

HL Organic Chemistry 1

1 Explain what is meant by the term *homologous series*.

A series of compounds with the same functional group, where each member differs from the next by $-\text{CH}_2-$.

The homologous series can usually be described by a general formula,

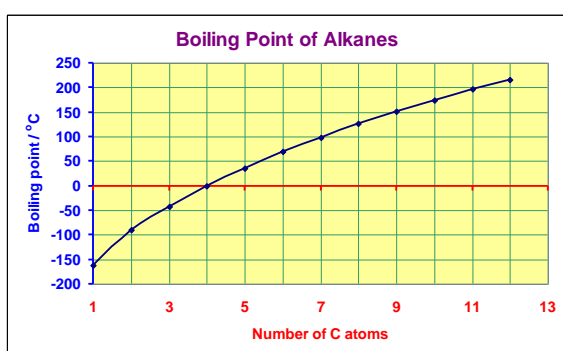
The members of the homologous series show similar chemical properties

The members of the homologous series show a gradation in physical properties such as boiling point.

2 Explain what is meant by the term *hydrocarbon*.

A compound containing *carbon* and *hydrogen only*

3 Sketch a graph of boiling point against number of carbons for the straight-chain alkane homologous series and explain the trend that is exhibited.



As relative molecular mass increases, London forces get stronger. Stronger forces between molecules – more energy has to be supplied to overcome these forces.

4 Draw full structural formulae, condensed structural formulae, skeletal formulae and state the names for the straight chain alkanes up to C_6 .

Name	Molecular formula	Skeletal Formula	Structural Formula	
			Condensed	Full
Methane	CH_4	No one would draw this – would be a dot .	CH_4	<pre> H H-C-H H </pre>
Ethane	C_2H_6	This is just a line —	CH_3CH_3	<pre> H H H-C-C-H H H </pre>
Propane	C_3H_8		$\text{CH}_3\text{CH}_2\text{CH}_3$	<pre> H H H H-C-C-C-H H H H </pre>
Butane	C_4H_{10}		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	<pre> H H H H H-C-C-C-C-H H H H H </pre>
Pentane	C_5H_{12}		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	<pre> H H H H H H-C-C-C-C-C-H H H H H H </pre>
Hexane	C_6H_{14}		$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	<pre> H H H H H H H-C-C-C-C-C-C-H H H H H H H </pre>

HL Organic Chemistry 2

5 Work out the molecular formula and empirical formulae of

- the alkane with 12 carbon atoms $C_{12}H_{26}$ empirical formula: C_6H_{13}
- the alkene with 10 carbon atoms $C_{10}H_{20}$ empirical formula: CH_2

6 Explain what is meant by the term *functional group*.

Atom/group of atoms in a molecule that gives it its characteristic chemical properties.

7 Explain what you understand by *structural isomers*.

Two or more compounds which have the same molecular formula but different structural formulae, i.e. a different arrangement of atoms.

8 Draw full structural formulae, condensed structural formulae, skeletal formulae and state the names of all the compounds with the molecular formula C_6H_{14} .

$\begin{array}{cccccc} H & H & H & H & H & H \\ & & & & & \\ H-C & -C & -C & -C & -C & -C-H \\ & & & & & \\ H & H & H & H & H & H \end{array}$			
Hexane			
$\begin{array}{cccccc} H & H & H & CH_3 & H & \\ & & & & & \\ H-C & -C & -C & -C & -C & -H \\ & & & & & \\ H & H & H & H & H & \end{array}$		$\begin{array}{cccccc} H & H & CH_3 & H & H & \\ & & & & & \\ H-C & -C & -C & -C & -C & -H \\ & & & & & \\ H & H & H & H & H & \end{array}$	
2-methylpentane		3-methylpentane	
$\begin{array}{cccccc} H & CH_3 & H & H & & \\ & & & & & \\ H-C & -C & -C & -C & -C & -H \\ & & & & & \\ H & CH_3 & H & H & & \end{array}$		$\begin{array}{cccccc} H & CH_3 & H & H & & \\ & & & & & \\ H-C & -C & -C & -C & -C & -H \\ & & & & & \\ H & H & CH_3 & H & & \end{array}$	
2,2-dimethylbutane		2,3-dimethylbutane	

9 Draw full structural formulae, condensed structural formulae, skeletal formulae and state the names of all alkenes with the molecular formula C_5H_{10} .

	$\begin{array}{ccccccc} H & & H & H & H & & H \\ & & & & & & \\ H-C & =C & -C & -C & -C & & -C-H \\ & & & & & & \\ H & & H & H & H & & H \end{array}$		$\begin{array}{ccccccc} H & & H & H & H & & H \\ & & & & & & \\ H-C & =C & -C & -C & -C & & -C-H \\ & & & & & & \\ H & & H & H & H & & H \end{array}$
pent-1-ene	$CH_2CHCH_2CH_2CH_3$	2-methylbut-1-ene	$CH_2C(CH_3)CH_2CH_3$
	$\begin{array}{ccccccc} H & H & & H & H & H & \\ & & & & & & \\ H-C & -C & =C & -C & -C & -C & -H \\ & & & & & & \\ H & H & H & H & H & H & \end{array}$		$\begin{array}{ccccccc} H & H & & H & H & H & \\ & & & & & & \\ H-C & -C & =C & -C & -C & -C & -H \\ & & & & & & \\ H & H & H & H & H & H & \end{array}$
pent-2-ene	$CH_3CHCHCH_2CH_3$	2-methylbut-2-ene	$(CH_3)_2CCHCH_3$

Note: *cis/trans isomers are also possible for pent-2-ene.*

10 State the general formula of each of the following:

alkanes C_nH_{2n+2}	alkenes C_nH_{2n}	alkynes C_nH_{2n-2}	alcohols $C_nH_{2n+2}O$
ketones $C_nH_{2n}O$	aldehydes $C_nH_{2n}O$	carboxylic acids $C_nH_{2n}O_2$	

HL Organic Chemistry 3

11 Give one example (structural formula) of a molecule in each of the classes of compounds and state the name of the functional group present in each

<p>alkane</p> <p>alkyl group</p>	<p>alkene</p> <p>alkenyl group</p>	<p>alkyne</p> <p>alkynyl group</p>	<p>halogenoalkane</p> <p>halo (bromo) group</p>	<p>alcohol</p> <p>hydroxyl group</p>
<p>ether</p> <p>ether group</p>	<p>aldehyde</p> <p>carbonyl group</p>	<p>ketone</p> <p>carbonyl group</p>	<p>ester</p> <p>ester group</p>	<p>carboxylic acid</p> <p>carboxyl group</p>
<p>amine</p> <p>amine group</p>	<p>amide</p> <p>carboxamide group</p>	<p>nitrile</p> <p>nitrile group</p>	<p>arene</p> <p>phenyl group</p>	

12 Write the molecular formula and identify the functional groups present in each of the following:

<p>carbonyl (aldehyde) alkenyl hydroxyl</p> <p>$C_6H_{10}O_2$</p>	<p>carbonyl (ketone) carboxyl amine</p> <p>$C_6H_{11}O_3N$</p>	<p>ester phenyl</p> <p>$C_8H_8O_2$</p>
<p>carbonyl (ketone) alkynyl hydroxyl nitrile</p> <p>$C_{11}H_{15}O_2N$</p>	<p>carbonyl (ketone) ether</p> <p>$C_6H_{12}O_2$</p>	<p>carboxamide</p> <p>$C_6H_{13}NO$</p>

13 Name each of the following compounds

Lower number given to hydroxyl group (group whose name comes at the end)

2,3-dimethylhexane	3-methylbut-1-ene	5-methylhexan-2-ol
1-ethoxypropane	methyl propanoate	3-methylhexan-2-one
propanal	2-chloro-3-methylbutane	pent-2-yne

