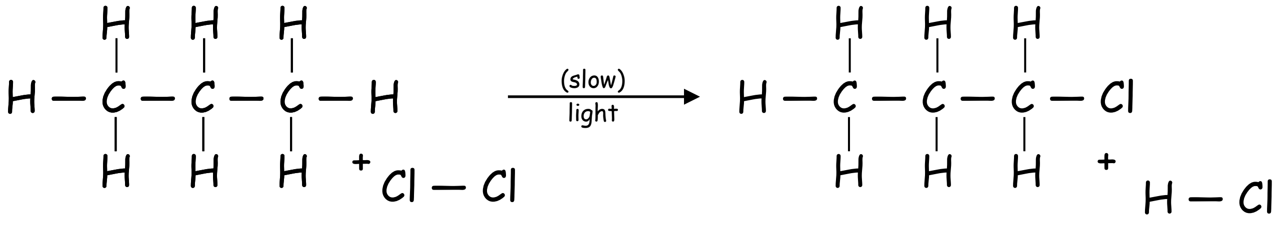
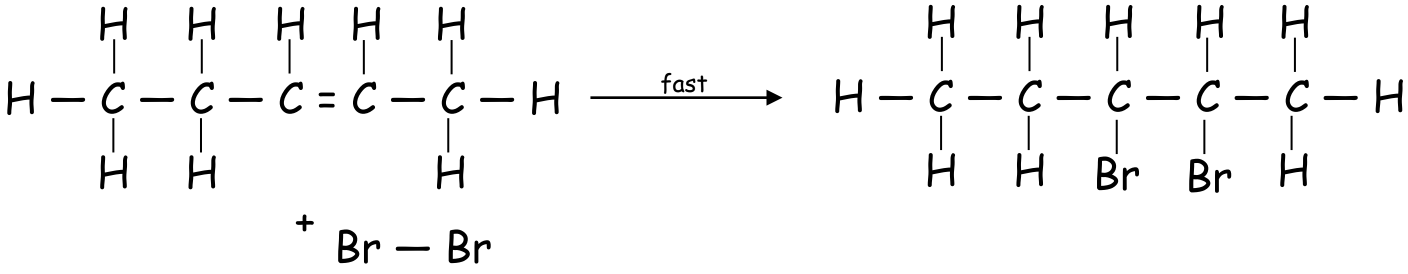
2.3 Synthesis

Types of Reaction

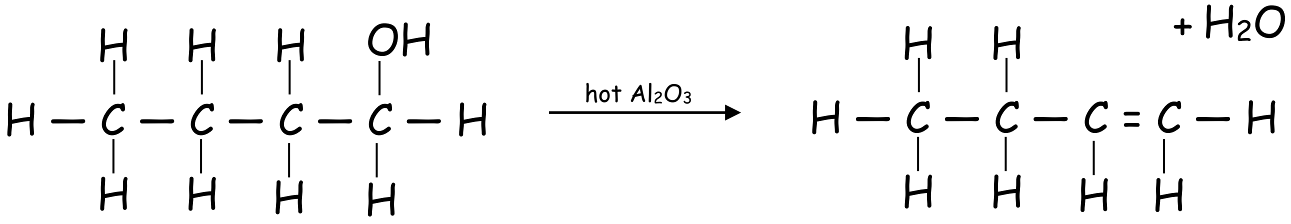
a) Substitution



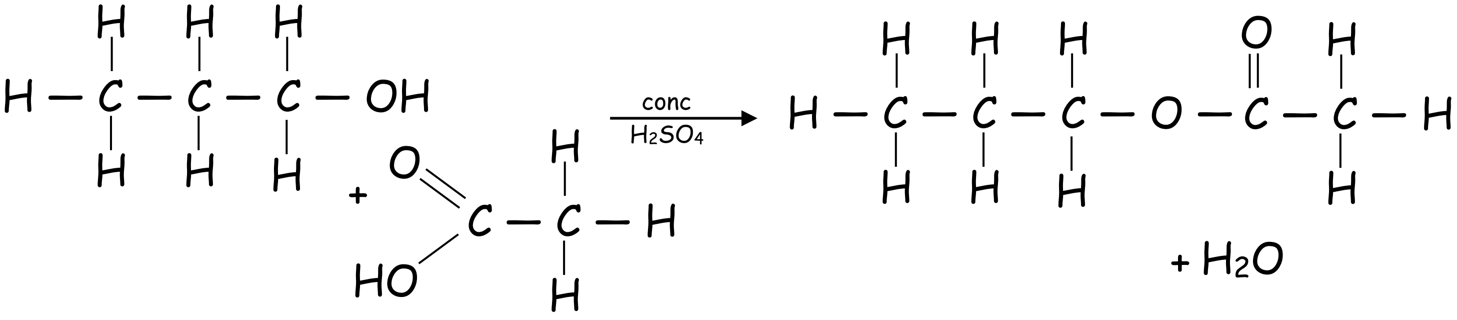
b) Addition



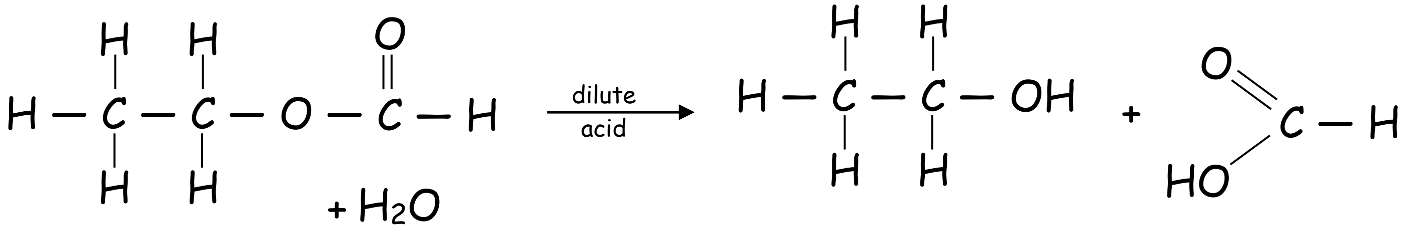
c) Elimination



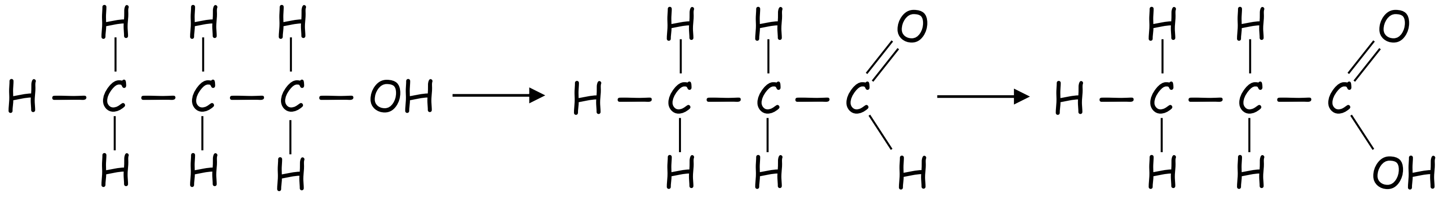
d) Condensation



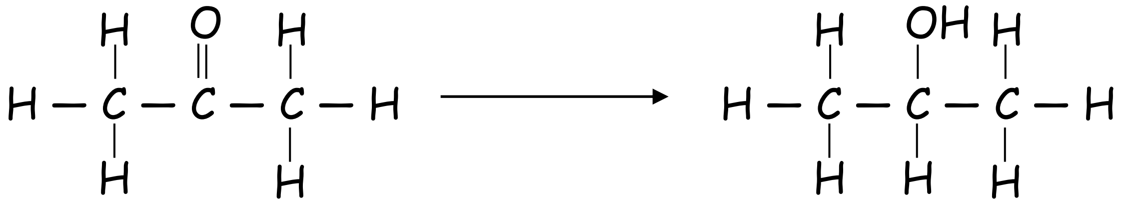
e) Hydrolysis



f) Oxidation



g) Reduction



Heterolytic and Homolytic Fission

a) Homolytic Fission

Homolytic fission is when two electrons in a covalent bond separate equally

e.g. hydrogen chloride

$$\mathrm{H} \overset{\bullet}{\underset{\bullet}{\text{——}}} \mathrm{Cl} \longrightarrow \mathrm{H}^{\bullet} + \mathrm{Cl}^{\bullet}$$

where • is an unpaired electron

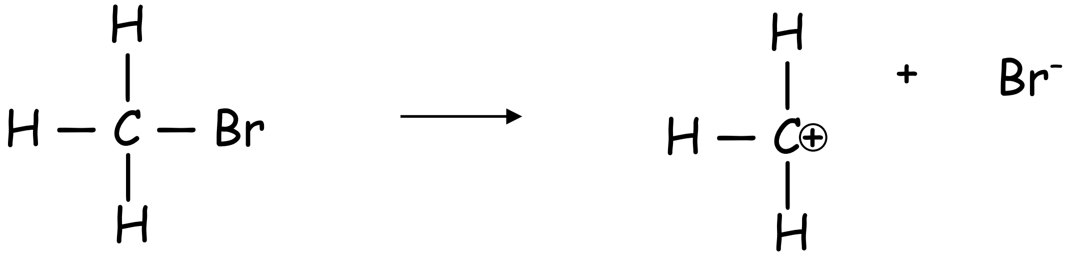
- Atoms are electrically neutral
    - number of protons = number of electrons
- Atoms are highly reactive as unpaired electrons have tendency to react with other unpaired electrons it encounters and they up pair up.
- Atoms with unpaired electrons are called **free radicals**
- Homolytic fission is more likely to happen in less polar bonds where electrons are evenly shared between the atoms.

b) Heterolytic Fission

- When a bond is broken, both the shared electrons transfer to just one of the atoms

$$\mathrm{H} \overset{\bullet}{\underset{\bullet}{\text{——}}} \mathrm{Br} \longrightarrow \mathrm{H}^{+} + \mathrm{Br}^{-}$$

- The more polar the covalent bond is, the more likely it is that heterolytic fission will take place.



$$\mathrm{CH_3Br} \longrightarrow \mathrm{CH_3}^{\oplus} + \mathrm{Br}^{-}$$

carbocation or carbonium ion

Reaction of Alkanes with Bromine/Chlorine

- Alkanes are relatively unreactive compounds
    - combustion is the main reaction of alkanes
- Alkanes react with bromine slowly
    - Light must be present
    - Chlorine is faster than bromine but still requires light
- Alkanes which react slowly with halogens react by a mechanism called **Free Radical Chain Reaction**

Free Radical Chain Reaction

- Free radicals contain an unpaired electron

Step 1: Initiation (Rate Determining Step)

unpaired electron

$$Br_2 \xrightarrow[\text{UV light/slow}]{\text{Homolytic fission}} Br^\bullet + Br^\bullet$$

saturated
single bonds
slow
substitution
sunlight

Step 2: Propagation

$$Br^\bullet + CH_4 \longrightarrow CH_3^\bullet + HBr$$

$$CH_3^\bullet + Br_2 \longrightarrow CH_3Br + Br^\bullet$$

Step 3: Termination

$$CH_3^\bullet + CH_3^\bullet \longrightarrow CH_3CH_3$$

$$CH_3^\bullet + Br^\bullet \longrightarrow CH_3Br$$

$$Br^\bullet + Br^\bullet \longrightarrow Br_2$$

- Light required to start reaction
    - Reaction continues in darkness once started
- Main products are bromomethane and hydrogen bromide
    - Some ethane is produced as two $CH_3^\bullet$ radicals join up with each other
- Bromoalkanes have significantly higher boiling point than alkanes
    - Separated by distillation

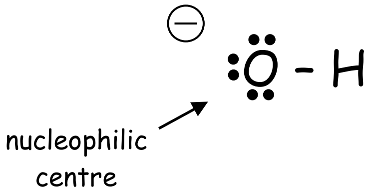
Nucleophiles and Electrophiles

Most organic reactions are between a nucleophile and an electrophile

- nucleophiles are electron-rich molecules
- electrophiles are electron-poor molecules

Charged particles are often nucleophiles and electrophiles

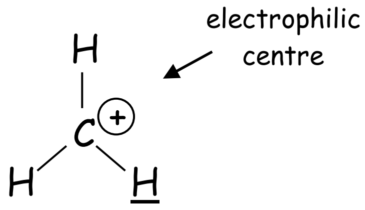
- an atom bearing a negative charge acts as a nucleophile



OH^- ion acts as a nucleophile

  - examples of nucleophiles include
    - carbanions R^-
    - other anions, e.g. OH^-, CN^-
    - molecules with lone pairs, e.g. NH_3
    - negatively polarised centres, e.g. O in H_2O

- an atom bearing a positive charge acts as an electrophile

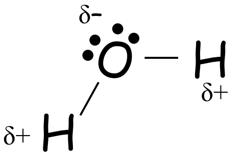


Carbocation acts as an electrophile

  - examples of electrophile include
    - carbocations R^+
    - other cations, e.g. H^+
    - electron-deficient centres
    - positively polarised centres, e.g. H in H_2O

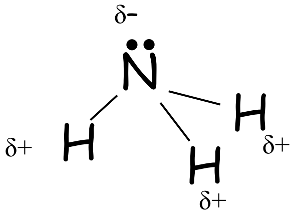
Molecules do not need to be charged to act as a nucleophile or an electrophile

- water is neutral but can act as both an electrophile or a nucleophile
    - oxygen atom has a greater share of electrons in the covalent bonds

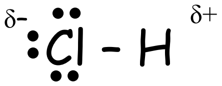


$\delta-$ nucleophilic centre
$\delta+$ electrophilic centre

- nitrogen in ammonia is more electronegative than the hydrogen



- hydrogen chloride molecules have nucleophilic and electrophilic centres

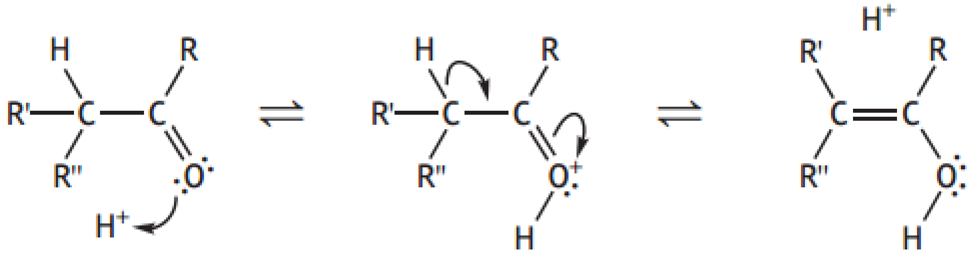


- nucleophilic strength is N > O > Cl
    - opposite to order of electronegativity

Curly Arrow Notation

a) Double Headed Arrows

- double headed arrow shows the movement of an electron pair
    - double headed arrow from the middle of a covalent bond indicated that heterolytic fission is occuring.



