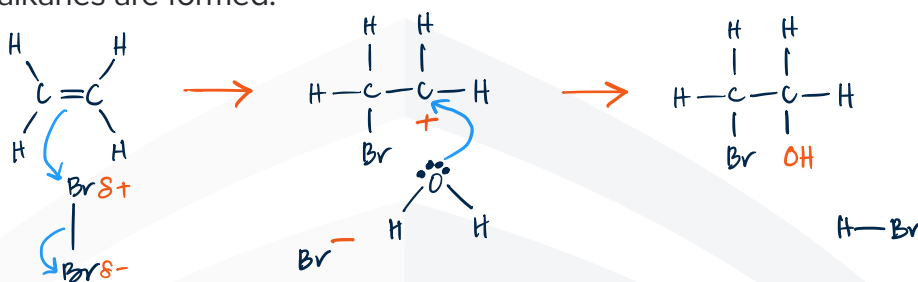
The mechanism is exactly analogous to the reaction of $\text{H}-\text{Br}$ with ethene, i.e. via a carbocation intermediate.



ALKENES WITH AQUEOUS BROMINE

Alkenes react with bromine water to form mainly bromoalcohols with a negligible amount of dibromoalkanes.

The reaction is similar to that of liquid bromine but the carbocation attacks the water molecule instead as it is found in large concentration. Small amounts of dibromoalkanes are formed.



25

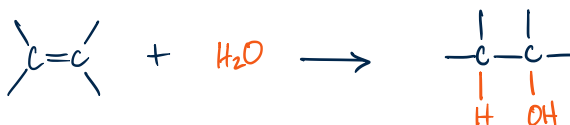
ALKENES WITH STEAM

Alkenes react with acid catalyst and steam at temperatures of around 350°C and pressures over 100 atm to form alcohols.

Reagent Steam and dil phosphoric acid (H_3PO_4)

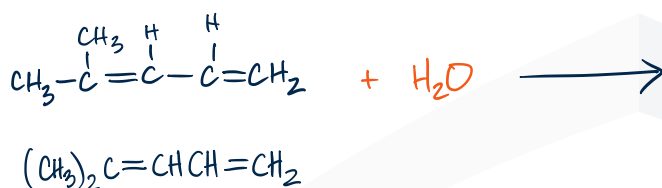
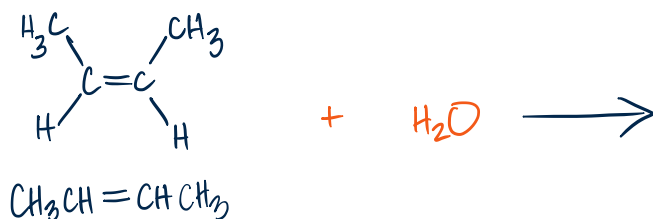
Condition 350 °C and 100 atm

Type Electrophilic addition



26

ETHENE WITH STEAM



27

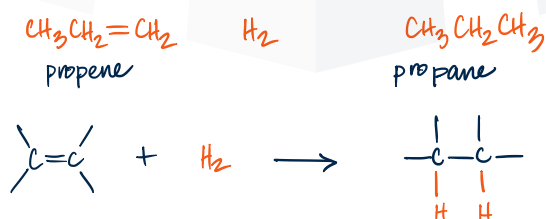
ALKENES WITH HYDROGEN

When a mixture of alkene and hydrogen is passed over Ni catalyst at 200°C to 300°C, an alkane is formed.

Reagent Hydrogen (H_2) and Nickel (Ni)

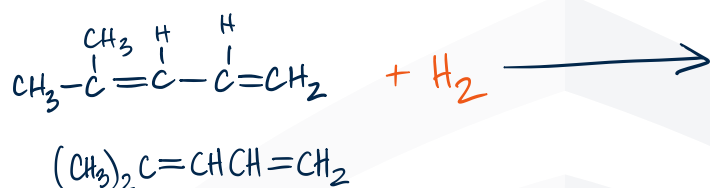
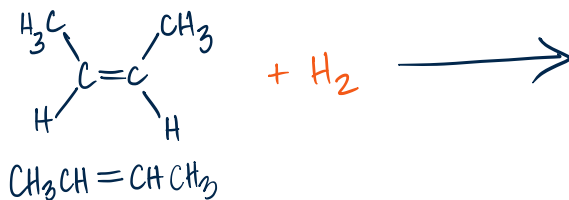
Condition 200 °C to 300 °C

