CHEM 110

Module 3 Organic Chemistry

Module Notes

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Organic Chemistry

Module 3

Topic 3A – Introduction

Key questions

Why is carbon so special? How is it that the vast majority of chemicals known today are made from carbon (and other elements)? Carbon chemistry is not only omnipresent in our society but it is emphatically the basis of life itself. In this topic we introduce you to the long history of the subject "carbon chemistry" or more widely known as "**organic chemistry**" as well as deal with the principles for breaking down such a vast field of science into understandable units.

Outline

The notes produced for the CHEM110 organic chemistry component of the unit are based on sections of the book *Introduction to Organic Chemistry*, William H. Brown (described as Brown in these notes). However, the Module notes do not necessarily follow exactly the order given in the text. We will also refer to both the Saunders *ChemOffice Web* CD-ROM (included with the Brown text) and the *General Chemistry* CD-ROM (included with your other main text, *Chemistry and Chemical Reactivity*, Kotz and Treichel, 5th edition). These CD-ROM references are not essential to learn this course, but we *highly* recommend their use to gain a better understanding of the principles involved.

Some topics have been expanded from these prescribed materials, and others given lesser emphasis or even omitted. This reflects *our* philosophy regarding the relative importance of the various aspects of organic chemistry to be covered in the unit.

The ordering adopted is based on that which has been found to be successful in teaching the internal unit. This permits the introduction of new topics and concepts to be used as a revision of earlier parts of the unit. Nonetheless, the endpoint arrived at is essentially the same as that of the prescribed text.

In the beginning........

Friedrich Wöhler expressed a view of organic chemistry with which some newcomers to the discipline might have some sympathy. In a letter to Jons Jacob Berzelius in 1835, he wrote:

"Organic Chemistry just now is enough to drive one mad. It gives me the impression of a primeval tropical forest, full of the most remarkable things; a monstrous and boundless thicket, with no way of escape, into which one may well dread to enter".

Berzelius in 1808 had been involved in the isolation and study of chemicals derived from living sources; the view at the time was that such "organic" substances as they were known could not be synthesised in the laboratory from "inorganic" materials, because it was believed that a "vital force" which was possessed only by living organisms was necessary to produce organic compounds.

This "Vital Force Theory" was challenged by Wöhler in 1828 when he heated the inorganic compound ammonium cyanate (NH_4OCN) and obtained *urea* which was recognised as being "organic" because it could be isolated from urine.

A few years later August Kekulé assigned the modern definition of organic chemistry - *organic compounds are those containing carbon.*

Likewise Leopold Gmelin in 1848 defined organic chemistry as "the chemistry of the compounds of carbon which occur naturally". This definition is too restrictive, however - although many organic compounds are of natural origin, the great majority owe their existence to the endeavours of academic and industrial chemists. Some may only have been synthesised in milligram quantities (or less!) whereas others are manufactured annually on the scale of millions of tonnes.

And let us not forget that all living matter is constructed of a multitude of (mainly very complex) organic chemicals and that life processes are the reactions of these chemicals.

In 1848 Wöhler was to write:

"The Philosopher of Chemistry will draw the conclusion that the production of all organic matters in our laboratories, in as much as they do not belong any more to the organism, must be regarded not only as probable but as certain. It is true we do not know the methods by which this final result will be reached, because the rudiments are unknown from which they are to be developed, but we shall know them in time".

A magnificent statement for 1848!

Wöhler indicated various target natural products, among them morphine: 80 years were to elapse before the structure of morphine was elucidated and a further 20 years before its synthesis was achieved.

How can we succeed?

What is the best way to study organic chemistry? In many ways it can be likened to learning a new language, and like the use of language communication is both oral and written.

The written component of the organic chemistry language is the structural formula, but while one can frequently get by with an ungrammatical sentence, a badly drawn (ungrammatical?) structure is useless.

The structure of a compound determines its reactivity, so the need for accuracy in drawing structures is paramount. This accuracy can only be achieved by practice with pen on paper: the task is rather like learning multiplication tables in primary school-eventually the correct structure will (we hope) be drawn automatically. Even professional chemists started this way and they communicate extensively by drawing structures. At least the written language is universal!

Production of correct pictures needs precision in drawing which leads to precision in thinking.

Why is carbon so special?

Read
Brown, Chapter 1.1 – 1.4

It is a characteristic of carbon that it forms strong covalent bonds with other carbon atoms, and with certain other elements, particularly hydrogen (carbon and hydrogen differ in electronegativity by only 0.4 on the Pauling scale). The **carbon - carbon bond energy** for a single bond is around **350 kJmol^{-1}**. This is among the strongest of covalent bonds between like atoms of any element.

Carbon can also form *multiple* **bonds**, that is, *double* and *triple* bonds readily.

General Chemistry CD-ROM Screen 11.3

The first point allows carbon to form an enormous variety of **chains** and **rings**, and this is the reason for the diversity of organic compounds. There are more than 10 million compounds listed in Chemical Abstracts, and most of these are organic. Fortunately we can classify them into a few dozen families. This classification is based on structural entities which have a chemical reactivity that is roughly predictable - so-called **functional groups**. We won't cover them all, but by the end of the course the principles will be well apparent to you.

Two of the simplest examples, both containing carbon chains are:
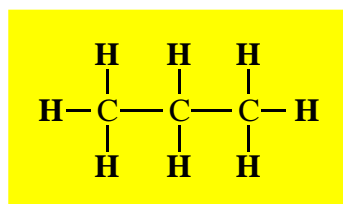

propane

and
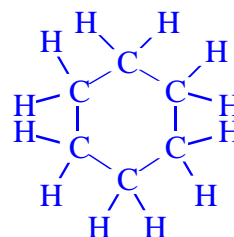
cyclohexane

Both these are **hydrocarbons** (as is methane), i.e. they contain only carbon and hydrogen.

Note that carbon is *tetravalent* in all cases, i.e. it forms four bonds to other atoms. In the above two examples some valencies are satisfied by bonding to other carbons and others by bonding to hydrogen.

As we have seen, Lewis structures of methane shown below are shorthand for the actual arrangement of atoms, which is a tetrahedron with angles of 109.5° between hydrogens. So not only is carbon tetravalent, but the four bonds have a definite orientation.

The arrangement in space about the central carbon can be explained in very simple terms. Each covalent bond contains two electrons and constitutes a region of negative charge. Since four such regions in space must repel one another, they will be as far apart as possible and this puts the hydrogens at the corners of a tetrahedron.
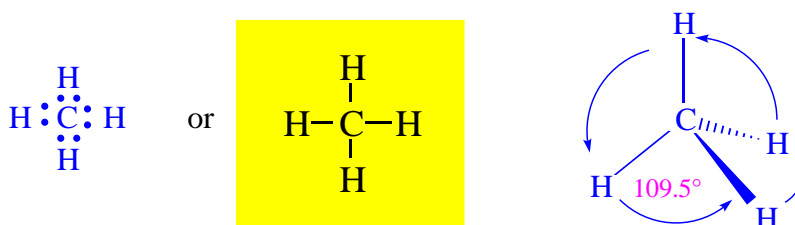
This principle, termed the *valence-shell electron pair repulsion (VSEPR)* model, has been dealt with in previous Modules.
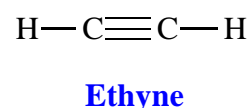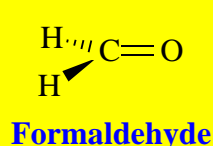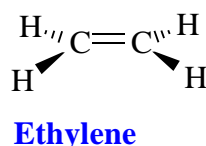
As you have also seen, carbon can form bonds in other ways. In double-bonded molecules such as **ethylene** and **formaldehyde** it lies at the centre of a triangle, while in triple-bonded molecules such as ethyne or in carbon dioxide it has a linear arrangement of bonds. VSEPR can explain these arrangements too but understanding of such geometries *and their chemistry* requires more understanding of the carbon valence shell and the concept of **hybridization.**

Self-Test Exercise 3.1

Complete *Practice Problem 1.8*, p.17 Brown:

(a)

(b)

(c)

A chemist's shorthand

Note that so far we have represented some structures mostly in two dimensions. This is adequate for many purposes, but often we need a more accurate representation in three dimension. *It is important to always remember that molecules are three-dimensional*! In methane, since the carbon is tetrahedral, the bond angles are all equal at 109.5°:

$109.5°$
tetrahedral bond angle
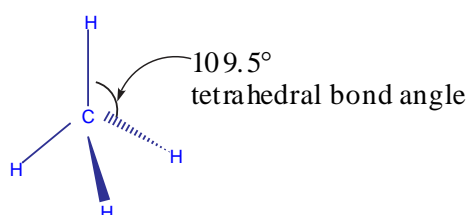
——— **represents a bond in the plane of the page**

◢ **represents a bond in front of the page**

⦙⦙⦙ **represents a bond behind the page**

You have reviewed the different ways of depicting chemical structures in previous Modules. It is worth reviewing the different depictions before closing this section.

General Chemistry CD-ROM Screen 3.4

There are other means of denoting structures, which are often written for convenience. Taking ethane as an example, its *empirical formula*, CH_3, represents its simplest form of elemental composition, i.e. that carbon and hydrogen are in the **ratio 1:3**. Empirical formulas are not very informative.

Ethane's *molecular formula* is C_2H_6. This is of course much more useful as it tells us the *actual number* of atoms in the molecule. However, the *structural formula* is even more informative, as it shows the bonding arrangement in the molecule.

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H$$
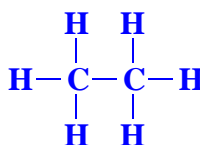
A disadvantage is that it takes time and space to write full structural formulas for every molecule we are discussing, and indeed Lewis structures take even longer.

Therefore we often use a ***condensed formula***:

$$CH_3-CH_3, \quad \text{or even more simply,} \quad CH_3CH_3$$
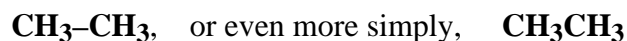
With larger molecules (and with some more experience) chemists will condense these even further!   They will use *skeletal* structural formula:

e.g. pentane, C_5H_{12}, or $CH_3CH_2CH_2CH_2CH_3$ will often be represented by

i.e. with only the bonds (and no atoms!) shown in a zig-zag, which implies tetrahedrality. The ends and angles represent carbon atoms, and the lines represent C–C bonds; the hydrogens and their bonds to the carbons are omitted completely! It is understood that there are **enough hydrogens to satisfy the tetravalency** on each carbon.

Resonance formulas depict structures which, together, best describe a particular electronic structure. These are dealt with in Chapter 1.5 of Brown.

Topic Highlights

You should be able to:

❏   recognise the broad features that lead to the diversity of carbon compounds;

❏   understand that carbon can form chains, rings, bond to atoms other than hydrogen and engage in different bonding arrangements.

Topic 3B - Bonding in carbon compounds

Key questions

How can carbon bond in three different geometries? How do three orthogonal p-orbitals and an s orbital allow this to happen? The answer lies in VB theory or, better still, MO theory. How does this theory enable carbon to bond, not only to hydrogen as in methane, but to other carbons and other elements as well?

Outline

You have dealt with much of this topic in the previous Topic 2C. If you are not yet comfortable with the concept of hybridization you should review this Topic again.

Valence bond models and hybridization

Read
Brown Chapter 1.6

sp^3 Hybridization — why carbon is tetravalent:

Carbon has an outer electronic configuration of $2s^2 2p^2$. However, carbon does not use these orbitals in bonding. By promotion of an electron from the 2s orbital to the vacant 2p orbital followed by **hybridization**, four equivalent orbitals are obtained - each lower in energy than the 2p orbitals, each containing one electron and each resembling a distorted 2p orbital.

*General Chemistry CD-ROM Screens 10.4, 10.5*
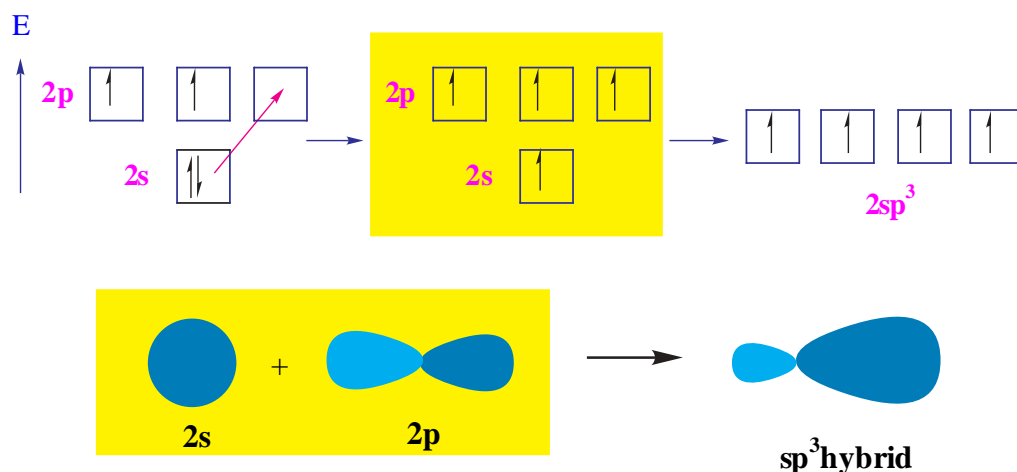
The **four equivalent** electrons can take part in the formation of strong covalent *single* bonds with other atoms. Carbon is said to be **sp^3 hybridized** (we omit the 2) when forming **single bonds** in this way.

Repulsion between the bonding pairs dictates that they must have maximal separation; thus, for four bonds around carbon, the carbon must be **tetrahedral**

in the same way that ammonia is tetrahedral at nitrogen and water is tetrahedral at oxygen.

Thus the **Valence Bond** description of the bonding in methane can be represented by covalent bonding between the appropriate sp^3 hybrid orbitals on carbon with 1s orbitals of each of four hydrogens (the reverse, smaller lobes of the hybrid orbitals are not shown for simplicity):
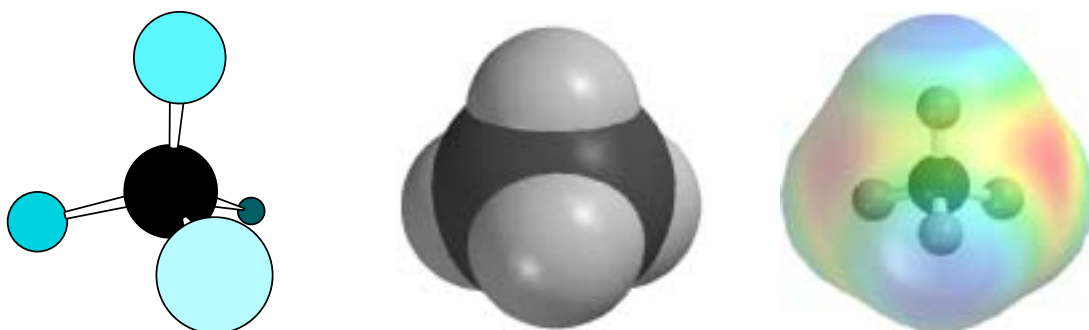

methane
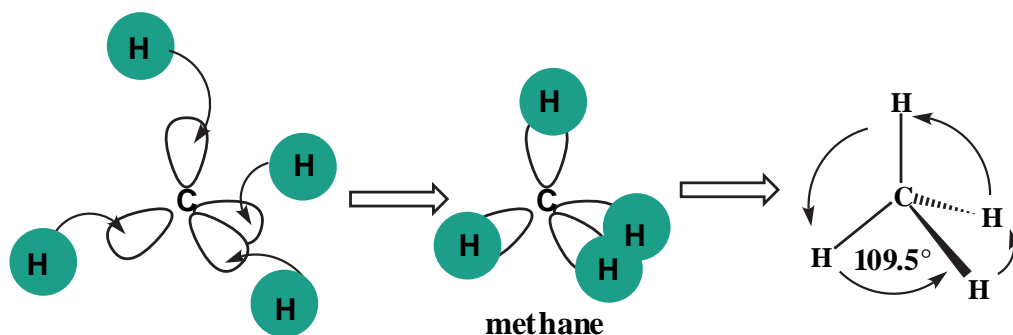
Each C–H bond has one electron from the 1s orbital of hydrogen and one from an sp^3 *hybrid* orbital of carbon.

In reality the hydrogen 1s and the sp^3 hybrid orbital are no longer separate identities and they combine to form a **sigma (σ) bonding molecular orbital** which encompasses both atoms and contains two electrons.
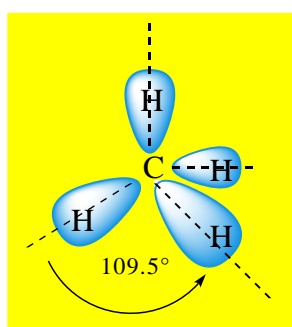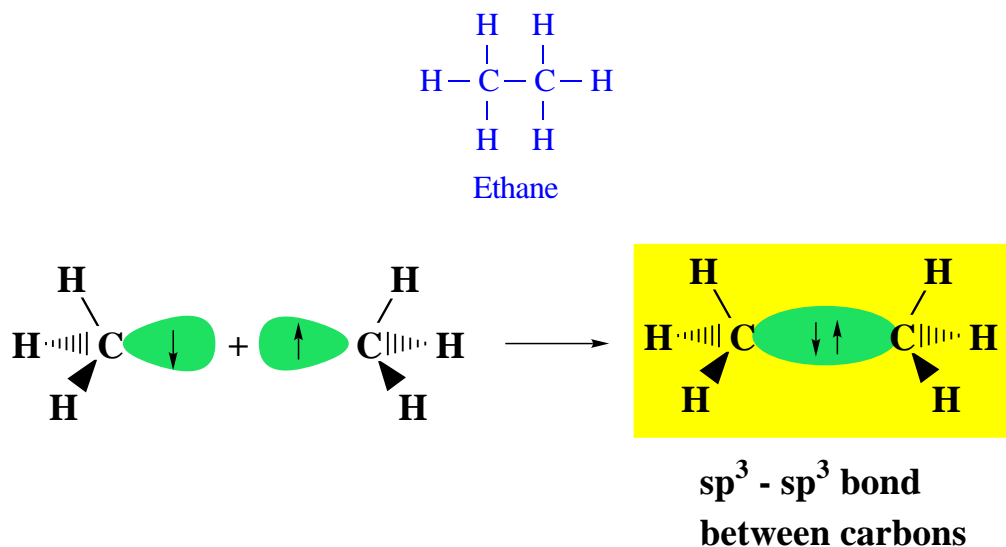

Methane

Two other representations of methane are shown below. The first is a 'ball and stick' model while the middle one is a more realistic 'space filling' model which fits the overall electron density surface that may be calculated and is shown on the right.

In **ethane** each carbon utilises three sp^3 hybrid orbitals in a similar fashion, but a C–C bond is formed by *end-on overlap* of two remaining carbon sp^3 orbitals:

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H$$
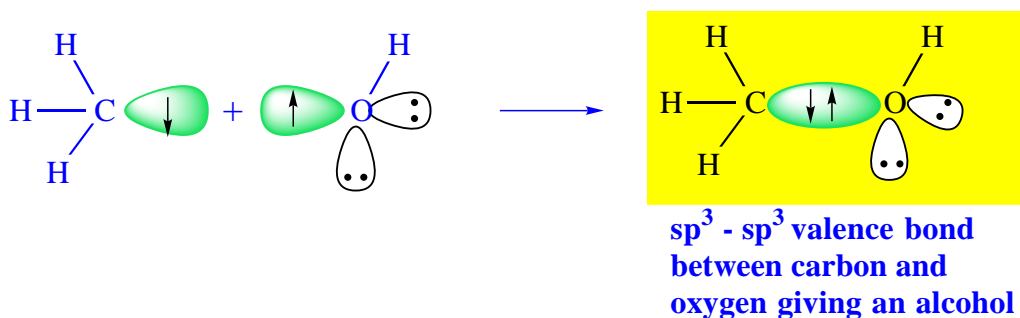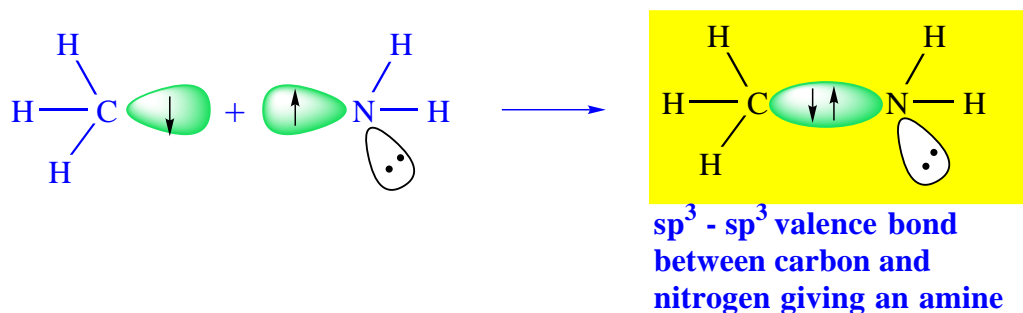
Ethane

sp^3 - sp^3 bond between carbons

Ball-and-stick and space-filling models of the ethane molecule are shown below:
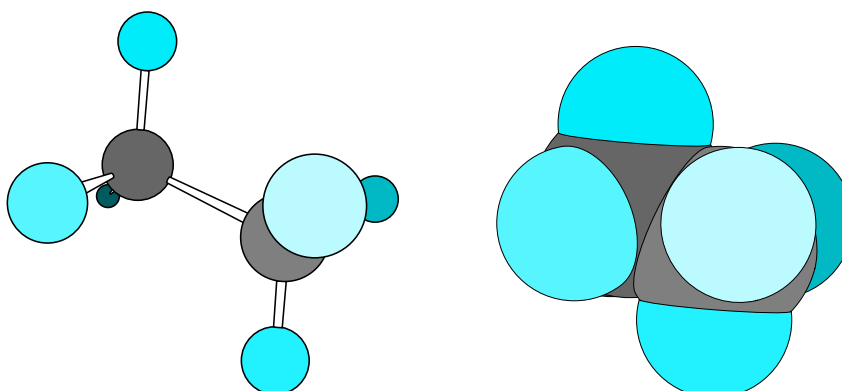
Naturally, three and more carbons can link up giving longer chains, so-called **alkanes**, which we will deal with in Topic 3B.

This process is not limited to bonding between carbon atoms. Sp^3 hybridised carbon and nitrogen, or carbon and oxygen, can covalently bond together in similar fashion to ethane:

sp^3 - sp^3 valence bond between carbon and oxygen giving an alcohol

sp^3 - sp^3 valence bond between carbon and nitrogen giving an amine

Thus, not only can pure carbon-hydrogen substances be made (called hydrocarbons), but also other types of organic molecules such as alcohols and amines (and many more).

sp2 Hybridisation — bonding in alkenes:

There are two other ways in which carbon (as well as oxygen and nitrogen) can hybridise - **sp^2 and sp hybridisation**, which result in **double** and **triple bond** formation.

The simplest organic molecule with a carbon-carbon double bond is ethene, represented by the structure below.