-
    - an arrow drawn with the head pointing to the space between two atoms indicates that a covalent bond will be formed between those atoms

b) Single Headed Arrows

- single headed arrows indicate the movement of a single electron
    - two single headed arrows starting in the middle of a covalent bond indicates that homolytic fission is occurring.

-

3.2a Haloalkanes

Organic compounds with halogen substituents are comparatively rare in nature

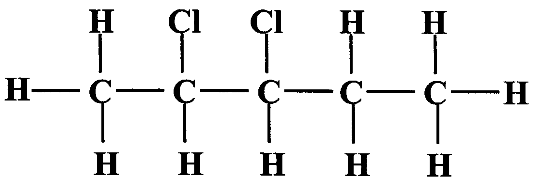
- these compounds need to be synthesised as they are widely used in Chemistry
    - medicines
    - anaesthetics e.g. chloroform
    - plastics e.g. PVC
    - agriculture e.g. pesticides
- serious problems of disposing of halogen-containing compounds
    - environmental damage of pesticides e.g. DDT
    - ozone layer depletion by CFCs

a) Naming Haloalkanes

- Haloalkanes are also known as
    - Halogenalkanes
    - Alkyl halides
- One or more hydrogens on an alkane have been replaced by a halogen atom
    - Can lead to higher degree of structural isomerism
    - Care must be take when naming and drawing haloalkanes

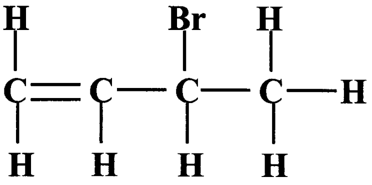
- Naming Examples of Haloalkanes

i)



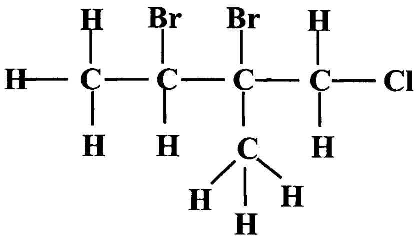
2,3-dichloropentane
(not *3,4-dichloropentane)*

ii)



3-bromobut-1-ene
(not *2-bromobut-3-ene*)

iii)



2,3-dibromo-1-chloro-2-methylbutane
NB bromo before chloro before methyl

Questions

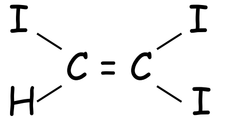
1. Draw full structural formulae for the following:
    a) 1-bromo-2,3-dimethylbut-2-ene

    b) 4-chloro-3,3-dimethylcyclohexene

    c) 4-bromo-1-chloro-2,3,5-trimethylhex-1-ene.

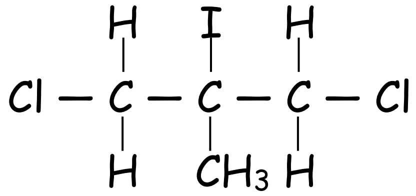
2. Name the following compounds:

a)



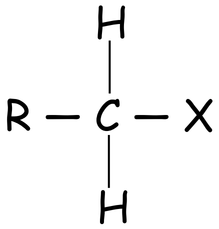
b) $BrCH_2CHCHCHBrCH_3$

c)



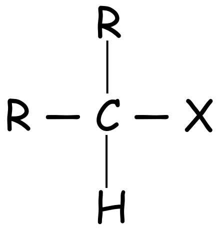
$$\begin{array}{ccccccccc} & & H & & I & & H & & \\ & & | & & | & & | & & \\ Cl & - & C & - & C & - & C & - & Cl \\ & & | & & | & & | & & \\ & & H & & CH_3 & & H & & \end{array}$$

b) <u>Position of Halogen in Haloalkanes</u>



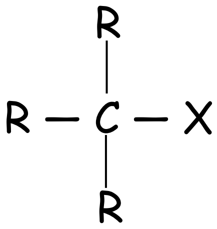
$$\begin{array}{c} H \\ | \\ R - C - X \\ | \\ H \end{array}$$

primary
halogenalkane



$$\begin{array}{c} R \\ | \\ R - C - X \\ | \\ H \end{array}$$

secondary
halogenalkane



$$\begin{array}{c} R \\ | \\ R - C - X \\ | \\ R \end{array}$$

tertiary
halogenalkane

- Where R is an alkyl group
    - methyl $-CH_3$, ethyl $-C_2H_5$, propyl $-C_3H_7$, etc.
- Where X is a halogen atom
    - fluoro –F, chloro –Cl, bromo –Br, iodo –I.

Reactions of Haloalkanes

Reactions of haloalkanes are largely dependent on two main factors:

- Which halogen is present
    - C-F bonds are the strongest and, therefore, the least reactive

Bond Strength: R – F > R – Cl > R – Br > R – I

strongest bond ⟶ weakest bond

Reactivity: R – I > R – Br > R – Cl > R – F

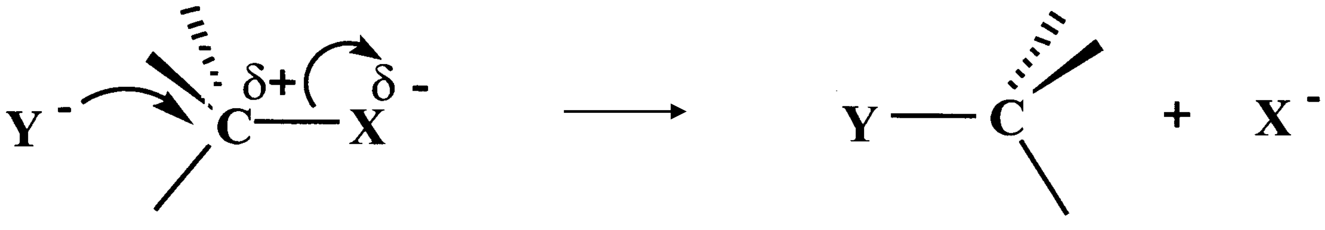
most reactive ⟶ least reactive

- The position of the halogen atom within the carbon compound
    - Primary, secondary or tertiary

Nucleophilic Substitution Reactions

Halogen atoms have a higher electronegativity than carbon

- C – X bond is polarised, where X is a halogen
- C – X bonds breaks heterolytically
    - Halogen ion X^- formed leaving behind a carbocation
    - Cl^-, Br^-, I^- ions are good leaving groups in chemical reactions



- Where Y^- is the attacking nucleophile
- Where X^- is the leaving halogen

Reactions of Nucleophilic Substitution

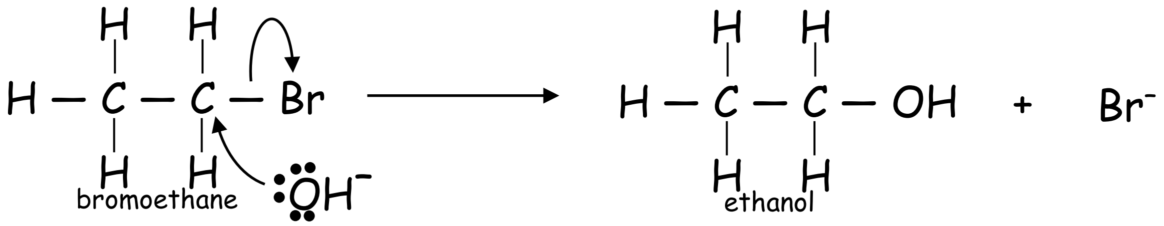
1. Using Alkalis to form Alcohols

$$\mathrm{R - X} \xrightarrow{\text{alkali}} \mathrm{R - OH}$$

halogen alkane alkanol

$$\mathrm{CH_3CH_2CH_2CH_2Cl} \xrightarrow{\text{alkali}} \mathrm{CH_3CH_2CH_2CH_2OH}$$

1-chlorobutane butan-1-ol



- Alcohols formed can be converted by oxidation to the corresponding aldehyde, ketone or carboxylic acid

2. Using Alcoholic Alkoxide to form Ethers

When sodium reacts with an alkanol, sodium alkoxide is formed

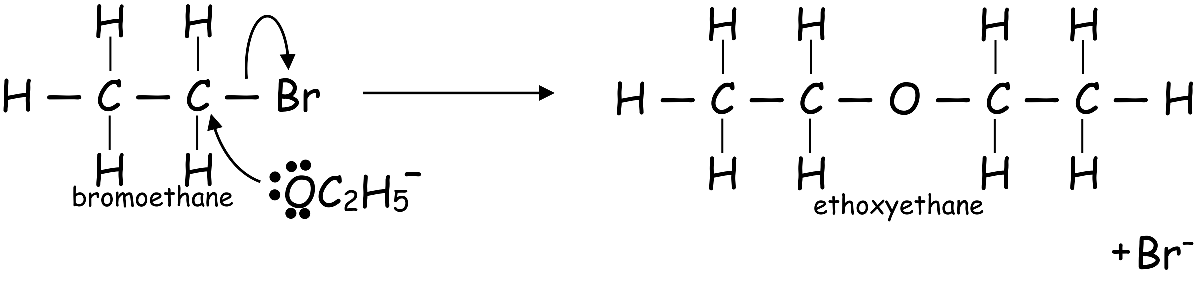
$$\mathrm{Na(s) + C_2H_5OH(l) \longrightarrow H_2(g) + C_2H_5O^-Na^+}$$

ethanol sodium ethoxide

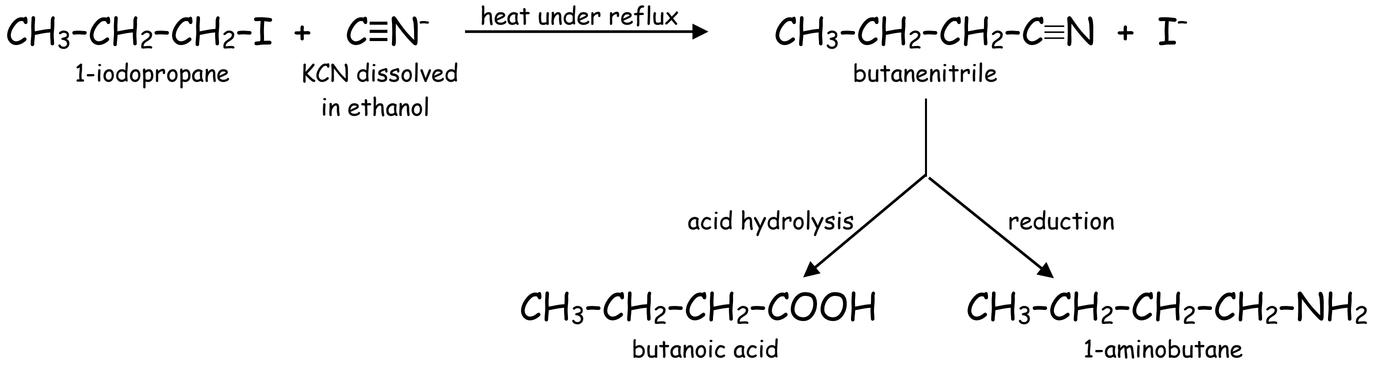
- Sodium alkoxides will react with haloalkanes to form ethers

$$\mathrm{C_2H_5O^-Na^+ + BrCH_2CH_3 \longrightarrow C_2H_5OCH_2CH_3 + Na^+Br^-}$$

sodium ethoxide bromoethane ethoxyethane (ether)



3. Reaction with Ethanolic Cyanide to form Nitriles



$$CH_3{-}CH_2{-}CH_2{-}I + C{\equiv}N^- \xrightarrow{\text{heat under reflux}} CH_3{-}CH_2{-}CH_2{-}C{\equiv}N + I^-$$

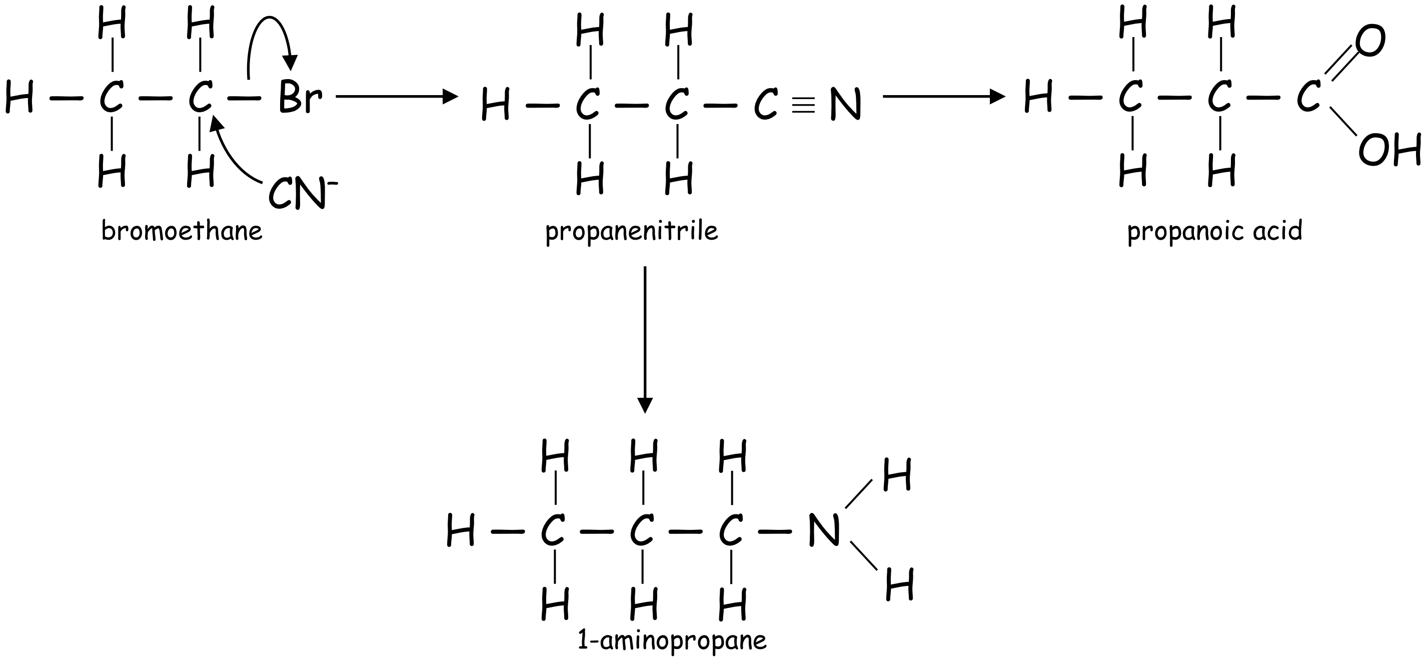
$$CH_3{-}CH_2{-}CH_2{-}C{\equiv}N \xrightarrow{\text{acid hydrolysis}} CH_3{-}CH_2{-}CH_2{-}COOH$$

$$CH_3{-}CH_2{-}CH_2{-}C{\equiv}N \xrightarrow{\text{reduction}} CH_3{-}CH_2{-}CH_2{-}CH_2{-}NH_2$$