Type Reduction



28

ALKENES WITH HYDROGEN



29

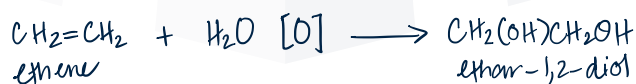
MILD OXIDATION OF ALKENES

When an alkene is passed through cold dilute alkaline manganate (VII), a diol is formed. During the reaction the purple colour of manganate (VII) is removed.

Reagent cold dilute alkaline (or acidic) potassium manganate (KMnO₄)

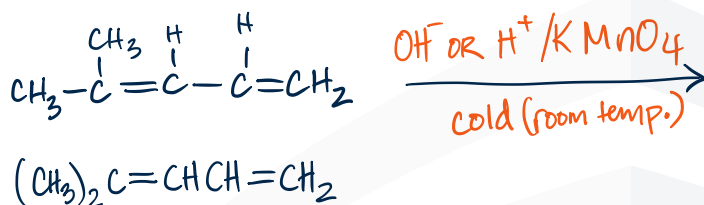
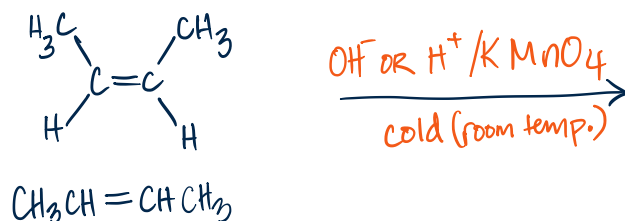
Condition cold (room temperature)

Type Oxidation



30

MILD OXIDATION OF ALKENES

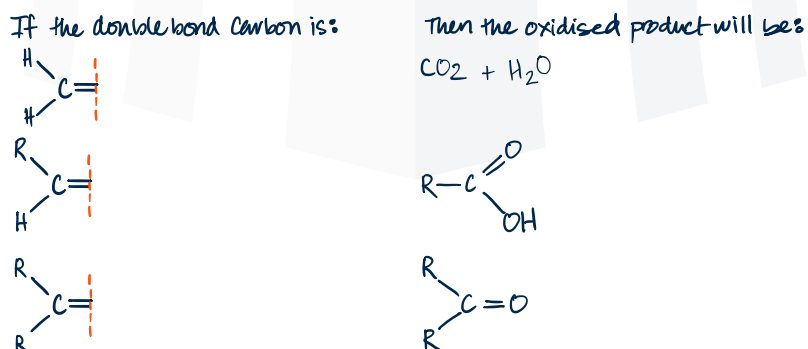


31

STRONG OXIDATION OF ALKENES

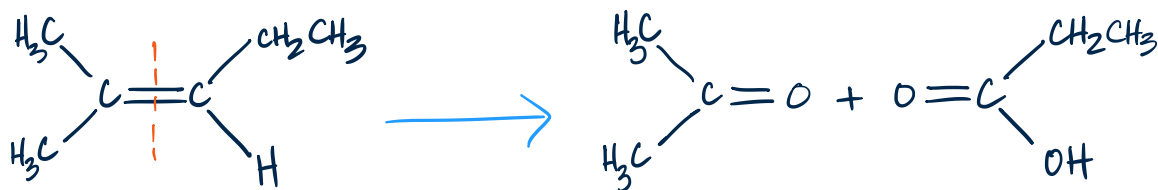
When an alkene is passed through hot concentrated acidified manganate (VII) the double bonds rupture giving two carbonyl compounds.

If the carbonyl compound is an aldehyde it is further oxidised to the corresponding acid.