Lower number given to species first in alphabet

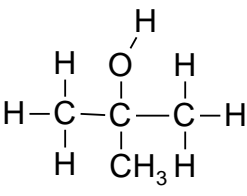
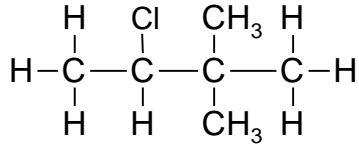
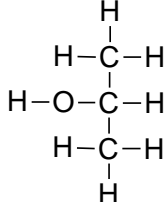
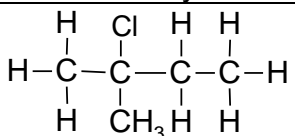
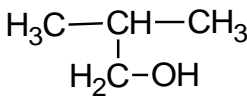
Commas between numbers, dashes between numbers and letter

14 Identify which of the molecules in 13 are saturated and which are unsaturated.

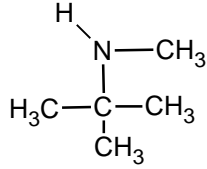
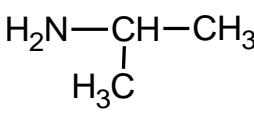
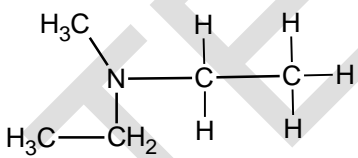
saturated	unsaturated	saturated
saturated	saturated	saturated
saturated	saturated	unsaturated

Saturated/unsaturated refers to the carbon skeleton – presence of C=C or C≡C

15 Classify each of the following as a primary, secondary or tertiary halogenoalkane/alcohol:

		
tertiary	secondary	secondary
		CH ₃ Br
tertiary	primary	primary

16 Classify each of the following amines as primary secondary or tertiary

		
secondary	primary	tertiary

17 Describe the structure of benzene

A planar hexagonal ring with all C-C bond lengths equal.

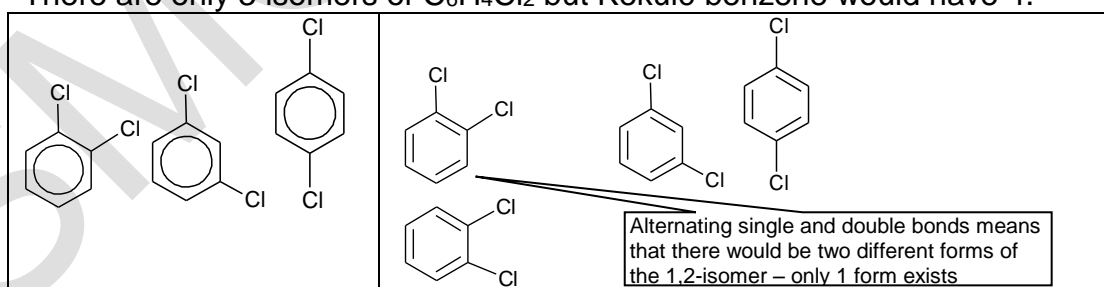
18 Explain (a) two pieces of physical evidence for the structure of benzene
(b) two pieces of chemical evidence for the structure of benzene

Benzene is an aromatic, unsaturated hydrocarbon. The initial suggestion was a structure that contained alternating C=C and C-C (Kekulé benzene/cyclohexa-1,3,5-triene) – this has been disproved by the following evidence



(a) X-ray crystallography shows that all C-C bond lengths are equal and between the length of C-C and C=C. Kekulé benzene would have alternating short and long C-C bonds.

There are only 3 isomers of C₆H₄Cl₂ but Kekulé benzene would have 4.



(b) The enthalpy change of hydrogenation for conversion of benzene (C₆H₆) to cyclohexane (C₆H₁₂) is substantially less exothermic than three times the enthalpy change of hydrogenation for cyclohexene (C₆H₁₀) to cyclohexane. This indicates that actual benzene is more stable than would be predicted by the Kekulé structure.

Benzene undergoes substitution reactions that maintain the stable aromatic ring system rather than addition reactions that would destroy it. For example, benzene does not react with bromine water to decolorize it as an alkene would.

- 19 Explain why alkanes are unreactive.

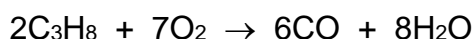
C-C and C-H bonds are strong meaning that it will generally be energetically unfavourable to break them in a reaction.

The molecules are essentially non-polar, therefore unlikely to attract polar molecules or ions.

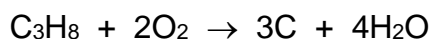
- 20 Write balanced equations for the complete combustion of propane and butane.



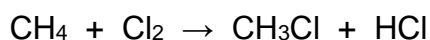
- 21 Write a balanced equation for the incomplete combustion of propane producing CO



- 22 Write a balanced equation for the incomplete combustion of propane producing soot (C)

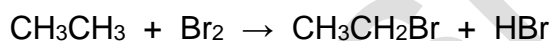


- 23 Write an equation for the reaction of methane with chlorine and state the conditions required for the reaction to occur.

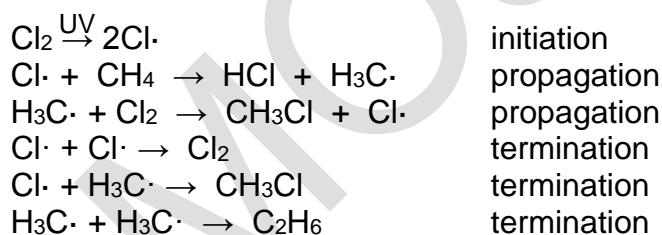


Conditions: UV light

- 24 Write an equation for the reaction of ethane with bromine



- 25 Write the mechanism for the reaction between methane and chlorine



- 26 Explain what is meant by a *chain reaction*, *homolytic fission* and *free radical*

chain reaction: one initial event causes a large number of subsequent reactions - the reactive species is regenerated in each cycle of reactions.

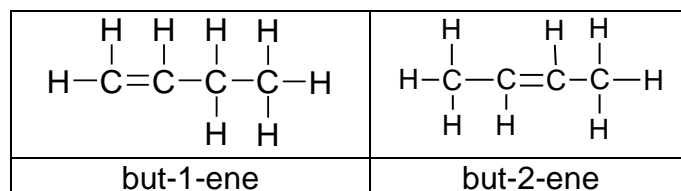
homolytic fission: when the covalent bond, made up of two electrons, breaks, one electron goes back to each atom making up the original covalent bond

Free radical: species (atoms or groups of atoms) with an unpaired electron. Free radicals are very reactive because of this unpaired electron.

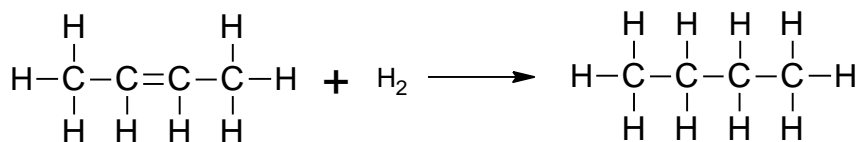
- 27 State the name of the two organic products of monochlorination of propane

1-chloropropane and 2-chloropropane

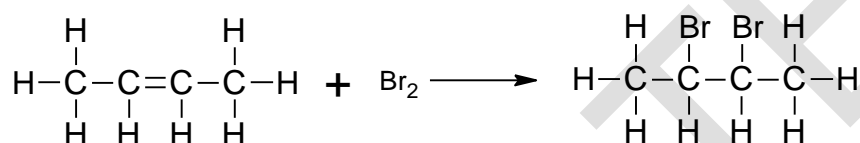
28 Draw the full structural formulae for but-1-ene and but-2-ene



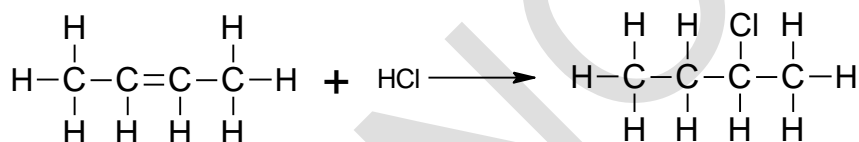
29 Write an equation, using full structural formulae, for the reaction of but-2-ene with hydrogen



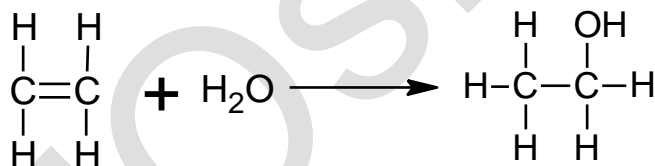
30 Write an equation, using condensed structural formulae, for the reaction of but-2-ene with bromine



31 Write an equation using full structural formulae for the reaction of but-2-ene with hydrogen chloride



32 Write an equation for the reaction of ethene with water under appropriate conditions



33 Explain how alkanes may be distinguished from alkenes in the laboratory.

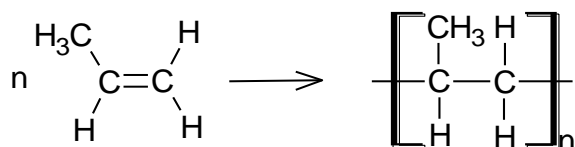
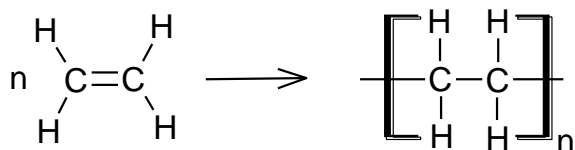
Shake with bromine water

The bromine water, which is orange, is decolorized to colourless, when shaken with an alkene, but there is no change in colour when an alkane is shaken with bromine water.