- acid hydrolysis of nitrile can produce alkanoic acid
    - this process lengthens the carbon chain length by one carbon

- reduction of nitrile can produce an amine
    - this process lengthens the carbon chain length by one carbon

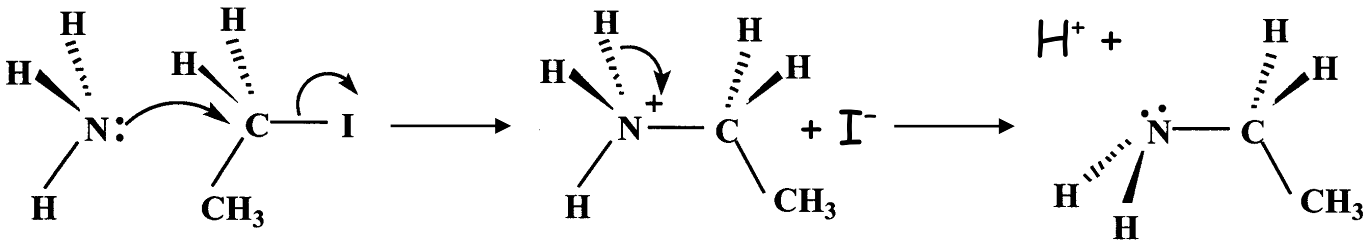
Mechanism:



4. Reaction With Ammonia to Form Amine

Not in Mandatory Course Key Areas

$$\underset{\text{haloalkane}}{R-X} + \underset{\text{ammonia}}{NH_3} \longrightarrow \underset{\text{amine}}{R-NH_2} + \underset{\text{hydrogen halide}}{HX}$$

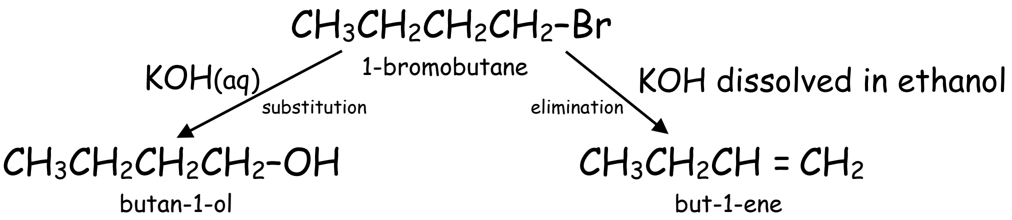


ammonia 1-iodoethane ethylammonium ion 1-aminoethane

Elimination Reactions

When monohaloalkanes are refluxed with alcoholic potassium hydroxide (KOH dissolved in C_2H_5OH)

- hydrogen halide molecules are eliminated
- C=C double bond is formed



$CH_3CH_2CH_2CH_2-Br$

1-bromobutane

KOH(aq) substitution

KOH dissolved in ethanol elimination

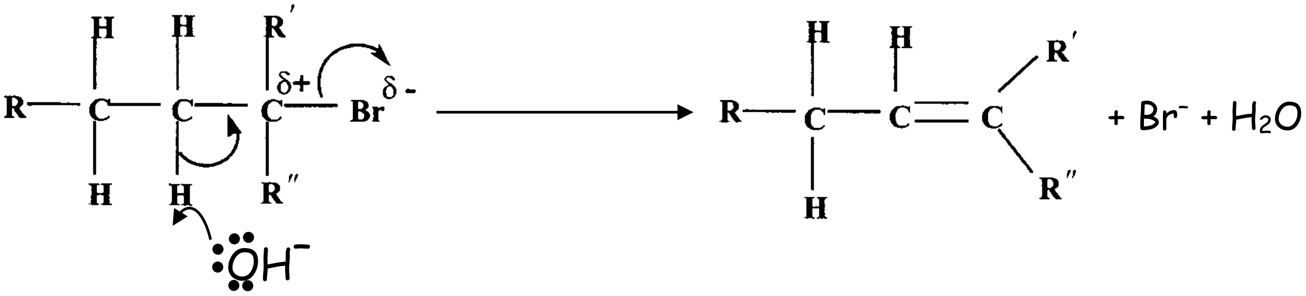
$CH_3CH_2CH_2CH_2-OH$

butan-1-ol

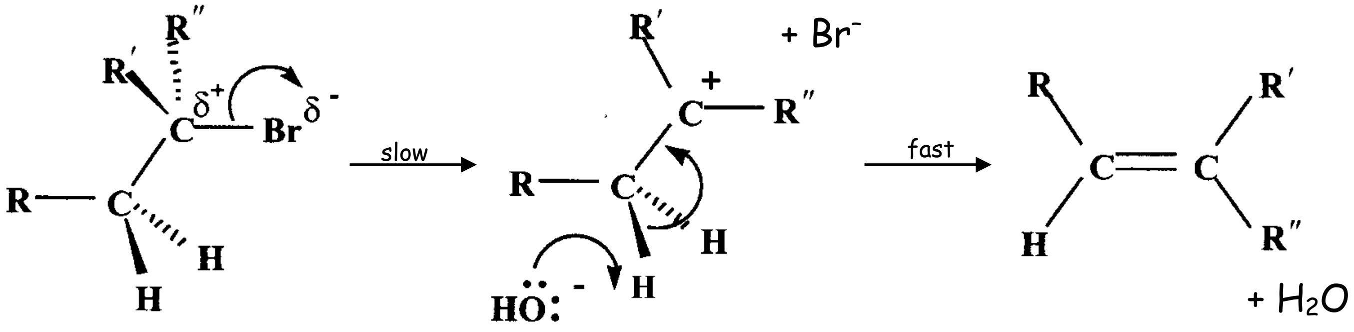
$CH_3CH_2CH = CH_2$

but-1-ene

E2 Mechanism: (2 molecules involved in Elimination RDS)



E1 Mechanism: (1 molecule involved in Elimination RDS)



Question

1. What are the possible products when 2-chloro-2-methylbutane is reacted with:

    a) aqueous potassium hydroxide

    b) a solution of potassium hydroxide in ethanol

    c) a solution of sodium ethoxide in ethanol?

Types of Nucleophilic Substitution Reactions

1. S_N2 Reaction: Hydrolysis of Primary Haloalkanes Using $OH^-(aq)$

$$C_2H_5Br(l) + OH^-(aq) \longrightarrow C_2H_5OH(aq) + Br^-(aq)$$

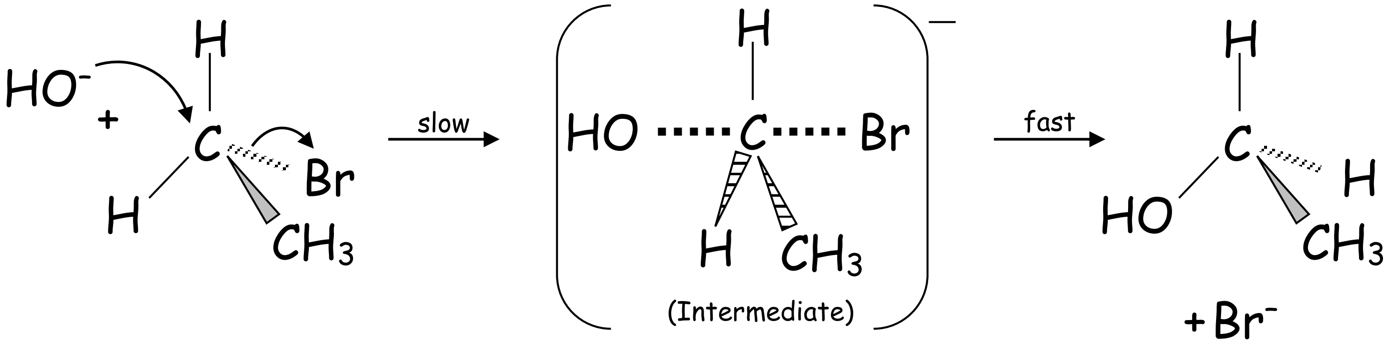
Experimental determination shows the kinetics of this reaction

- 1st order with respect to OH^-
- 1st order with respect to C_2H_5Br

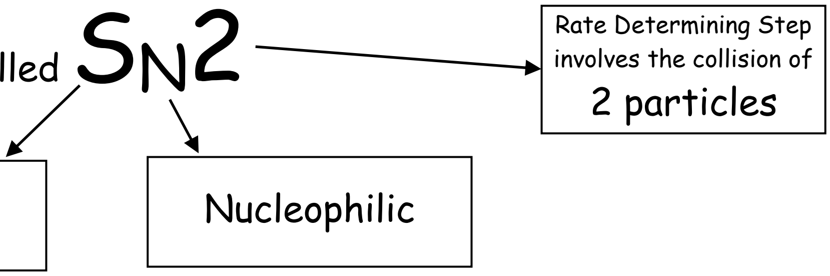
- rate = k $[C_2H_5Br]\,[OH^-]$

- rate determining step involves
  - 1 molecule of C_2H_5Br
  - 1 molecule of OH^-

- OH^- ion nucleophilically attacks the slightly positive (∂+) carbon in C_2H_5Br from the opposite side of the C_2H_5Br molecule to where the Br atom is located
- As OH^- approaches the central carbon, C – Br begins to weaken
- If collision has sufficient energy an intermediate is formed where
  - C – O bond is half-formed
  - C – Br bond is half-broken
- But as C – O bond becomes 100% formed, C – Br bond breaks completely



This reaction type is called S_N2

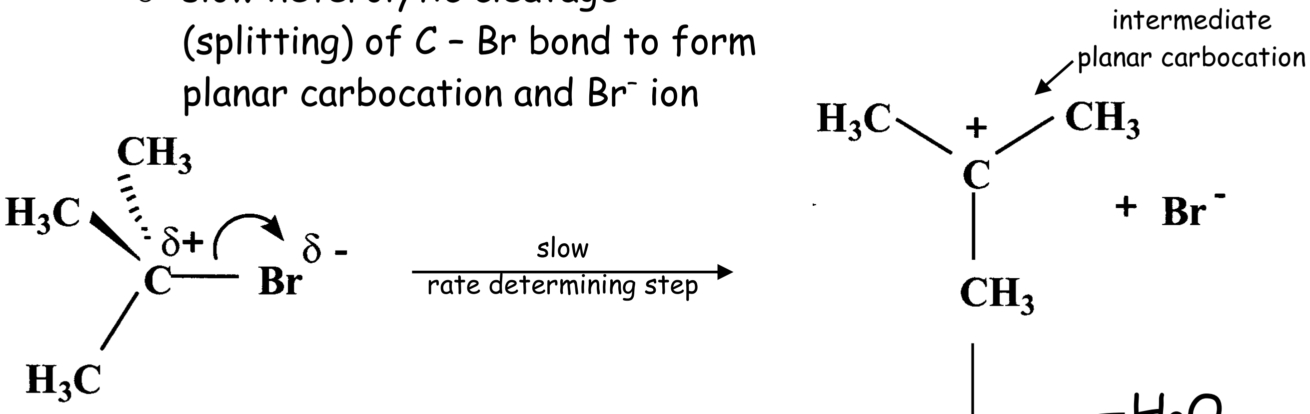


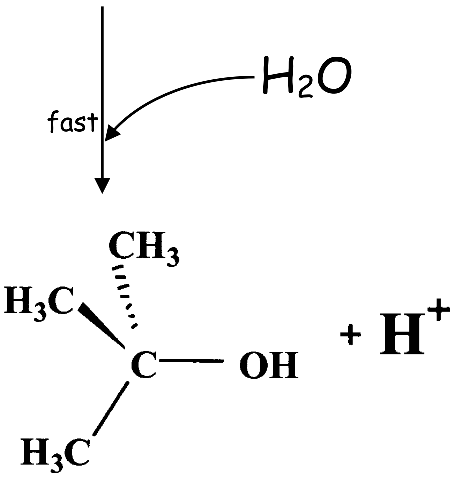
2. S_N1 Reaction: Hydrolysis of 2-bromo-2-methylpropane

$$\underset{\text{tertiary haloalkane}}{(CH_3)_3CBr(l)} + H_2O(l) \longrightarrow \underset{\text{tertiary alkanol}}{(CH_3)_3COH(aq)} + HBr(aq)$$

Experimental determination shows the kinetics of this reaction

- 1st order with respect to $(CH_3)_3CBr$
- Zero order with respect to H_2O (i.e. independent of $[H_2O]$)
- rate = $k [(CH_3)_3CBr]$
- rate determining step involves only $(CH_3)_3CBr$
  - slow heterolytic cleavage (splitting) of C – Br bond to form planar carbocation and Br^- ion





- rate of reaction is determined by the rate of the formation of the intermediate carbocation
  - rate of the 2nd step in the mechanism is very fast compared to the rate determining 1st step.
- If the molecule is chiral (see Unit 3.7)
  - Planar carbocation ion can be attacked from either side
  - Both chiral forms of $(CH_3)_3COH$ are formed and a racemic mixture of stereoisomers are formed (See Unit 3.7)

This reaction type is called S_N1

Substitution reaction

Nucleophilic

Rate Determining Step involves the collision of 1 particle

2.3b Alcohols

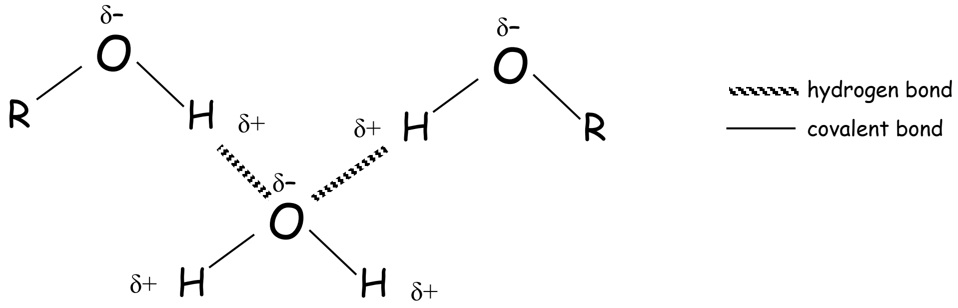
- alkanols are a subset of bigger family called alcohols
  - homologous series of alkanols: $C_nH_{2n+1}OH$

- alcohols have general formula R-OH
  - where R is a hydrocarbon group or substituted hydrocarbon

- position of –OH group decides type of alcohol
  - primary 1 carbon directly attached to the carbon with the –OH group
  - secondary 2 carbons directly attached to the carbon with the –OH group
  - tertiary 3 carbons directly attached to the carbon with the –OH group

- boiling point increases as chain length of R group increases

- -OH group is polar
  - hydrogen bonding between water and alcohol molecules



  - lower alcohols are miscible with water

Alcohol	Solubility (g/100 g of H_2O)
Methanol	∞
Ethanol	∞
Propan-1-ol	∞
Butan-1-ol	7.9
Pentan-1-ol	2.3
Hexan-1-ol	0.6
Heptan-1-ol	0.2
Decan-1-ol	0

