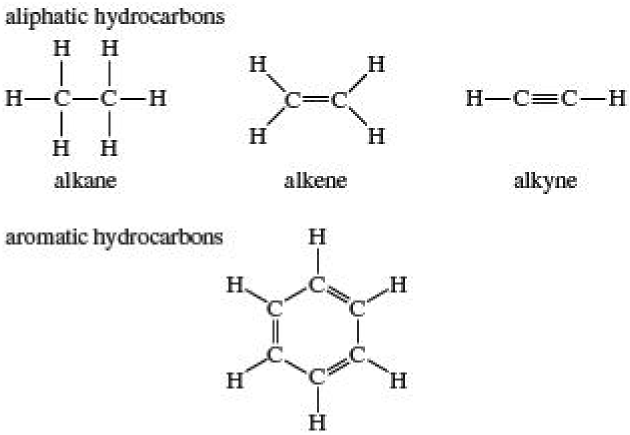
UNIT 7

INTRODUCTION TO ORGANIC CHEMISTRY

PART 3 – SIMPLE REACTIONS OF HYDROCARBONS



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Key words: addition, substitution, saturated, unsaturated, petrochemicals, aromatic, resonance, ozone layer

1) Alkanes

(a) Sources and industrial preparation

Methane is the main component of natural gas.
Most other alkanes are obtained industrially by the fractional distillation, cracking and reforming of crude oil as described in Unit 7 Part 2.

(b) Laboratory Preparation

Alkanes can be made in the laboratory by:

(i) the addition of hydrogen to an alkene
eg $C_2H_4 + H_2 \rightarrow C_2H_6$

(ii) the addition of hydrogen to a haloalkane
eg $C_2H_5I + H_2 \rightarrow C_2H_6 + HI$

(c) Uses and chemical reactions

(i) Fuels

Alkanes are mainly used as fuels for transport, domestic heating and electricity production as described in Unit 7 Part 2.

(ii) Manufacture of Petrochemicals

Alkanes are also used as the starting point in the manufacture of a wide variety of organic products. The use of alkanes to manufacture other useful chemicals is known as the petrochemical industry.

The first step is to convert alkanes into haloalkanes. One or more hydrogen atoms on the alkane are replaced by halogen atoms in presence of UV light:

Eg $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
$CH_4 + 2Cl_2 \rightarrow CH_2Cl_2 + 2HCl$
$C_3H_8 + Br_2 \rightarrow C_3H_7Br + HBr$
$C_3H_8 + 2Br_2 \rightarrow C_3H_6Br_2 + 2HBr$

These reactions are called **substitution** reactions because they involve the replacement of a hydrogen by a halogen.

These reactions tend to produce a wide variety of different haloalkanes because:

- The number of halogen atoms replacing hydrogen atoms on each hydrocarbon can vary; in other words reacting CH_4 and Cl_2 will result in a mixture of CH_3Cl, CH_2Cl_2, $CHCl_3$ or CCl_4
- The position of the halogen atoms on the carbon skeleton can vary; in other words reacting C_3H_8 with Br_2 will result in a mixture of 1-bromopropane and 2-bromopropane, as well as a number of dibromoalkanes, tribromoalkanes etc

2) Alkenes

(a) Laboratory preparation

Alkenes are usually prepared in the laboratory by the dehydration of alcohols. The alcohol is heated using concentrated sulphuric acid as the dehydrating agent:

Eg $C_2H_5OH \rightarrow H_2O + C_2H_4$

$C_2H_5CH_2OH \rightarrow H_2O + C_3H_6$

(b) Chemical reactions

(i) Addition Reactions

Alkanes can also be used as the starting point in the manufacture of a wide variety of petrochemicals. The C=C double bond in alkenes can be easily broken and other atoms can be added to the carbon skeleton. The reactions are known as **addition** reactions because atoms are added to the carbon skeleton but no atoms are removed.

The atoms being added must join the skeleton on the two carbon atoms where the double bond used to be. This means that the products are much easier to predict and control – only one or two products will ever be formed.