34 Explain the terms *saturated* and *unsaturated*.**unsaturated** - contain C=C/C≡C multiple bonds**saturated** - only C-C single bonds - no C-C multiple bonds

35 Write an equation using structural formula to show the formation of a polymer from

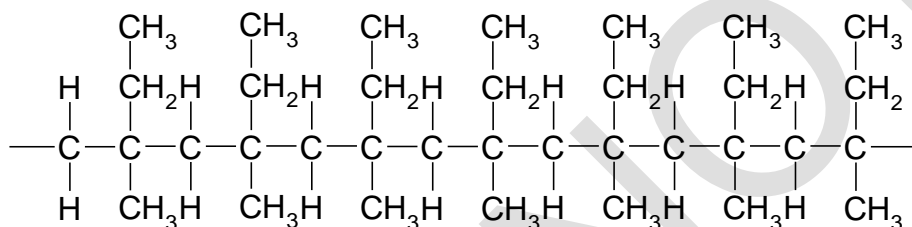
- ethene
- propene



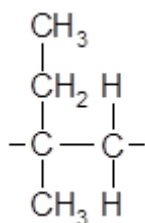
36 What type of polymerisation reaction is involved in 35

Addition polymerisation

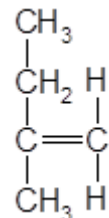
37 Draw the repeating unit and monomer for the polymer shown



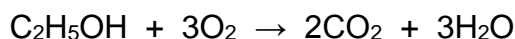
Repeating unit:



monomer:



38 Write an equation for the complete combustion of ethanol

39 Draw full structural formulae and name all the isomers of $\text{C}_4\text{H}_{10}\text{O}$ that are alcohols

$\begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \\ & & & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{O} & \\ & & & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & & \end{array}$	$\begin{array}{ccccccc} & & & & \text{H} & & \\ & & & & & & \\ & \text{H} & \text{O} & \text{H} & \text{H} & \text{H} & \\ & & & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{H} & \\ & & & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & & \end{array}$	Full structural formula must show O-H bond
butan-1-ol	butan-2-ol	
$\begin{array}{ccccccc} & & & \text{H} & & & \\ & & & & & & \\ & \text{H} & \text{O} & \text{H} & \text{H} & \text{H} & \\ & & & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{H} & & \\ & & & & & & \\ & \text{H} & \text{H} & \text{C} & -\text{H} & \text{H} & \\ & & & & & & \\ & & & \text{H} & & & \end{array}$	$\begin{array}{ccccccc} & \text{H} & & \text{H} & & \text{H} & \\ & & & & & & \\ \text{H} & -\text{C} & - & \text{C} & - & \text{C} & -\text{O}-\text{H} \\ & & & & & & \\ & \text{H} & \text{H} & \text{C} & -\text{H} & \text{H} & \\ & & & & & & \\ & & & \text{H} & & & \end{array}$	
2-methylpropan-2-ol	2-methylpropan-1-ol	

40 Classify each of the alcohols in 39 as primary, secondary or tertiary

$\begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \\ & & & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{O} & \\ & & & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & & \end{array}$	$\begin{array}{ccccccc} & & & & \text{H} & & \\ & & & & & & \\ & \text{H} & \text{O} & \text{H} & \text{H} & \text{H} & \\ & & & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{H} & \\ & & & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & & \end{array}$	
primary	secondary	
$\begin{array}{ccccccc} & & & \text{H} & & & \\ & & & & & & \\ & \text{H} & \text{O} & \text{H} & \text{H} & \text{H} & \\ & & & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{H} & & \\ & & & & & & \\ & \text{H} & \text{H} & \text{C} & -\text{H} & \text{H} & \\ & & & & & & \\ & & & \text{H} & & & \end{array}$	$\begin{array}{ccccccc} & \text{H} & & \text{H} & & \text{H} & \\ & & & & & & \\ \text{H} & -\text{C} & - & \text{C} & - & \text{C} & -\text{O}-\text{H} \\ & & & & & & \\ & \text{H} & \text{H} & \text{C} & -\text{H} & \text{H} & \\ & & & & & & \\ & & & \text{H} & & & \end{array}$	
tertiary	primary	

41 For the oxidation of alcohols, state the

- names and formulae of 2 different oxidising agents that can be used
- the required conditions
- the colour changes observed

name	formula	conditions	colour change
acidified dichromate(VI)	$\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$	acidified + heat	orange to green
acidified manganate(VII)	$\text{MnO}_4^-/\text{H}^+$	acidified + heat	purple to colourless

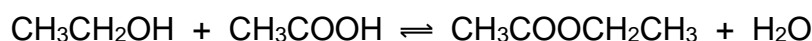
- 45 Explain how the conditions for oxidation of a primary alcohol can be varied to allow for a better yield of the aldehyde or the carboxylic acid.

For better yield of aldehyde use distillation and excess alcohol

For better yield of carboxylic acid use reflux and excess oxidising agent

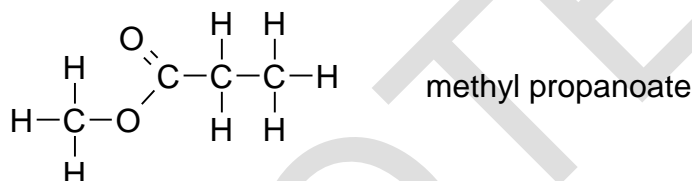
The aldehyde does not have hydrogen bonding between molecules (no H joined directly to O) therefore has a lower boiling point than the alcohol and distils off as soon as it is formed – before it can be oxidised further

- 46 Write an equation for the reaction of ethanol with ethanoic acid and state the essential conditions for the reaction



Heat with concentrated sulfuric acid catalyst

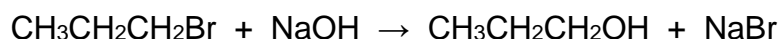
- 47 Draw the structural formula of and name the ester formed when propanoic acid reacts with methanol



- 48 State the name of the type of reaction occurring in 46 and 47.

Condensation/esterification/nucleophilic substitution

49 Write an equation for the reaction of 1-bromopropane with aqueous sodium hydroxide



50 State the name of the type of reaction occurring in 49

nucleophilic substitution/hydrolysis

51 Explain why halogenoalkanes are more reactive than alkanes.

The C-X (where X is a halogen atom) bond is polar and nucleophiles are attracted to $\text{C}^{\delta+}$
 X^- is a better leaving group than H^-

The C-Cl/C-Br/C-I bonds are weaker than C-C and C-H bonds

52 Explain what a *nucleophile* is.

A molecule/negatively charged ion, possessing a lone pair of electrons, which is attracted to a more positively charged region in a molecule (region with lower electron density) and donates a lone pair of electrons to form a covalent bond.