Preparation of Alcohols

a) Fermentation of Sugars

$$C_6H_{12}O_6 \xrightarrow[\text{No } O_2]{\text{enzymes in yeast}} 2CO_2 + 2C_2H_5OH$$

b) Substitution of Haloalkanes

$$C_2H_5I + NaOH \longrightarrow C_2H_5OH + NaI$$

c) Hydration of Alkenes

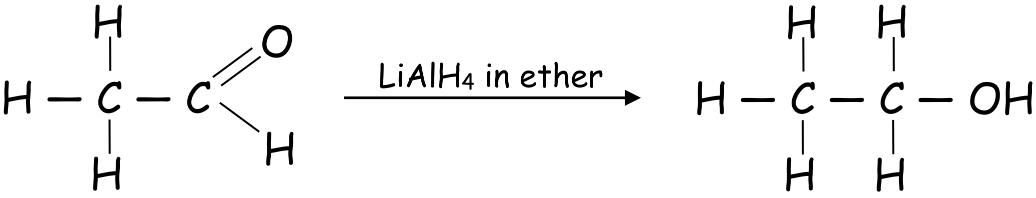
$$\underset{\text{propene}}{C_3H_6} + H_2O \xrightarrow{\text{acid}} \underbrace{\underset{\substack{\text{propan-1-ol}\\ \text{Minor Product}}}{CH_3CH_2CH_2OH} + \underset{\substack{\text{propan-2-ol}\\ \text{Major Product}}}{CH_3CHOHCH_3}}_{\text{Markovikov's Rule}}$$

- This is the industrial method of making alcohols
    - Methanol CH_3OH is made from react synthesis gas ($CO + H_2$)

d) Reduction of Aldehydes/Ketones by Lithium Aluminium Hydride

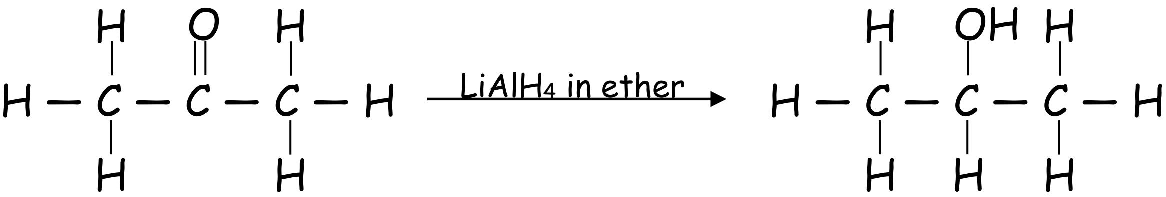
Lithium Aluminium Hydride $LiAlH_4$ dissolved in ether can

- reduce aldehydes to primary alcohols



ethanal ethanol

- reduce ketones to secondary alcohols



propanone propan-2-ol

- $NaBH_4$ also reduces aldehydes and ketones

Chemical Properties of Alcohols

Alcohols (R-OH) and water (H-OH) have similar reactions as both contain the hydroxyl group (-OH group)

a) Reaction with Sodium to form Alkoxides

$$\underset{\text{ethanol}}{2C_2H_5OH} + 2Na \longrightarrow \underset{\text{sodium ethoxide}}{2Na^+C_2H_5O^-} + H_2$$

$$\underset{\text{water}}{2HOH} + 2\ Na \longrightarrow \underset{\text{sodium hydroxide}}{2Na^+OH^-} + H_2$$

b) Reaction with Phosphorus Pentachloride

Not in Mandatory Course Key Areas

$$\underset{\text{ethanol}}{C_2H_5OH} + \underset{\text{phosphorus pentachloride}}{PCl_5} \longrightarrow \underset{\text{phosphorus oxychloride}}{POCl_3} + HCl + \underset{\text{chloroethane}}{C_2H_5Cl}$$

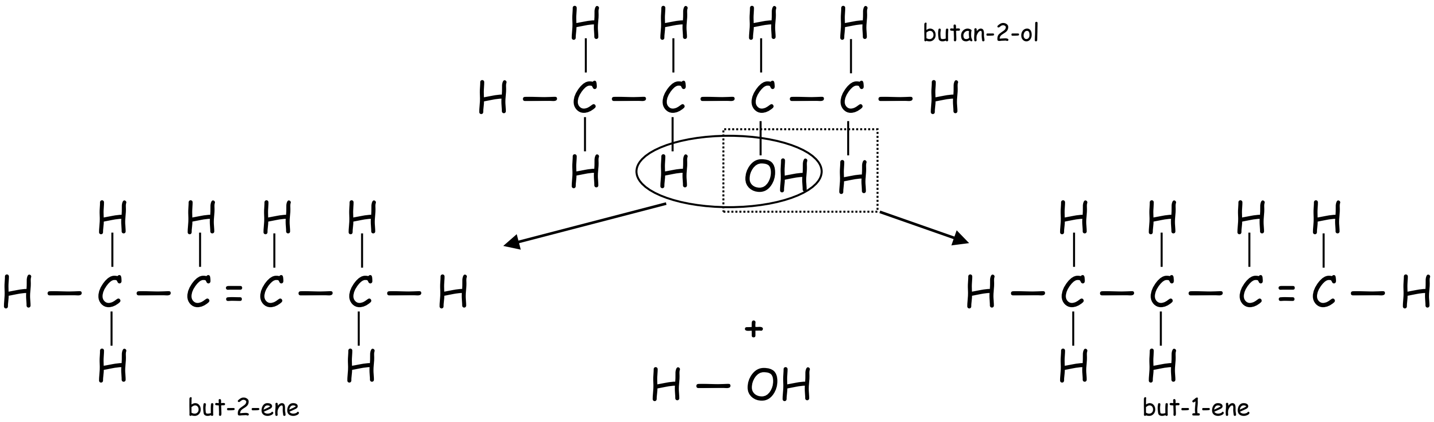
$$HOH + PCl_5 \longrightarrow POCl_3 + HCl + HCl$$

- Dense white fumes of HCl gas are produced
    - HCl fumes produced when PCl_5 is added is a positive test for the –OH group
- PBr_3 used instead of PCl_5 produces bromoalkanes instead of chloroalkanes

c) Dehydration of Alcohols to Alkenes

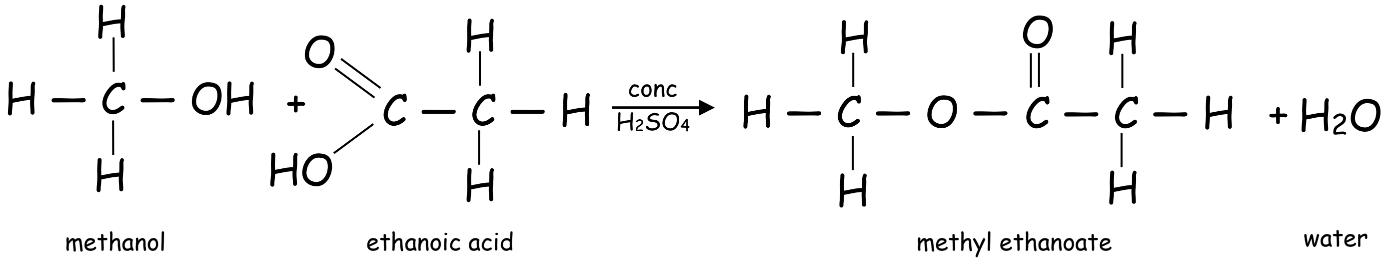
Dehydration of alcohols to alkenes can be achieved by two methods

1. Passing alcohol vapour over hot Al_2O_3
2. Heating Alcohol with excess conc. H_2SO_4

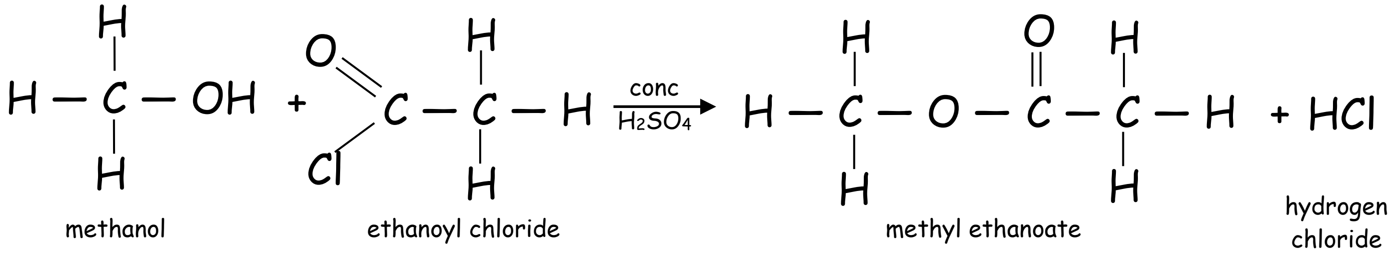


d) Ester Formation

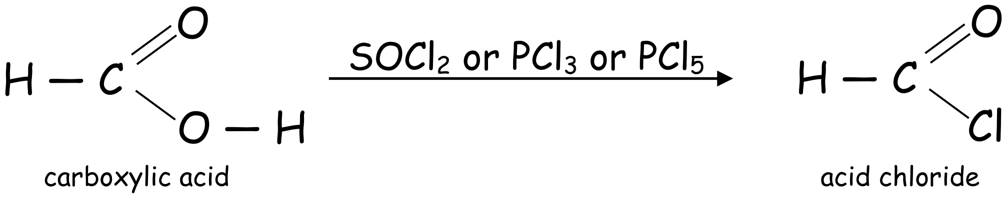
Alcohols react with both alkanoic acids and acid chlorides to form esters by condensation (also known as esterification)



- when acid chlorides are used, the reaction is faster and more vigorous



- Acid chlorides can be prepared from alkanoic acids



- The chlorine atom in an acid chloride makes the carbon atom more susceptible to nucleophilic attack by the alcohol molecule during esterification

e) Oxidation of Alcohols

Primary Alcohol $\xrightarrow{\text{oxidation}}$ Aldehyde $\xrightarrow{\text{oxidation}}$ Carboxylic Acid

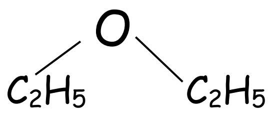
Secondary Alcohol $\xrightarrow{\text{oxidation}}$ Ketone $\cancel{\xrightarrow{\text{oxidation}}}$

Tertiary Alcohol $\cancel{\xrightarrow{\text{oxidation}}}$

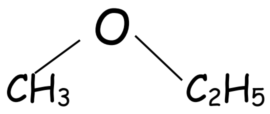
2.3c Ethers

Ethers are compounds with the general formula R′ — O — R″

- where R′ and R″ are alkyl groups
- if R′ = R″ symmetrical ether e.g. ethoxyethane



- if R′ ≠ R″ asymmetrical ether e.g. methoxyethane

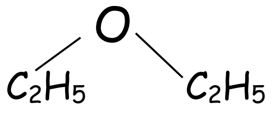


Ethers have low melting and boiling points

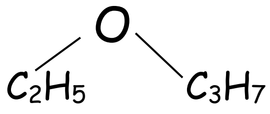
- no hydrogen bonding between molecules of ether in pure ether
- only small ethers are *slightly* soluble in water
- very flammable
- form explosive peroxides (R′—O—O—R″) on long term storage

a) Naming Ethers

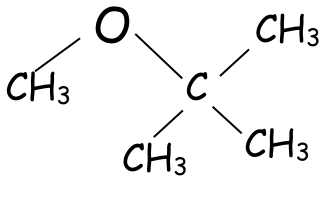
- Larger alkyl R group provides base name of ether
  - Smaller alkyl R substituent group is used to get the alkoxy part of name



ethoxyethane



ethoxypropane

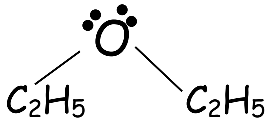


methoxy-2-methylpropane

- ethoxyethane is the most common ether
  - frequently called just ‘ether’

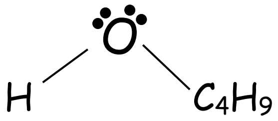
b) Properties of Ethers

- Compare ethoxyethane and butan-1-ol



ethoxyethane

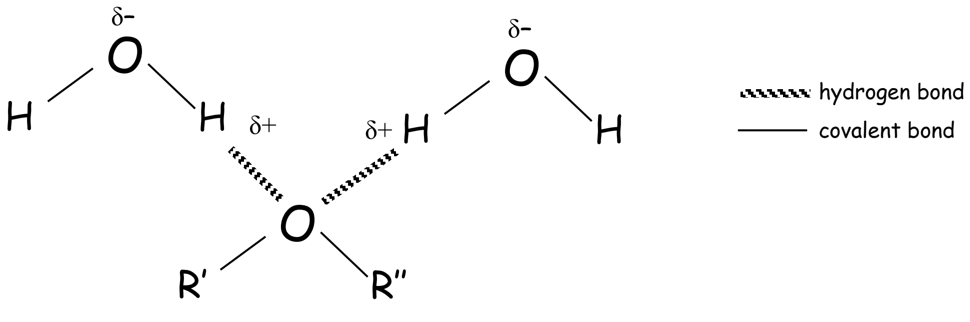
Formula mass = 74g
Boiling Point = 34.5°C
Solubility = 8g per 100g H_2O



butan-1-ol

Formula mass = 74g
Boiling Point = 119°C
Solubility = 7.9g per 100g H_2O

- Same formula mass of 74g (they are isomers)
    - Ether lacks a hydroxyl –OH group
    - Ether lacks hydrogen bonding between ether molecules
    - Ether has lower boiling point than its isomeric alcohol
- Ether C – O – C is non-linear
    - Ether is effectively an H_2O molecule with the hydrogens replaced by alkyl groups
    - C – O bonds are polar so ether molecules are polar
    - Polarity of ether is low and has little effect on boiling point
        - Boiling points of ethers are similar to boiling points of alkanes of similar mass
- Water can from hydrogen bonds with smaller ether molecules
    - Smaller ethers are soluble in water to some extent



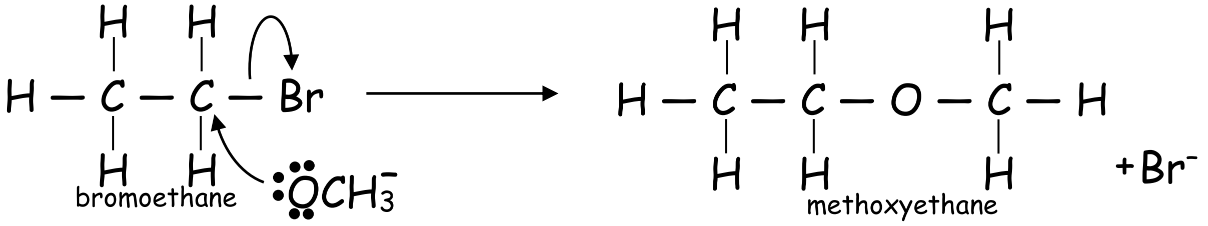
c) Preparation of Ethers

- Ethers can be prepared by nucleophilic attack of an alkoxide ion on a haloalkane

$$2Na + 2CH_3OH \longrightarrow 2CH_3O^-Na^+ + H_2$$

methanol sodium methoxide

- Sodium methoxide is dissolved in methanol and reacted with monohaloalkane



d) Uses of Ethers

Ethers do not dissolve ionic species

- ethers will dissolve most non-polar (organic) compounds
- ethers are relatively unreactive and do not react with potential solutes
  - ethers are not polar enough to be susceptible to attack by nucleophiles or electrophiles
  - ethers can not be oxidised or reduced
- ethers are used for solvent extraction
- ethers of low formula mass are easily removed by distillation
- ethers have high flammability and high volatility and can explode
  - exposure to air can produce explosive peroxides
  - can happen towards the end of distillation
  - ethers are more dense than air and can gather in sinks, etc.