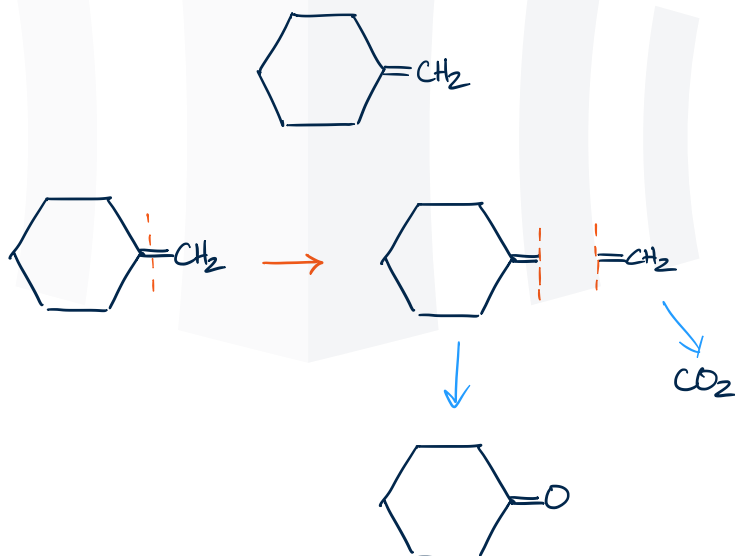
32

STRONG OXIDATION OF ALKENES



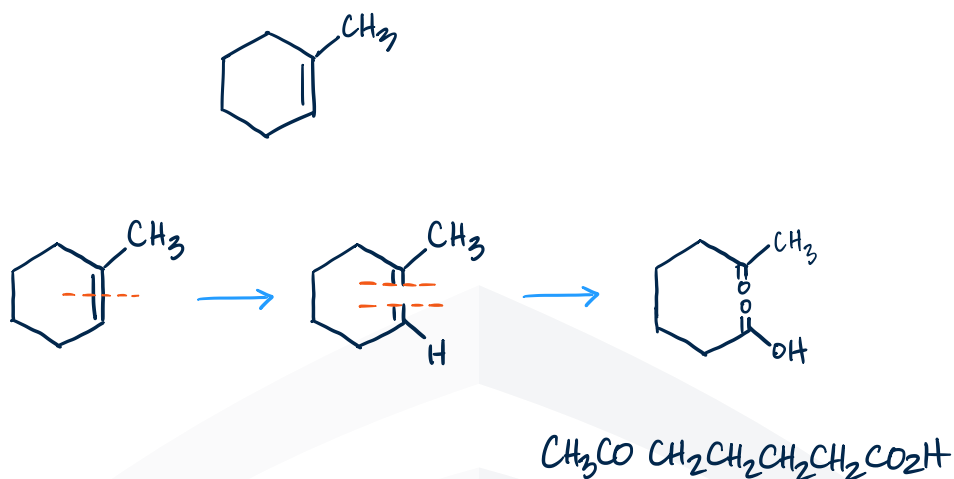
33

STRONG OXIDATION OF ALKENES



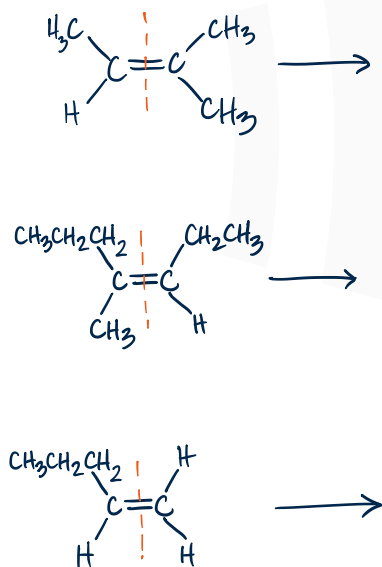
34

STRONG OXIDATION OF ALKENES



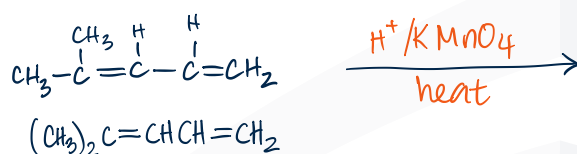
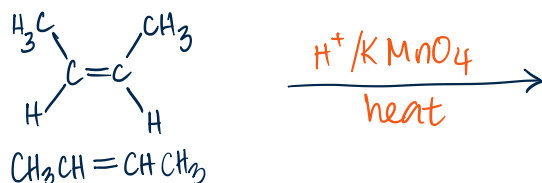
35