With halogens (X_2), only one product is formed:

Eg $C_3H_6 + Br_2 \rightarrow C_3H_6Br_2$ (1,2-dibromopropane only)

With hydrogen halides (HX) and bromine water (Br-OH), two products are formed if the alkene is unsymmetrical around the double bond (eg propene, but-1-ene). One product is formed if the alkene is symmetrical around the double bond (eg ethene, but-2-ene):

Eg $CH_3CH{=}CHCH_3 + HCl \rightarrow CH_3CHClCHClCH_3$ (2,3-dichlorobutane only)

Eg $CH_3CH{=}CHCH_3 + HOBr \rightarrow CH_3CH(OH)CHBrCH_3$ (3-bromobutan-2-ol only)

Eg $CH_2CH{=}CH_3 + HBr \rightarrow CH_3CHBrCH_3$ or $CH_3CH_2CH_2Br$

(2-bromopropane or 1-bromopropane)

(ii) Hydroxy-oxidation reactions

Alkenes can also be converted to diols using $KMnO_4$ in alkaline solution. Two -OH groups are added across the double bond to give a single organic product:

Eg $C_3H_6 + [O] + H_2O \rightarrow HOCH_2CH(OH)CH_3$ (propan-1,2-diol only).

These reactions are known as hydroxyoxidation because oxygen is added in the form of -OH groups.

(c) Laboratory detection

There are two tests for alkenes:

(i) Br_2/CCl_4

When bromine is shaken with an alkene in the presence of an inert organic solvent such as CCl_4, the mixture turns from orange to colourless (ie it decolorises). This is because the orange bromine is involved in an addition reaction with the alkene. When the bromine reacts, its colour disappears.

(ii) $KMnO_4$

When potassium manganate (VII) is shaken with an alkene in acidic aqueous conditions, the mixture turns from purple to colourless (ie it decolorises). This is because the purple manganate (VII) ion is involved in a hydroxyoxidation reaction with the alkene. When the manganate (VII) ion reacts, its colour disappears.

3) Alkynes

(a) Industrial preparation

Ethyne is manufactured by adding water to calcium carbide (CaC_2):

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

(b) Uses

(i) The most important use of ethyne is to manufacture ethanal:
$C_2H_2 + H_2O \rightarrow CH_3CHO$

(ii) Ethyne is also used to make chloroethene, which is in turn used to make polychloroethene:
$C_2H_2 + HCl \rightarrow CH_2{=}CHCl$

(c) Laboratory detection

Alkynes show many of the characteristic reactions of alkenes; alkynes decolorise both bromine (addition) and $KMnO_4$ (hydroxyoxidation). This reaction can be used to distinguish alkenes and alkynes from alkanes.

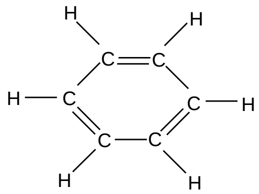
Ethyne can be distinguished from alkenes and alkanes because it will give a yellow-white precipitate (of Ag_2C_2) when bubbled through an aqueous ammoniacal solution of $AgNO_3(aq)$.

This happens because ethyne is weakly acidic, dissociating very slightly in aqueous solution to form H^+ ions: $C_2H_2\ (aq) == 2H^+(aq)\ + C_2^{2-}(aq)$. This dissocation happens more in the presence of ammonia.
The resulting carbide (C^{2-}) ion will react with Ag^+ ions to give a yellow-white precipitate of Ag_2C_2:
$Ag^+(aq) + C^{2-}(aq) \rightarrow Ag_2C_2(s)$
Neither ethane nor ethene are acidic. They therefore do not give this reaction.

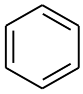
4) Benzene

(a) Structure

Benzene is a cyclic hydrocarbon containing six carbon atoms and six hydrogen atoms. It was originally thought to be a ring of six carbon atoms containing alternate single and double bonds as follows:



This molecule has the IUPAC name cyclohex-1,3,5-triene. It has the molecular formula C_6H_6 but is usually represented as its skeletal formula:



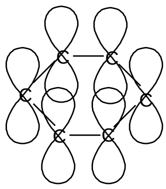
This structure is often known as the Kekule structure.

Double and single bonds do not have the same length; in double bonds, the extra overlap of the π–orbitals brings the atoms closer together and the bond is shorter:

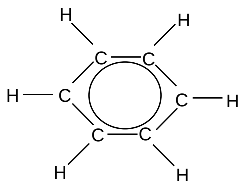
bond	Length/nm
C-C	0.154
C=C	0.134

The double bonds would be expected to be shorter than the single bonds in cyclohexa-1,3,5-triene.