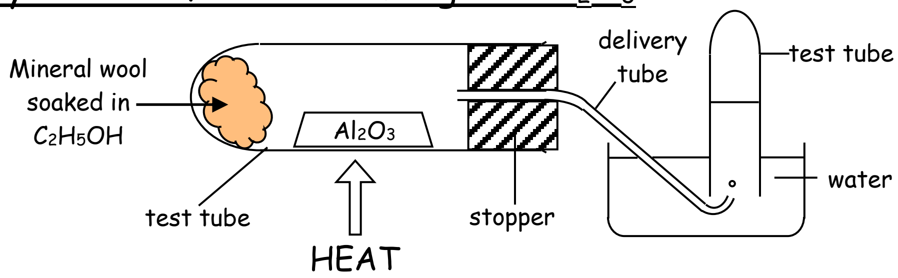
Ethers must be used with care

2.3d Alkenes

Synthesis of Alkenes

Alkenes can be produced the elimination reaction of alcohols

a) Dehydration of Alcohols using hot Al_2O_3



b) Dehydration of Alcohols using conc H_2SO_4

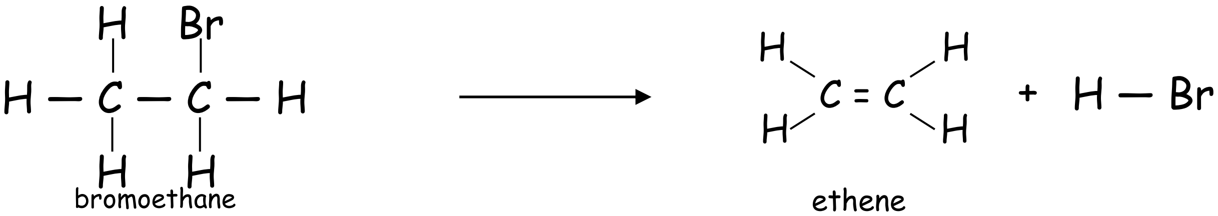
$$\underset{\text{butan-1-ol}}{C_4H_9OH} \xrightarrow{\text{conc } H_2SO_4} \underset{\text{but-1-ene}}{C_4H_8} + H_2O$$

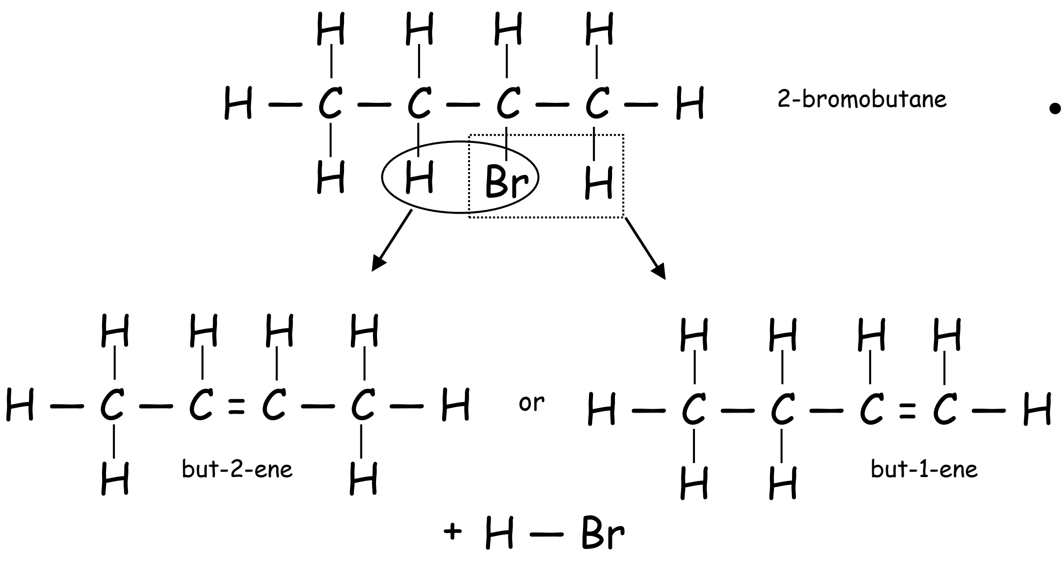
c) Dehydration of Alcohols using phosphoric acid

$$\underset{\text{propan-2-ol}}{C_3H_7OH} \xrightarrow[\text{acid}]{\text{orthophosphoric}} \underset{\text{propene}}{C_3H_6} + H_2O$$

d) Elimination of hydrogen halides from monohaloalkanes

- reaction is base-induced as base will react with HBr formed





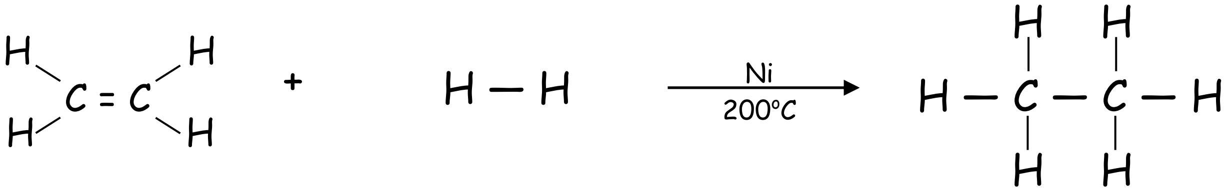
- Alkene produced depends on which H-Br molecule is eliminated from the original molecule.

Reactions of Alkenes

a) Catalytic Addition of Hydrogen

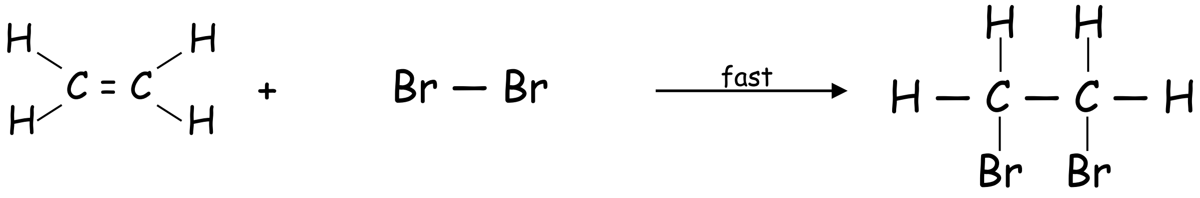
- Also known as hydrogenation

ethene + hydrogen $\xrightarrow[200^\circ C]{Ni}$ ethane

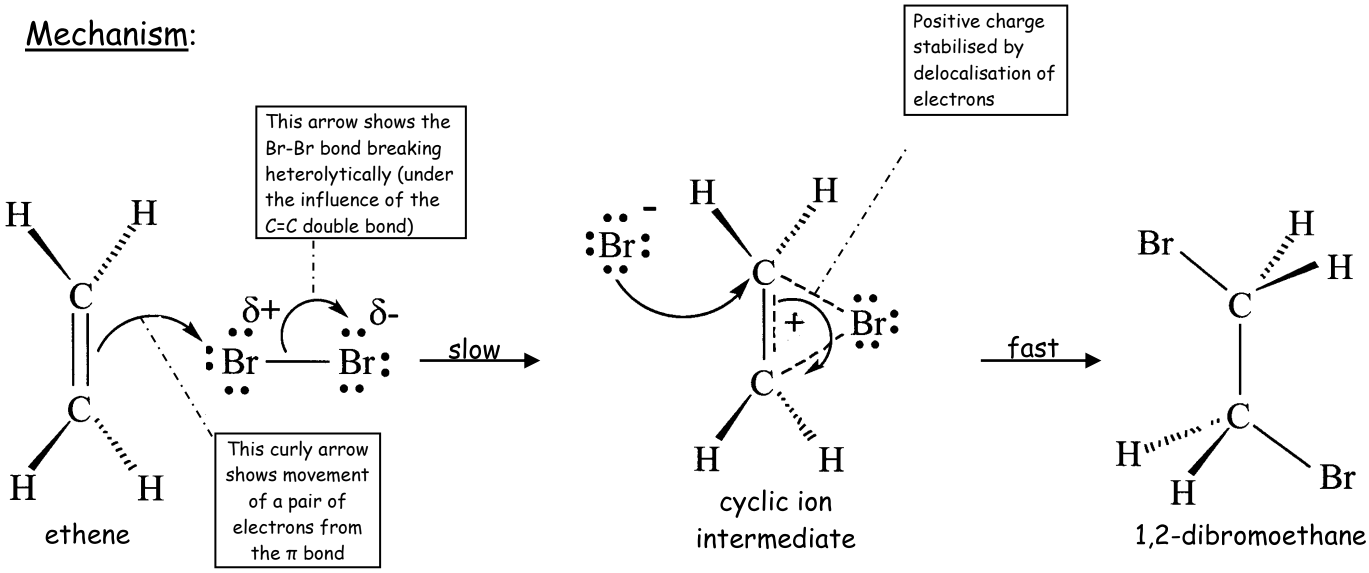


b) Addition of Halogens

ethene + bromine $\longrightarrow$ 1,2-dibromoethane



Mechanism:

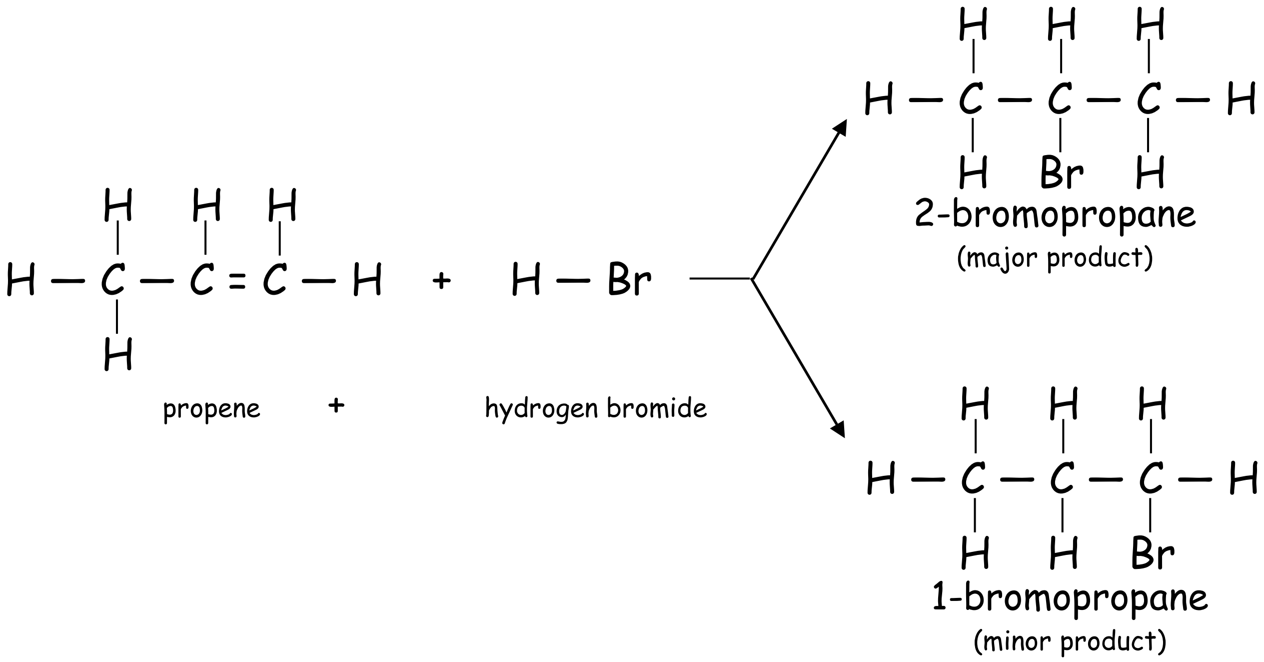


This arrow shows the Br-Br bond breaking heterolytically (under the influence of the C=C double bond)

This curly arrow shows movement of a pair of electrons from the π bond

Positive charge stabilised by delocalisation of electrons

c) Addition of Hydrogen Halide

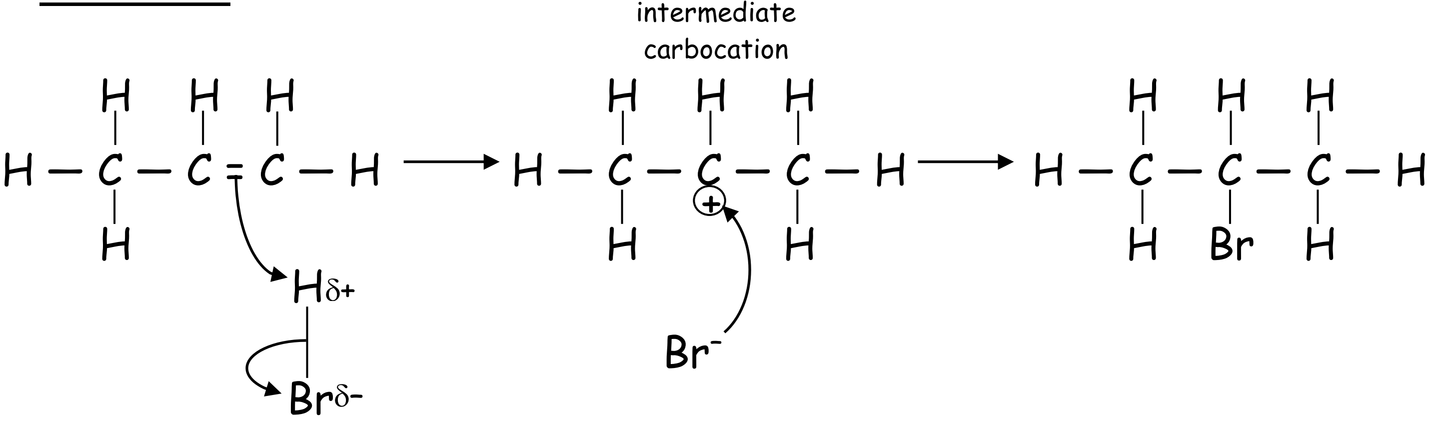


Markovnikov's Rule

The major product of the above reaction is 2-bromopropane:

- when a hydrogen halide molecule H–X is added across a C=C double bond
    - hydrogen becomes attached to the carbon atom of the C=C double bond that is already bonded to the greater number of hydrogen atoms
    - Note: not all molecules have differing numbers of hydrogens attached to the carbons of the C=C double bond, e.g. but-2-ene.