STRONG OXIDATION OF ALKENES



36

STRONG OXIDATION OF ALKENES



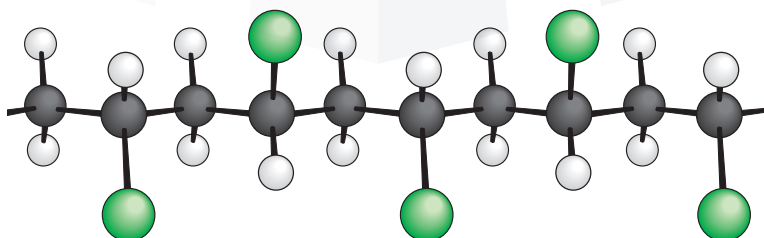
37

ADDITION POLYMERISATION

Alkenes undergo addition polymerisation, in which a large number of monomers are joined together into a polymer chain.

It is important to realise from this reaction that it is only the C=C group that reacts when the polymerisation reaction occurs – all the other groups attached to the C=C are unaffected.

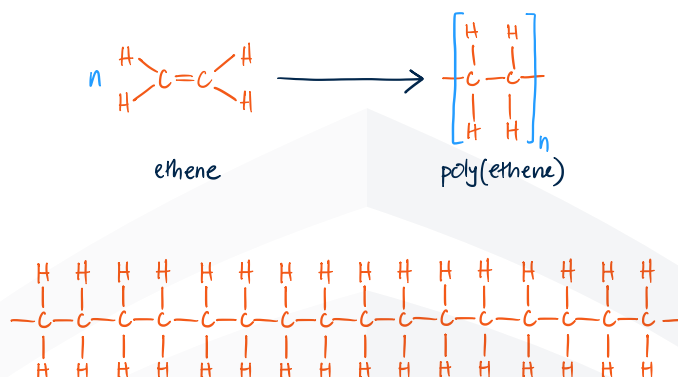
A 3D displayed formula of part of the poly(chloroethene) molecule



38

POLY(ETHENE)

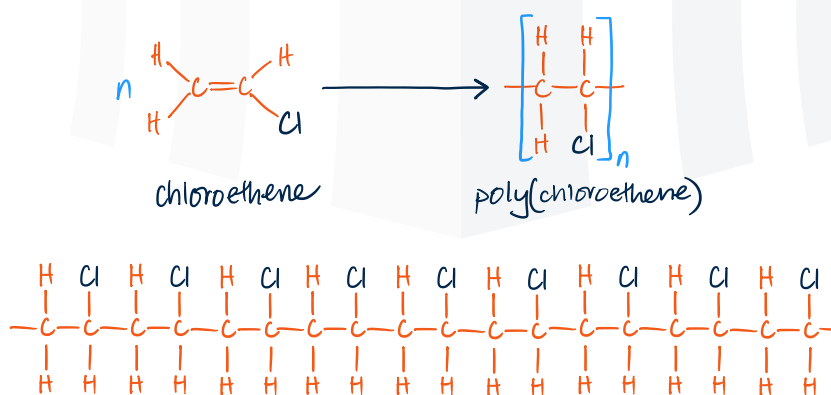
Poly(ethene), commonly called polythene, is termed an addition polymer because one molecule is made from many ethene units. Poly(ethene) is used to make bags, electrical insulation, dustbin liners, bottles, etc.



39

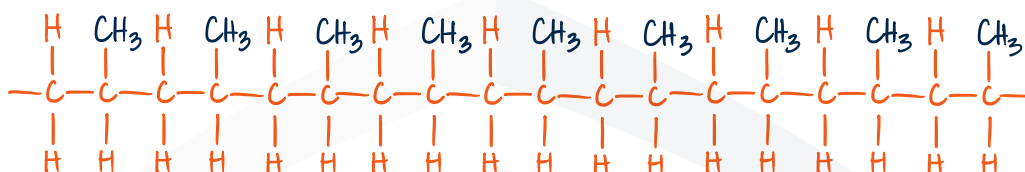
POLY(CHLOROETHENE)

poly(chloroethene), commonly called PVC [poly(vinylchloride)], is used to make guttering, water pipes, window frames, floor coverings.