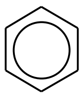
Analysis of the molecule, however, shows that this is not in fact the case; the bonds all have a length of 0.142 nm, intermediate between single and double. It was proposed that the structure did not in fact contain alternate single and double bonds but contained delocalized electrons in six overlapping orbitals:



This delocalisation of electrons is known as **resonance**. The delocalized electrons can be represented as a circle within the hexagonal ring:



This molecule is known as benzene. It is usually represented by its skeletal formula:



The electrons are completely delocalized. The carbons atoms each form three covalent bonds making the angle between the atoms 120^o and the molecule planar.

The structure of benzene thus has the following key features:

- All six –bonded electrons are delocalized
- All six C-C bonds have the same length, intermediate between single and double
- The molecule is planar

Any molecule containing the benzene ring can be described as **aromatic**.

(b) Stability and Reactions

The delocalization (resonance) of the electrons in benzene makes the molecule more stable than expected for a molecule with three double bonds.

As benzene contains carbon-carbon double bonds, it might be expected to behave like alkenes; i.e. react readily with bromine and hydrogen to undergo addition reactions, but this is not the case. Benzene will not decolorise bromine water. Neither will benzene readily undergo any other addition reactions. Addition reactions will break up the delocalized system and are therefore not as favoured.

Benzene thus tends to undergo substitution, rather than addition reactions. In this its reactivity is more similar to alkanes than to alkenes.

(i) Substitution reactions of benzene

In the presence of a catalyst such as $AlCl_3$ or $FeBr_3$, benzene can undergo a substitution reaction with a halogen:

Eg $C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$
bromobenzene

(ii) Addition reactions of benzene

In more extreme conditions (high pressure, high temperature and UV light), benzene can be persuaded to undergo an addition reaction with a halogen:

Eg $C_6H_6 + 3Cl_2 \rightarrow C_6H_6Cl_6$

It can also be persuaded to undergo an addition reaction with hydrogen:

$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$

Summary of Reactions of Alkanes, Alkenes and Arenes:

	addition	**substitution**
alkanes	**no**	**yes**
alkenes	**yes**	**no**
arenes	**yes**	**Yes**

(c) Uses of benzene

Benzene is used to make ethylbenzene, which is in turn used to make polystyrene.

Benzene is also added to gasoline to improve its octane number.

Benzene is used as the starting point in the manufacture of a variety of petrochemicals, including pharmaceutical products and dyes.

5) Haloalkanes

(a) Uses

Haloalkanes are generally toxic and are widely used as insecticides.

Chlorofluorocarbons (or CFCs), which are haloalkanes in which all of the hydrogen has been substituted by halogen atoms (such as CCl_4 or $C_2Cl_2F_4$), are widely used as refrigerants and aerosols. They are useful for both purposes because they are unreactive, non-toxic and volatile.

(b) Pollution Effects

CFCs are responsible for a serious global environmental problem – the destruction of the ozone layer.

The ozone layer is a thin layer of ozone (O_3) high up in the atmosphere. Ozone absorbs UV light from the sun, and this is important because UV light can cause skin cancer in humans.

CFCs, because of their unreactivity at ground level, tend to rise intact through the atmosphere until they eventually reach the ozone layer. They are then broken up by UV light from the sun to from free Cl and F atoms, and it is these atoms which cause the destruction of the ozone layer:

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

The overall reaction is $O_3 + O \rightarrow 2O_2$. This reaction causes the destruction of the ozone layer – the Cl and F atoms from CFCs are catalysts for this reaction.

Test Your Progress: Topic 7 Part 3 Exercise 1

1. Write equations to show:
   (a) the reaction of ethane with chlorine to produce chloroethane
   (b) the reaction of propene with bromine
   (c) the reaction of benzene with chlorine to produce chlorobenzene
   (d) the reaction of benzene with hydrogen to produce cyclohexane
   (e) the reaction of but-1-ene with $KMnO_4$ (aq)

2. For each of the reactions in Question 1, state the type of reaction occurring.

3. Write equations to show:
   (a) the laboratory preparation of propane
   (b) the laboratory preparation of propene
   (c) the industrial preparation of ethyne