Ethene (carbon sp^2)
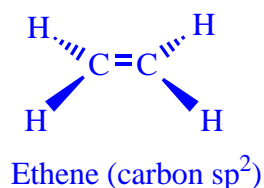
In sp^2 hybridisation, **only two of the 2p orbitals (2p$_x$ and 2p$_y$)** become hybridised with the **2s** orbital. This produces **three** identical sp^2 hybrid orbitals of lower energy than the 2p$_z$ orbital, which remains unaltered in shape and energy:
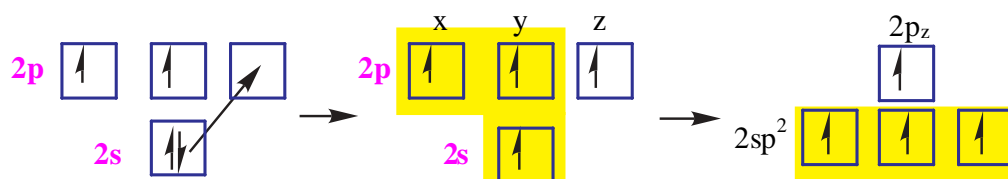
So for the valence electrons of each carbon atom, three are in the sp^2 orbitals and the one remaining is in the 2p$_z$ orbital. The three sp^2 hybrid orbitals minimise electron repulsion by spreading apart in the *xy* plane at angles of 120° around the carbon atom.

sp² hybrid

C2p$_z$

sp² hybrid

sp² hybrid

120°

An sp² hybridised carbon atom.
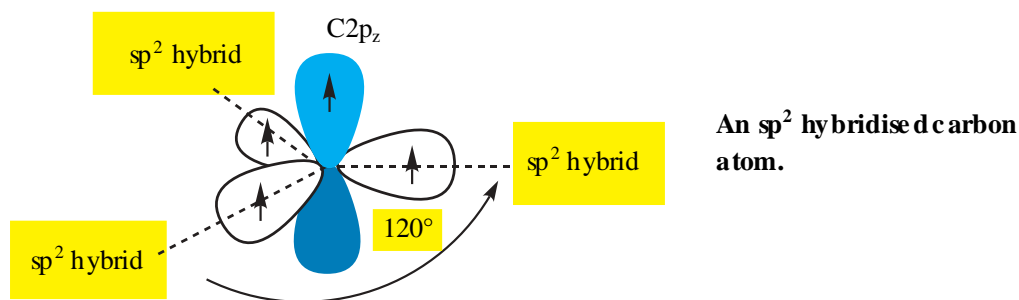
As we have seen, σ bonding of each carbon in ethene involves the sp² electrons forming two **C–H σ-bonds** and one **C–C σ-bond**:


C2p$_z$

C2p$_z$
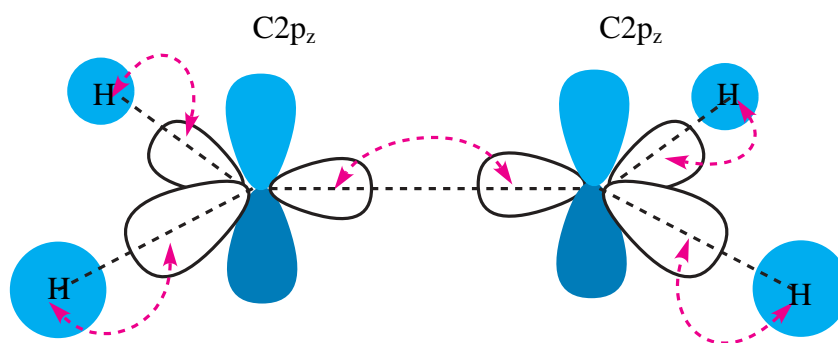
General Chemistry CD-ROM Screen 10.7

The *second C–C bond* is formed by the less efficient sideways overlap of the remaining p-orbitals, giving a second bond between the two carbons - **a π (pi) - bond**:


C2p$_z$

C2p$_z$

H

H

H

H

CC σ-bond
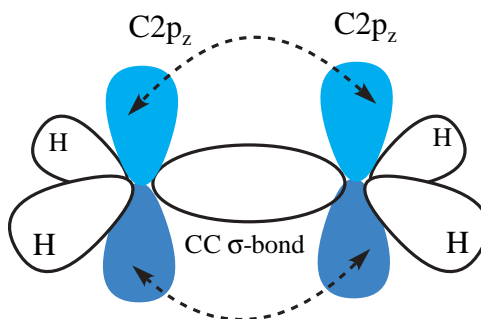
MO theory of π-bonding in ethylene gives us, by the usual overlap of two atomic orbitals (in this case 2p$_z$ orbitals), a pi-bonding molecular orbital, **π**, lower in energy; and a pi-antibonding molecular orbital, **π***, higher in energy then the constituent 2p$_z$ orbitals. The two electrons originally from the C2p$_z$ orbitals go into the lower energy π-bonding molecular orbital and become more stable. It is this increased stability that makes the formation of a π-bond favourable.

One $\pi*$-molecular orbital

One π-molecular orbital
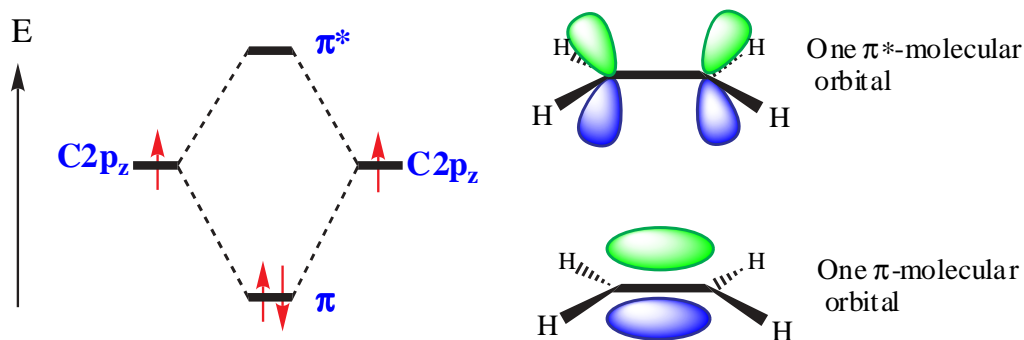
A space-filling drawing of ethene and the computed electron density surface illustrates the planarity of the molecule, as well as the π-electron density between the carbon atoms above and below that plane:
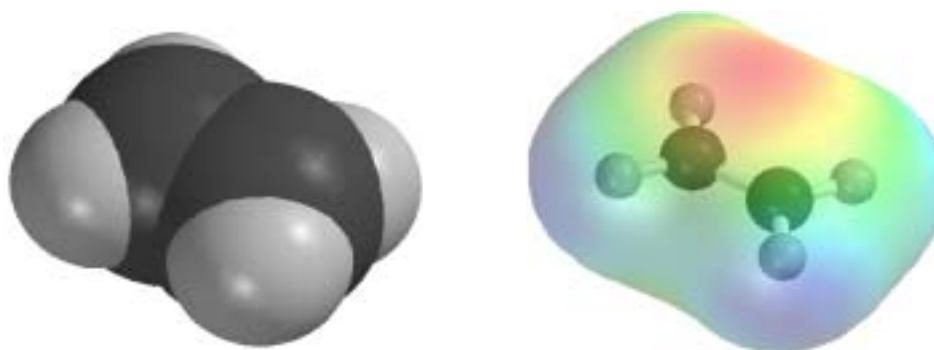

Ethylene is invariably written as:
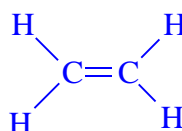
This implies that both bonds in the double bond are identical, but it must be remembered that they are not the same and that there is an sp^2-sp^2 **σ bond** and a p_z—p_z **π-bond**.

The consequence of this bonding is that the carbon and hydrogen atoms are in a **planar** arrangement, with bond angles of approximately 120° as expected from a **trigonal planar geometry**. However, the differences in electronegativities of C and H mean that there is some slight distortion from the ideal geometry. In addition, the CC double bond is significantly shorter than the CC single bond:
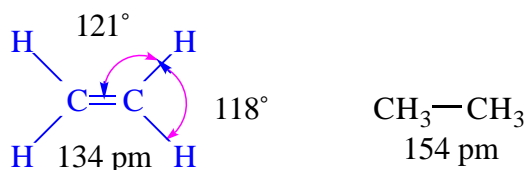
Other heteroatoms can also hybridise in an sp^2 fashion to enable double bond formation. You have already seen how a carbon—oxygen double bond can form in **formaldehyde**. Carbon-nitrogen double bonds can also form from sp^2 hybridised carbon and nitrogen in **imines:**
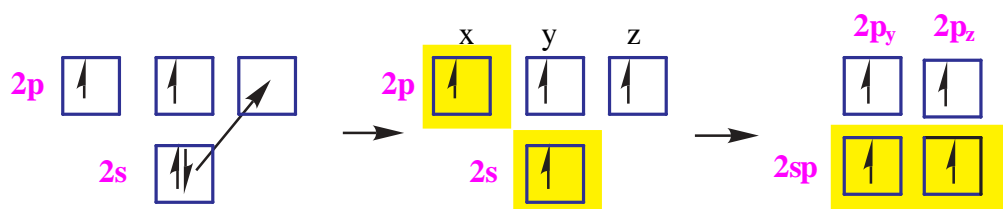

Formaldehyde   An imine
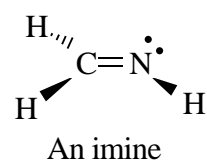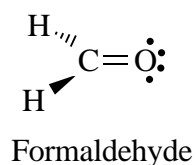
Sp hybridization - bonding in alkynes:

Alkynes contain C—C triple bonds. The simplest alkyne is *ethyne*:

$$H–C≡C–H$$

A third manner in which carbon can hybridise is shown below, and results in formation of **sp** hybrid orbitals leaving *both* the $2p_y$ and $2p_z$ orbitals unchanged:

To minimise electron repulsion these orbitals are colinear (angle of 180°):

An sp hybridised carbon atom
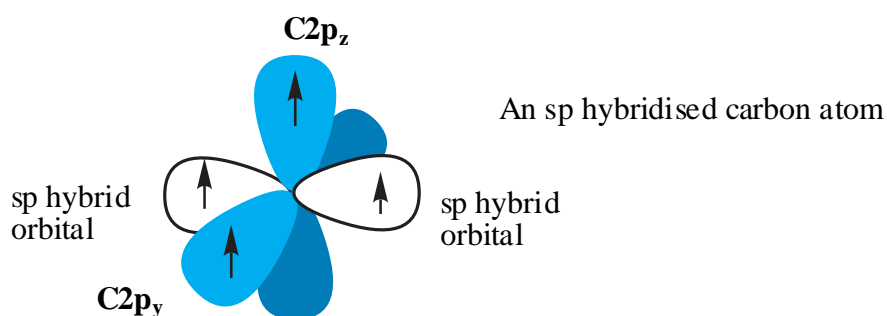
For the bonding in ethyne we have the **sp** electrons of each carbon forming one **C–H σ-bond** and one **C–C σ-bond**:
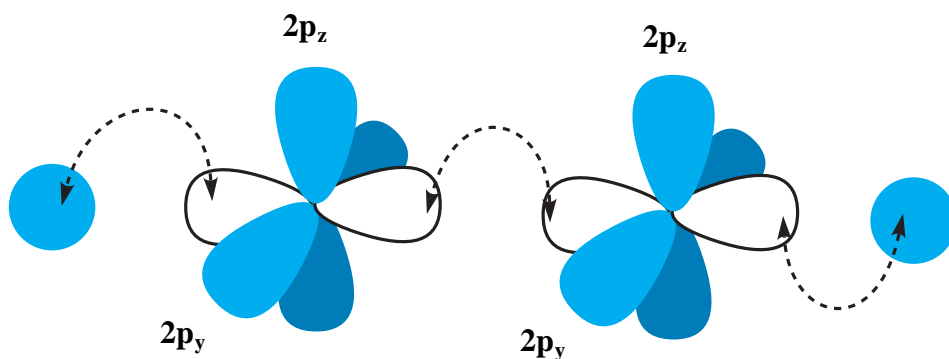
Alkynes are characterised by a carbon-carbon **triple bond** comprising the **carbon-carbon σ-bond** from overlap of sp orbitals on the two carbons and **two**

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weaker π bonds, π_z and π_y formed by overlap of two sets of perpendicular p-orbitals:
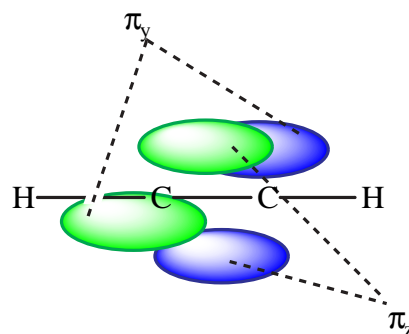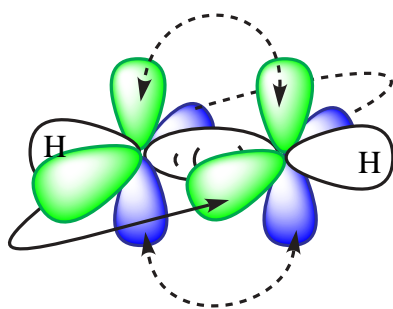
This results in a barrel of electron density around the σ-bond. A space-filling model and the electron density surface depicts this clearly:
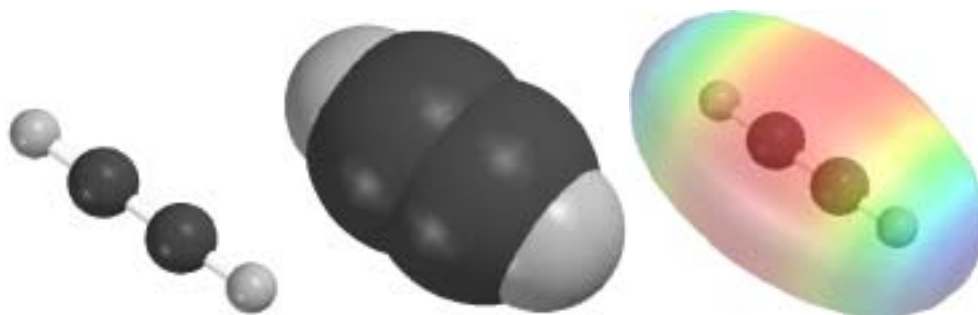
The two carbon atoms and the two atoms attached to the triple bond form a *linear* arrangement.

Triple C—C bonds are stronger than double bonds, which are in turn stronger than single C—C bonds. Bond length decreases from single to double to triple bond, and bond strength increases from single to double to triple bond.
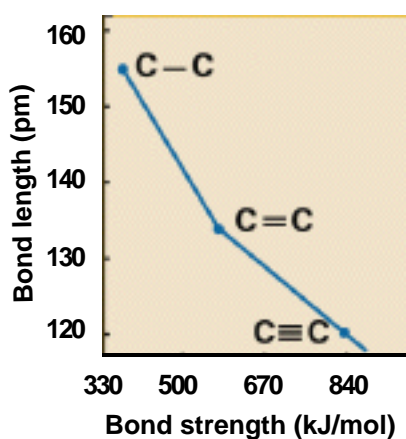
In **nitriles**, a triple bond is formed between carbon and nitrogen:

Acetonitrile
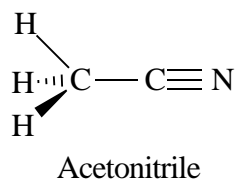
Self-Test Exercise 3.2

Complete *Practice Problem 1.12*, p.27 Brown:

(a)

(b)

Topic Highlights

You should be able to:

❏   reproduce the ways in which carbon hybridises and how it uses these hybridisations to from single, double and triple bonds both with itself and with other heteroatoms (oxygen and nitrogen);

❏   understand the trends in properties of carbon-carbon single, double and triple bonds, such as bond length and energy;

❏   draw and understand the various representations of hydrocarbon structures.

Topic 3C - Alkanes

Key questions

Alkanes; hydrocarbons; saturated hydrocarbons. What are these? Why are they so prevalent, and what are their structural features and their chemical properties? In this section we will explore the simplest class of organic substances.

Outline

Alkanes constitute the first class of organic substances we will discuss in this module. Each section of the module from this one, 3C, will deal with a particular class of organic chemicals. There will be more detail than is to be found in Kotz and Treichel and there will be many more examples of structures and nomenclature but this is essential to enable you to progress further to CHEM120.

Introduction

> **Read**
> **Brown Chapter 3.1 – 3.3**

There are various subdivisions in the classification of hydrocarbons. One family of hydrocarbons is called the **alkanes**, or sometimes **paraffins** (from the Latin *parum affinis*, meaning "little affinity" and thus implying a lack of reactivity) or **aliphatics** (from the Greek word *aleiphar* meaning "fat or oil"). They are also called **saturated hydrocarbons**. This means that they are saturated with *hydrogen,* and that they do not react with hydrogen. We will see the significance of this later.

Constitutional or structural isomerism:

We encountered methane and ethane in Section 3B. Propane is the next one in the series. Here the central carbon is bonded to two other tetrahedral carbons:

Methane	CH_4	
Ethane	CH_3CH_3	C_2H_6
Propane	$CH_3CH_2CH_3$	C_3H_8

So far, we can consider this progression from methane to propane as a stepwise *replacement of a hydrogen by a* CH_3 - this is called a **methyl group**.

In methane and ethane all the hydrogens are identical, so it is immaterial which one is replaced by a methyl group. In propane however, the two hydrogens on

the central carbon are obviously in a different environment to those on the end carbons:

$$CH_3CH_2CH_3$$

2 identical hydrogen atoms

differently situated hydrogen atoms

6 identical hydrogen atoms
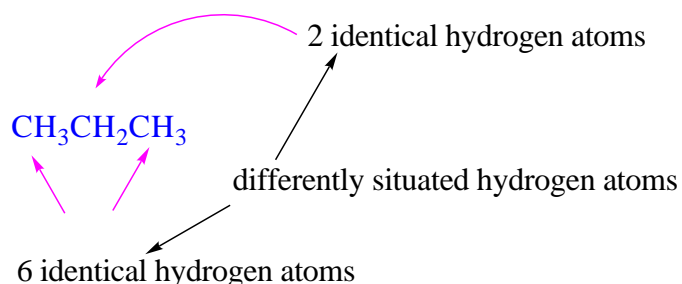
When we come to the next alkane after propane (butane, which has four carbons and has a molecular formula C_4H_{10}) we can derive two different structures by the replacement of a hydrogen atom by a methyl group giving:

$$CH_3CH_2CH_2CH_3$$ butane or *n*-butane

and

$$CH_3CHCH_3$$
$$|$$
$$CH_3$$ isobutane

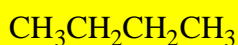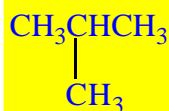Note that these alkanes have the same *molecular formula*, but different *structural formulas*. ('*n*-' indicates a normal straight chain arrangement while the '*iso*-' indicates an arrangement containing a $(CH_3)_2CH-$ group).

These isomers are called **constitutional or structural isomers** and have differing physical and chemical properties.

This indicates another reason why there are so many organic compounds - except for a few simple members in each family, constitutional isomerism multiplies the number of structural possibilities for a given molecular formula. When the carbon atoms of a hydrocarbon are linked end to end, we refer to them as being **straight chain** compounds; a better description is **unbranched chain** to distinguish **branched chain** possibilities.

At this stage you might notice a trend occuring in the molecular formulas; all alkanes that are open chain (not rings) have the **general formula C_nH_{2n+2}**, where **n** is an integer. All the carbons in the chain are bonded to two carbons and two hydrogens - except for the terminal carbons, where an extra hydrogen is needed to satisfy the tetravalency.

Now consider the next highest member of the alkane family, pentane C_5H_{12}.

Thus $CH_3CH_2CH_2CH_2CH_3$ is pentane or *n*-pentane, and we also have

$$CH_3CHCH_2CH_3$$
$$|$$
$$CH_3$$

and

$$CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_3$$
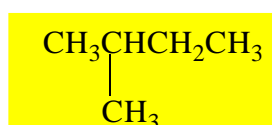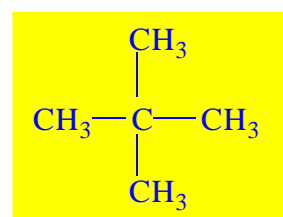
isopentane

neopentane

which are constitutional isomers of pentane, having the same molecular formula C_5H_{12}.

For C_6H_{14} there are five constitutional isomers, for C_7H_{16} there are nine, and for $C_{10}H_{22}$ there are seventy five! It should be apparent that very soon we would run out of distinguishing prefixes *and* the ability to remember their application.

For $C_{40}H_{82}$ we can calculate that there are 62×10^{12} constitutional isomers! Although very few of these have been synthesised or isolated from natural sources, the very possibility of their existence illustrates the enormous scope of organic chemistry.

Self-Test Exercise 3.3

Complete *Practice Problem 3.1*, p.58 Brown:

(a)

(b)

Self-Test Exercise 3.4

Complete *Practice Problem 3.2*, p.58 Brown:

Nomenclature

How do we name this multitude of alkanes, and indeed all organic compounds?

If they were given individual, unrelated names we could never derive the structure from the name; nor could we remember which structure fitted which name. Although so-called *trivial names* are known for many organic compounds, they are used colloquially and where it is simplest. There is however a **systematic nomenclature** system that chemists use. This has been drawn up by the International Union of Pure and Applied Chemistry (IUPAC) and is internationally accepted as the standard. As a basic premise, under this system one name fits one structure, and each name identifies a structure unambiguously.

A systematic name consists of three parts:
- a *prefix*
- a *stem* identifying the longest carbon chain
- a *suffix* to identify the type of compound.

Naming alkanes:

A **suffix** -*ane* on the name of an organic compound indicates an **alkane**.

The main part of the name, or **stem**, gives an indication of the particular alkane on which the name is based and indicates the number of carbon atoms in the longest carbon chain present in the compound:

For a stem of	**1C**	we use the stem name **meth**
	2C	**eth**
	3C	**prop**
	4C	**but**
	5C	**pent**
	6C	**hex**
	7C	**hept**
	8C	**oct**
	9C	**non**
	10C	**dec**

Stems are available for more carbons, (any number you may wish), and we will meet some of these as we progress, although ten carbons is enough for the level of a first-year course.

Before the stem name, a **prefix** indicates a **substituent** (a substituent may be regarded as a group replacing hydrogen in the parent alkane).

Both the **nature and position** of a substituent must be indicated and are included in the name.

Examples will indicate the application of the concepts used - further necessary features will become obvious as we progress. For example,

$$CH_3$$
$$|$$
$$CH_3CH_2CH_2CH_2CH_2CH_3$$

is an alkane with 6 carbons in its longest chain, ∴ *hexane*

Now number along the chain to give the **lowest number for the position of the substitutuent.**

$$CH_3$$
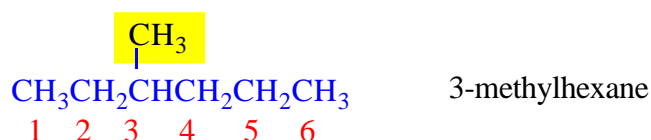$$CH_3CHCH_2CH_2CH_2CH_3$$
$$1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6$$
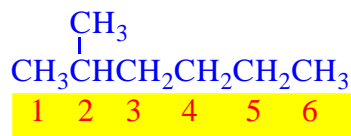
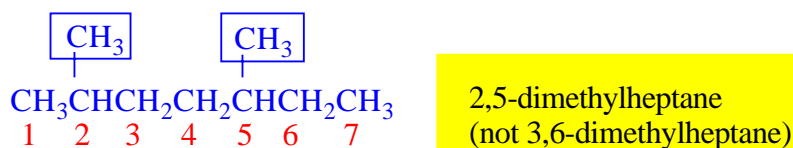Next name the substituent and indicate its position (by a prefix)

∴   the correct and unambiguous name is **2-methylhexane**

The name of the prefix *methyl* comes from methane: it is an alk**yl** substituent.