40

POLY(PROPENE)



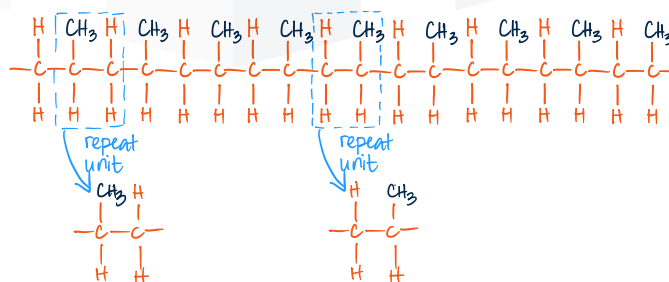
41

REPEAT UNITS

The repeat unit or repeating unit of a polymer is the basic unit from which the whole polymer chain can be made up.

In each of the equations seen so far, this has been shown in brackets.

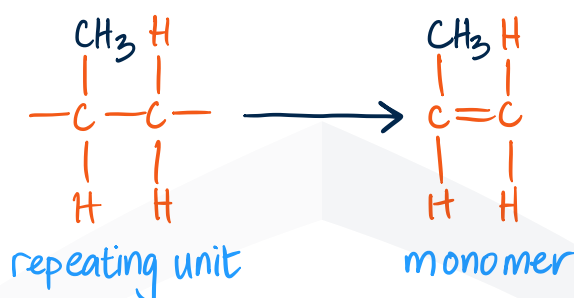
The repeat unit for a polymer may be obtained simply by taking any two adjacent carbon atoms in the main polymer chain.



42

REPEAT UNITS

The monomer for a polymer can be derived by simply placing a double bond between the carbons of the repeat unit.



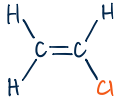
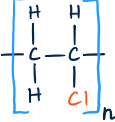
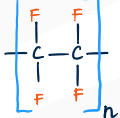
43

POLYMERS

Monomer	Polymer repeat unit	Properties	Uses
ethene $\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	poly(ethene) $\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right]_n$	Light Flexible Easily moulded Transparent Good insulator Resistant to water, acids and alkalis	Plastic bags and bottles Insulation for cables
propene $\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{CH}_3 \end{array}$	poly(propene) $\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{CH}_3 \end{array} \right]_n$	Tough Easily moulded Easily coloured Very resistant to water, acids and alkalis	Fibre for ropes and carpets Crates Toys

44

POLYMERS

Monomer	Polymer repeat unit	Properties	Uses
chloroethene 	poly(chloroethene) [PVC] 	Tough Rigid or flexible Very resistant to water, acids and alkalis	Clingfilm Guttering and window frames Insulation for cables Waterproof clothing Flooring
tetrafluoroethene 	poly(tetrafluoroethene) (ptfe) 	Tough Rigid Low friction solid Resistant to water, acids and alkalis	Coating for non-stick pans and skis Low friction surfaces for bridges to move as metals expand and contract

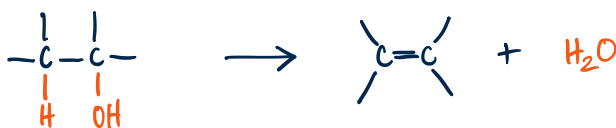
45

ALKENES FROM ALCOHOLS

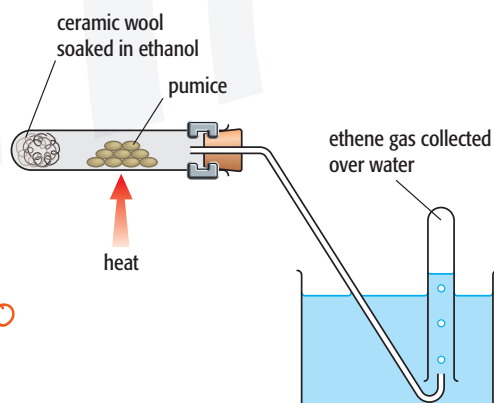
When an alcohol is heated with excess concentrated sulphuric acid at around 200 °C an alkene is formed. (Refer to the notes on Alkenes).