53 State what type of reactions benzene undergoes.

Substitution (not addition)

54 Draw the structural formulae and name all the isomers of $\text{C}_4\text{H}_9\text{Cl}$

$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{Cl} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	$\begin{array}{cccc} \text{H} & \text{Cl} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$
1-chlorobutane	2-chlorobutane
$\begin{array}{ccc} \text{H} & \text{Cl} & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & \\ \text{H} & \text{H}-\text{C}-\text{H} & \text{H} \\ & & \\ & \text{H} & \end{array}$	$\begin{array}{ccc} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{Cl} \\ & & \\ \text{H} & \text{H}-\text{C}-\text{H} & \text{H} \\ & & \\ & \text{H} & \end{array}$
2-chloro-2-methylpropane	1-chloro-2-methylpropane

55 State whether each of the halogenoalkanes in 54 is primary, secondary or tertiary.

$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{Cl} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	$\begin{array}{cccc} \text{H} & \text{Cl} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$
primary	secondary
$\begin{array}{ccc} \text{H} & \text{Cl} & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & \\ \text{H} & \text{H}-\text{C}-\text{H} & \text{H} \\ & & \\ & \text{H} & \end{array}$	$\begin{array}{ccc} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{Cl} \\ & & \\ \text{H} & \text{H}-\text{C}-\text{H} & \text{H} \\ & & \\ & \text{H} & \end{array}$
tertiary	primary

56 Explain whether each of the halogenoalkanes in 54 will react with aqueous sodium hydroxide via an $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ mechanism

$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{Cl} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	$\begin{array}{cccc} \text{H} & \text{Cl} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$
$\text{S}_{\text{N}}2$	$\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}1$
$\begin{array}{ccc} \text{H} & \text{Cl} & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & \\ \text{H} & \text{H}-\text{C}-\text{H} & \text{H} \\ & & \\ & \text{H} & \end{array}$	$\begin{array}{ccc} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{Cl} \\ & & \\ \text{H} & \text{H}-\text{C}-\text{H} & \text{H} \\ & & \\ & \text{H} & \end{array}$
$\text{S}_{\text{N}}1$	$\text{S}_{\text{N}}2$

57 Explain what is meant by S_N1 and S_N2 reactions

S_N1 nucleophilic substitution unimolecular

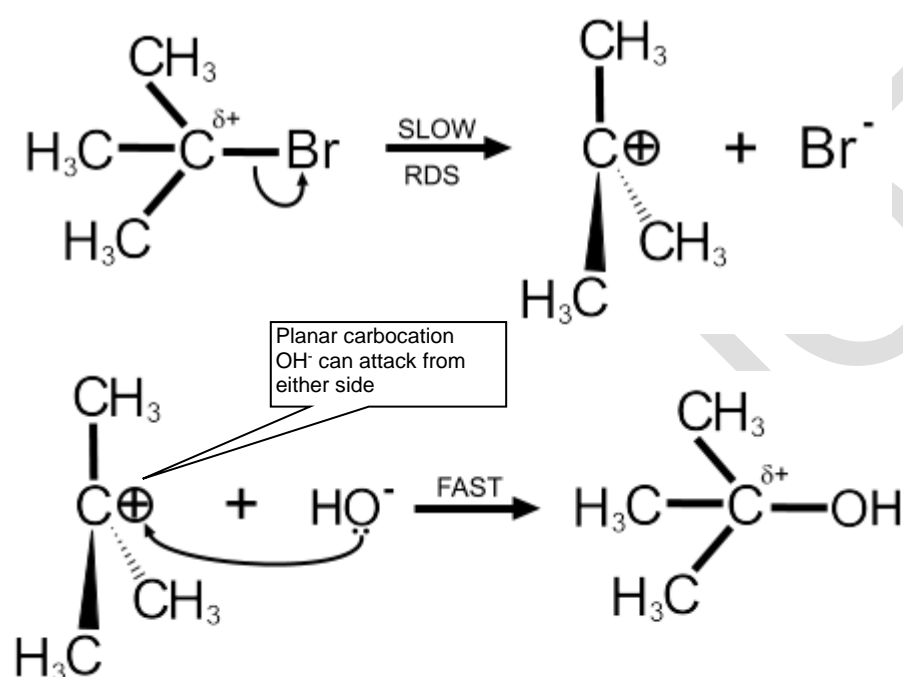
S_N2 nucleophilic substitution bimolecular

Substitution – one atom/group is replaced by another atom/group

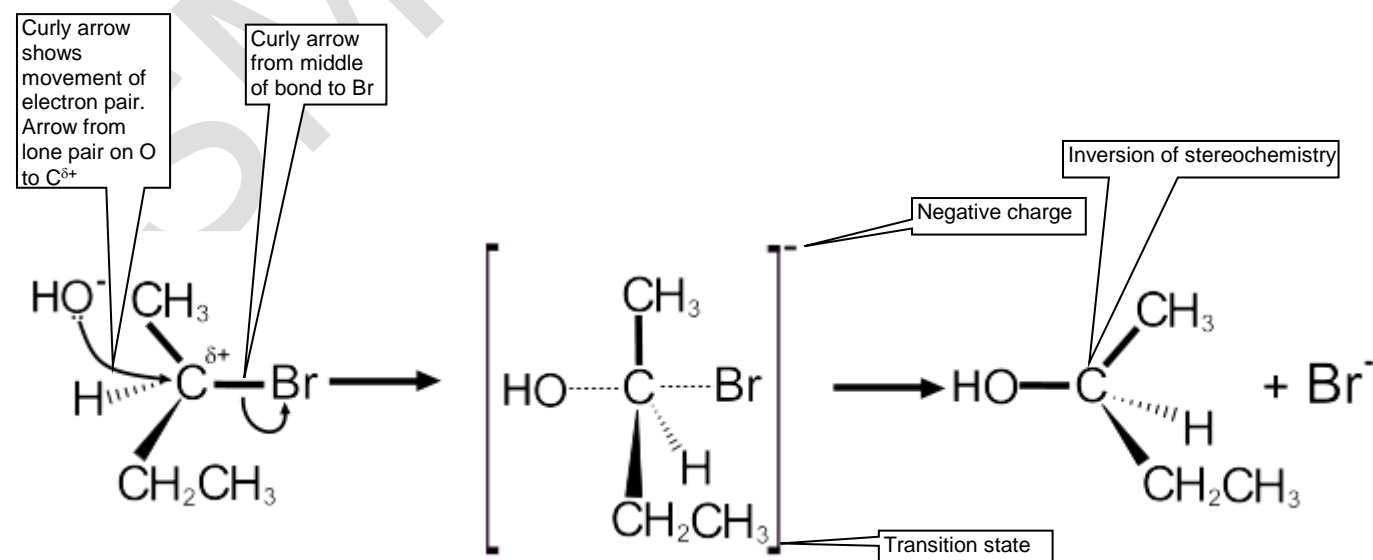
Nucleophile - a molecule/negatively charged ion, possessing a lone pair of electrons, which is attracted to a more positively charged region in a molecule (region with lower electron density) and donates a lone pair of electrons to form a covalent bond.

58 Draw out S_N1 and S_N2 mechanisms for suitable halogenoalkanes reacting with aqueous sodium hydroxide

S_N1



S_N2

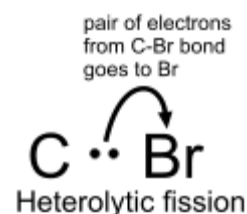


- 59 Explain what is meant by the term *heterolytic fission* and explain how it is different to *homolytic fission*.

heterolytic fission – a bond breaks so that both electrons go to the same atom.



homolytic fission – a bond breaks so that one electron goes to each atom.



- 60 State and explain why the rate of S_N2 reactions depends on whether the halogenoalkane is primary, secondary or tertiary

S_N2 reactions are faster for primary halogenoalkanes and slowest for tertiary halogenoalkanes. The more highly substituted the C the slower the rate of the S_N2 reaction. This is due to steric effects - alkyl groups surrounding the central C make it much more difficult for the nucleophile to get in to attack the central C.

- 61 State and explain why the rate of S_N1 reactions depends on whether the halogenoalkane is primary, secondary or tertiary

S_N1 reactions are faster for tertiary halogenoalkanes and slowest for primary halogenoalkanes. The more highly substituted the C the faster the rate of the S_N1 reaction. This is due to the stability of the intermediate carbocation. The order of stability of carbocations is:

Tertiary carbocations > secondary carbocations > primary carbocations

Alkyl groups have an electron-releasing effect (positive inductive effect) – the more electron-releasing alkyl groups around the positively-charged C, the more stable the carbocation.