The compound we have named is *different* from and *isomeric* with

$$CH_3$$
$$CH_3CH_2CHCH_2CH_2CH_3 \qquad \text{3-methylhexane}$$
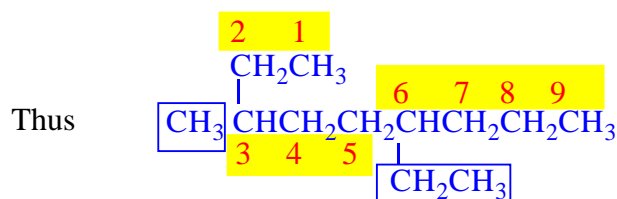$$1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6$$

For multiple substituents we give each substituent a number to indicate its position, and indicate how man*y* substituents by the appropriate prefix:

$$\boxed{CH_3} \qquad \boxed{CH_3}$$
$$CH_3CHCH_2CH_2CHCH_2CH_3 \qquad \text{2,5-dimethylheptane}$$
$$1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \qquad \text{(not 3,6-dimethylheptane)}$$

We operate similarly for tri-, tetra-, and higher substitution.

We arrange different substituents in alphabetical order:

$$2 \quad 1$$
$$CH_2CH_3$$
$$6 \quad 7 \quad 8 \quad 9$$
Thus $\boxed{CH_3}\,CHCH_2CH_2CHCH_2CH_2CH_3$
$$3 \quad 4 \quad 5$$
$$\boxed{CH_2CH_3}$$

is named 6-**e**thyl-3-**m**ethylnonane
(**e** comes before **m** alphabetically)

Note the punctuation: a "hyphen" separates numbers from words (i.e., the substituent and the parent alkane), words are linked and not broken with spaces. Remember that we must still use the lowest numbers of any possible choices. Note that, as in the preceding example, the longest carbon chain is not always written horizontally: this is usually simply a printer's convenience or sometimes a lecturer testing students! Try rewriting the structure with the longest carbon chain horizontal.

The multiplier "di" is not considered in the alphabetizing. Hence, the name of the following alkane is 5-ethyl-2,3-dimethylheptane:

$$CH_3CHCHCH_2CHCH_2CH_3$$

with CH_3 above (boxed), CH_3 and CH_2CH_3 below (boxed)
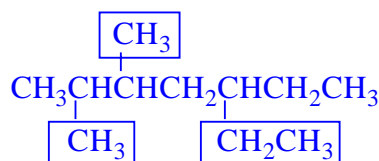
Note the punctuation: - a comma separates the numbers.

An isomer of this compound is named 5-ethyl-2,2-dimethylheptane:

$$CH_3\,C\,CH_2CH_2CHCH_2CH_3$$

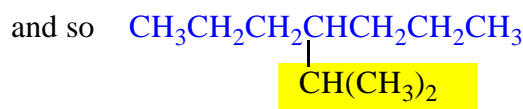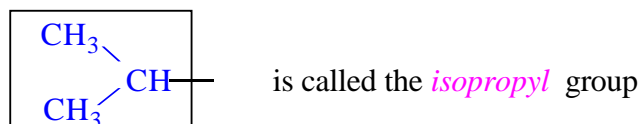with CH_3 above, CH_3 and CH_2CH_3 below
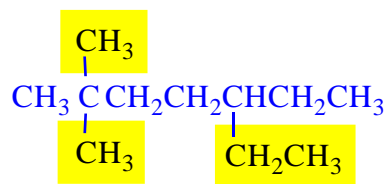
Here both the methyl substitutents are attached to carbon number 2, so we must repeat the "2" for a complete description.
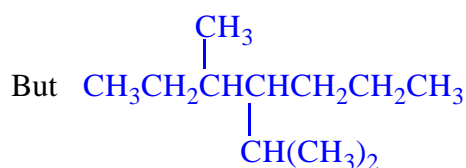
Note the simple relationship between naming alkanes and the corresponding groups as substituents. For any alk**ane**, the correponding group is termed an alk**yl** substituent.

CH_4	Meth**ane**	CH_3-	Meth**yl**
CH_3CH_3	Eth**ane**	CH_3CH_2-	Eth**yl**
$CH_3CH_2CH_3$	Prop**ane**	$CH_3CH_2CH_2$-	Prop**yl**
$CH_3(CH_2)_2CH_3$	But**ane**	$CH_3(CH_2)_2CH_2$-	But**yl**
$CH_3(CH_2)_3CH_3$	Pent**ane**	$CH_3(CH_2)_3CH_2$-	Pent**yl**
R-H	Alk**ane**	R-	Alk**yl**

Some trivial nomenclature is retained for simple branched substituents. Thus

$$\begin{array}{c} CH_3 \\ \diagdown \\ CH- \\ \diagup \\ CH_3 \end{array}$$ is called the *isopropyl* group

and so $CH_3CH_2CH_2CHCH_2CH_2CH_3$

with $CH(CH_3)_2$ below

is named 4-*isopropyl*heptane
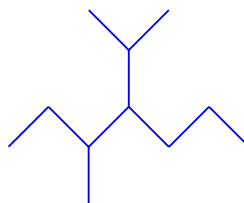
But $CH_3CH_2CHCHCH_2CH_2CH_3$

with CH_3 above and $CH(CH_3)_2$ below

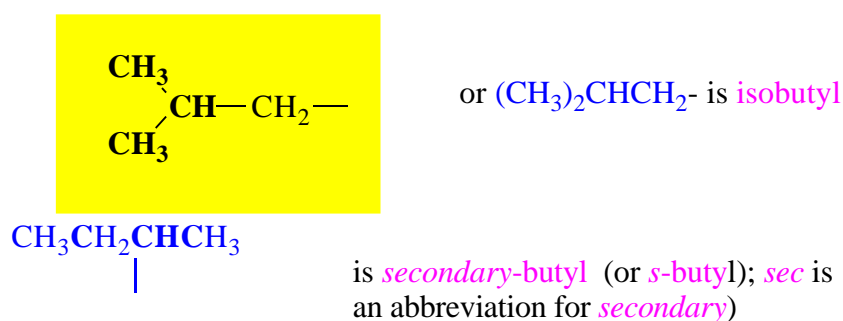is named 4-**i***sopropyl*-3-**m**ethylheptane

(Note the alternative representation of the isopropyl group).

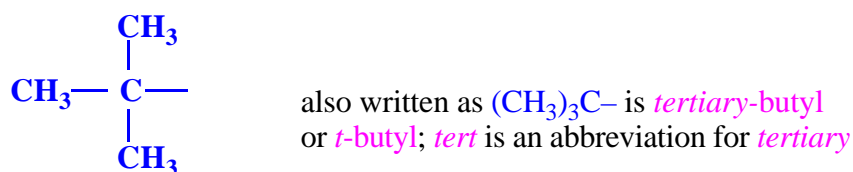We can represent the last formula as a skeletal formula:

This representation is much faster to write, but some familiarity is needed with the method before it will become second nature.

The other common trivially named substituents, are:

$$CH_3$$
$$\diagdown$$
$$CH-CH_2-$$
$$CH_3 \diagup$$
or $(CH_3)_2CHCH_2$- is isobutyl

$CH_3CH_2\mathbf{CH}CH_3$ | is *secondary*-butyl (or *s*-butyl); *sec* is an abbreviation for *secondary*)

and

$$CH_3$$
$$|$$
$$CH_3-C-$$
$$|$$
$$CH_3$$
also written as $(CH_3)_3C-$ is *tertiary*-butyl or *t*-butyl; *tert* is an abbreviation for *tertiary*

This leads us to a convention for describing and naming **substituent groups**:

$$CH_3$$
$$|$$
$$CH_3-C-$$
$$|$$
$$CH_3$$
← **tertiary (3°)**: 3 carbons bonded to carbon attached to chain

$$H$$
$$|$$
$$CH_3-C-$$
$$|$$
$$CH_3$$
← **secondary (2°)**: 2 carbons bonded to carbon attached to chain

$$H$$
$$|$$
$$CH_3-C-$$
$$|$$
$$H$$
← **primary (1°):** 1 carbon bonded to carbon attached to chain.
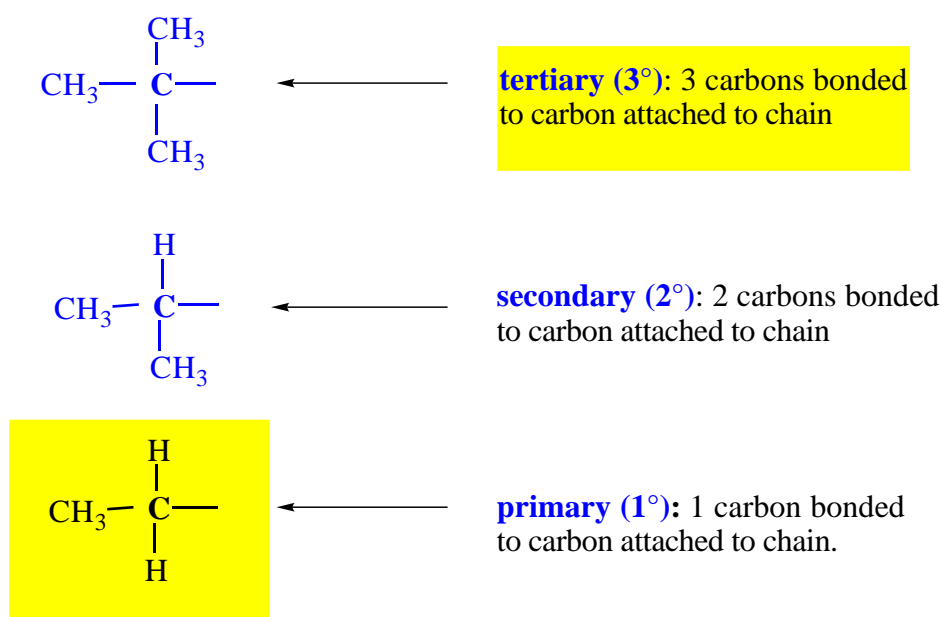
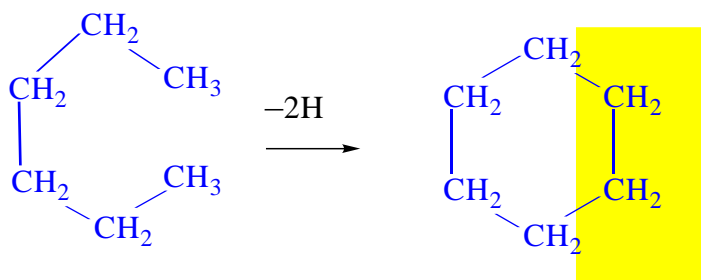# Ring structures - cycloalkanes

Read
Brown Chapter 3.4 – 3.7

In addition to straight-chain or branched hydrocarbons, terminal carbons can be joined together to form rings. In *ring* structures the prefix *cyclo-* indicates presence of a ring of carbon atoms. Such compounds are termed **cycloalkanes**. These have the general formula C_nH_{2n}. Examples are:

cyclobutane formed from butane:
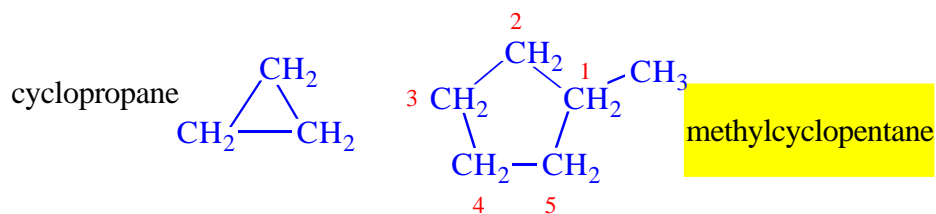
$$CH_3 \quad CH_3 \qquad -2H \qquad CH_2—CH_2$$
$$| \qquad | \qquad \longrightarrow \qquad | \qquad |$$
$$CH_2—CH_2 \qquad\qquad\qquad CH_2—CH_2$$
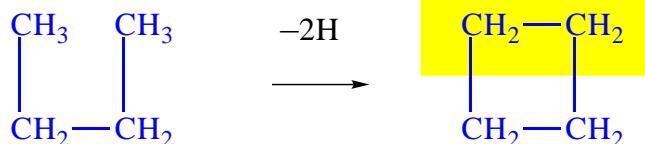
cyclohexane formed from hexane:

(structure of hexane) $-2H$ → (structure of cyclohexane)

And a few more:

cyclopropane

methylcyclopentane

Note that as all carbons are identical in the above examples, we don't need to number them. However, sometimes numbering is necessary to define the name unambiguously and the convention is to assign the position bearing the substituent as **1**. Where more than one substituent is on the ring, the positions of the substituents must be specified in the name, e.g.
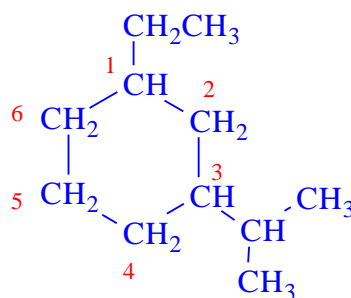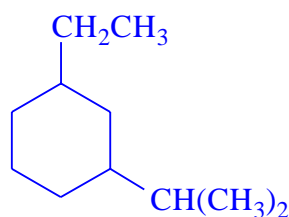
is 1-ethyl-3-isopropylcyclohexane. Note how we number around the ring so as to give the substituents the lowest number.

Skeletal structures are more commonly used for cyclic compounds - the above examples become:
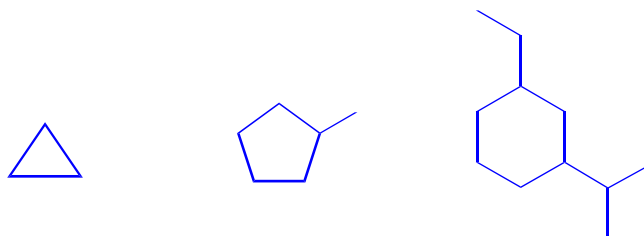
alternatively, hybrids of the two conventions are often used, e.g.

CH_2CH_3

$CH(CH_3)_2$

From the above and your reading of Chapter 3.6, you will notice that not all cycloalkanes are planar (flat). Angle strain forces cyclopentane into an "envelope" shape, and a cyclohexane ring is puckered into a "chair" shape. However, cyclopropane, cyclobutane and also cyclopentane **are** planar.

Rings can present two faces (an upper and a lower face), and substituents on the ring can be on the same face or opposite faces. This is designated by naming them "*cis*" and "*trans*" isomers.

Examples:

Cis-1,2-dimethylcyclopropane   Trans-1-ethyl-3-methylcyclohexane
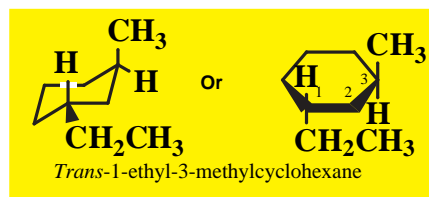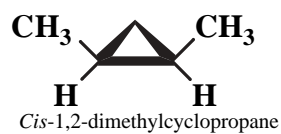
Note that rings as substituents are treated in the same way as other alkanes:

Ring	Group
Cyclopropane	Cyclopropyl-
Cyclobutane	Cyclobutyl-
Cyclopentane	Cyclopentyl-
Cyclohexane	Cyclohexyl-

Self-Test Exercise 3.6

Complete *Practice Problem 3.4*, p. 64 Brown:

(a)

(b)

Properties of the alkanes

> **Read**
> **Brown Chapter 3.8 and 3.9 (for interest)**

Physical properties of alkanes and cycloalkanes:

Alkanes are colourless and water-insoluble. Their boiling point increases with molecular weight, e.g.

	CH_4	$n\text{-}C_4H_{10}$	$n\text{-}C_7H_{16}$	$n\text{-}C_{10}H_{22}$
bp (°C)	– 162	0	98	174

Table 3.4 in Brown (p.78) shows the states of various alkanes at room temperature. Note that the lower molecular weight alkanes are gases.

Unbranched hydrocarbons have higher boiling points than their branched isomers. For example:

$CH_3(CH_2)_3CH_3$

bp 36°

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

bp 10°

The unbranched chain alkanes can align themselves more closely, and hence can develop stronger intermolecular forces and associations than are possible when branching of the chain is present. The greater the association between the molecules, the higher the boiling point

Compare the neatly packed nonane with its constitutional isomer 2,3,4-trimethylhexane:

Nonane
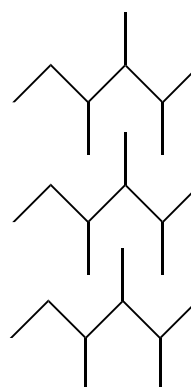
2,3,4-Trimethylhexane

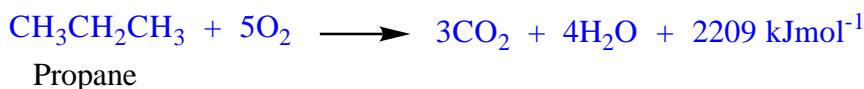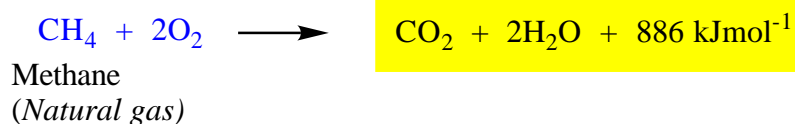## *Chemical properties of alkanes and cycloalkanes:*

As their alternative name 'paraffin' implies, alkanes are inert to most common chemical reagents, including:

- Strong acids
- Strong alkalis
- Oxidising agents (under normal laboratory conditions)
- Halogens (in the dark)

Candle wax and petroleum jelly (Vaseline) are two high formula weight alkanic compounds that you are familiar with. Apart from their combustibility they are pretty stable and unreactive chemicals. As far as laboratory chemists are concerned, alkanes are often considered a synthetic dead end! However, both of the latter two reactions are performed daily on an enormous scale:

Oxidation:

The combustion (burning) of alkanes is a familiar phenomenon:

$$CH_4 \; + \; 2O_2 \; \longrightarrow \; CO_2 \; + \; 2H_2O \; + \; 886 \; kJmol^{-1}$$

Methane
(*Natural gas*)

$$CH_3CH_2CH_3 \; + \; 5O_2 \; \longrightarrow \; 3CO_2 \; + \; 4H_2O \; + \; 2209 \; kJmol^{-1}$$

Propane

Similar equations can be written for petrol, which is being oxidised in enormous quantities daily in internal combustion engines. Petrol consists mainly of a complex and variable (depending on its source) mixture of alkanes.

While complete combustion of petrol would normally form just carbon dioxide and water, in reality limited oxygen supplies leads to incomplete combustion and the formation of the toxic gas carbon monoxide and carbon (soot).

Another important industrial oxidation reaction of alkanes can be represented by

$$CH_3\!-\!CH_3 \;\; - \;\; 2H\bullet \; \xrightarrow[\text{catalyst}]{\text{heat}} \;$$
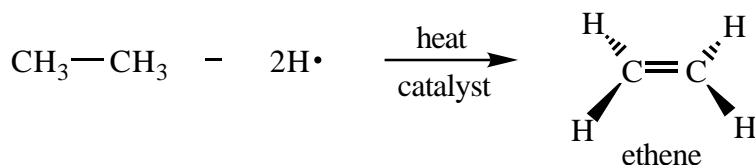
ethene

Ethene is an *alkene;* we will consider this latter reaction's significance and the chemistry of alkenes (another family of hydrocarbons) later.
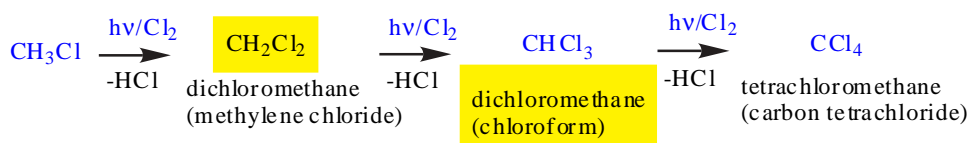
Reactions with halogens:

> This section is not covered specifically in *Brown*, but we will introduce it here. As well as being an important reaction of alkanes it will introduce us to *haloalkanes*, which we will be dealing with in greater detail later in the unit.

The simplest representative alkane, methane, reacts with chlorine when heated or in the presence of visible light:

$$CH_4 + Cl_2 \xrightarrow[\text{light (h}\nu)]{\Delta} \boxed{CH_3Cl} + HCl$$

chloromethane
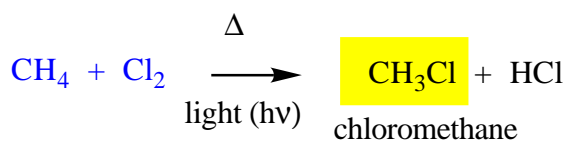
Note that this reaction (and the oxidation reactions) needs the input of energy - either electrical, thermal, or radiant (the symbols Δ and $h\nu$ are used to indicate that the reaction is heated or irradiated, respectively).

After the first hydrogen atom has been replaced, the reaction can proceed further:

$$CH_3Cl \xrightarrow[\text{-HCl}]{h\nu/Cl_2} \boxed{CH_2Cl_2} \xrightarrow[\text{-HCl}]{h\nu/Cl_2} CHCl_3 \xrightarrow[\text{-HCl}]{h\nu/Cl_2} CCl_4$$

dichloromethane   dichloromethane   tetrachloromethane
(methylene chloride)   (chloroform)   (carbon tetrachloride)

We have given both the systematic and (in brackets) trivial names for the products.

In practice, we would expect to get a mixture of products by chlorination of methane gas, and indeed we do. It is possible to separate the products by utilising their difference in boiling points, via **fractional distillation**.

Molecular fluorine, bromine and iodine can undergo the same reaction with light but F_2 is explosively reactive and I_2 barely reacts at all.

Halogenation of Other Alkanes:

Chlorine will also react by the same mechanism with other alkanes. For example with ethane:

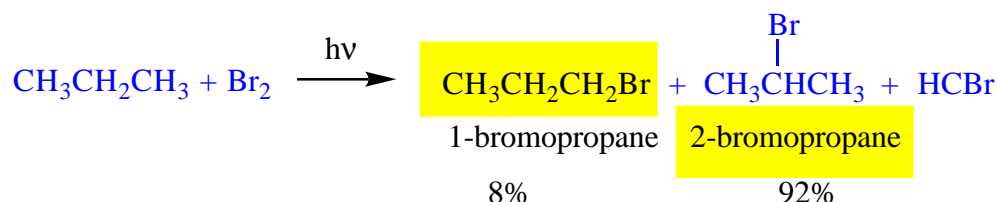$$CH_3-CH_3 \rightarrow CH_3CH_2Cl + HCl$$

chloroethane
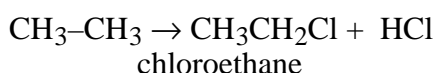
All the hydrogens in ethane are identical, so it is immaterial which one is abstracted initially. Thus there is only one product, but with further reaction we see now that all the hydrogens are not identical, and which product is formed will depend on which hydrogen is replaced.
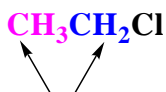
CH₃CH₂Cl

Two different sets of hydrogen

Thus we obtain two products, CH_3CHCl_2 (1,1-dichloroethane) and $ClCH_2CH_2Cl$ (1,2-dichloroethane). These dichloroethanes are constitutional isomers.