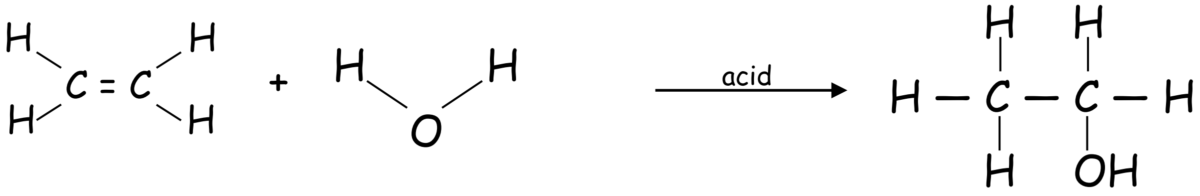
Mechanism:



d) Acid-Catalysed Hydration

- Also known as Addition of Water

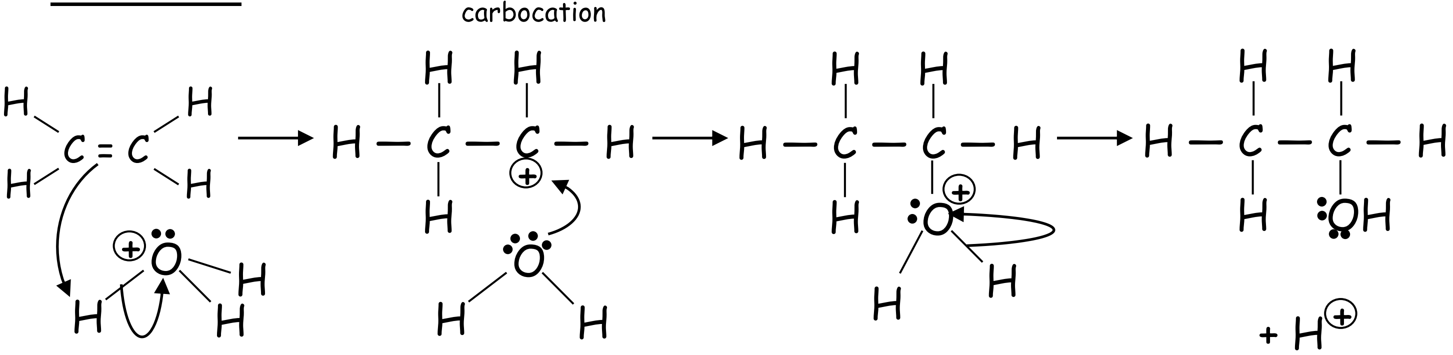
ethene + water $\xrightarrow{acid}$ ethanol



- H_3O^+ hydronium ion in acid acts as catalyst and seeks out C=C double bond
  - H_3O^+ ion is acting as an electrophile

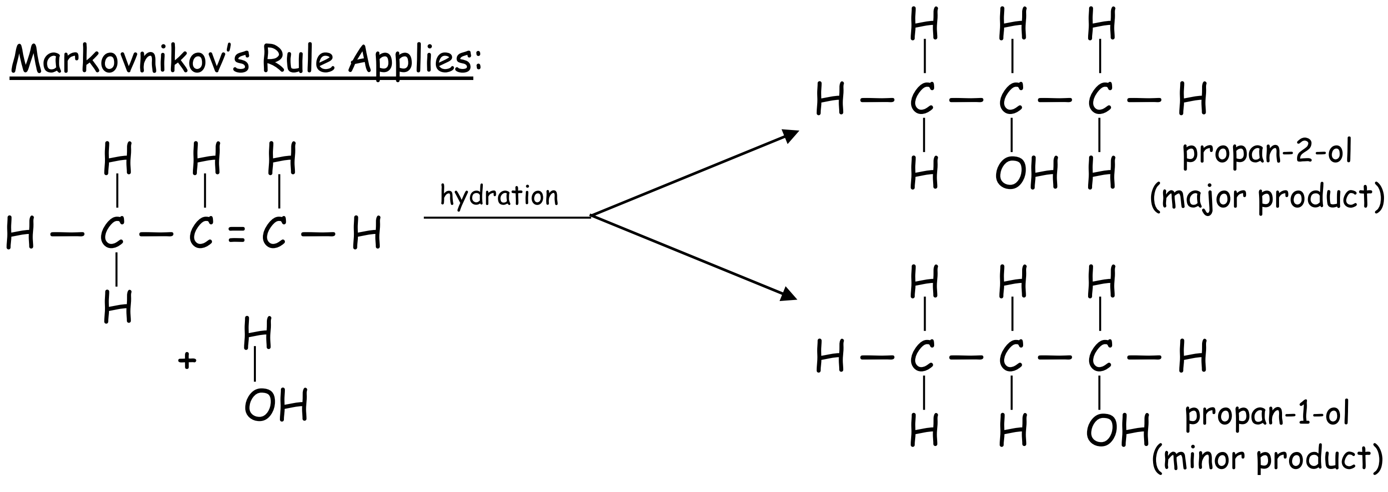
- carbocation intermediate is formed

Mechanism:



- H_2O acts as a nucleophile
  - Lone pair of electrons attracted to the positive charge of carbocation

Markovnikov's Rule Applies:



Questions

1. Propane was reacted with chlorine. The following products were obtained:
    i. hydrogen chloride
    ii. two compounds of formula C_3H_7Cl
    iii. four compounds of formula $C_3H_6Cl_2$ (labelled A, B, C and D).
    a) What type of reaction has taken place and what type of bond fission occurred?
    b) Draw full structural formulae for all the organic compounds.
    c) Each of the dichlorocompounds was further treated with chlorine. A gave one trichloro product. B gave two trichloro products and C and D both gave three trichloro products. The product obtained from A was also produced by C but not by D.
    Identify which of the dichloro structures are A, B, C and D.

Bond	C–C	C=C	C≡C
Bond Enthalpy (kJ mol^{-1})	337	607	828
Bond Length (nm)	0.154	0.134	0.121

2. The above table shows that the C≡C bond is stronger than the C-C bond but not three times as strong. The ethyne molecule (H-C≡C-H) is known to be linear. Describe in terms of hybridisation how the C≡C bond could be formed.

3. Ethene is reacted with a solution of bromine in methanol. As well as the expected product, some $Br\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_3$ is also obtained. By considering the mechanism of the reaction, account for the formation of the second product.

4. Name and draw structures for the products of the following reactions, in each case stating which product will be formed in the higher yield:
    a) the reaction of propene with hydrogen bromide
    b) the reaction of 2-methylbut-2-ene with hydrogen chloride
    c) the catalytic hydration of 2-methylbut-1-ene
    d) the addition of hydrogen bromide to 3-methylbut-1-ene.

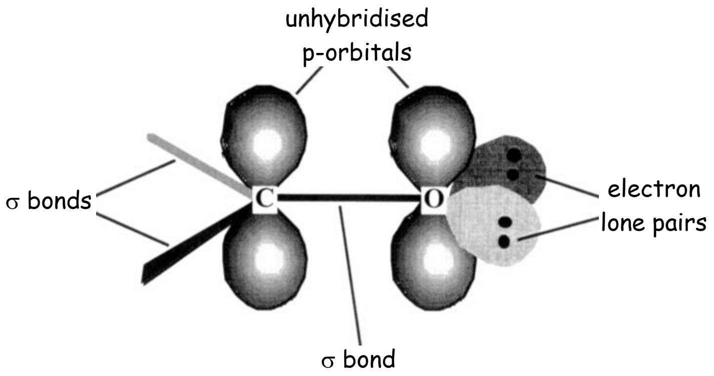
2.3e Carboxylic Acids

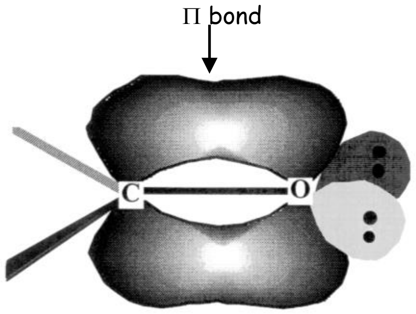
Each of the following groups contain the carbonyl C=O group

- aldehydes
- ketones
- carboxylic acids

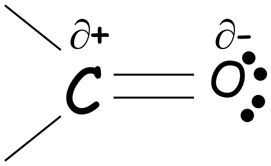
The carbonyl C=O bond is similar in construction to the C=C double

- central sigma (σ) bond
- sp^2 hybridisation in the carbon atom
- overlap of hybridised p-orbital to form Π - bond



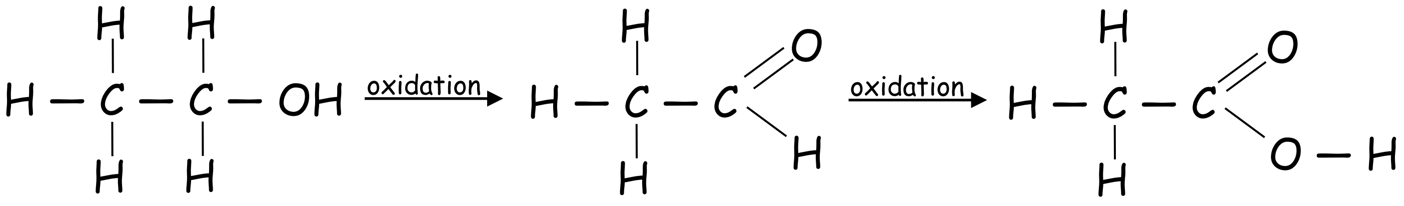


- carbonyl bond is polar
    - high dipole moment



a) Preparation of Carboxylic Acids

1. Oxidation of Primary Alcohols and Aldehydes



ethanol primary alcohol

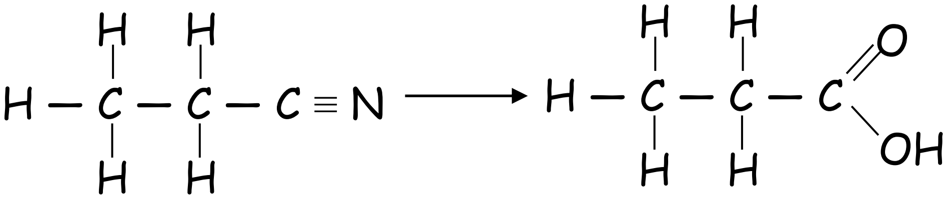
ethanal aldehyde

ethanoic acid carboxylic acid

- Suitable oxidising agents for both oxidation reactions above:
  - acidified dichromate solution (orange → green)
  - acidified permanganate solution (purple → clear/slight pink)
  - hot copper (II) oxide
- Suitable oxidising agents for aldehyde to carboxylic acid only:
  - Tollen's reagent (silver mirror produced)
  - Fehling's solution (blue → brick red)

2. Hydrolysis of Nitriles

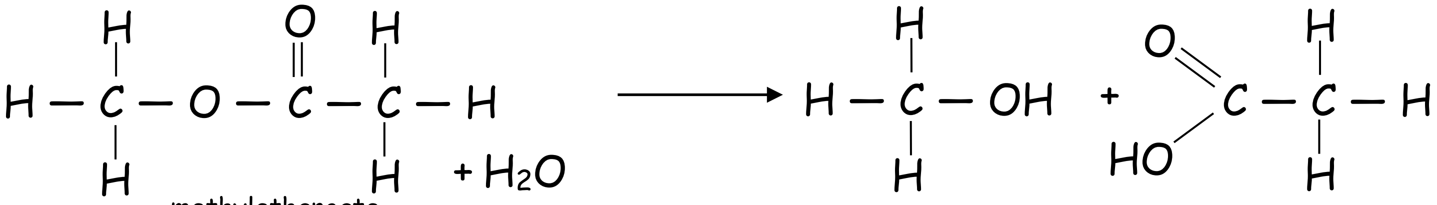
- refluxing a nitrile with strong acid or a base can hydrolyse a nitrile to a carboxylic acid



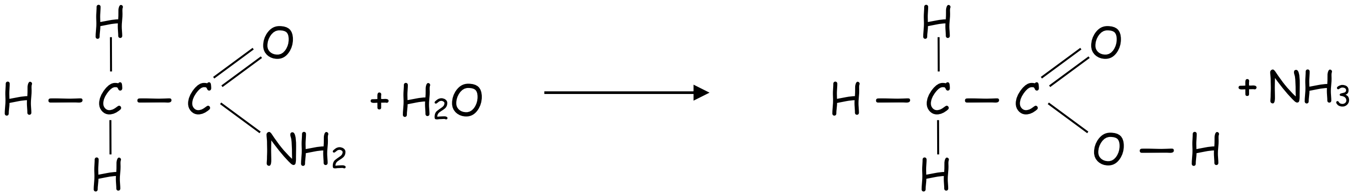
propanenitrile

propanoic acid

3. Hydrolysis of Esters and Amides



methylethanoate

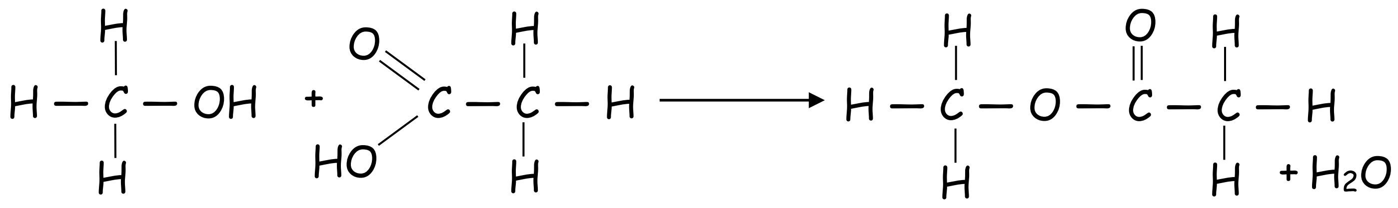


ethanamide

b) Reactions of Carboxylic Acids

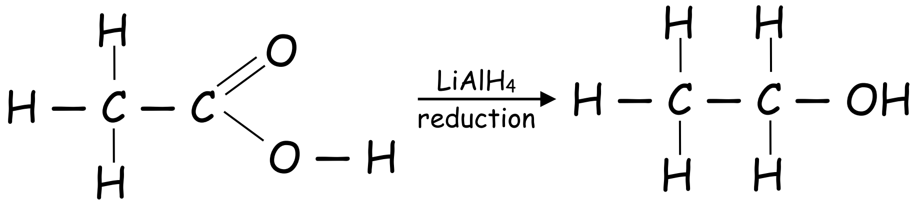
1. Condensation Reactions to form Esters