Dehydration of the alcohol can also be carried out by passing the alcohol vapour over alumina at 350 °C.

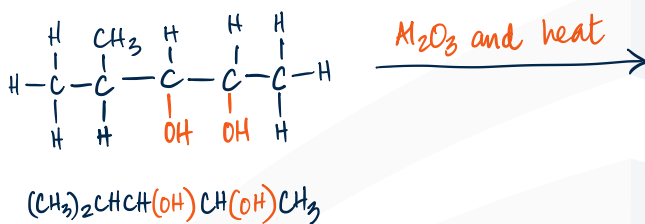
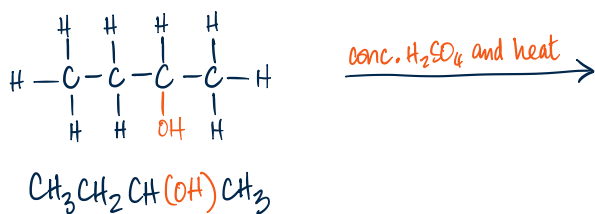
Reagent	conc H ₂ SO ₄
Condition	200 °C
Alternatively	Alumina at 350°C.
Type	elimination



46

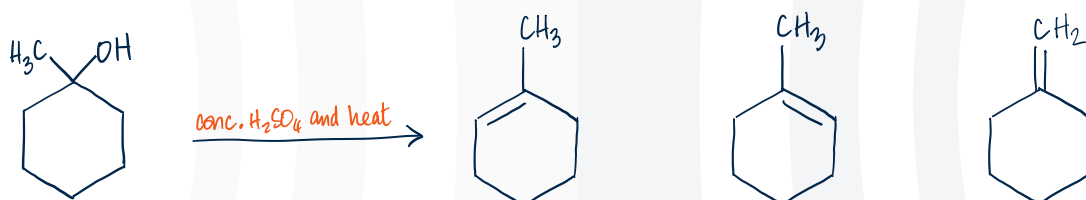


ALKENES FROM ALCOHOLS



47

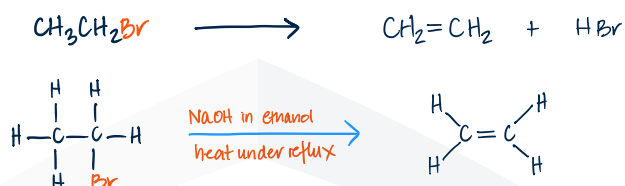
ALKENES FROM ALCOHOLS



48

ALKENES FROM HALOGENOALKANES

Reagent	sodium (or potassium) hydroxide dissolved in ethanol
Condition	heat under reflux
Product	Alkene
Type	elimination

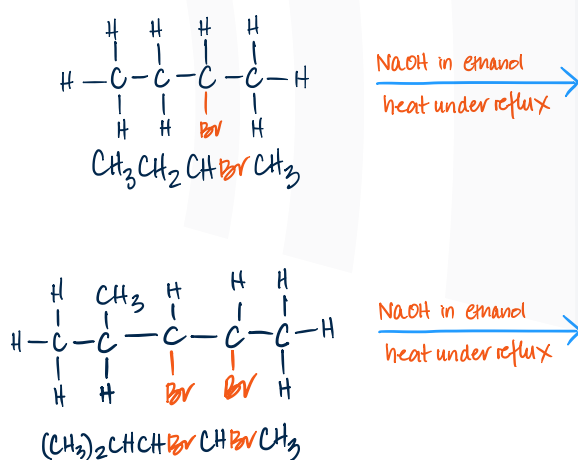


The OH^- removes a proton from a carbon atom adjacent the C bearing the halogen.

If the haloalkane is unsymmetrical (e.g. 2-bromobutane) a mixture of isomeric alkene products is obtained.

49

ALKENES FROM HALOGENOALKANES



50