For propane, even the first halogenation step gives the possibility of two isomeric products:

$$CH_3CH_2CH_3 + Br_2 \xrightarrow{h\nu} CH_3CH_2CH_2Br + CH_3\overset{\overset{\displaystyle Br}{|}}{C}HCH_3 + HCBr$$

<div align="center">

1-bromopropane   2-bromopropane

8%   92%

</div>

Bromine is said to be **regioselective** in this reaction, preferring to replace the secondary hydrogen much more than a primary hydrogen (a regioselective reaction is a reaction in which one region of the molecule is more reactive than another, thus leading to selective product formation).

In this reaction, two different types of C–H bonds are broken and the relative amounts of product are dependent upon three factors:

1. The ease with which the different kinds of hydrogens react with the halogen;
2. The number of each kind of hydrogen in the molecule;
3. The type of halogen.

Factor two is easy to understand. The more hydrogens there are of any one type, the greater is the probability of the halogens reacting with them.

<div align="center">

2 secondary H's

CH₃CH₂CH₃

6 primary H's

</div>
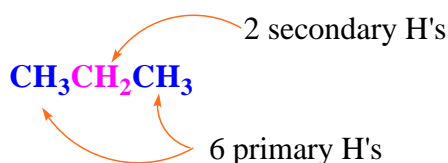
Thus the chlorine atom has greater chance of colliding with a primary hydrogen than a secondary, so that more 1-chloropropane should be produced. *Not only is collision between molecules of importance, but collision between certain parts of molecules can also have relevance in the course of a reaction.*

Since in the above reaction less replacement of the more numerous hydrogens occurs, this clearly cannot be the only factor of importance. To understand how Factors (1) and (3) affect the product *regioselectivity* we have to look a little deeper at the reaction processes that are involved. How does the halogenation reaction proceed? What is its mechanism? Indeed what *is* a mechanism?

How reactions happen – mechanisms:

A mechanism is a theory that must explain the observed experimental facts and must predict results for other analogous reactions. We cannot really hope to absolutely prove a mechanism but we can eliminate alternatives that are not in accord with the facts. As new experimental data emerge, the failure of predictions can give insight into a more correct mechanism.

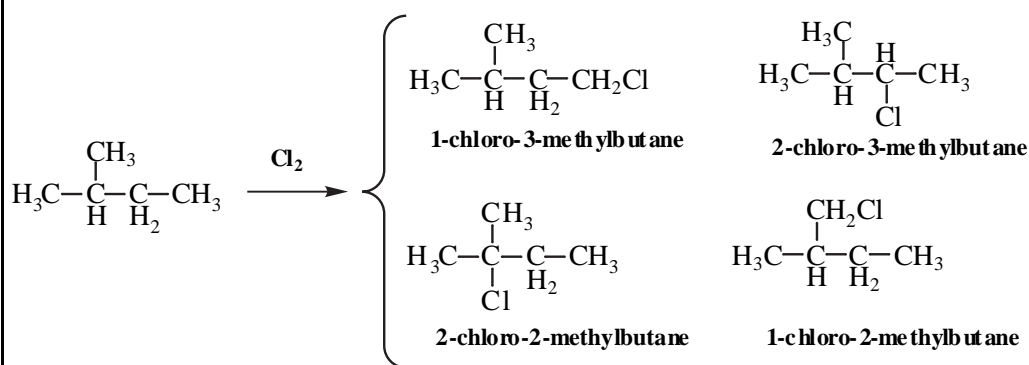It is easiest to start by stating the obvious. In an organic reaction:
- we break bonds and form bonds, and
- these bonds are covalent; electron pairs are involved

It is the sequence in which bond breaking and bond formation occurs as well as how the energy of the system changes during a process which defines the mechanism of a reaction. We will deal with a more mechanistic approach to some of the reactions described in this course in CHEM120.

Draw and name all the possible products from monochlorination of 2-methylbutane (isobutane) using Cl_2 in the presence of a light source:

Answer:

$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{}{}}{\underset{\underset{\displaystyle H_2}{|}}{C}}-CH_2Cl$

1-chloro-3-methylbutane

$H_3C-\overset{\overset{\displaystyle H_3C}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-CH_3$

2-chloro-3-methylbutane

$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-\overset{}{\underset{\underset{\displaystyle H_2}{|}}{C}}-CH_3$

2-chloro-2-methylbutane

$H_3C-\overset{\overset{\displaystyle CH_2Cl}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{}{\underset{\underset{\displaystyle H_2}{|}}{C}}-CH_3$

1-chloro-2-methylbutane

Topic Highlights

You should be able to:

❏   Draw structural formulas of alkanes and cycloalkanes, and understand how to generate different **structural isomers**;

❏   understand and be able to use the IUPAC nomenclature system for naming unbranched, branched, substituted alkanes and cycloalkanes;

❏   recognise **primary, secondary** and **tertiary** carbons;

❏   recognise that cycloalkanes can have *cis* and *trans* substituents;

❏   understand the effect of structure on the physical properties of alkanes;

❏   write equations for the combustion of simple hydrocarbons in oxygen;

❏   draw and name products from free radical chlorination of alkanes.

Topic 3D - Alkenes and Alkynes

Key questions

How do we name compounds with C—C double and triple bonds? What are the structural consequences of the strength of the double bonds? Double bonds are reactive because the pi-electrons are not as tightly bound as σ-electrons. What sorts of reactions do alkenes undergo? Do triple-bonded hydrocarbons, so-called *alkynes*, react similarly?

Outline

Once again the texbook provides the framework for this topic but we will go into somewhat more detail on certain aspects than is found in the text. This additional material should be understood to be a part of the syllabus and, unless where indicated, is examinable.

Bonding in alkenes

> **Read**
> **Brown Chapter 5.1**

In ethene, the **two carbon atoms are linked by a double bond where each carbon atom is sp^2 hybridised.**

In Module 2 and Topic 3B we looked at the bonding in ethene and learnt that a double bond is comprised of a σ-bond formed from overlap of two sp^2 hybrid orbitals and a π-bond formed by overlap of two $2p_z$ atomic orbitals.

Covalent bond formation in ethene (ethylene)
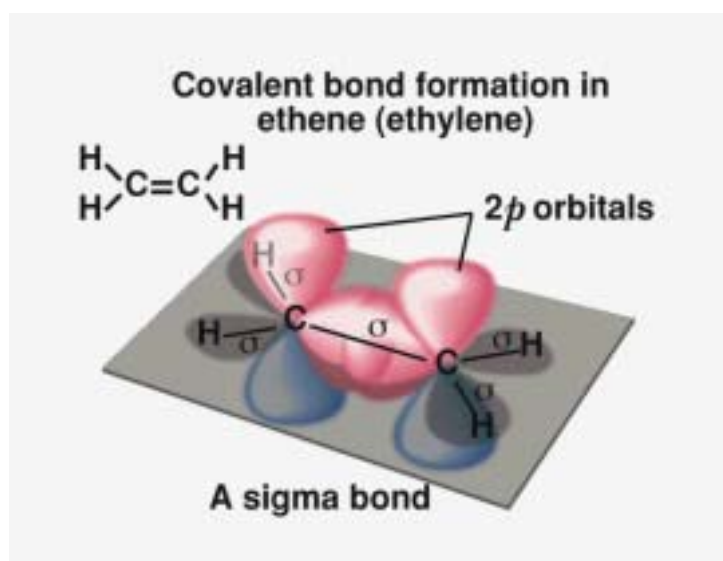
The difference in the **σ- and π-bonds** is reflected in their bond energies; the total C=C bond energy is 681 kJ mol^{-1}, but if it is assumed that the sp^2-sp^2

bond energy is not too dissimilar from a typical sp^3-sp^3 bond energy (for example in ethane), and thus estimated at 397 kJ mol^{-1}, then this leaves the **π-bond with a bond energy of 284 kJ mol^{-1}**. Thus the **π-bond is weaker** and consequently easier to break than the σ-bond. From this we would expect alkenes to be **more reactive than alkanes**. They are, and dramatically so! In simple terms, electrons in the p_z obitals on the carbon are higher in energy then the electrons in the sp^2 hybrid orbitals. Electrons in p-orbitals are **further from the nucleus** than s electrons and are less tightly bound. All the reactivity of alkenes can then be expected to involve these p_z electrons, or the π-bond.

Apart from bond length, another major difference between alkenes and alkanes is that in alkenes the bond is **rigid**, whereas in alkanes there is **free rotation** about the single bond. This can give rise to different **conformers** (arrangements) of alkanes:

"staggered" conformation   "eclipsed" conformation
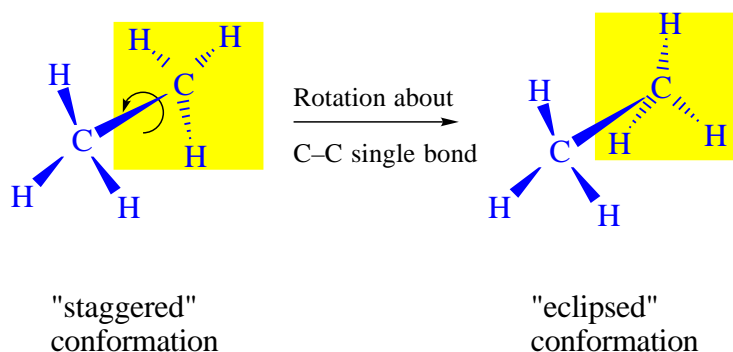
These structures represent the two extremes of the possible three-dimensional arrangements in which the "staggered" conformation is most stable (the C–H bonds, and hence their bonding electrons are as far apart as possible), and the "eclipsed" is least stable due to electrostatic repulsion of bonding electrons. However, the energy barrier to rotation is small (*ca* 11 kJmol^{-1}), and it is not possible to isolate the different conformers of simple alkanes; at room temperature rotation around the carbon–carbon single bond is very rapid (millions of rotations per second), and only an "averaged" structure can be identified. In other words, the thermal energy at room temperature is more than sufficient (much more) to overcome the barrier to rotation.

Conversely in **alkenes, a bond must be broken** to allow free rotation, so much greater energies are involved. In fact, **a chemical reaction (involving bond breaking and reformation) is the only way in which rotation around a C=C can occur**. In Module 2 you saw that the barrier to rotation about the **double** bond in 2-butene was 233 kJmol^{-1} (which is close to the 284 kJmol^{-1} calculated above).

Conceptually, the situation can be likened to two planks nailed together - a single nail (bond) allows free rotation, but two nails (bonds) fix the planks rigidly in place, and to rotate them requires removal of one of the nails (bond-breaking).

One nail
(bond)

Two nails
(bonds)

rigid

Geometrical isomerism:
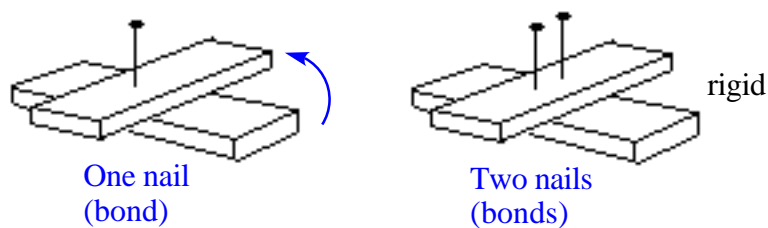
*Chemoffice
Web (Brown)
CD-ROM
Models 5.3–5.4*

This has important consequences for double bonded compounds with two *different* groups or atoms on *both* ends of the double bond.

Take a four-carbon system with a double bond between the middle two carbons: 2-butene. When we write out the structures in full, we see there are two possible arrangements or **configurations** of the substituents about the double bond:
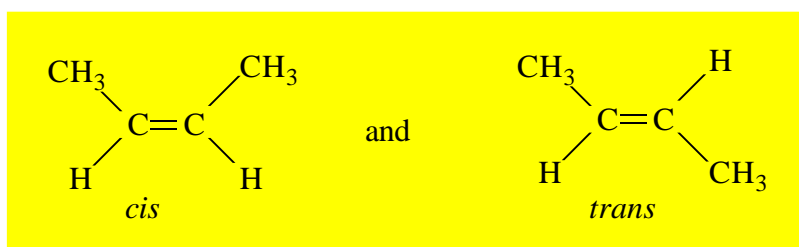
The methyl groups (and of course the hydrogens) may be on the *same side* or the *opposite side* of the double bond. Since a great deal of energy is needed to rotate around a double bond (at room temperature, and well above room temperature), these arrangements will not interconvert and the two forms are actually completely different molecules.

These *different compounds* need distinguishing names. We call the left-hand isomer *cis*-**2-butene** (from the Latin *cis* meaning **'same side'**) and the right-hand isomer *trans*-**2-butene** (from the Latin *trans*, meaning **'opposite side'**). For more complicated alkenes a more rigorous, **E/Z**, naming system is used.

Note that if only one carbon has different groups, geometrical isomerism is precluded.
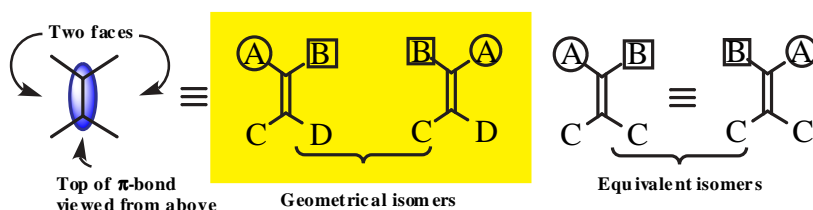
This is an example of what is known as **geometrical isomerism**. We observe **a** similar type of isomerism in **cycloalkanes**.

Rotation around a double-bond is critical in reactions that allow us to see. Vitamin A, also called retinol, isomerises to 11-*trans*-retinal, which in turn isomerises to 11-*cis*-retinal. This *cis* retinal reacts with a protein in the eye (opsin) to give a pigment called rhodopsin, which absorbs the blue-green frequencies of visible light.

Light striking the pigment triggers rotation around a carbon-carbon double bond, transforming rhodopsin into metarhodopsin II. The change in molecular shape causes a nerve impulse to be sent to the brain, which is translated into a visual image. Eventually (after 1/10 of a second) metarhodopsin II decomposes into 11-*trans*-retinal and the cycle begins again.

Another example of the importance of *cis* and *trans* isomers in living creatures is described in *Chemical Connections*, p. 130.

Nomenclature of alkenes and alkynes

Read
Brown Chapter 5.2

The same principles that were used for the naming of alkanes apply to alkenes. The suffix -*ene* is used to indicate an alkene. Thus prop**ene** is:

$$CH_3CH{=}CH_2$$

(note that this carbon is sp^3 hybridised)
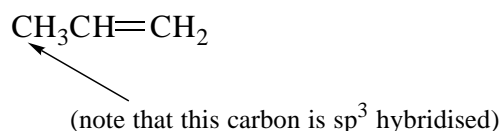
But for butene there are two structural isomers, as the double bond can be positioned between C(1) and C(2) or between C(2) and C(3).

Hence 1-but**ene** is:

$$CH_3CH_2CH{=}CH_2$$
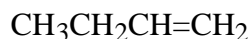
(Note that the name must be that with the lowest carbon number for the position of the double bond. Furthermore we only give the number of the lowest numbered carbon atom of the two that comprise the double bond).

$$CH_3CH{=}CHCH_3 \qquad \text{is 2-but\textbf{ene}}$$
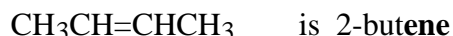
There is one minor variation from alkane nomenclature - in selecting the longest carbon chain we choose that which contains the double bond. Thus:

$$CH_3CH_2CH_2$$
$$\underset{CH_3CH_2CH_2CH_2}{}C{=}CHCH_3$$
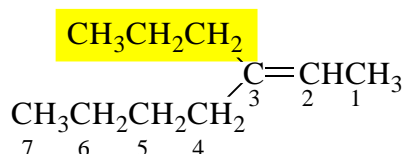
is named 3-propyl-2-heptene even though there is an 8 carbon chain in the compound.

### The E-Z system:

The geometrical isomers can be identified as **Z** (which stands for *zusamen*) or **cis,** and **E** (which stands for *entgegen*) or **trans** if one of the groups *on each carbon* is given preference. When these are on the same side we have the **Z-isomer** and when they are on opposite sides we have the **E-isomer**. A system of ranking substituents in preference (to be described in detail in dealing with

*General
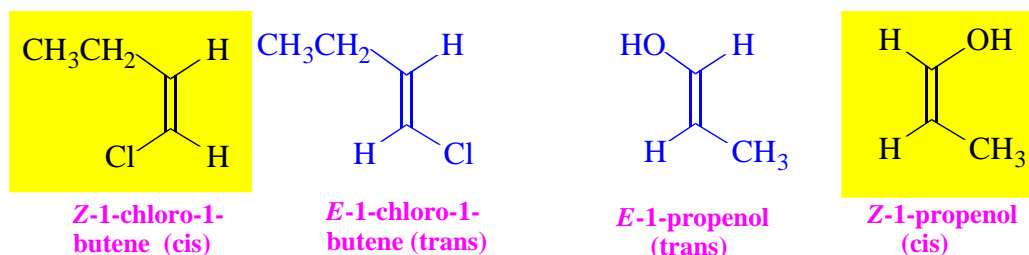Chemistry
CD-ROM
Screen 10.13*

optical isomers in CHEM120) is used, but when each carbon of the double bond bears a hydrogen, preference is always given to the other groups.

Thus for 2-butene the **Z**-isomer has both methyls on one face. The **E**-isomer has the methyls on opposite faces:

Z-2-butene
(cis)   **E-2-butene**
(trans)   **2-methyl-2-butene**
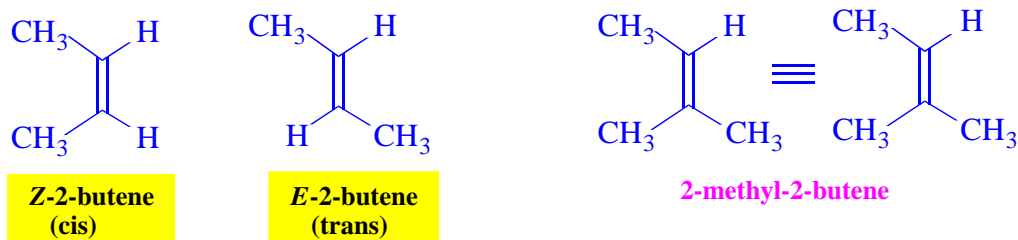
2-Methyl-2-butene does not display geometrical isomerism. In more complicated alkenes, the atomic number of the atoms directly attached to the end of the double bond are compared and that with highest atomic number has priority. If, at one end, the same atoms are directly attached, then we assign priority based on the atomic numbers of atoms attached to the first atom.
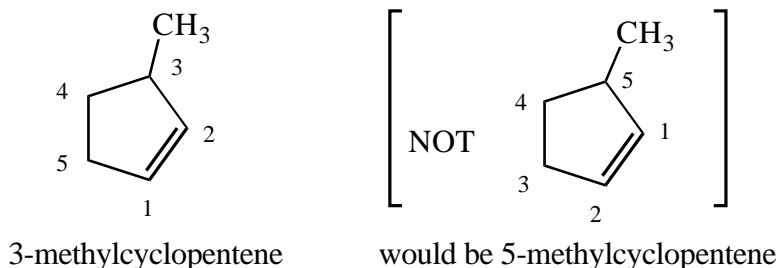
Other examples:

Z-1-chloro-1-butene (cis)   **E-1-chloro-1-butene (trans)**   **E-1-propenol (trans)**   **Z-1-propenol (cis)**
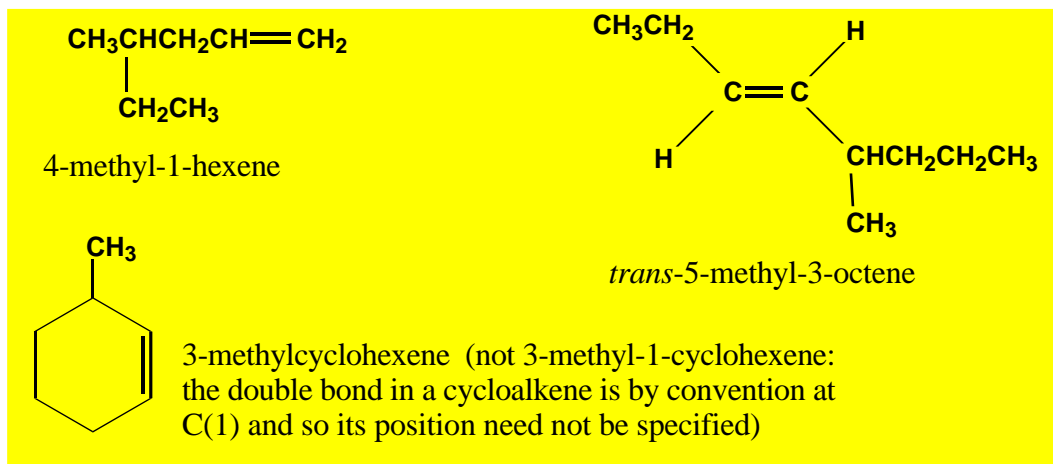
E-2 pentene is depicted in Screen 11.3 of the *General Chemistry* CD-ROM under alkenes. Also, the influence of rigid double bonds in "Unsaturated fats" is shown on the CD-ROM on Screen 11.7.

Geometrical isomers, of course, have different physical and chemical properties.

In **cycloalkenes**, the the carbon atoms of the ring double bond are numbered 1 and 2 in the direction of the nearest substituent so that the substituent is on the lowest numbered position in the ring.

3-methylcyclopentene   would be 5-methylcyclopentene

Some more examples of alkene nomenclature:

$CH_3CHCH_2CH{=}CH_2$

CH_2CH_3

4-methyl-1-hexene

trans-5-methyl-3-octene

CH_3

3-methylcyclohexene (not 3-methyl-1-cyclohexene: the double bond in a cycloalkene is by convention at C(1) and so its position need not be specified)

Naming alkynes:

The alkynes have a similar nomenclature to alkenes with the suffix *-yne* indicating the presence of a carbon-carbon triple bond. For example:

ethyne	$H–C{\equiv}C–H$
propyne	$CH_3–C{\equiv}C–H$
1-butyne	$CH_3CH_2C{\equiv}CH$
2-butyne	$CH_3C{\equiv}CCH_3$

Since alkynes are linear, unlike alkenes, they do not display *geometrical isomerism*.

Self-Test Exercise 3.8

Complete *Practice Problem 5.4* p.127-128 Brown:

(a)

(b)

(c)

Reactivity of alkenes

Although chemically reactive, alkenes are not particularly polar. Consequently, their physical properties are very similar to those of the alkanes.
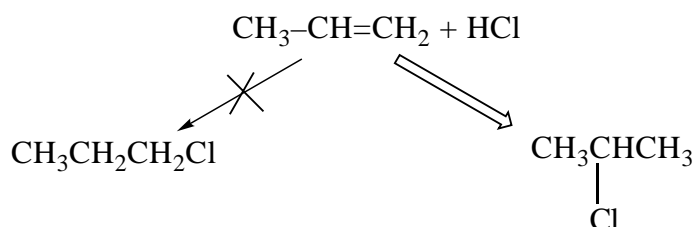
Addition of hydrogen halides:

Alkenes react with **hydrogen halides**.   For instance, HBr reacts with ethylene giving ethyl bromide or bromoethane (an alkyl halide).

$$CH_2\!\!=\!\!CH_2 \quad + \quad H\!\!-\!\!Br \quad \longrightarrow \quad CH_3\!\!-\!\!CH_2\!\!-\!\!Br$$
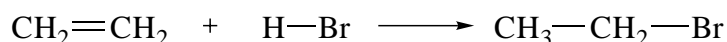
General Chemistry CD-ROM Screen 11.4

Similarly, hydrochloric acid might react with propene. Now we are posed with a problem: does the reaction of propene with hydrogen chloride yield 1-chloropropane or 2-chloropropane, or a mixture of the two?   Whatever the result, why?

$$CH_3\!\!-\!\!CH\!\!=\!\!CH_2 + HCl$$

$$CH_3CH_2CH_2Cl \qquad\qquad CH_3CHCH_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad Cl$$

In fact only the latter product is formed in this reaction. We can explain this because of the known mechanism of the reaction, which you will study in detail in CHEM120. For the purposes of this course, you need only remember that the hydrogen (the positively charged ion) **adds to the side of the double bond bearing the most hydrogens.** This is called "the Markovnikov Rule" after the chemist who discovered it.