- 62 Match the rate equation with the type of reaction mechanism:

Rate = $k[\text{halogenoalkane}][\text{hydroxide ion}]$	Rate = $k[\text{halogenoalkane}]$
S_N2 – the halogenoalkane and hydroxide ion both involved in the only (therefore RDS) step.	S_N1 – only the halogenoalkane involved in mechanism up to and including the RDS - hydroxide ion only involved in a fast step after the RDS

- 63 One enantiomer of an optically active halogenoalkane reacts with aqueous sodium hydroxide and a racemic mixture is formed. Explain what type of mechanism occurred.

An S_N1 mechanism occurred – a planar carbocation is formed – the hydroxide ion is equally likely to attack from either side therefore both enantiomers of the product formed in equal concentrations – a racemic mixture.

The S_N2 mechanism is stereospecific and would have resulted in the formation of just one enantiomer and not a racemic mixture.

64 Classify each of the following solvents as *non-polar*, *aprotic polar* or *protic polar*

(CH ₃) ₂ SO	NH ₃	(CH ₃) ₂ CO	H ₂ O
<i>aprotic polar</i>	<i>protic polar</i>	<i>aprotic polar</i>	<i>protic polar</i>
CCl ₄	C ₆ H ₁₄	CH ₃ OH	CH ₃ CN
<i>non-polar</i>	<i>non-polar</i>	<i>protic polar</i>	<i>aprotic polar</i>

65 State whether each of the solvents in 64 would favour S_N1 or S_N2 reactions

(CH ₃) ₂ SO	NH ₃	(CH ₃) ₂ CO	H ₂ O
S _N 2	S _N 1	S _N 2	S _N 1
CCl ₄	C ₆ H ₁₄	CH ₃ OH	CH ₃ CN
S _N 2	S _N 2	S _N 1	S _N 2

66 Explain, using one example of each *type* of solvent, your answer to question 65

Protic polar solvents - able to solvate both negative and positive ions. Negative ions are solvated by interaction with the H atoms attached to the O or N through hydrogen bonding.

Ion-solvent interactions stabilise the intermediates in the S_N1 reaction.

In the S_N2 reaction, the negatively-charged nucleophile will be solvated by solvent molecules and will thus not be a very effective nucleophile - it is being kept away from the δ⁺ C by the solvent molecules which are surrounding it – more energy has to be supplied to strip away solvent molecules – higher activation energy.

Non-polar solvent – does not solvate the negatively-charged nucleophile very well so it can more easily attack the δ⁺ C – less energy to strip away solvent molecules – lower activation energy. Therefore S_N2 favoured. Does not stabilise the ionic intermediates in the S_N1 reaction – S_N1 not favoured.

Aprotic polar solvent – does not solvate the negatively-charged nucleophile very well (no hydrogen bonding) so it can more easily attack the δ⁺ C – less energy to strip away solvent molecules – lower activation energy. Therefore S_N2 favoured. Does not stabilise the negatively charged intermediate in the S_N1 reaction – S_N1 not favoured as much as with protic polar solvents.

67 State whether 1-chlorobutane or 2-chloro-2-methylpropane reacts faster with aqueous sodium hydroxide

2-chloro-2-methylpropane reacts faster – S_N1 reactions are generally faster than S_N2.

68 Explain whether 1-chlorobutane or 1-iodobutane will react more quickly with aqueous sodium hydroxide

1-iodobutane reacts faster. The C-I bond is weaker than the C-Cl bond. The rate determining step involves breaking the C-halogen bond.

69 Explain whether water or the hydroxide ion will react more rapidly with 1-bromobutane.

S_N2 mechanism. Hydroxide ion is negatively charged but water is neutral. Hydroxide ion more strongly attracted to δ⁺ C. Therefore hydroxide ion reacts more rapidly.

70 Explain what is meant by the term *electrophile*.

A reagent (a positively charged ion or the positive end of a dipole) which is attracted to regions of high electron density and accepts a pair of electrons to form a covalent bond.

71 Explain whether an electrophile is a Lewis acid or Lewis base

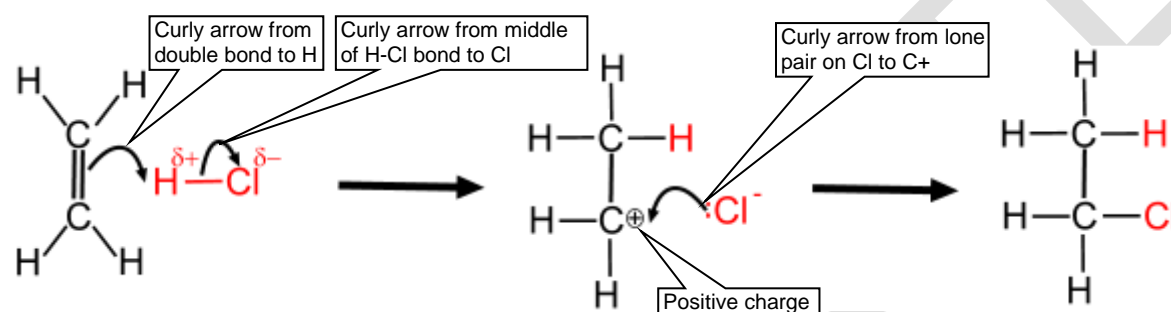
An electrophile is a Lewis acid – a Lewis acid is an electron pair acceptor and an electrophile accepts a pair of electrons in an organic reaction.

A nucleophile is a Lewis base – donates a pair of electrons.

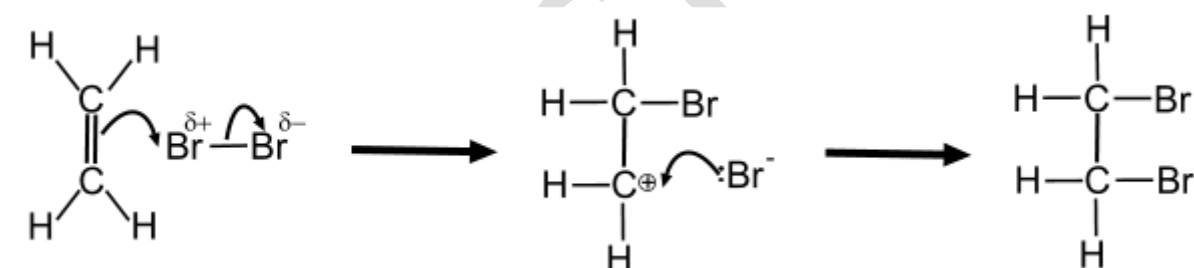
72 State the name of the type of reaction mechanism that occurs when ethene reacts with hydrogen halides or halogens

Electrophilic addition

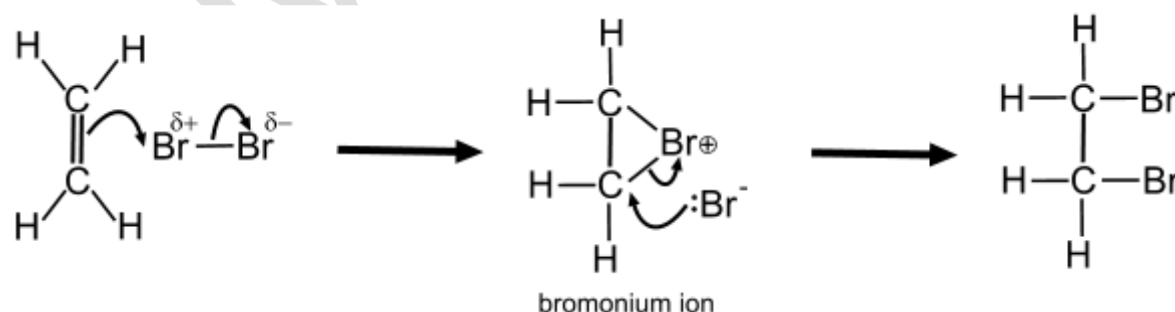
73 Draw out the mechanism for the reaction of ethene with hydrogen chloride