- Also called esterification



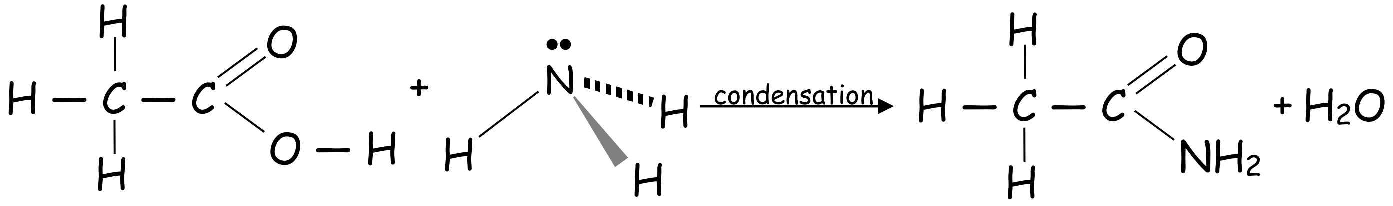
- conc H_2SO_4 shifts equilibrium to Right Hand Side by removing the H_2O produced by the forward reaction

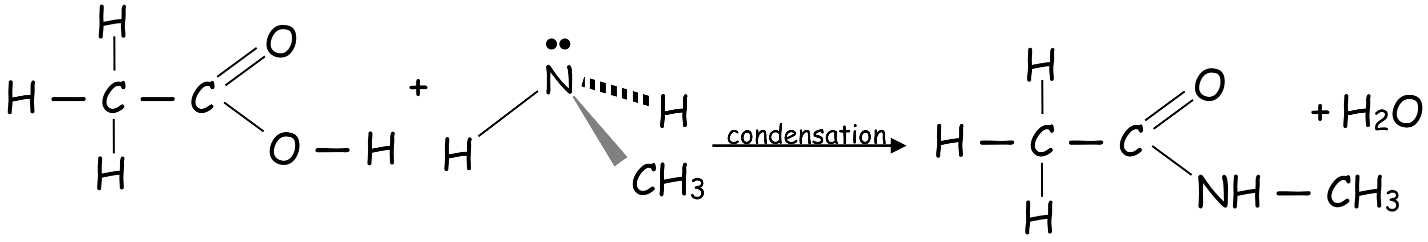
2. Reduction with Lithium Aluminium Hydride



3. Reaction with Ammonia to form Amides

- Carboxylic acids from amides when heated with ammonia





4. Formation of Salts by Reactions with Metals or Bases

- React with MAZIT metals

$$\underset{\text{ethanoic acid}}{Mg + 2CH_3COOH} \longrightarrow \underset{\text{magnesium ethanoate}}{Mg^{2+}(CH_3COO^-)} + H_2$$

- Neutralisation of Bases

$$\underset{\text{ethanoic acid}}{CH_3COOH} + NaOH \longrightarrow \underset{\text{sodium ethanoate}}{Na^+CH_3COO^-} + H_2O$$

2.3f Amines

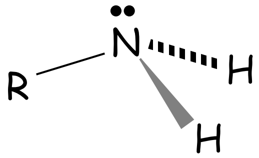
Classification of Amines

Amines are compounds based on ammonia NH_3 where one or more of the hydrogens have been replaced by

- an alkyl group
- an aryl group (aromatic benzene-based ring)

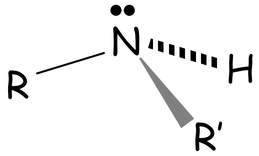
a) Primary Amine

- One of the hydrogens in NH_3 has been replaced with a carbon group R



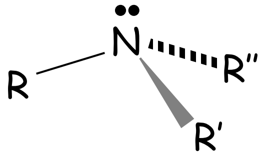
b) Secondary Amine

- Two of the hydrogens on NH_3 have been replaced with carbons groups R and R'



c) Tertiary Amine

- All 3 hydrogens in NH_3 have been replaced with carbon groups R, R' and R''



Naming Amines

There are two commonly used naming systems for amines

a) removing the –**e** from the parent alkane name, then add the suffix –**amine**.

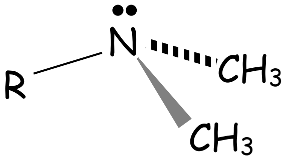
e.g.	$C_2H_5NH_2$	ethanamine
	$C_4H_9NH_2$	butanamine

b) Adding the suffix –**amine** to the name of the substituent alkyl group

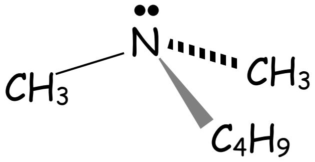
e.g.	$C_2H_5NH_2$	ethylamine
	$C_4H_9NH_2$	butylamine

This system is better naming secondary and tertiary amines

e.g.



dimethylamine

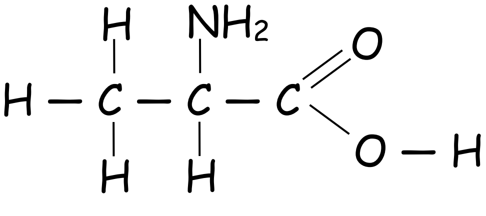


butyldimethylamine

In amino acids and other compounds where the amino group is not the principal group

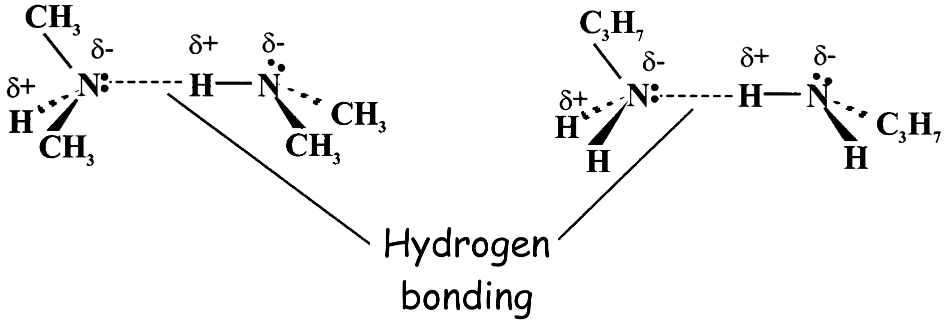
- Amino prefix is used

e.g. 2-aminopropanoic acid



3.5.3 Properties of Amines

Primary and secondary amines have hydrogen bonding between their molecules



- primary and secondary amines have a higher melting points compared to
    - tertiary amines of similar mass
    - hydrocarbons of similar molecular mass

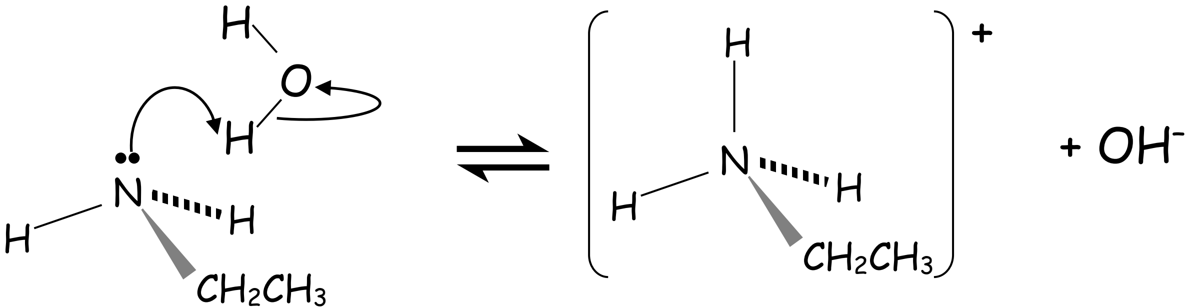
Amine	Amine Type	Relative Formula mass	Boiling Point (°C)	Alkane	Relative Formula mass	Boiling Point (°C)
CH_3NH_2	Primary	31	-7.5	CH_3CH_3	30	-89
$(CH_3)_2NH$	Secondary	45	7.5	$CH_3CH_2CH_3$	44	-42
$(CH_3)_3N$	Tertiary	59	3	$CH_3CH_2CH_2CH_3$	58	-1
$CH_3CH_2CH_2NH_2$	Primary	59	49	$CH_3CH_2CH_2CH_3$	58	-1

- shorter primary and secondary amines are water soluble due to hydrogen bonding
    - solubility decreases as chain length(s) increase

- amines can act as proton acceptors

$$\underset{\text{ethylamine}}{CH_3CH_2NH_2} + \underset{\text{water}}{H_2O} \rightleftharpoons \underset{\text{ethylammonium hydroxide}}{CH_3CH_2NH_3^+ + OH^-}$$

- ionisation of base is incomplete
    - amines are weak bases

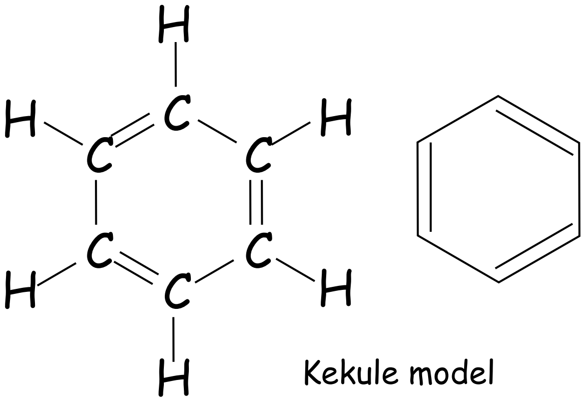


2.3g Aromatics

Aromatic originally referred to a group of pleasant-smelling compounds

- other compounds were discovered with a similar structure but with unpleasant smells
- all contain a benzene ring structure
- known as arenes

Structure of Benzene



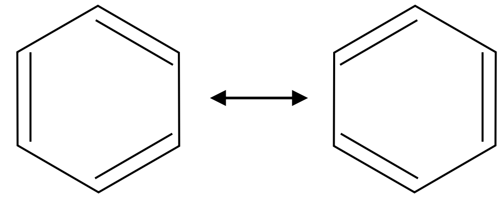
Benzene was found to have a formula of C_6H_6.

- Original hypothesis was that benzene was a highly unsaturated ring structure with three C=C double bonds
- Each corner on the hexagon ring is a carbon atom with one hydrogen atom sticking off it.

But the evidence of further investigation showed that this model was incorrect:

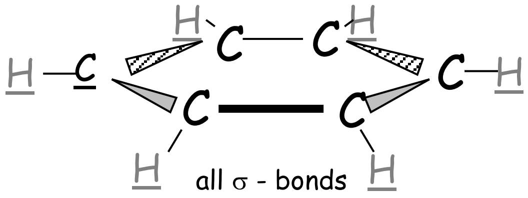
1. X-ray analysis of benzene shows 6 carbons atoms form a regular hexagon.
   - Benz*ene* is not an alkene.
2. Benzene does <u>not</u> decolourise bromine water quickly.
   - Benzene in not unsaturated and has not C=C double bonds.
3. All carbons and hydrogen atoms lie in the same plane.
   - Cyclohexane carbon ring is not a planar.
4. X-ray analysis shows carbon to carbon bond lengths are of equal length.
   - Carbon to carbon bond length in benzene lies between bond lengths for C–C single bond and C=C double bond.

However, despite not being an accurate representation of the structure of benzene, this model of benzene is still used at times in reaction mechanisms.

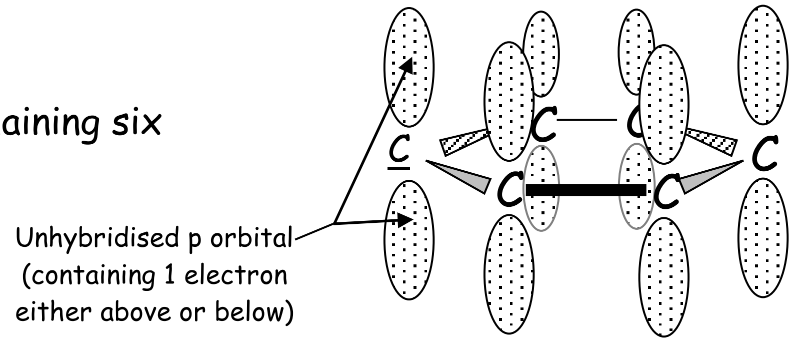


Benzene's ring structure contains sp^2 hybridisation

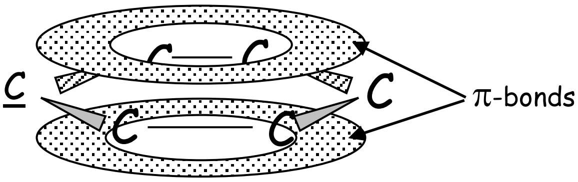
- 6 carbons and 6 hydrogen lie in same plane
    - 120° angle between carbons and hydrogens in molecule
    - all bonds shown are sigma σ-bonds (single bonds)



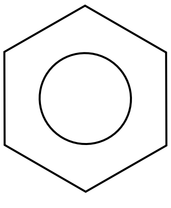
- 6 electrons in left in remaining six unhybridised p-orbitals



- 6 electrons in remaining unhybridised p-orbitals form π–bonds
    - electrons are described as delocalised
    - 6 electrons form 2 electron rings
        - 3 electrons above carbon ring
        - 3 electrons below carbon ring
    - stability of benzene attributed to the clouds of delocalised electrons
    - Electron repulsion between delocalised electron rings flatten benzene structure so carbon ring becomes planar



- The term aromatic was redefined to describe a ring of atoms stabilised by delocalised electrons.
    - Benzene diagram was redesigned to reflect the electron delocalisation



Reactions of Benzene

The high electron density of the delocalised electron clouds in benzene:

- Attract electrophile to the benzene ring
  - Benzene rings undergo **electrophilic substitution** reactions