Acid-catalysed hydration:

For the purposes of understanding this reaction, water can be regarded as [H^+ HO^-] and H^+ therefore adds to the end carbon while HO^- adds to the middle carbon.

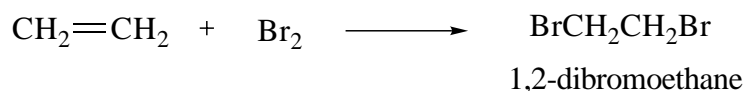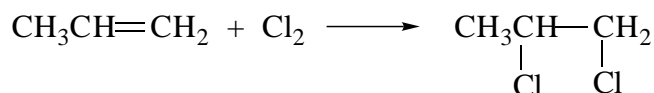Dilute sulfuric acid reacts in a similar manner and the reaction obeys Markovnikov's rule.

$$CH_3CH\!\!=\!\!CH_2 + H_2O \quad\xrightarrow{\text{ }H^+\text{ }}\quad CH_3CHCH_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

2-propanol
(an alcohol)
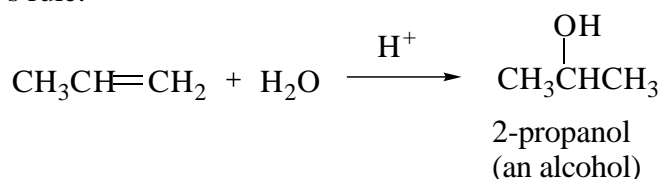
Once again the mechanism will be discussed later, in CHEM120.

Reaction with halogens (X₂):

Alkenes react readily with halogens *at room temperature* in an **addition reaction** (compare the reactivity of alkanes where halogens using light energy actually replace a hydrogen!)

$$CH_2{=}CH_2 \ + \ Br_2 \longrightarrow BrCH_2CH_2Br$$

1,2-dibromoethane

and

$$CH_3CH{=}CH_2 \ + \ Cl_2 \longrightarrow \underset{\underset{Cl}{|}}{CH_3CH}{-}\underset{\underset{Cl}{|}}{CH_2}$$

Both reactants are gases but the products are oily liquids; hence the older (and still used) name for alkenes - **olefin** (oil forming).

Actually the reaction with bromine proceeds by an unusual "**mechanism**" which you need not know for this course but serves as an example of a reaction that proceeds by a specific sequence of events. Initially a "**bridging bromonium ion**" is formed and the counter ion then attacks from the opposite face. In writing *mechanisms*, we illustrate the movement of electrons in forming and breaking bonds using double-headed arrows as shown below.
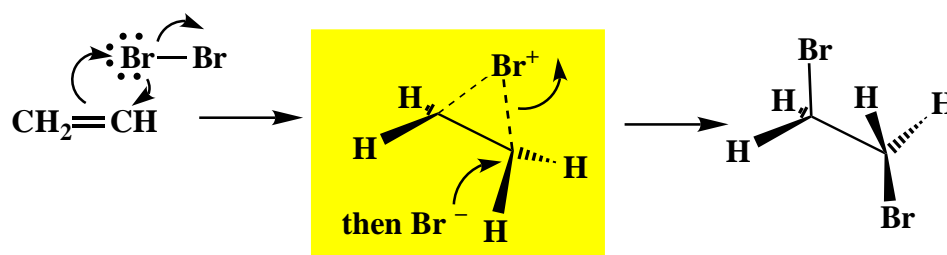
This mechanism is animated on Screen 11.4 of the *General Chemistry* CD-ROM.

A consequence of this mechanism, and good evidence for it, is that cycloalkenes always afford the *trans*-adduct:


trans-1,2-dibromocyclohexane
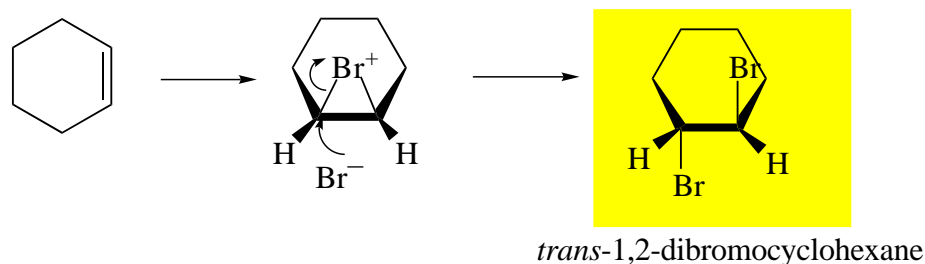
## *Hydrogenation of alkenes — a reduction reaction*

> **Read**
> **Brown Chapter 6.3A (p.150), B (p.156), C (p.158-159)**

Hydrogen can add across a double bond under certain circumstances and the reaction is exothermic ($\Delta H = -120$ kJ mol^{-1}), i.e. heat is evolved. But hydrogenation reactions typically have high energies of activation, so that an alkene and hydrogen will not react simply on mixing. The use of a catalyst (finely divided Pt, Pd, Ni, Rh, Ru usually adsorbed on charcoal) is required.

Catalytic hydrogenation proceeds in the following manner. Hydrogen is adsorbed on the surface of the metal, which weakens the H$_2$ single bond and the hydrogens become atom-like:
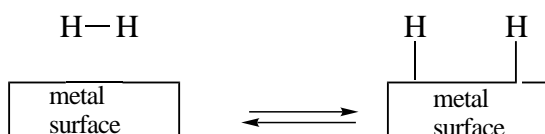
As the alkene approaches the surface the pi bond breaks and two C-H bonds form:
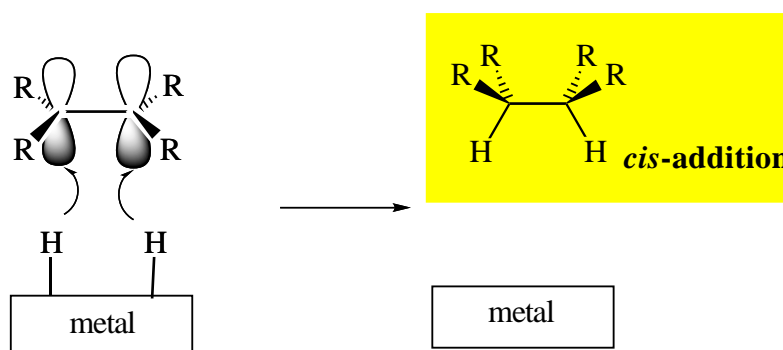
Note the use of **half-headed arrows** as hydrogen atoms are involved and each has one electron. Since hydrogen transfer occurs on the surface we get *cis*-addition. Also note that the symbol "**R**" represents a general organic group. You will see this used very often as a general representation of a molecule.

With a suitable substrate we can demonstrate the "stereochemistry" of the reaction:

cis-1,2-dimethylcyclohexane
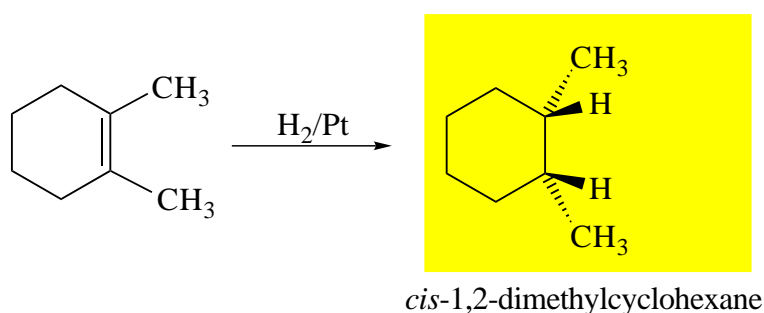
Since the hydrogen has added *on one face of the alkene*, the ***cis***- isomer is formed exclusively.

Self-Test Exercise 3.9

Complete *Practice Problem 6.6* p.159 Brown:
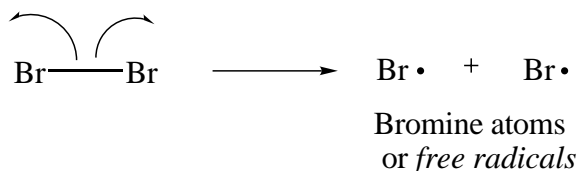
(a)

(b)

Polymerisation of alkenes

Read
Brown Chapter 15.5, p. 427-428

One of the most widely used industrial reactions today is free radical polymerisation of alkenes. An enormous variety of polymers are manufactured today but very many of these, so-called addition polymers, are made from alkenes. It is worth pausing here to describe exactly what a **free radical** is.
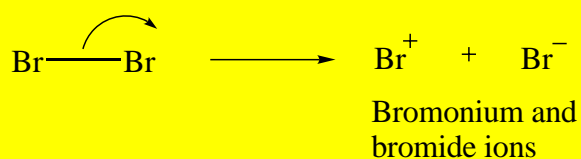
A *free radical* is an atom or a part of a molecule bearing one unshared electron. They are often formed by breaking a covalent bond "homolytically" - down the middle, one electron going into each atom. This may require heat energy or light energy.

To depict this type of bond-breaking process in organic chemistry we use **half-headed** arrows, as illustrated below for the cleavage of bromine molecules:

Homolytic cleavage:

$$Br\!-\!\!-\!Br \longrightarrow Br\bullet \;\; + \;\; Br\bullet$$

Bromine atoms
or *free radicals*

Heterolytic cleavage:

$$Br\!-\!\!-\!Br \longrightarrow Br^+ \;\; + \;\; Br^-$$

Bromonium and
bromide ions

Heterolytic cleavage on the other hand involves movement of electron pairs and results in formation of ions.

Radical polymerisation involves a *free radical chain* process which is initiated by a homolytic cleavage reaction in some initiator (generalised as In—In here). There are three steps to these reactions:
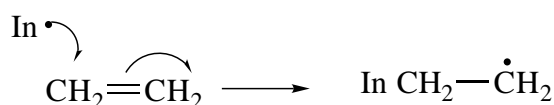
Step 1 —Initiation:

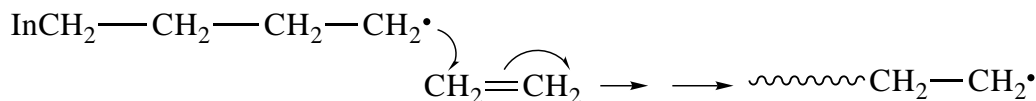An initiator free radical is first formed (In•) which adds to an alkene.
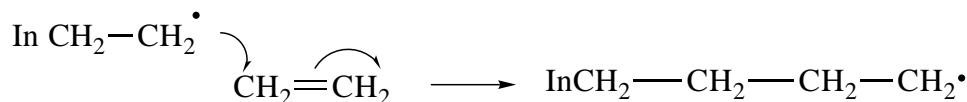
First:

$$In-In \longrightarrow In\bullet \ + \ In\bullet$$

Then:

$$In\bullet \quad CH_2=CH_2 \longrightarrow In\ CH_2-\overset{\bullet}{C}H_2$$

Step 2—Propagation:

The radical formed in the first step adds to a second alkene.

$$In\ CH_2-\overset{\bullet}{C}H_2 \quad CH_2=CH_2 \longrightarrow InCH_2-CH_2-CH_2-CH_2\bullet$$

$$InCH_2-CH_2-CH_2-CH_2\bullet \quad CH_2=CH_2 \longrightarrow \longrightarrow \sim\sim\sim CH_2-CH_2\bullet$$

The polymer grows by repetition of this process until two chains collide in a chain *termination* process.

Step3 — Termination:

$$\sim\sim\sim CH_2-CH_2\bullet \ + \ \sim\sim\sim CH_2-CH_2\bullet$$
$$\longrightarrow \sim\sim CH_2-CH_2-CH_2-CH_2\sim\sim$$
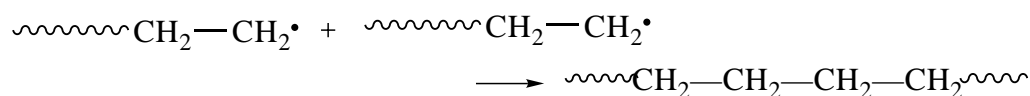
Polymers derive their characteristics from the monomer alkene from which they are made. Table 15.1 p. 427 shows the various, well known items and the monomers from which they are derived.

Reactivity of alkynes

The reactions of alkynes can mostly be regarded as the same as alkenes, except the product alkene can react further. This is not specifically dealt with in Brown, but we will cover it here.

You will see that the addition reactions are very similar to those of alkenes, but after the first addition to an alkyne an alkene is formed which then undergoes a second addition reaction.

Addition of halogens:

As with alkenes. electrophilic addition reactions characterise the chemical reactivity of alkynes. Thus, alkynes undergo addition reactions with halogens. For example:
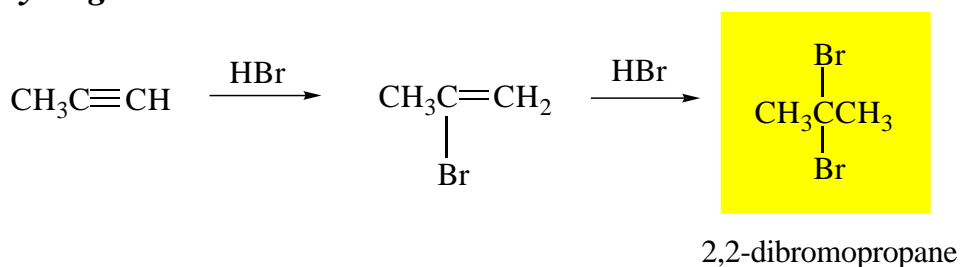
$$H-C\equiv C-H \ + \ Br_2 \ \longrightarrow$$
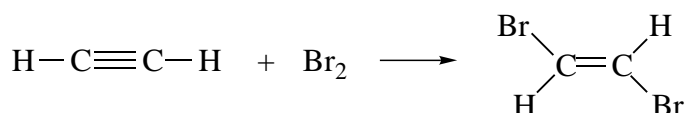
But the product is an alkene, so a second addition reaction takes place:

$$+ \ Br_2 \ \longrightarrow \ Br_2CH-CHBr_2$$

1,1,2,2-tetrabromoethane
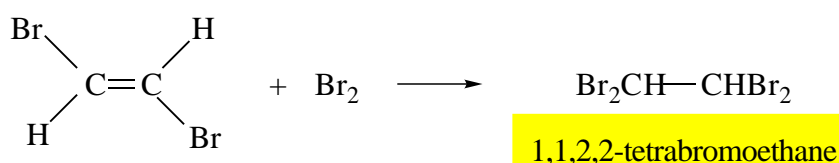
Again, Markovnikov's rule is obeyed in addition reactions with unsymmetrical alkynes.

Addition of hydrogen halides:

$$CH_3C\equiv CH \ \xrightarrow{HBr} \ CH_3C{=}CH_2 \ \xrightarrow{HBr} \ CH_3\overset{\textstyle Br}{\underset{\textstyle Br}{C}}CH_3$$

(with Br on the middle carbon of $CH_3C{=}CH_2$)

2,2-dibromopropane

Compare the reactions of alkenes and alkynes with halogens (and hydrogen halide acids) with the reaction of alkanes with halogens (alkanes don't react with hydrogen halides). Much milder reaction conditions are needed with alkenes and alkynes and there is a *well-defined route to a single product* - not mixtures, as with alkanes.

Addition of hydrogen:

Hydrogenation of alkynes eventually yields an alkane by uptake of *two* moles of hydrogen. However using a less active catalyst, such as Pd on $BaSO_4$ that has been 'poisoned' with sulfur allows us to stop the hydrogenation at the alkene stage. Since hydrogenation is *syn* addition we get the *cis*-alkene:
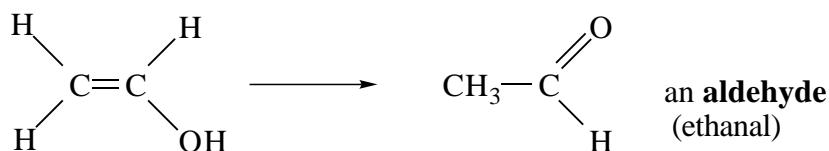
$$R-C\equiv C-R' \; + \; H_2 \longrightarrow \underset{H}{\overset{R}{\diagdown}} C = C \underset{H}{\overset{R'}{\diagup}}$$
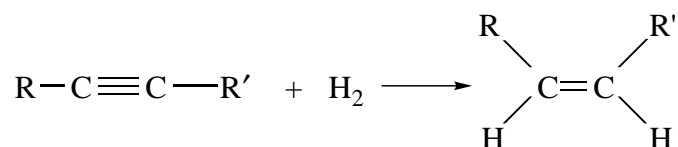
Addition of water:

The addition of water (using aqueous H_2SO_4) also requires a catalyst, namely mercury(II) sulfate $HgSO_4$:

$$H-C\equiv C-H \; + \; H_2O \; \xrightarrow[HgSO_4]{H_2SO_4} \; \underset{H}{\overset{H}{\diagdown}} C = C \underset{OH}{\overset{H}{\diagup}}$$
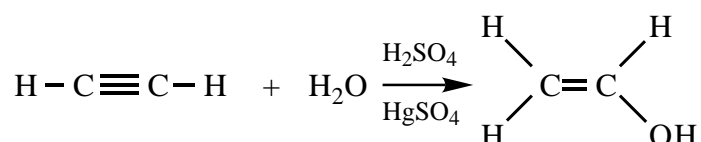
The product is an **enol** (from -en signifying a double bond, and -ol an alcohol), but in this case a second molecule of water does not add. Structural reorganisation of the initial adduct (we call this a *rearrangement*) occurs:

$$\underset{H}{\overset{H}{\diagdown}} C = C \underset{OH}{\overset{H}{\diagup}} \longrightarrow CH_3 - C \overset{\diagup O}{\underset{\diagdown H}{}} \quad \text{an **aldehyde**} \atop \text{(ethanal)}$$

The rearrangement results in a shift in the position of a hydrogen atom and of a pair of bonding electrons to give a more stable structure. Again with unsymmetrical alkynes the addition obeys Markovnikov's rule. You will encounter alcohols and aldehydes later in this module.

Acidity of alkynes:

Before we leave these unsaturated functional groups, one unusual feature of terminal alkynes needs to be understood. A terminal alkyne is *acidic*, albeit very weakly so, and can be deprotonated by treatment with a strong base to yield a **carbanion** (a negatively charged organic ion).

$$R-C\equiv C-H \; \xrightarrow{-H^+} \; R-C\equiv C:^-$$
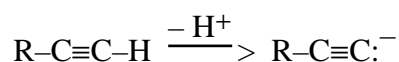
The *strong base* that is often used is sodium amide in liquid ammonia. It is the *amide anion* that affects the deprotonation:

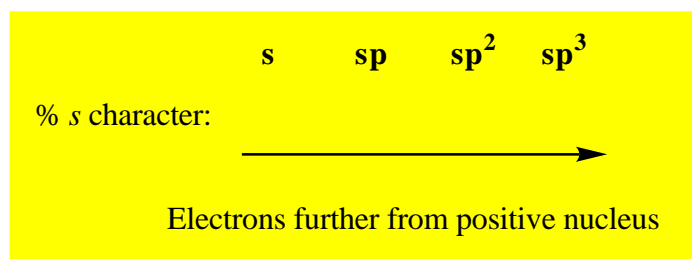$$R-C\equiv C-H \quad :\ddot{N}H_2 \longrightarrow R-C\equiv C\mathrel{:}^- + NH_3$$

We should note that anhydrous conditions are essential – otherwise, the anion itself will immediately react with any water present:

$$R-C\equiv\bar{C}: \quad H-OH \longrightarrow R-C\equiv CH + HO^-$$

The alkyne is regenerated and hydroxide ion is formed; in other words, water is a stronger (much stronger) acid than a terminal alkyne.

Why can we form an **alkynide ion** apparently so readily? The carbon is sp hybridised and as such has a greater percentage of s character than the sp^2 or sp^3 hybridised carbon. The electrons in the sp hybrids are therefore closer to the positively-charged nucleus, resulting in a carbon that can better tolerate a negative charge.

<div style="background-color:yellow">

| | s | sp | sp^2 | sp^3 |

% *s* character:

$\longrightarrow$

Electrons further from positive nucleus

</div>

Alkynes can also form metal derivatives of silver(I) and copper(I). These are made by treating the alkyne with an aqueous solution of complex silver(I) or copper(I) salts, resulting in the metallo-derivatives:

$$R–C\equiv C–Ag \ \text{ or } \ R–C\equiv C–Cu$$
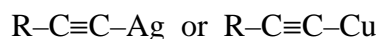
The metal derivatives in this case are *not* carbanions. The carbon is *covalently* bound to the metal.

Self-Test Exercise 3.10

Explain the following differences in reactivity:

(a) Propane ($CH_3CH_2CH_3$) does not react with sodium amide ($NaNH_2$), but propyne ($CH_3C\equiv CH$) reacts to form the sodium alkynide, $CH_3C\equiv C^- Na^+$.

(b) 1-butene ($CH_3CH_2CH{=}CH_2$) reacts with one equivalent of molecular bromine, but 1-butyne consumes two equivalents.
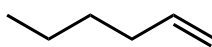
Index of hydrogen deficiency

This section is not covered in Brown, but is a very useful tool for deciding structural formulas given an empirical formula.

We saw earlier that alkanes had the general formula C_nH_{2n+2}, and cycloalkanes C_nH_{2n}. Alkenes have the general formula C_nH_{2n} also, and similarly alkynes and dienes are C_nH_{2n-2} (as are cycloalkenes). When working with an unknown hydrocarbon we can obtain a considerable amount of information if we know its molecular formula and its **index of hydrogen deficiency.**

This is defined as the number of pairs of hydrogen atoms that need to be subtracted from the molecular formula of the corresponding *alkane* to give the molecular formula of the compound under consideration.

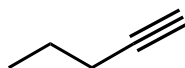Thus for example, 1-hexene and cyclohexane have the same molecular formula C_6H_{12}.

| 1-pentene | cyclohexane |
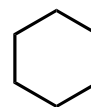
Thus:

C_6H_{14}:   corresponding alkane (hexane)

$- C_6H_{12}$:   1-hexene or cyclohexane

$\overline{}$

H_2 $\equiv$ 1 pair of hydrogen atoms

$\therefore$ index of hydrogen deficiency $= 1$.

Similarly, 1-pentyne and cyclopentene have the same molecular formula, C_5H_8:

1-pentyne   cyclopentene

$$C_5H_{12} - C_5H_8 = 2 \times H_2$$

The index of hydrogen deficiency = 2. It is easy to see that each unit is equivalent to one π-bond or one ring.