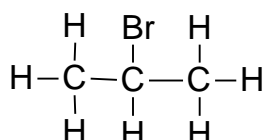
74 Draw out the mechanism for the reaction of ethene with bromine



Or

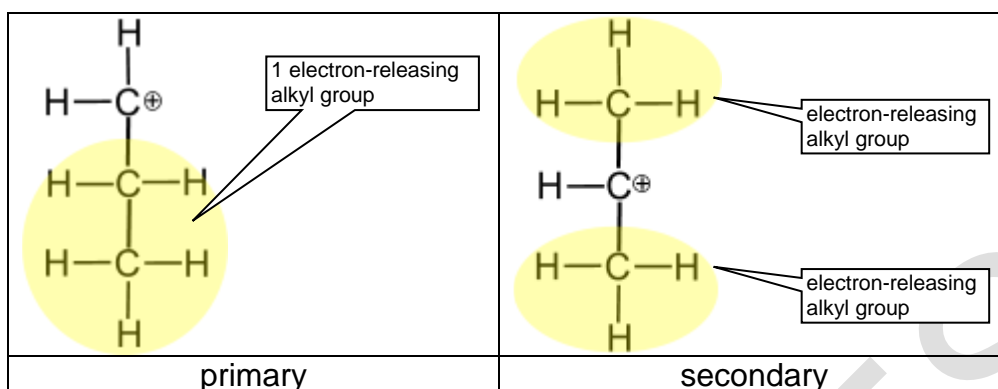


75 Draw structural formula of the major product when propene reacts with hydrogen bromide



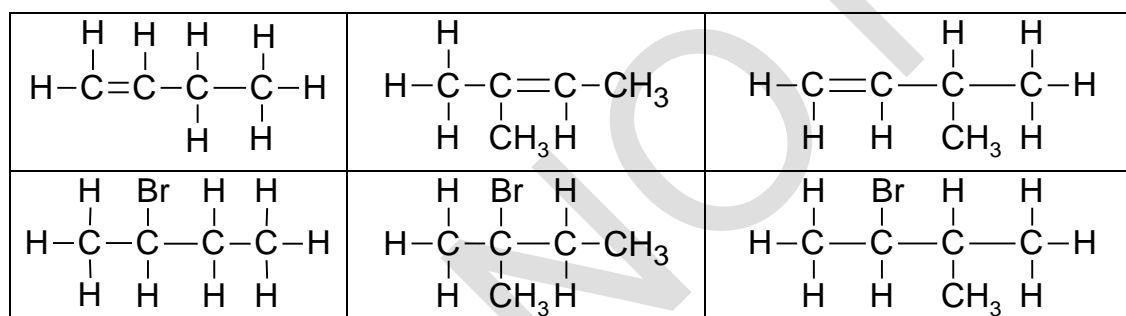
76 Explain the formation of a major product when propene reacts with hydrogen bromide

2 possible carbocations can be formed: primary and secondary

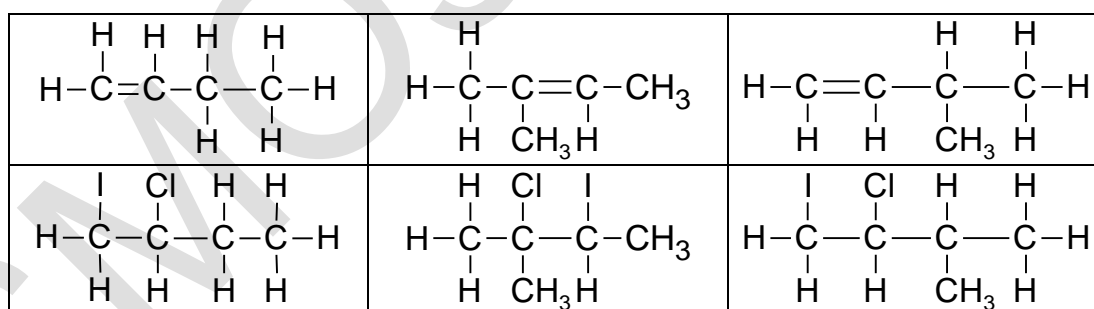


Secondary carbocation is more stable as there are *more* electron-releasing alkyl groups around the positively-charged C

77 Predict the major product when each of the following alkenes reacts with hydrogen bromide



78 Predict the major product when each of the following alkenes reacts with iodine monochloride (ICl)



79 Explain the bonding in benzene and state what the C-C bond order is.

An aromatic compound with a π -delocalised system containing 6 electrons. The π -delocalised system is formed when a p orbital, containing 1 electron, on each C overlaps side-on with p orbitals on adjacent C atoms in the ring.

Bond order is 1.5

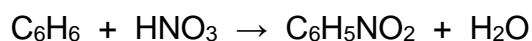
80 For the nitration of benzene:

- state the reagents and conditions
- write a chemical equation for the reaction
- draw the mechanism for the reaction

➤ **state the reagents and conditions**

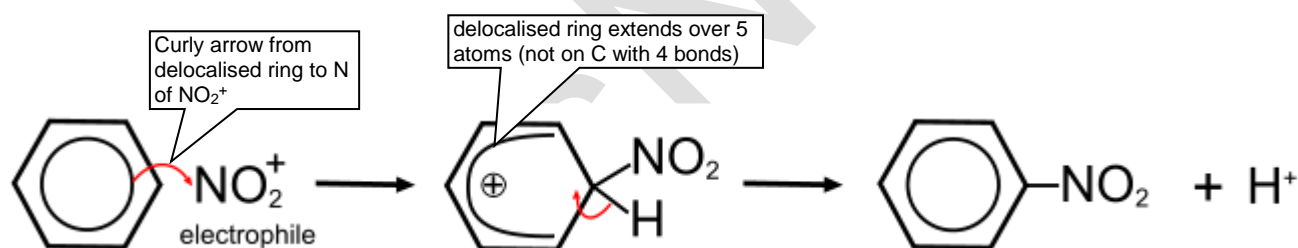
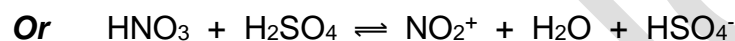
concentrated nitric acid, concentrated sulfuric acid, heat under reflux

➤ **write a chemical equation for the reaction**



➤ **draw the mechanism for the reaction**

Formation of the electrophile:



81 State the *type* of mechanism that benzene undergoes

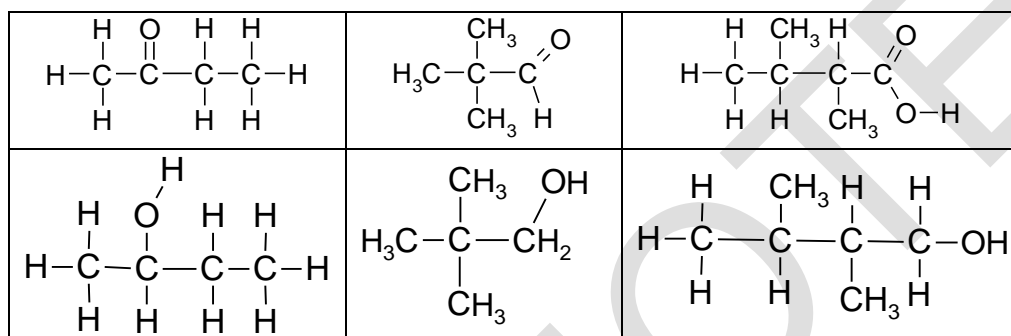
Electrophilic substitution

82 State the reagents and conditions for

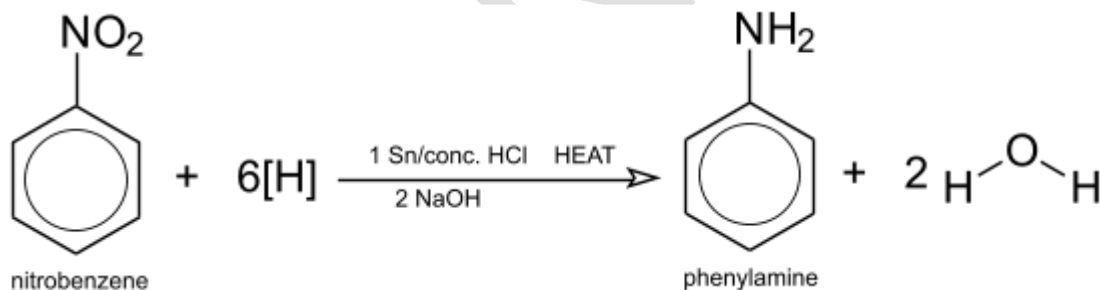
- reduction of a carboxylic acid
- reduction of an aldehyde or ketone

➤ **reduction of a carboxylic acid**stage 1 – LiAlH_4 (lithium aluminium hydride) in dry ethoxyethane solventstage 2 – $\text{H}^+(\text{aq})$ ➤ **reduction of an aldehyde or ketone** NaBH_4 (sodium borohydride) in methanol solvent

83 Give the structural formulae of the products formed when each of the following is reduced using the reagents and conditions in 82.