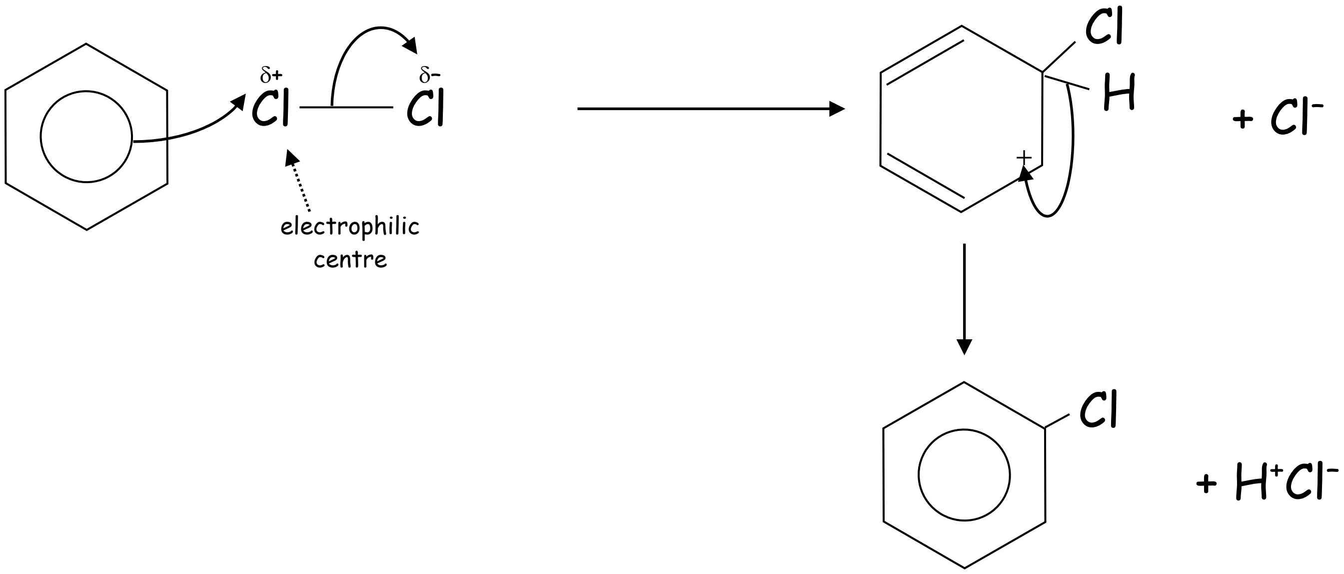
a) Chlorination of Benzene

$$\text{Benzene + chlorine} \xrightarrow[\text{catalyst}]{FeCl_3 \text{ or } AlCl_3} \text{chlorobenzene}$$

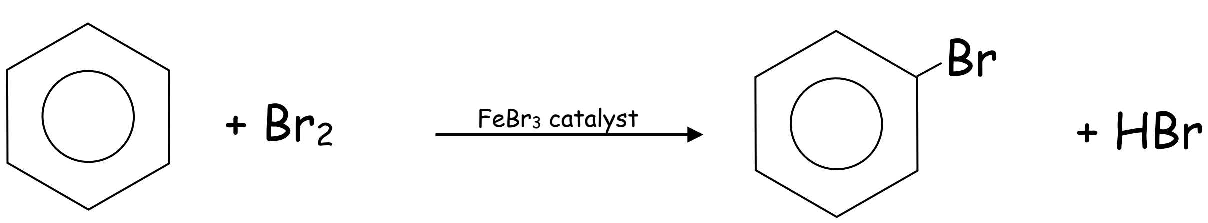
- Catalyst required to induce polarisation with halogen molecule

$$\overset{\delta+}{Cl} — \overset{\delta-}{Cl} \;\text{IIIIIIIIIII}\; FeCl_3$$

- Electrophilic substitution reaction

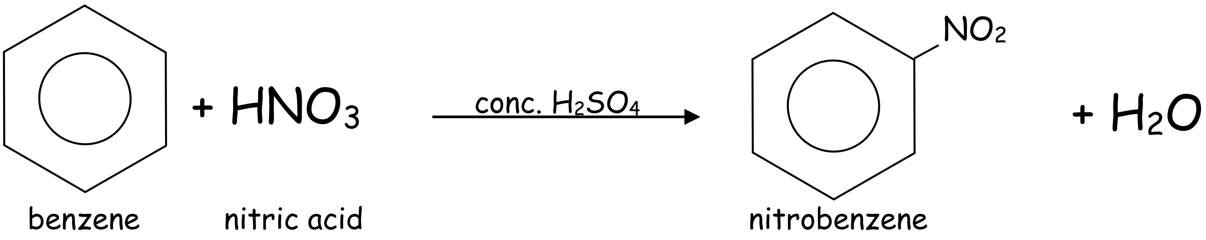


- Also bromination of benzene by similar mechanism.



b) Nitration of Benzene

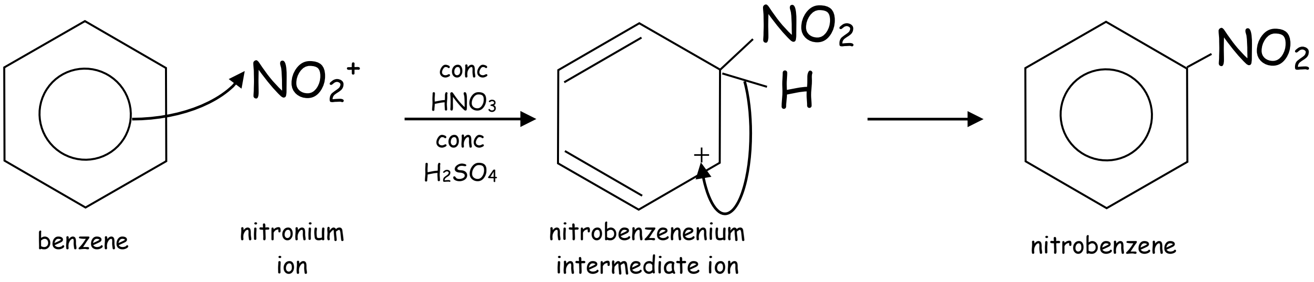
- Benzene reacts with a mixture of conc nitric acid and conc sulphuric acid to form nitrobenzene



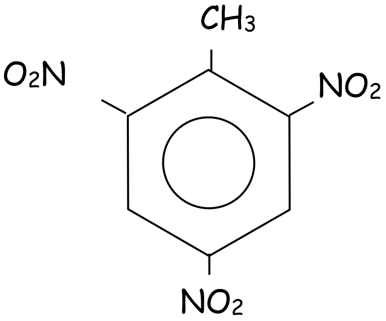
- Electrophilic species NO_2^+ nitronium ion is formed on mixing conc HNO_3 and conc H_2SO_4.

$$HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

- Nitronium ion attacks electron-rich benzene ring to give nitrobenzene



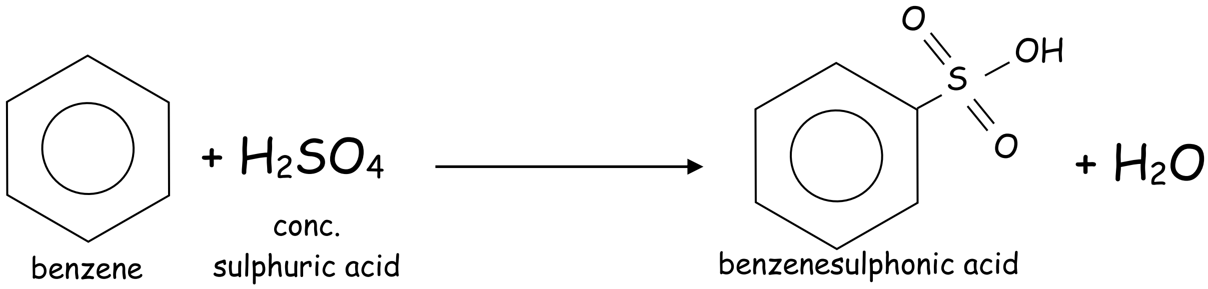
- Other nitro-groups can be added
    - e.g. Trinitrotoluene (aka T.N.T.)
-

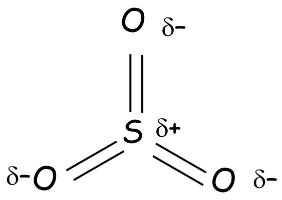


trinitrotoluene

c) Sulphonation of Benzene

- Benzene and conc H_2SO_4 form benzenesulphonic acid when heated under reflux

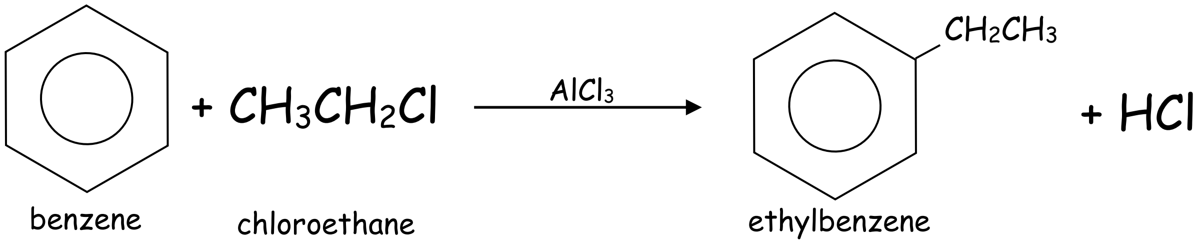




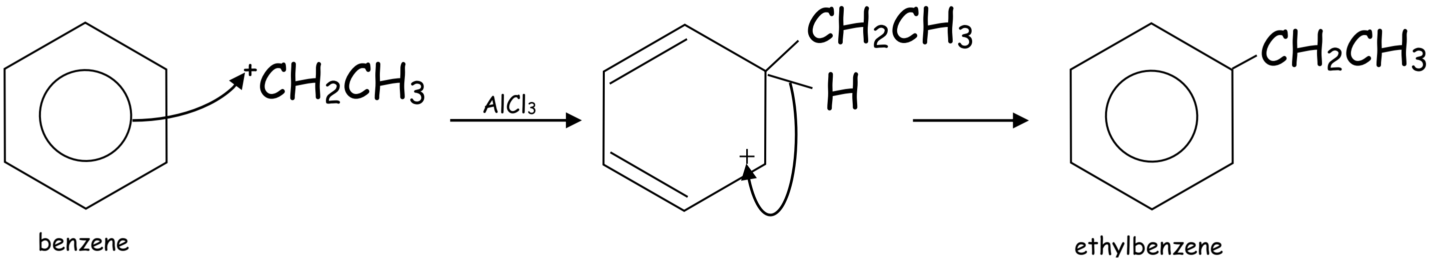
- SO_3 is a powerful electrophile, despite being neutral
- this is an important process in the production of detergents

d) Alkylation of Benzene

- Alkylbenzenes are formed when benzene reacts with a haloalkane
  - Catalyst $AlCl_3$ must be present



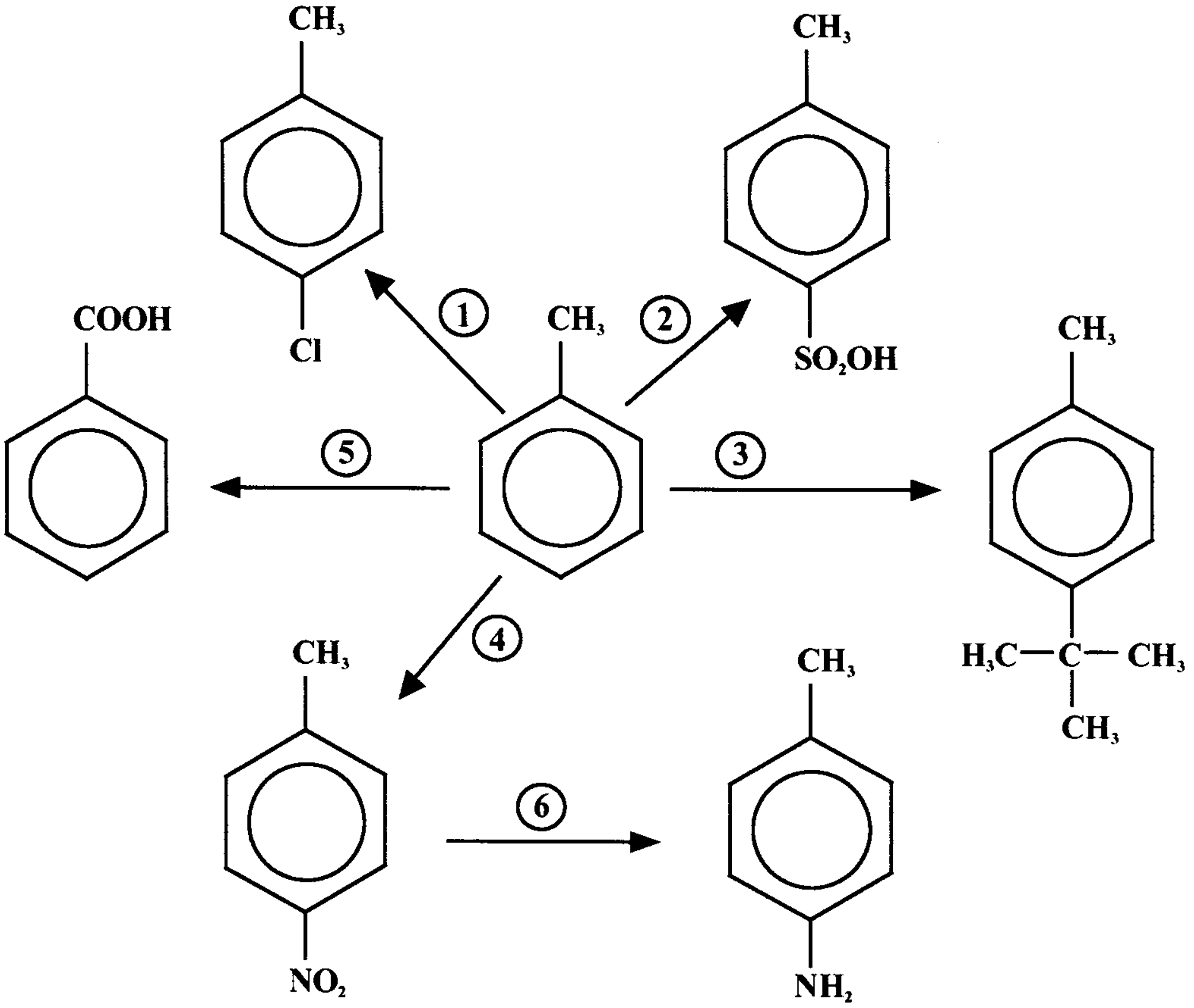
- $AlCl_3$ increases the polarity of the $\overset{\delta+}{C} - \overset{\delta-}{X}$ bond in haloalkane
  - $AlCl_3$ generates the positive electrophilic species $CH_3CH_2^+$
  - Heterolytic fission of CH_3CH_2Cl
  - known as Friedel-Craft alkylation



- This process is used in the production of detergents, nylon and phenol

Questions

1. Study the reaction scheme below and then answer the following questions



a) What type of reaction is involved in reactions 1,2,3 and 4?
b) For the reactions 1 to 4, state the conditions required and in each case identify the electrophile involved.
c) Identify the type of reaction involved in
    i. Reaction 5
    ii. Reaction 6
d) Methylbenzene undergoes a free radical substitution with chlorine to give an isomer of the product of Reaction 1.
   What conditions would be required for this reaction and what would be the product?