We can also determine the number of double (or triple) bonds by hydrogenating the compound. Each double bond consumes one molar equivalent of hydrogen; each triple bond two molar equivalents, and the rings are unaffected. Thus in our examples, 1-hexene consumes *one* molar equivalent of H_2, and is thus an *alkene*. Cyclohexane is unaffected.

Similarly in the second example 1-pentyne would consume *two* molar equivalents of hydrogen, and cyclopentene only *one* molar equivalent. (Note that the bicyclic compound:
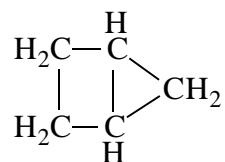
which has two rings and no double bonds, is also C_5H_8 and would be unaffected).

How do we determine molecular formulas? By combustion analysis:

A known weight of the compound is burned (about 3-5 mg) in pure oxygen and the amount of carbon dioxide and water produced is measured:

$$C_xH_y \ + \ O_2(\text{excess}) \ \rightarrow \ xCO_2 \ + \ yH_2O$$
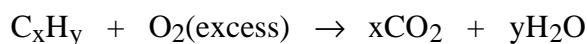
By simple proportions we can calculate the percentage composition by weight of carbon and hydrogen. Next we calculate the empirical formula by dividing the percentages by the atomic weights. For example say we have found
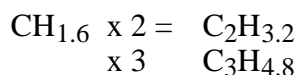
C: 88.16%
H: 11.84%

Then

$$C = \frac{88.16}{12.01} = 7.341$$

$$H = \frac{11.84}{1.008} = 11.75$$

Dividing by the lowest number yields $CH_{1.6}$, which is clearly nonsense. However through multiplication (by factors 2,3.......etc.) we find that integral numbers for both carbon and hydrogen are obtained for a C_5 compound.

$$CH_{1.6} \ \times 2 = \ C_2H_{3.2}$$
$$\times 3 \quad C_3H_{4.8}$$

$$x\ 4 \quad C_4H_{6.4}$$
$$x\ 5 \quad C_5H_8$$

Thus the empirical formula is C_5H_8.

Note that there is no drastic rounding off (e.g., not C_2H_3 or C_3H_5) - combustion analysis yields results with an accuracy of $\pm\ 0.2\%$.

Next we determine the molecular weight of the compound (usually by a technique known as **mass spectrometry**). If the molecular weight is 68 (= C_5H_8) then the empirical formula and the molecular formula are the same, but for a found molecular weight of 136 the molecular formula would be $C_{10}H_{16}$.

Finally we proceed to spectroscopic and sometimes chemical analysis to determine the structural formula of the compound. You will learn more about this next year.

Self-Test Exercise 3.11

What is the index of hydrogen deficiency of:

(a) C_6H_6

(b) C_6H_{10}

Topic Highlights

You should be able to:

❏   understand the effect of pi-bonding in alkenes upon structure; why they are rigid;

❏   understand what *cis* and *trans* **geometrical isomers** are;

❏   name straight-chain and cycloalkenes as well as designate geometrical isomers as *E* and *Z* forms;

❏   name alkynes;

❏ understand and be able to write down products from the addition to alkenes of Br_2 (trans addition to a ring), H_2 (*cis* additions), hydrogen halides (Markovnikov addition) and water (acid catalysed);

❏ understand the concept of free radical polymerisation of alkenes and the three steps that are involves in the process;

❏ give the products from addition reactions of bromine, hydrogen halides to alkynes and hydrogenation and hydration of alkynes and note differences to the corresponding reactions of alkenes.

❏ understand that terminal hydrogens of alkynes are acidic;

❏ determine the *index of hydrogen deficiency* for hydrocarbons;

❏ understand the significance between double- and single-headed arrows to depict electron movement.

Topic 3E - Aromatic compounds

Key questions

Aromatic substances undergo substitution reactions rather than the addition reactions we saw for alkenes and alkynes. The key question is—why? What is the difference? What is an aromatic compound? Why are they so stable? How do we name aromatic substances?

Outline

We need to understand more about aromatics and aromaticity than the textbook suggests, but aromatic reactivity is dealt with in much more detail in CHEM120. You have encountered the nature of bonding in benzene already (Module 2) and you should review this where indicated.

What is an aromatic compound?

> **Read**
> **Brown Chapters 9.1, 9.2**

The term "aromatic compounds" was originally used to describe compounds with distinctive odors. In organic chemistry, the term now has a special meaning: *aromatic* is used to describe the type of bonding in certain compounds.

Generally aromatic compounds are **cyclic, planar** compounds that can be represented by structural formulas **containing alternate single** and **double bonds**. The term aromatic is contrasted with the term *aliphatic*, which is used to describe non-aromatic compounds, such as alkanes.

Typical Aromatic Compounds:

| benzene | naphthalene (moth balls) | benzaldehyde oil of almonds | acetyl salicyclic acid (aspirin) | styrene |
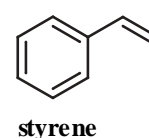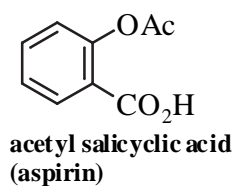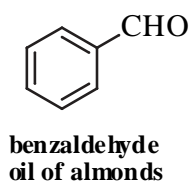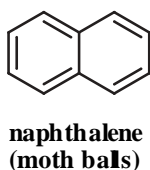
Like alkanes and alkenes, most aromatic compounds used in commerce and industries are obtained from the refining of petroleum.

Bonding in benzene:

In 1825 the English chemist Michael Faraday isolated an oily liquid from London gas lines. This compound was shown to have a molecular formula of C_6H_6 and was subsequently named **benzene**. It was not until 40 years later that the German chemist Fredrich August Kekulé conceived a workable structure

for this compound. Almost another 75 years elapsed before the modern structure of benzene was developed.

The early problems in devising a workable structure for benzene stemmed from the fact that an adequate structure cannot be drawn when conventional line-bond formulas are used. Today we know that the **six carbons of benzene are sp^2 hybridized and are arranged in a six-membered ring.** Each carbon atom bears a *p* orbital containing one electron. We might expect these six *p* electrons to be in three double bonds.
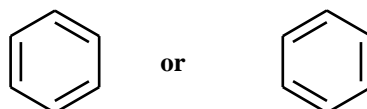
However, these formulas do not explain why benzene does not undergo reactions typical of alkenes.
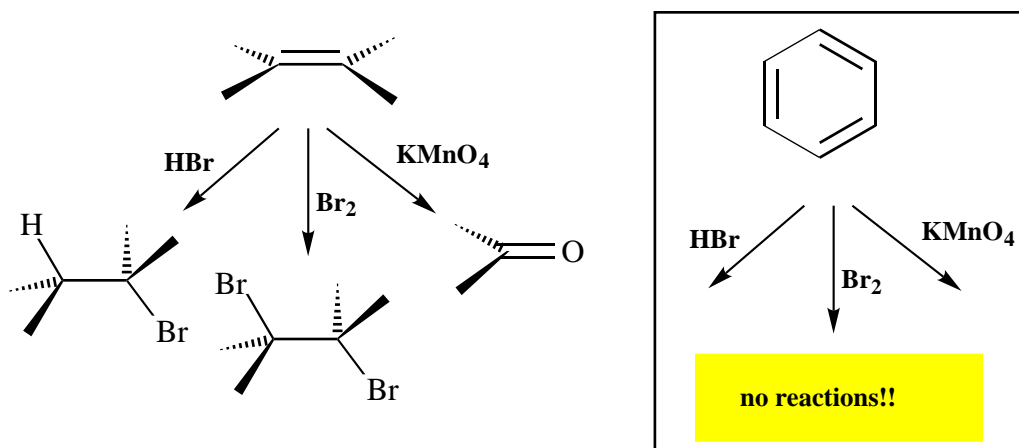

Furthermore, all the C–C bond lengths in benzene are the same – we know from X-ray diffraction that benzene does not contain three shorter double bonds and three longer single bonds.

Benzene as a Resonance Hybrid:

In 1865 Kekulé proposed a hexagonal structure with three double bonds for benzene. In 1872 he further proposed (incorrectly) that benzene is a mixture of two six-membered-ring compounds, each with three double bonds, in equilibrium with each other. This proposal was accepted as fact for almost 50 years, and even today we call these the **Kekulé structures** of benzene.

General Chemistry CD-ROM Screen 10.7 A Closer Look
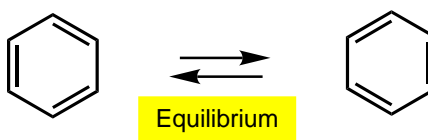
Kekulé's equilibrium proposal by itself does not explain all the unusual properties of benzene. However, if we consider Kekulé's structures as *resonance structures,* we can explain benzene's properties. **The real structure of benzene is a resonance hybrid** described by the two Kekulé structures. Benzene contains no true carbon-carbon single bonds or double bonds; instead, **all six pi electrons are shared equally by six carbons,** making all the carbon-carbon bond lengths identical.
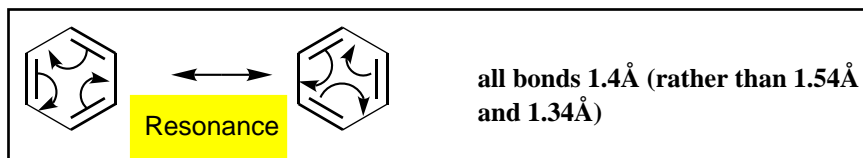

Molecular Orbital Picture Of Benzene:

Benzene is a flat six-membered ring of sp^2-hybridized carbon atoms. Each carbon is bonded to one hydrogen, and each carbon has one $2p$ orbital perpendicular to the ring, as shown below. The six p orbitals contain a total of six $2p$ electrons.

Because benzene is symmetrical, the p orbitals do not overlap to form three pi bonds. Instead, each p orbital overlaps equally with each of its neighbours.

This results in **six** molecular orbitals which together form two doughnut-like π-clouds, one on each face of the benzene skeleton. Because the electronic charge is evenly distributed, the molecular orbital is referred to as an **aromatic pi cloud**.
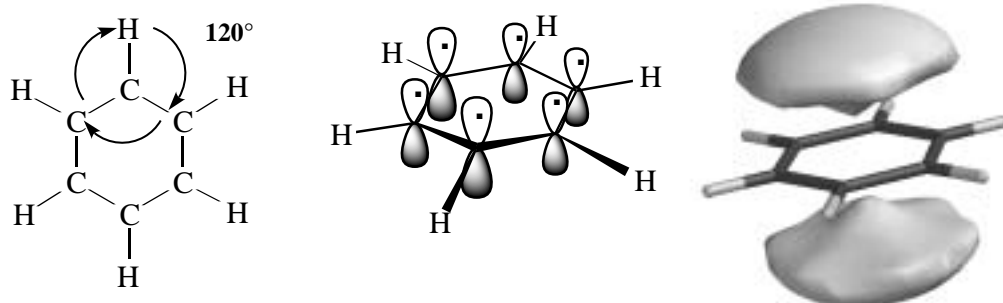
We will use two types of benzene formulas - those with lines for bonds (the Kekulé symbols above) when we want to keep track of electrons or one with a circle in the ring, which emphasizes the aromatic pi cloud.
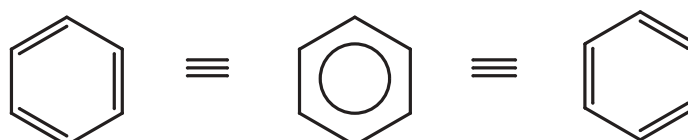
A space filling drawing and electron density surface gives a better view of the benzene structure:
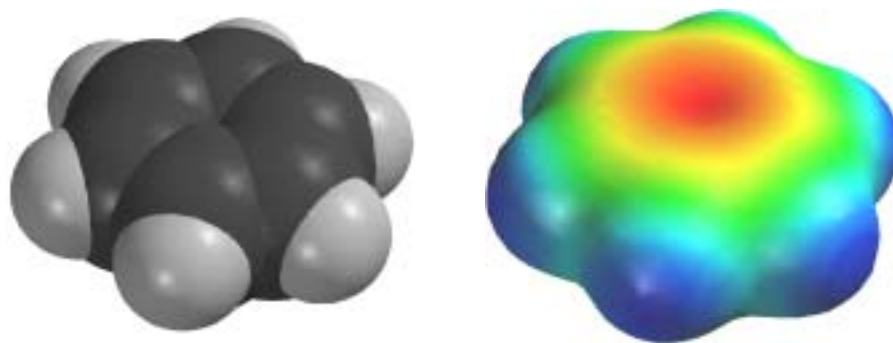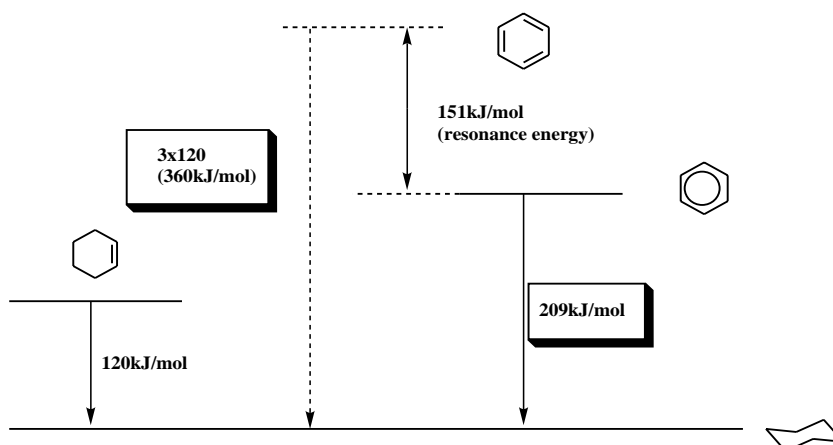
Stability of the Benzene Ring:

Because delocalization of electronic charge stabilizes a structure, the benzene ring is more stable (lower in energy) than a hypothetical cyclic triene. The energy of stabilization for an aromatic compound, called the **resonance stabilisation energy**, is 151 kJ/mol for benzene.

The value for the resonance energy of an aromatic compound can be determined experimentally. Cyclohexane liberates 120 kJ/mol when hydrogenated. The hypothetical cyclohexatriene would therefore theoretically liberate 3 x 120, or 360 kJ/mol. However, benzene liberates only 209 kJ/mol. The difference, 151 kJ/mol, is the resonance energy.

These energy changes can be illustrated graphically:

The resonance stabilization of the benzene ring is the principal reason that benzene does not undergo alkene addition reactions. If a reagent is added to the ring, the aromaticity would be lost and a less stable product would result.

The Hückel 4n+2 rule:

To be aromatic, an all-carbon compound must be **planar, cyclic and fully conjugated** (alternating single and double bonds). However, not all cyclic compounds containing sp^2-hybridized atoms in a ring system are aromatic. For example, the following two compounds are *not* aromatic.
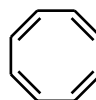
cyclobutadiene   **cyclooctatetraene**

In 1931 the German chemist Erich Hückel put forth the following rule to evaluate which compounds are aromatic and which are not.

> **Hückel Rule:** To be aromatic, a planar, monocyclic compound with alternating single and double bonds must contain **(4***n* **+ 2)** pi electrons, where **n is an integer** (0, 1, 2, 3, etc).

According to the Hückel rule, a compound containing 2, 6, 10, or 14 pi electrons can be aromatic, but a compound with 4, 8, or 12 pi electrons cannot.

The Hückel rule works very well for most common aromatic compounds including heteroaromatic compounds (aromatic rings with atoms other than carbon - see later this topic). Why the Hückel rule works can be explained by modern molecular orbital theories, which we will discuss in the second-year course on aromaticity.
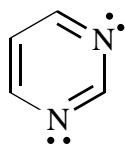
Aromatic heterocyclic compounds:

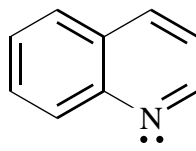*Chemoffice Web (Brown)*
CD-ROM
Model 9.2

In biological systems, aromatic rings containing carbon and nitrogen as ring atoms are common. These compounds are called **aromatic heterocyclic compounds**. The adjective *heterocyclic* refers to any ring in which the ring atoms are not all the same element (usually carbon). Some common rings found in aromatic heterocyclic compounds are shown below:
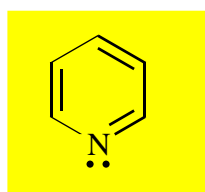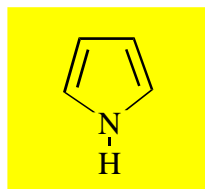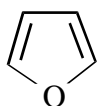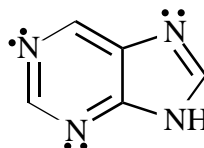

Pyridine   **Pyrimidine**   **Quinoline**

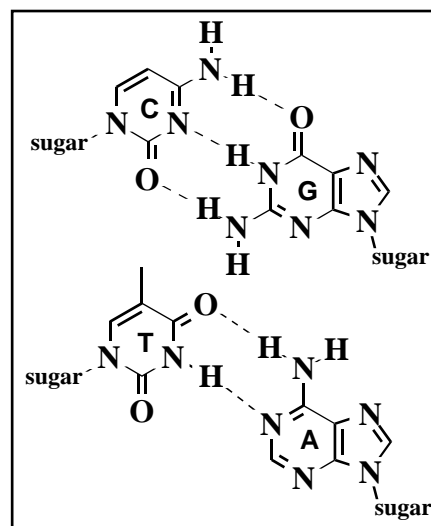**Pyrrole**   **Furan**   **Purine**

The components responsible for hydrogen bonding in DNA and the transmission of the genetic code are heterocyclic aromatic molecules. Guanine (G) and cytosine (C) always pair together as do adenine (A) and thymine (T). The dotted lines show the hydrogen bonds between groups on these ring systems. **C** and **T** are pyrimidines and **G** and **A** are purines.

The bonding in pyridine is very similar to the bonding in benzene (a [4n+2] system). A difference between pyridine and benzene is that the nitrogen in pyridine contains an unshared pair of valence electrons as shown above. Pyridine, like aliphatic amines, can act as a base. The electron density picture shows this lone pair quite clearly. There is also a mushroom of pi electron density above and below the ring as for benzene but it is not shown in this picture.
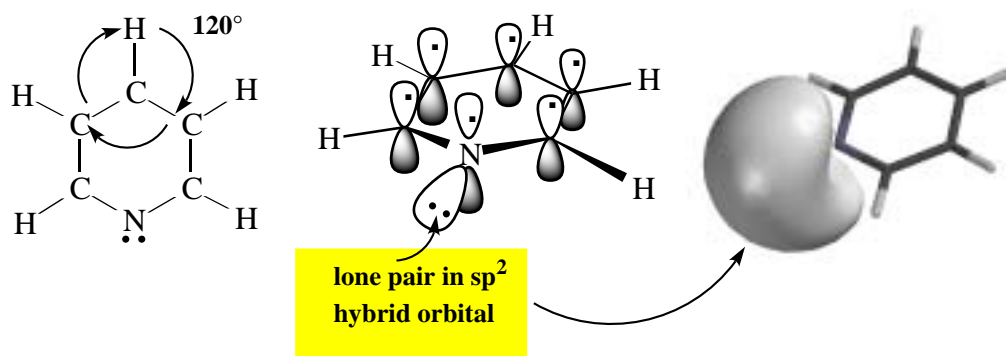
Pyrrole is a **five-membered** ring containing nitrogen. The bonding in pyrrole is somewhat different from that in benzene or in pyridine. From its valence bond formula, pyrrole does not appear aromatic because the nitrogen does not appear to have a double bond to it. The lone pair on nitrogen is however in a p-orbital and together with the four electrons from carbon, the total is **six electrons** (a 4n+2 system). Note the pi electron cloud above and below the ring as for benzene.
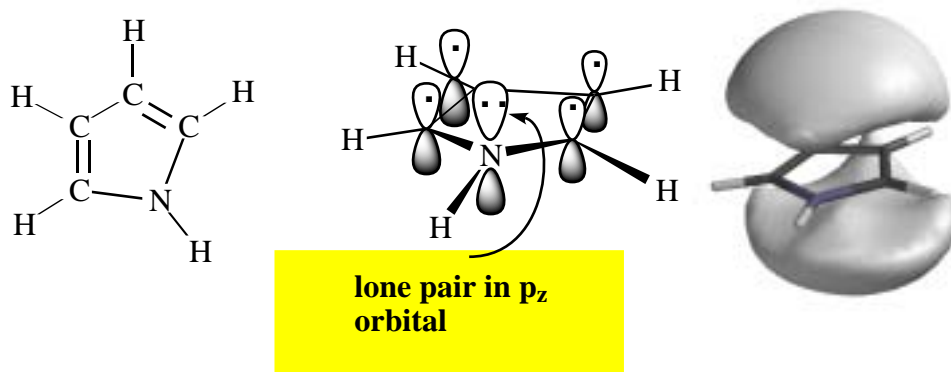
Nomenclature of substituted benzenes

Read
Brown Chapter 9.3

The original trivial names of many common aromatic compounds have been accepted by the IUPAC as systematic names. A few of these are listed below.
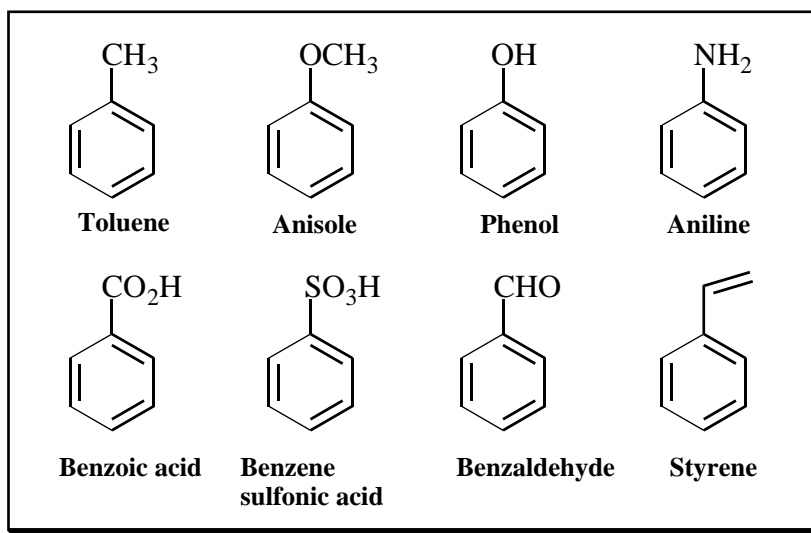
Aside from the trivial names, we usually name **monosubstituted benzenes** with benzene as the parent. The name of the substituent is prefixed to the parent name.
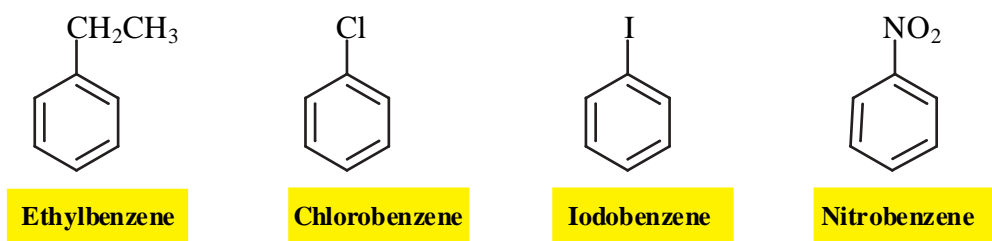
A **disubstituted benzen**e can be named with prefix numbers or by the **ortho, meta, para system**, which shows the positional relationships of the two groups to each other on the ring.
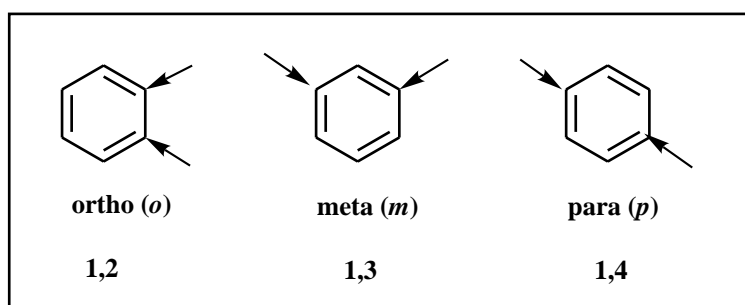
The following examples show how these prefixes are used:

**o-dichlorobenzene   m-nitrochlorobenzene   p-methoxytoluene   4-amino-2-ethyl-
benzoic acid**

In the third and fourth examples, a substituted benzene is used as the parent. In these compounds, the principal substituents of the parent ($-CH_3$ and $-CO_2H$) are **considered to be at position 1.**

The *o-*, *m-*, *p-* system is used only for disubstituted benzenes and **never for substituted cyclohexanes** or other compounds.
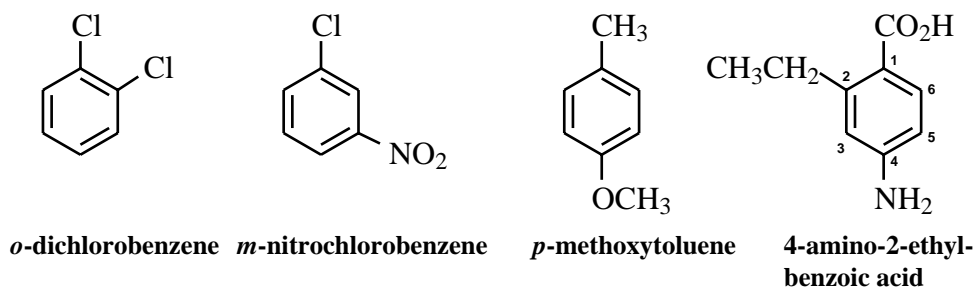
A benzene with more than two substituents is more conveniently named using prefix numbers to specify the location of the groups on the ring, as in the fourth example.