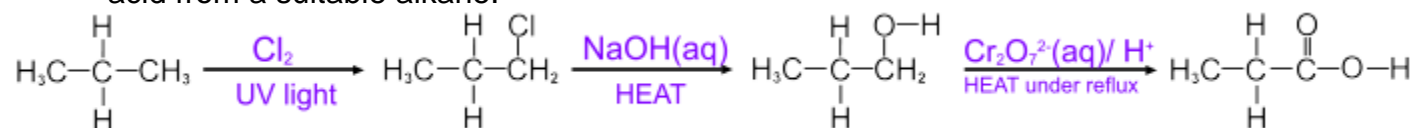
84 Write a balanced equation showing structures, reagents and conditions for the conversion of nitrobenzene to phenylamine.



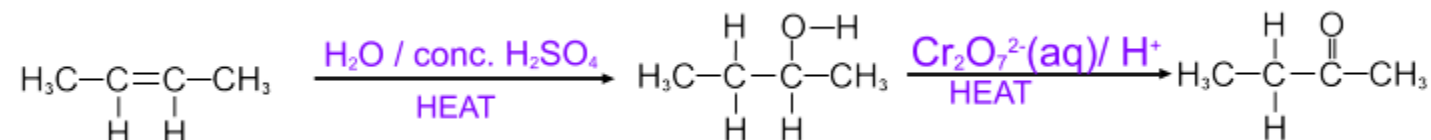
85 Explain what is meant by the *retro-synthetic* approach

Chemists start with the target molecule that they are trying to make and work backwards using known reactions to an appropriate, readily available starting material.

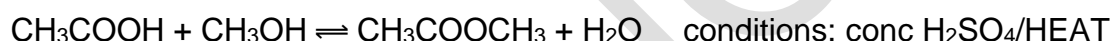
86 Give a reaction scheme showing structures, reagents and conditions for making propanoic acid from a suitable alkane.



87 Give a reaction scheme showing structures, reagents and conditions for making butanone from an alkene.



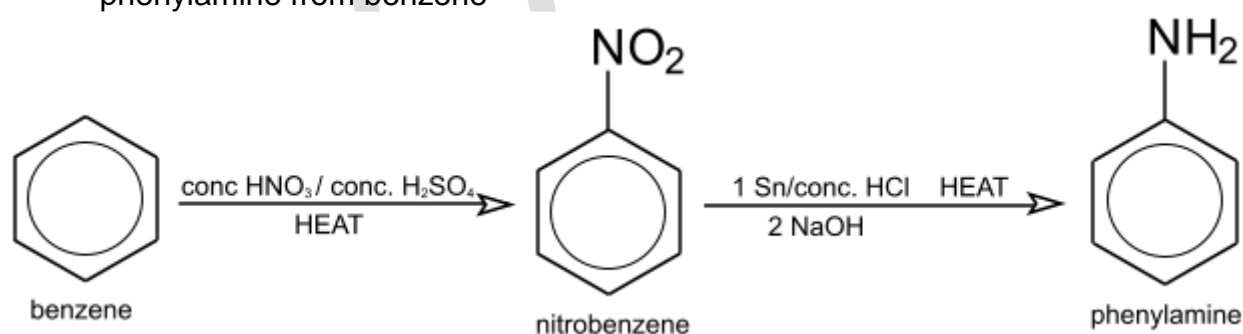
88 Give a reaction scheme showing condensed structural formulae, balanced equations and conditions for making methyl ethanoate from suitable hydrocarbons.



Alternatively, ethanol can be made as follows:



89 Give a reaction scheme showing structures, reagents and conditions for making phenylamine from benzene



90 Explain what is meant by the term *stereoisomerism*

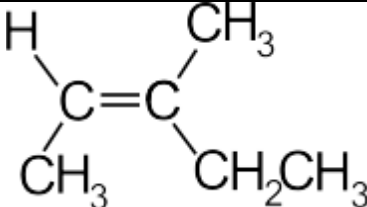
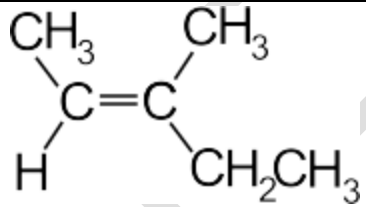
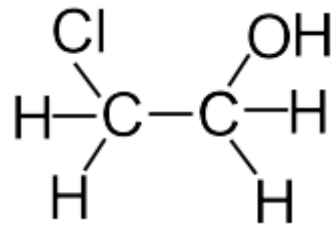
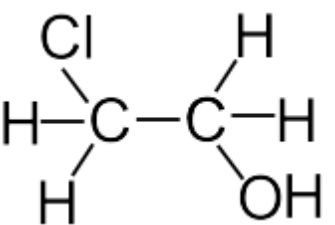
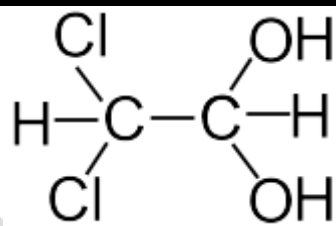
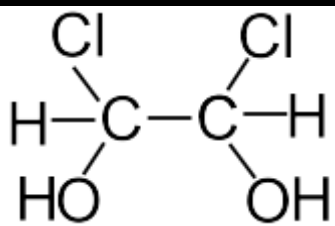
Molecules have same structural formula (i.e. the atoms are joined together in the same way – same connectivity) but the atoms are arranged differently in space.

91 Explain the difference between conformational and configurational stereoisomers

Conformational isomers are the **same molecule** in different conformations due to rotation about a σ bond

Configurational isomers - different molecules that can only be interconverted by breaking and re-forming a covalent bond.

92 Explain whether each of the following pairs represent configurational or conformational stereoisomers or structural isomers

1		
configurational stereoisomers		
2		
conformational stereoisomers		
3		
structural isomers		

93 Explain what is meant by *cis-trans isomerism*.

Molecules which exhibit *cis-trans* isomerism have the same structural formula (atoms joined together in the same way) but the atoms/groups are arranged differently in space relative to a reference plane (C=C or a ring of atoms)

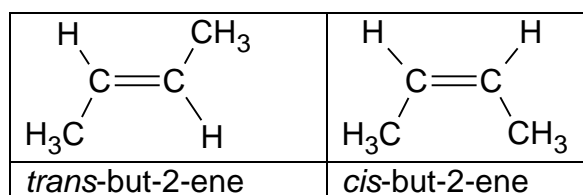
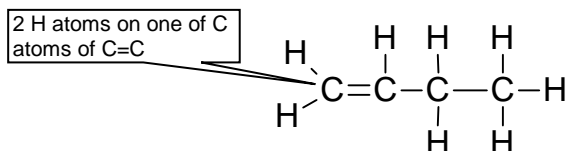
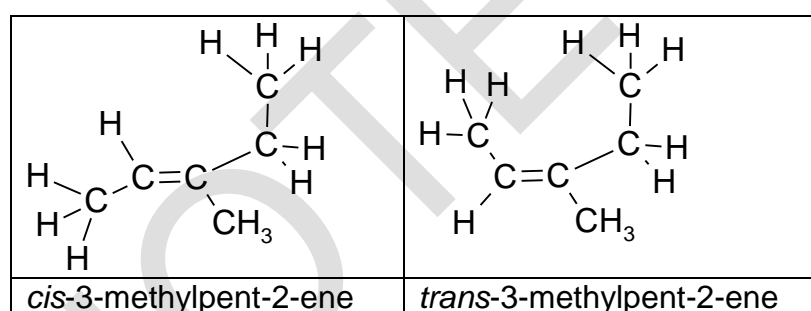
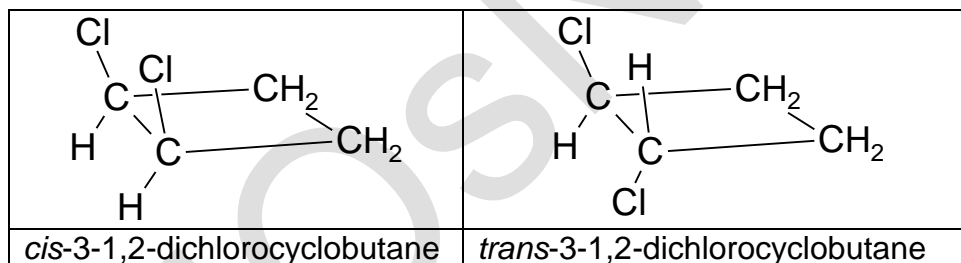
94 Explain how *cis-trans isomerism* arises in alkenes.