When a benzene ring is bonded to a chain or to a more important parent, the ring is referred to as a **phenyl group** (this should be differentiated from a **benzyl group**):

Phenyl

2-Phenylpropanol

**2-(2-chloro-4-hydroxyphenyl)-
propene**

Benzyl

4-(p-nitrophenyl)-1-pentene
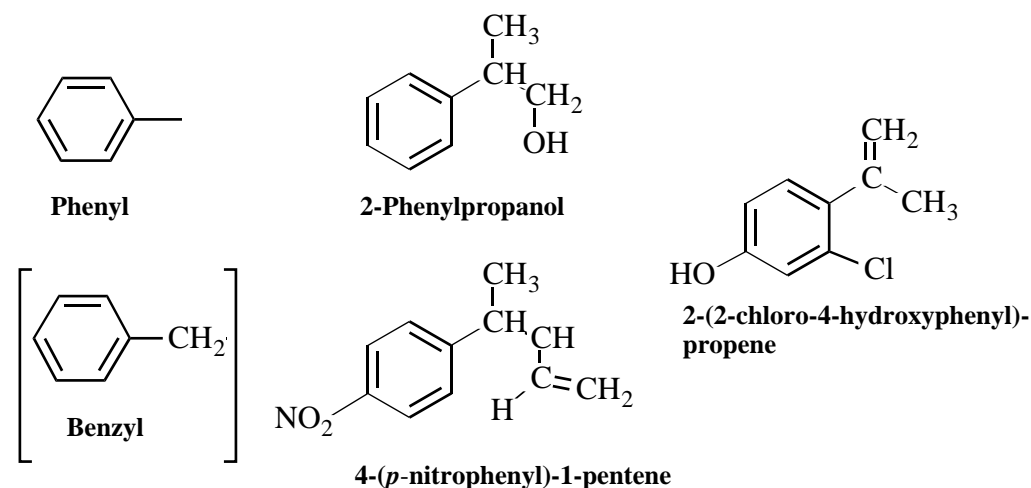
Polycyclic aromatic compounds:

A *polycyclic* aromatic compound is a compound containing "fused rings" (rings sharing carbons) that are aromatic. Resonance structures can be drawn for any of these aromatic compounds. We have already mentioned naphthalene (a moth repellent), and anthracene is used in dye manufacturing. Benzo[a]pyrene is a potent mutagen and carcinogen found in soot, tar and cigarette smoke.
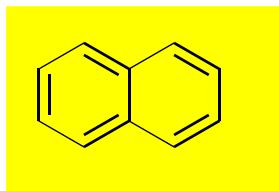
Naphthalene
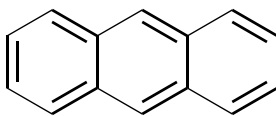
Anthracene
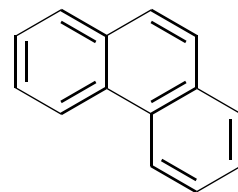
Phenanthrene
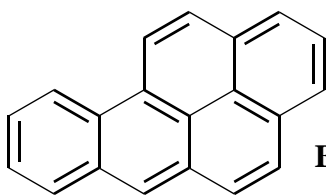
Benzo[a]pyrene

Self-Test Exercise 3.12

Complete *Practice Problem 9.1* p. 245 Brown:

(a)

(b)

(c)

Self-test Exercise 3.13

Draw and name systematically the (three) structural isomers of bromobenzaldehyde:

Aromatic substitution reactions

Read
Brown Chapter 9.6

In CHEM120 you will learn more about this reaction and that the group that goes onto the ring starts off as an electron acceptor, an **electrophile**. The process is more correcly known as **elecrophilic aromatic substitution.**

As described earlier benzene does not undergo addition reactions as do alkenes, but substitution reactions of benzene are common. In these, a group or an atom is **substituted for a ring H** – hence the reaction is referred to as an **aromatic substitution reaction**.

As stated at the beginning of this topic, reactions with benzene are difficult and so all reactions are acid-or Lewis-acid catalysed. Lewis acids are dealt with in Section 17.11 and later in the course you will learn that they are electron acceptors.
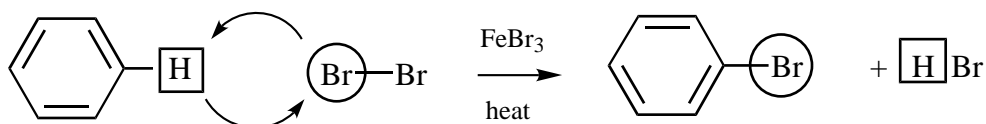
Halogenation:

Treatment of benzene with bromine (Br_2) in the presence of an iron(III) halide catalyst yields **bromobenzene**, as shown above. Using chlorine gives **chlorobenzene**:

$$\text{benzene} \quad + \quad \text{Cl-Cl} \quad \xrightarrow[\text{heat}]{\textbf{FeBr}_3} \quad \text{C}_6\text{H}_5\text{—Cl} \quad + \quad \text{HCl}$$

bromobenzene
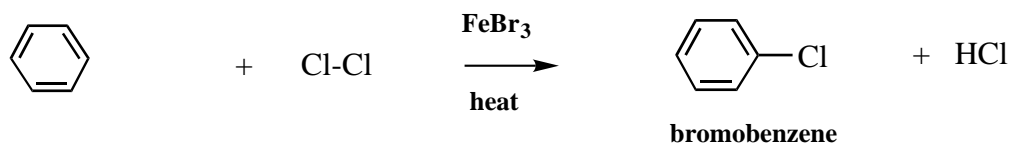
Nitration:

If benzene is treated with concentrated nitric acid, with concentrated sulfuric acid as the catalyst, **nitrobenzene** is formed.

$$\text{benzene} \quad + \quad \text{HNO}_3 \quad \xrightarrow[\text{heat}]{\textbf{H}_2\textbf{SO}_4} \quad \text{C}_6\text{H}_5\text{—NO}_2 \quad + \quad \text{H}_2\text{O}$$

Nitrobenzene

Sulfonation:

Treatment of benzene with fuming sulfuric acid gives **benzenesulfonic acid**.

$$\text{benzene} \quad + \quad \boxed{\text{H}_2\text{SO}_4} \quad \underset{\xleftarrow{\hspace{1cm}}}{\overset{\text{heat}}{\xrightarrow{\hspace{1cm}}}} \quad \text{C}_6\text{H}_5\text{—SO}_3\text{H} \quad + \quad \text{H}_2\text{O}$$
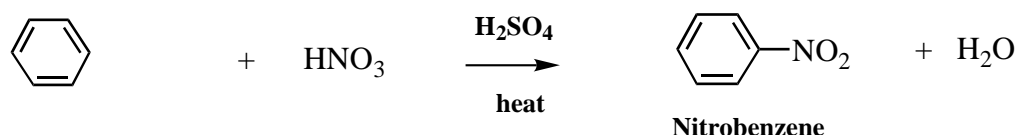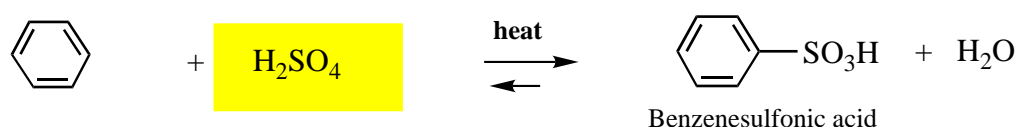
Benzenesulfonic acid

Alkylation:

When treated with a alkyl halides, denoted by R—X (see next topic) and a Lewis acid catalyst (AlX$_3$ in this reaction), benzene is converted to an **alkylbenzene**. This reaction is called a **Friedel-Crafts alkylation** after Charles Friedel, a French chemist, and James Crafts, an American chemist, who developed this reaction in 1877. The term *alkylation* means substitution by an alkyl group.

$$\text{benzene} \quad + \quad \text{EtCl} \quad \xrightarrow{\boxed{\textbf{AlCl}_3}} \quad \text{C}_6\text{H}_5\text{—Et} \quad + \quad \text{HCl}$$
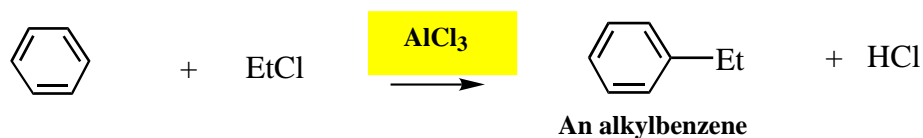
An alkylbenzene

Acylation:

Friedel and Crafts developed a reaction similar to the alkylation reaction above. This type of reaction is called a **Friedel-Crafts acylation** because an *acyl* group (see later) , not an alkyl group, is substituted on the benzene ring. The symbol "*R*" is used commonly in organic chemistry to denote an alkyl substituent.

$$\text{benzene} \quad + \quad \underset{R}{\overset{O}{\underset{\|}{\text{C}}}}\text{—Cl} \quad \xrightarrow{\boxed{\textbf{AlCl}_3}} \quad \text{C}_6\text{H}_5\text{—}\underset{R}{\overset{O}{\underset{\|}{\text{C}}}} \quad + \quad \text{HCl}$$

An acylbenzene
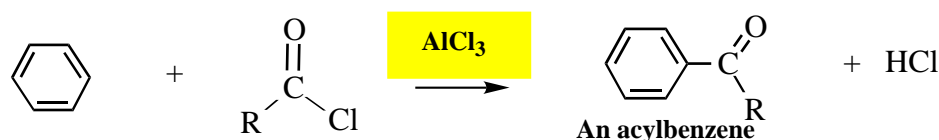
Give the reagents required to:

(a) chlorinate benzene

(b) nitrate benzene

(c) sulfonate benzene

Topic Highlights

You should be able to:

❏   draw and name the structures of benzene and substituted benzenes;

❏   understand the nature of the bonding in benzene from a valence bond and molecular orbital viewpoint;

❏   understand and be able to calculate the **resonance stabilisation energy** of benzene;

❏   determine whether a simple cyclic system is aromatic from the Hückel 4n+2 rule;

❏   understand that benzene undergoes **substitution** rather than addition reactions and know what reagents are needed to put onto the ring, in place of hydrogen, —Br, —Cl, —NO$_2$, —SO$_3$H, alkyl and acyl (carbonyl) groups

❏   understand the structures of polycyclic aromatics and the heteroaromatics, pyridine and pyrrole.

3F Alkyl halides

Key questions

What is an alkyl halide? How do we name them systematically? What sorts of reactions do they undergo?

Outline

Thus far we have dealt with the properties of hydrocarbons (alkanes, alkenes, alkynes and aromatics). Brown p.27 categorises derivatives of hydrocarbons by so-called "functional groups", groups which add functionality to the hydrocarbons and which are generally reactive if substituted on a hydrocarbon chain or ring.

We will now touch on the properties of each of these starting with alkyl halides, which have been made in several reactions of hydrocarbons. They are, however, a very important class of organic substances and are very useful in synthetic organic chemistry, so we must learn something about them here. The module notes will suffice from this point of view but the textbook will also be of help. Note that many of the reactions of alkyl halides are common to alcohols, which we will deal with in Topic G.

What is an alkyl halide?

The *alkyl halides* are a class of compounds with the general formula

$$R \!-\! X \qquad \begin{array}{l} R = \text{alkyl group,} \\ X = \text{halogens, F, Cl, Br and I} \end{array}$$
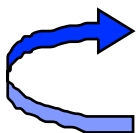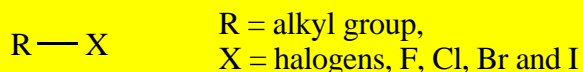
Topics 3B and 3C

We have already encountered this family of organic compounds as products of the reactions of hydrocarbons, where we saw that they may be prepared by the following routes:

(1)   Radical halogenation of alkanes

e.g. $\qquad CH_4 + Cl_2 \xrightarrow{\ h\nu\ } CH_3Cl + HCl$

and $\qquad CH_3CH_2CH_3 + Cl_2 \xrightarrow{\ h\nu\ } CH_3CH_2ClCH_3 + HCl$

(2)   Addition of hydrogen halides to alkenes

e.g. $\qquad CH_3CH\!=\!CH_2 \ + \ HBr \ \longrightarrow$

$$\begin{array}{c} CH_3 \quad CH_3 \\ \diagdown CH \diagup \\ | \\ Br \end{array}$$
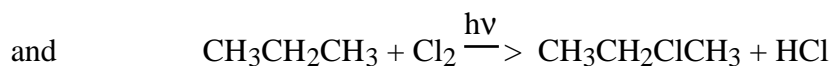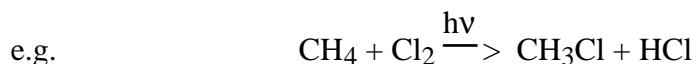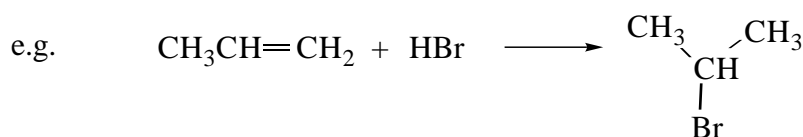
Remember that the addition also proceeds according to *Markovnikov's Rule.*

Similarly addition of halogens (Cl_2, Br_2 and I_2) to alkenes or alkynes gives rise to polyhaloalkanes (alkenes bearing more than one halogen atom).

Nomenclature of alkyl halides

Read
Brown Chapter 7.1

Initially we will confine our discussion to simple alkyl halides and mostly those with only one halogen atom. We name them as *halo alkanes*: commonly used trivial names are given in brackets.
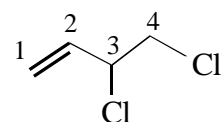
Thus:

chloromethane is CH_3Cl (methyl chloride),
bromoethane is CH_3CH_2Br (ethyl bromide),
2-iodopropane is CH_3CHICH_3 (isopropyl iodide)
1-bromo-5-chloro-2-iodohexane is $BrCH_2CHICH_2CH_2CHClCH_3$
and **3,4-dichloro-1-butene** is

Note that we list our substituents alphabetically using the lowest possible numbers just as we did when naming alkanes. The chlorine atoms are substituents on the alkene rather than the other way around.

Physical properties of alkyl halides:

Except for a few of the lower molecular weight members, the alkyl halides are colourless liquids that are heavier than water. Comparison of the boiling point (°C) of a few examples reveals the expected trend of increasing boiling point with increasing molecular weight.

CH_3Cl: 24° CH_3Cl: 24° C_2H_5Cl: 13° $CH_3CH_2CH_2Cl$: 46°

CH_2Cl_2: 40° CH_3Br: 5° C_2H_5Br: 38° $CH_3CH_2CH_2Br$: 71°

$CHCl_3$: 61° CH_3I: 42° C_2H_5I: 72° $CH_3CH_2CH_2I$: 102°

CCl_4: 77°

For isomers, as we observed with the alkanes, chain branching results in a lower boiling point, e.g.:

$CH_3CH_2CH_2CH_2Cl$: 77° $CH_3CH_2CHClCH_3$:   69°

$(CH_3)_2CHCH_2Cl$:   69° $(CH_3)_3CCl$:   51°

The carbon halogen bond energies are informative:

C–F   456 kJ/mol^{-1} bond length   1.39 Å
C–Cl   351   1.78
C–Br   293   1.93
C–I   235   2.14

From these values we may anticipate (correctly) that alkyl iodides are the most reactive of the alkyl halides. We also note that the bond length increases with increasing atomic radius of the halogen atom.

General Chemistry CD-ROM Screen 11.9

Generally alkyl fluorides are very inert (this is very useful in the case of **teflon**, the polymer of tetrafluoroethene ($-CF_2-CF_2-)_n$, whose chemical inertness makes it useful not only for lining frying pans but also in the construction of apparatus used in corrosive chemical reactions. In fact polyfluorinated alkanes are both stable and able to dissolve oxygen. As shown on p.179, they can even be used as **artificial blood**! Alkyl fluorides require special methods for their preparation and we will not consider them further.

Polarisation of the carbon-halogen Bond

Read
Brown Chapter 1.2C, 1.4

Unlike carbon-carbon and carbon-hydrogen bonds the carbon-halogen bonds are polarised. Observe this polarisation in the C—Cl bond of methyl chloride:
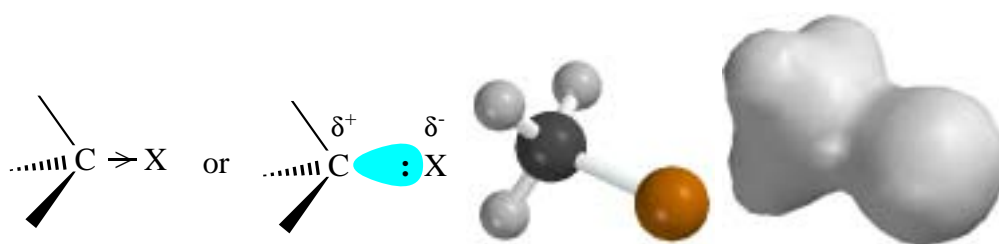
Halogens are much more *electronegative* than carbon and so the electron pair of the covalent bond is more associated with the halogen atom than the carbon atom. This means that halogens have an inductive *electron-withdrawing* effect, which we symbolise as a **–I** effect. Any group that attracts electrons towards itself is classified as **–I**. Conversely, alkyl groups repel electrons in covalent bonds and are classified as being positvely inductive or **+I**. You will encounter inductive effects often when dealing with reactivity in CHEM120.

We can think of a polar covalent bond as a covalent bond trying to become ionic. The significance of this polarization is that the carbon atom is susceptible to attack by negatively charged species (nucleophiles) and readily undergoes substitution reactions: a characteristic reaction of alkyl halides is *nucleophilic substitution*.
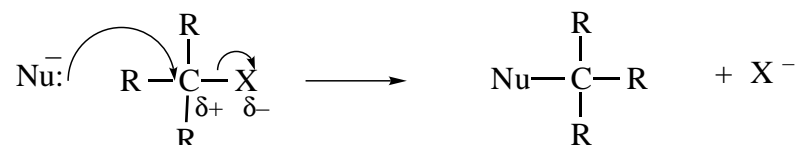
Nucleophilic substitution reactions

Read
Brown Chapter 7.2

A **nucleophile** is an **electron-rich ion or molecule** that reacts at a positive or positively polarised centre in a molecule. They can be represented as either a negatively charged ion or a neutral, electron rich molecule:

Nu:⁻   e.g. hydroxide ion, HO^- or cyanide ion, ^-CN
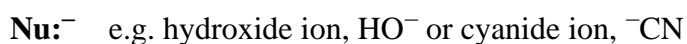
Nu: e.g. water, H_2O or ammonia, NH_3, each of which have a lone pair of electrons that constitute an electron-rich region.

A nucleophilic substitution reaction of an alkyl halide involves the replacement of the halogen atom by a suitable nucleophile. The positive polarity at the carbon of the C—X bond attracts the electron-rich nucleophile. We can write the reaction in a general form:

We break the carbon-halogen bond liberating a halide anion (the polarity helps) and form of a carbon-nucleophile bond (actually to the negatively charged atom of the nucleophile). In nucleophilic substitution, the group (or atom X in this case) that is displaced is called the ***leaving group***. The reaction is depicted in "arrow" notation above. Remember, the double-headed arrows are used to indicate the **movement of electrons** and not the movement of atoms.
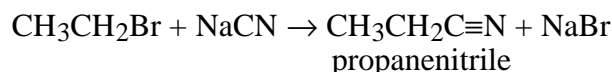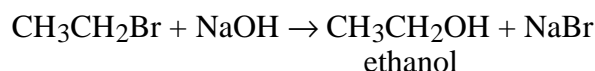
Some of the most commonly used *strong* nucleophiles are:

HO^-	(as NaOH in aqueous or organic solution)
$N\equiv C^-$	(as NaCN in aqueous or organic solution)
H_2N^-	(as $NaNH_2$ in liquid ammonia)
$R_3N:$	(as ammonia, R=H or amines (see later))
$R–C\equiv C^-$	(as $R–C\equiv CNa$ in liquid ammonia; recollect the acidity of terminal alkynes)

Two weaker nucleophiles are:

H_2O	(water)
R—OH	(alcohols, see later)

Thus, if we take bromoethane as a representative alkyl halide reacting with hydroxide or cyanide, the products are an **alcohol** (ethanol) and a **nitrile** (propanenitrile) respectively:

$$CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$$
$$\text{ethanol}$$
$$CH_3CH_2Br + NaCN \rightarrow CH_3CH_2C\equiv N + NaBr$$
$$\text{propanenitrile}$$

(Note here that with the nitrile group (a carbon-nitrogen triple bond), the carbon atom is included in the carbon count for carbon chain when naming the compound).

With amide (NH_2^-) we obtain an ***alkylamine*** *(ethanamine or ethylamine)*:
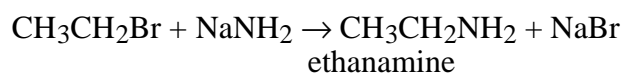
$$CH_3CH_2Br + NaNH_2 \rightarrow CH_3CH_2NH_2 + NaBr$$
$$\text{ethanamine}$$

and with a metal salt of an alkyne, we can generate other disubstituted alkynes:

$$CH_3CH_2Br + NaC{\equiv}CCH_3 \rightarrow CH_3CH_2C{\equiv}CCH_3 + NaBr$$
2-pentyne
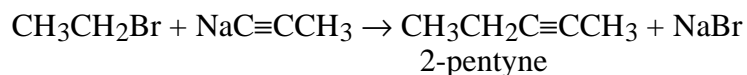
In nucleophilic substitution our curly arrow symbolism does not give us a total picture of the reaction. It tells us about the fate of the electrons, but nothing about the *timing* of the movement of the electron pairs. We obtain further information about the mechanism from investigation of the *kinetics* of the reaction. This tells us which reactants are involved in the **rate determining step** - the slow step of the reaction.