Alkenes exhibit *cis-trans* isomerism if they have **two different groups** on **both** carbon atoms of a double bond. The *cis*-isomer has two groups on the same side of the C=C and the *trans*-isomer has them on opposite sides of C=C.

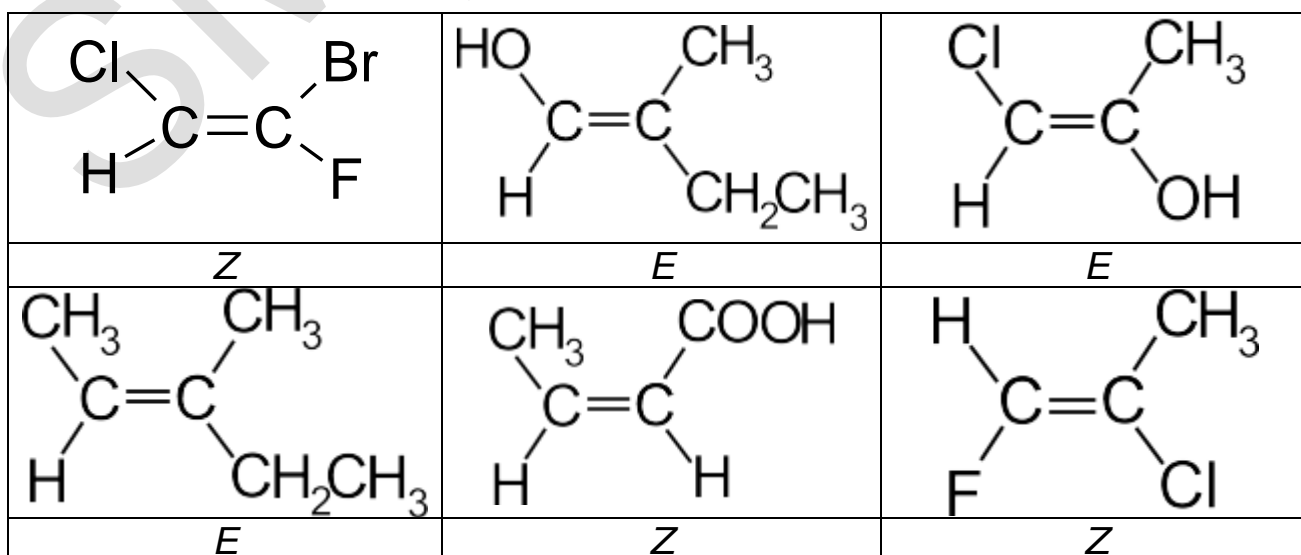
Cis-trans isomerism occurs because the π component of the C=C **prevents rotation of groups about the C=C bond** – the groups cannot be rotated around the bond without breaking the π component.

95 Explain which of the following will exhibit *cis-trans* isomerism

but-2-ene but-1-ene 3-methylpent-2-ene

but-2-ene: exhibits *cis-trans* isomerism - two different groups on each C atom making up C=C**but-1-ene:** does not exhibit *cis-trans* isomerism - two groups the same on one of the C atoms making up C=C**3-methylpent-2-ene:** exhibits *cis-trans* isomerism - two different groups on each C atom making up C=C96 Draw the structures of the *cis-trans* isomers of 1,2-dichlorocyclobutane and explain why they exist

The ring structure prevents rotation of groups - Cl atoms cannot rotate around the C-C bond without breaking the C-C bond.

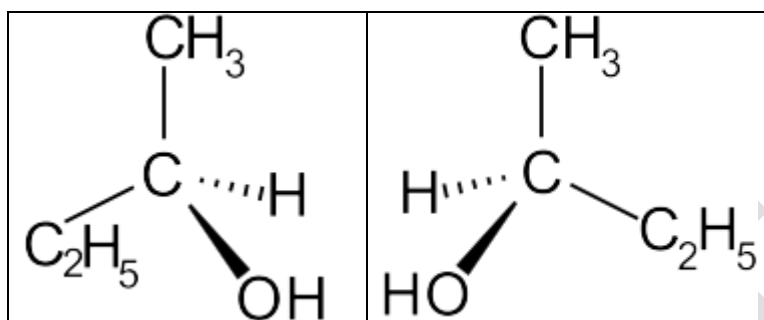
97 Classify each of the following as *E* or *Z*

98 Explain what is meant by *optical isomerism*.

Molecules that are optical isomers have the same structural formula (atoms joined together in the same way) but the atoms/groups are arranged differently in space so that mirror images are not superimposable

The molecule possesses a chiral centre - four different atoms/groups attached to a C atom. Optical isomers rotate the plane of plane polarised light in opposite directions by equal amounts.

99 Draw clear 3-D diagrams showing the optical isomers of butan-2-ol



100 Explain which of the following will exhibit optical isomerism

1-bromobutane

2-bromobutane

$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{COOH}$

<p>does not exhibit optical isomerism – no chiral centre</p>	<p>exhibits optical isomerism – chiral centre</p>	<p>exhibits optical isomerism – chiral centre</p>

101 Explain what is meant by the terms *enantiomer* and *chiral centre*

enantiomers - the individual optical isomers of an optically active compound – enantiomers are non-superimposable mirror images of each other

chiral centre - a carbon atom with four different atoms or groups attached

102 Explain what is meant by plane-polarised light.

Light that vibrates in one plane only.

103 State how the two enantiomers of butan-2-ol interact with plane-polarised light

They rotate the plane of plane polarised light in opposite directions by equal amounts (assuming they are present at equal concentration)

104 Explain how a polarimeter may be used to distinguish between optical isomers

Plane polarised light is passed through the individual isomers (usually dissolved in a solvent) in a polarimeter. The optical isomers rotate the plane of plane polarised light in opposite directions by equal amounts (assuming they are present at equal concentration)

105 Explain what a racemic mixture is

An equimolar mixture of the two enantiomers of a chiral compound.

A racemic mixture has no effect on plane-polarised light since the rotations of the two enantiomers cancel each other out.

106 Describe the similarities and differences in the physical and chemical properties of enantiomers.

Physical properties such as melting point, boiling point, solubility are identical. The only difference in physical properties is in the direction of rotation of the plane of plane-polarised light.

The chemical properties of enantiomers are identical for reactions with compounds which are not optically active. Enantiomers may, however, react differently with other optically active compounds.

107 Explain whether *cis*- or *trans*-1,2-dichlorocyclopropane exhibits optical isomerism

Only *trans*-1,2-dichlorocyclopropane exhibits optical isomerism.

cis-1,2-dichlorocyclopropane has a plane of symmetry meaning that the mirror images are superimposable and it does not exhibit optical isomerism.

108 Explain what *diastereomers* are

Diastereomers are stereoisomers that are not mirror images of each other.

The molecules have the same structural formula (atoms joined together in the same way) and the atoms/groups are arranged differently in space but diastereomers are not mirror images of each other.

Diastereomers have different physical properties and can have different chemical properties.

109 State whether each of the following pairs are enantiomers, diastereomers or identical