From measurements of the rates of reaction of various alkyl halides with nucleophiles, we find that nucleophilic substitution can take place by two different mechanisms. A major factor influencing which mechanism is adopted is the structure of the alkyl halide. One mechanism operates for primary and secondary alkyl halides whereas another mechanism occurs with tertiary alkyl halides.

[Primary (1°) alkyl halides have general formula

$$R{-}CH_2X$$

secondary (2°) alkyl halides
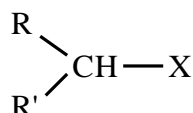
and tertiary (3°) alkyl halides
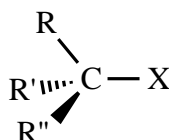
Where R, R' and R" are alkyl groups which may be the same or different.]

Elimination reactions —synthesis of alkenes

Read
Brown Chapter 7.6

Alkenes can be synthesised from alkyl halides by **loss of hydrogen halide** (*dehydrohalogenation*).

Here **X** stands for one of the **halogen atoms Cl, Br or I**. Remember, the symbol '**R**' represents some organic group of unspecified structure.

The reaction is called an ***elimination reaction*** and you will deal with the mechanism of this reaction in CHEM120.
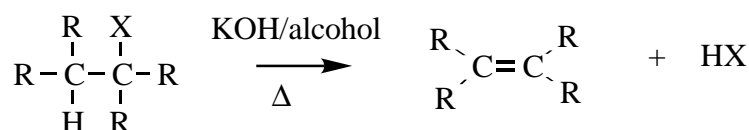
We have just seen that the nucleophilic substitution reaction of a primary alkyl halide with warm aqueous sodium hydroxide yields an alcohol by a substitution process. If however we change our reaction conditions and use a higher temperature and a more concentrated sodium hydroxide in ethanol instead of water, elimination occurs.

Thus with 2-bromopropane:

$$NaOH \ + \ CH_3CHCH_3 \ \xrightarrow{\text{ethanol}} \ CH_3CH{=}CH_2 \ + \ NaBr \ + \ H_2O$$
$$\underset{Br}{|}$$
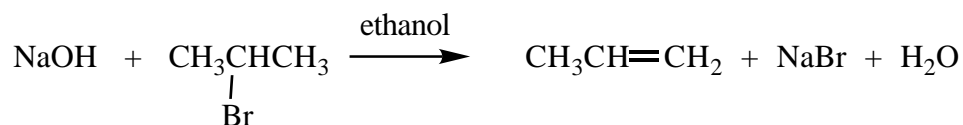
The overall result is removal of hydrogen bromide (dehydrobromination: generally dehydrohalogenation) to yield propene. Here our hydroxide ion is behaving like a base (reaction with a proton) rather than as a nucleophile (reaction at carbon).

Self-Test Exercise 3.15

Give reagents you would use to make the following from butyl bromide ($CH_3CH_2CH_2CH_2Br$):

(a) $CH_3CH_2CH_2CH_2NH_2$
   Butanamine
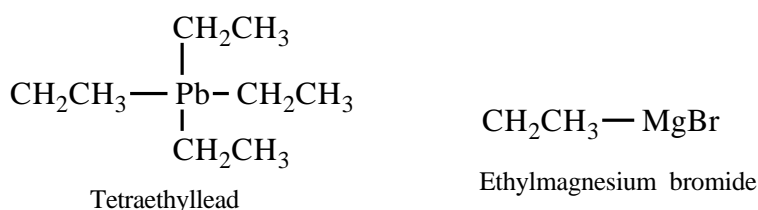
(b) Butanol

(c) 3-Octyne

(d) $CH_3CH_2CH_2CH_2C{\equiv}N$
   pentanenitrile

(e) 1-Butene

Organometallic compounds
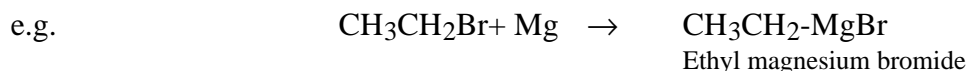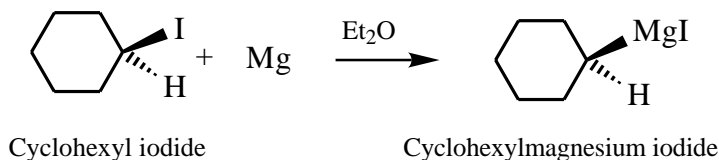
One final reaction of alkyl halides is of major importance: their reaction with metals when an *organometallic compound* is formed which contains a covalent metal to carbon bond. The anti-knock additive to petrol is one such compound in which four ethyl groups are bonded to a central lead atom:

$$CH_2CH_3 — Pb — CH_2CH_3$$

with CH_2CH_3 above and CH_2CH_3 below the Pb.

Tetraethyllead

$$CH_2CH_3 — MgBr$$

Ethylmagnesium bromide

Probably the most important class of organometallics, however, is where the metal is magnesium or lithium. Reaction of an alkyl halide with magnesium metal in a dry inert solution (usually diethyl ether [$C_2H_5OC_2H_5$]) yields an **alkyl magnesium halide** or **Grignard** reagent. An example is the formation of ethylmagnesium bromide above.

e.g. $$CH_3CH_2Br + Mg \rightarrow CH_3CH_2\text{-}MgBr$$

Ethyl magnesium bromide

and

Cyclohexyl iodide   Cyclohexylmagnesium iodide

For now we note that the effect of the insertion of an electropositive magnesium atom between the carbon and halogen atoms changes the partial charge on the carbon atom.

$$\overset{\delta^-}{-}C\overset{\delta^+}{-}MgX \quad \text{instead of} \quad \overset{\delta^+}{-}C\overset{\delta^-}{-}X$$
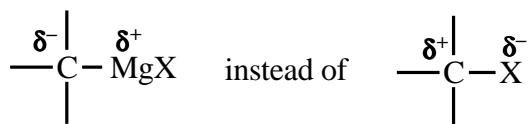
Polarisation in the sigma bond is reversed:

$$\overset{\delta^-}{-}C\mathbf{:}\overset{\delta^+}{MgX} \quad \text{instead of} \quad \overset{\delta^+}{-}C\mathbf{:}\overset{\delta^-}{X}$$
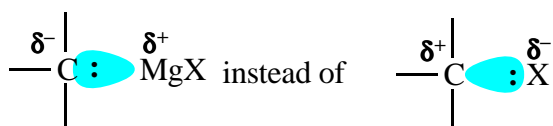
As a consequence Grignard reagents behave like **negatively charged carbons** (**R⁻**)**,** or what are termed in organic chemistry **carbanions**. **T**hese have very wide synthetic utility, as we shall see when we discuss other functional groups. One important property to note here is that such Grignard reagents are also strongly basic and will react readily with proton sources such as water.

Halogens attached to double bonds (vinyl halides) and aromatic rings (aryl halides) are also reactive.

Topic Highlights

You should be able to:

❏ draw and name various simple alkyl halides;

❏ understand their properties in terms of bond strengths of the various alkyl halides and polarity of the carbon-halogen bonds;

❏ recognise why they undergo substitution reactions and write the products from reaction with —OH^-, —CN^-, —NH_2^-, and alkynides;

❏ recognise that they undergo elimination reactions;

❏ understand what a Grignard reagent is.

Topic 3G - Alcohols

Key questions

What is an alcohol? How do we name them and what are their properties? They are soluble in water — why? What is hydrogen bonding? What reactions involve replacement of the OH group? What is a nitrite ester? Are alcohols acidic?

Outline

Alcohols are very common organic reagents that are widely used in synthesis. Their chemistry is similar in some ways to alkyl halides you have just studied. In this Topic we explore basic chemistry of the alcohol functionality.

What is an alcohol?

Read
Brown Chapters 8.1, 8.2, 8.3 (Alcohols only)

Alcohols contain the **-OH** or **hydroxyl group**. Note, particularly, the two *non-bonding valence electrons* on the oxygen atom. These have an important role to play in the chemistry of this functional group:

$$R - \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} - H$$
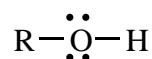
Nomenclature of alcohols:

The presence of a hydroxy group on an alk**ane** is denoted by the suffix **-anol**. In all but methane and ethane, a prefix number is used to designate the position of substitution. For some simple compounds, the older trivial nomenclature is still used where it takes the form of alkyl alcohol.

Thus:

CH_3OH	methanol	methyl alcohol
CH_3CH_2OH	ethanol	ethyl alcohol
$CH_3CH_2CH_2OH$	1-propanol	*n*-propyl alcohol
$CH_3CH_2(OH)CH_3$	2-propanol	*sec*-butyl alcohol
$CH_3CH_2CH_2CH_2OH$	1-butanol	*n*-butyl alcohol
$CH_3CH_2CH(OH)CH_3$	2-butanol	*sec*-butyl alcohol
$(CH_3)_2CHCH_2OH$	2-methyl-1-propanol	isobutyl alcohol
$(CH_3)_3COH$	2-methyl-2-propanol	*tert*-butyl alcohol

In more complex alcohols, the position of the hydroxyl group is given the lowest number in the carbon chain. Thus the structure below is 5-methyl-3-hexanol and not 2-methyl-4-hexanol.
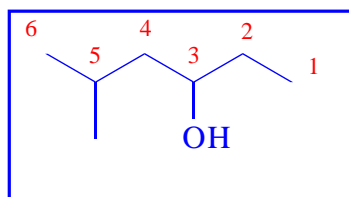
Alcohols are classified in a similar manner to the alkyl halides. Thus 1-propanol, methanol, ethanol etc., are primary (1°) alcohols (general formula $R–CH_2OH$), 2-propanol and 2-butanol are secondary (2°) alcohols (R_2CHOH) and 2-methyl-2-propanol (*tert*-butyl alcohol) is a tertiary   (3°) alcohol (R_3COH).

Note that alcohols have the general formula $C_nH_{2n+2}O$ (or more descriptively $C_nH_{2n+1}OH$). Thus 1-propanol and 2-propanol are structural isomers with formulas C_3H_8O, and the four butyl alcohols are structural isomers with formula $C_4H_{10}O$.

Self-Test Exercise 3.16

Complete *Practice Problem 8.2* p. 205 Brown:
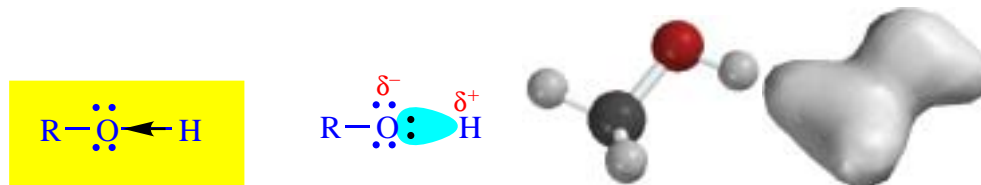
(a)

(b)

(c)

(d)

Properties of alcohols:

The **electronegativity of oxygen is very high**, hence the -O-H bond is strongly polarised. The electron cloud between the oxygen and the hydrogen atom is greatly distorted towards the oxygen atom.

Observe the distortion in O–H bond of the methanol molecule:

The group "R" can be an alkane, an alkene, an alkyne, or an aromatic ring. In aliphatic compounds the **suffix '–ol' is used to denote the presence of this group** (on occasions it is necessary to use the prefix hydroxy).

Unlike the organic compounds we have encountered so far, **alcohols are soluble in water**. The low molecular weight alcohols are totally miscible with water; then the solubility decreases with increasing molecular weight.

Alcohols also have a higher boiling point than hydrocarbons or alkyl halides of comparable molecular weight:

CH_3OH: 65° CH_3Cl: 24° CH_3CH_3: -88°

CH_3CH_2OH: 78° CH_3CH_2Cl: 13° $CH_3CH_2CH_3$: -45°
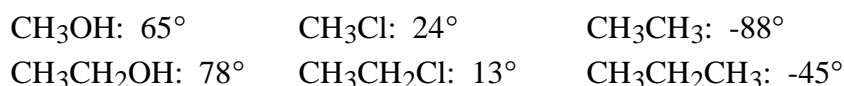
Both these physical properties are a consequence of **intermolecular hydrogen bonding** (weak bonding between the electron-rich oxygen of one molecule and the electron-deficient hydrogen of another). Such bonding involves donation of one of the lone pairs of oxygen towards a hydrogen of another alcohol, which thus becomes partly bonded to both molecules. However, the longer the hydrocarbon chain, the less soluble the alcohol will be.
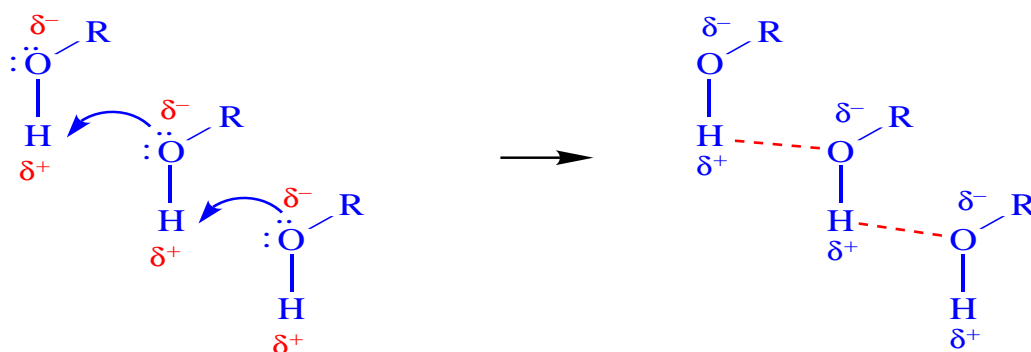
In order to vaporise we have to provide energy to break the intermolecular hydrogen bonds between the alcohol molecules.

The water solubility of alcohols derives from the ability of the hydroxyl group to hydrogen bond to water in a like manner. The **hydroxyl group is** said to be **hydro*philic*** (water loving). **Alkyl groups**, being non-polar, contribute to water insolubility. They are said to be **hydro*phobic***. Indeed, alcohols can be pictured as being water with one of its hydrogens replaced by an alkyl group.

As you saw in Topic 3D, hydrogen bonding is a vital process which is responsible for the way in which DNA - deoxy ribonucleic acid - is held

together and is able to transfer genetic information during cell division and protein synthesis.
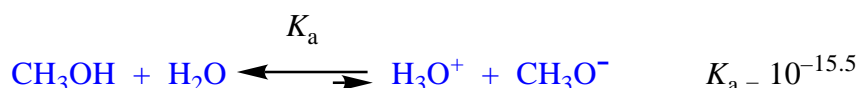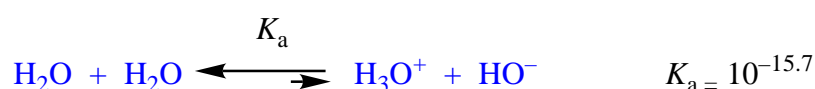
Synthesis and reactions of alcohols

We have already encountered two syntheses of alcohols:

> Hydrolysis of alkyl halides;
> Acid catalysed hydration (addition of water) to alkenes.

In first-year chemistry we are primarily concerned with the reactions rather than the preparation of organic compounds. (We will use such introductory syntheses as a means of revision of reactions already discussed and we will meet other routes to alcohols as the course proceeds).

Acidity and basicity:

Like water alcohols can act as a proton donor, although under normal aqueous conditions they are not very well ionised at all:

$$H_2O + H_2O \xrightleftharpoons{K_a} H_3O^+ + HO^- \qquad K_a = 10^{-15.7}$$

$$CH_3OH + H_2O \xrightleftharpoons{K_a} H_3O^+ + CH_3O^- \qquad K_a = 10^{-15.5}$$

With strong bases though, they can be ionised to give very strongly basic alkoxide ions:

Strong base   Alkoxide ion
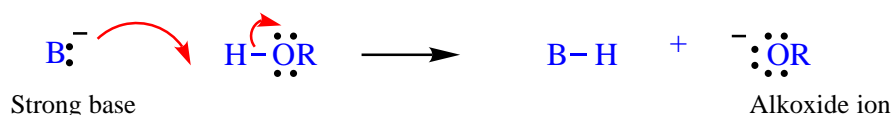
A base stronger than hydroxide is required.

The lone pairs on the alcohol oxygen make alcohols *weakly* basic, but they are readily protonated in the presence of strong acids:

A protonated alcohol
or an *oxonium ion*
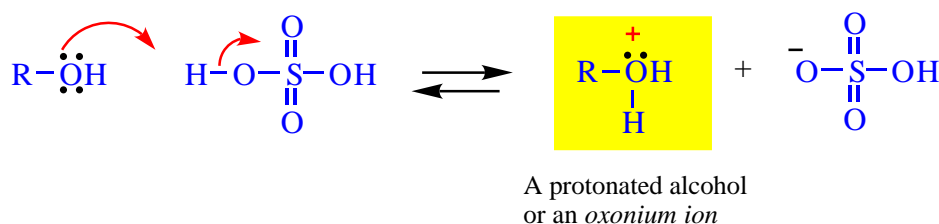
2

This is the starting point for many reactions where the hydroxyl group is replaced by another kind of substituent (see below).

Nucleophilic substitution:

Like the halogens, oxygen is *much more* electronegative than carbon. This means that alcohols like alkyl halides will undergo nucleophilic substitution reactions. However they do so much less readily, because the hydroxyl group is a very poor **leaving group**.

> For a group (or atom in the case of halogens) to be displaced in nucleophilic substitution reactions it must be stable in solution (i.e. a weak base).
> Hydroxide ion is a strong base.

Nonetheless, we can make alcohols undergo nucleophilic substitution reactions: but the leaving group is not a hydroxide ion. We must conduct the reactions under *acidic* conditions where the alcohol is protonated on the oxygen atom (alcohols, like water, are weak bases).
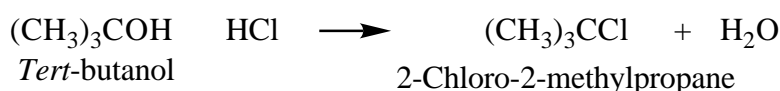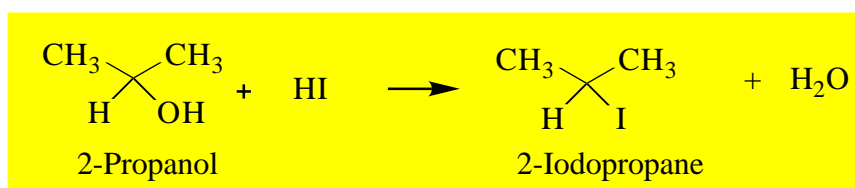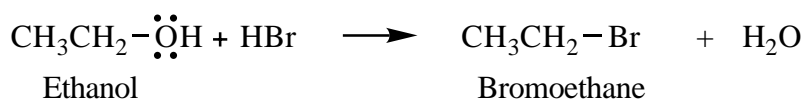
After protonation the reaction parallels that of the alkyl halides, with the nucleophile displacing water. Water is an excellent leaving group being a very weak base.
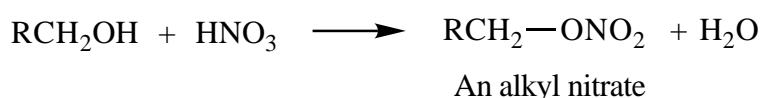
$$R-\ddot{O}H + H^+ \rightleftharpoons R-\overset{+}{\underset{\underset{H}{|}}{\ddot{O}H}} \xrightarrow{Nu\ddot{:}^-} Nu-R \ + \ H_2O$$
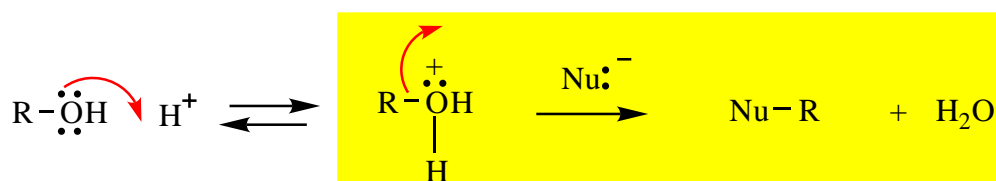
The *oxonium ion* becomes
a good leaving group

Chloride, bromide and iodide ions however are *weak* bases (the conjugate acids HCl, HBr and HI are strong acids which readily ionise) and the order of reactivity of alkyl halides is: alkyl iodide > alkyl bromide > alkyl chloride, paralleling the order of basicity of the anions. Iodide ions are more stable than bromide and chloride ions.

Alcohols therefore react readily with HCl, HBr and HI producing alkyl halides.

$$CH_3CH_2-\ddot{O}H + HBr \longrightarrow CH_3CH_2-Br \ + \ H_2O$$

Ethanol   Bromoethane

$$\underset{\text{2-Propanol}}{\overset{CH_3 \diagdown \diagup CH_3}{H \diagup \diagdown OH}} + \ HI \longrightarrow \underset{\text{2-Iodopropane}}{\overset{CH_3 \diagdown \diagup CH_3}{H \diagup \diagdown I}} + \ H_2O$$

$$\underset{Tert\text{-butanol}}{(CH_3)_3COH} \quad HCl \longrightarrow \underset{\text{2-Chloro-2-methylpropane}}{(CH_3)_3CCl} \ + \ H_2O$$

Nitric acid can function in a similar manner to yield a nitrate ester.

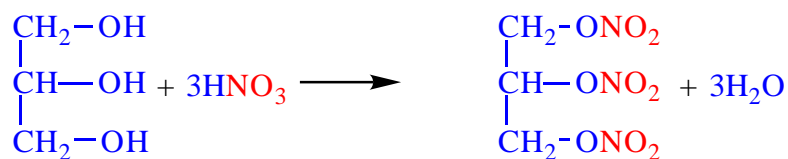$$RCH_2OH \ + \ HNO_3 \longrightarrow RCH_2-ONO_2 \ + H_2O$$

An alkyl nitrate

Thus with 1,2,3-propanetriol (trivial name glycerol) we obtain 1,2,3-propanetriyl trinitrate. This is otherwise called *nitroglycerine*, a colourless oily liquid which is sensitive to slight shock - which results in violent detonation. The synthesis reaction is performed in the presence of concentrated sulfuric
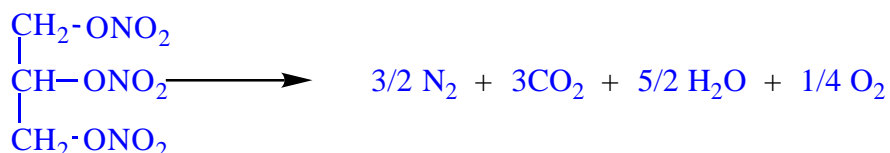

General Chemistry CD-ROM Screen 11.6

The sudden liberation of this large volume of gas in a space initially occupied by the liquid substance gives a shock wave of enormous pressure. The name *nitroglycerine* is misleading: it is not a nitro compound as these are bonded to carbon through the nitrogen.

acid to absorb the water formed in the reaction, needs super-efficient cooling, and agitation using compressed air to mix the reactants:

$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + 3HNO_3 \longrightarrow \begin{array}{l} CH_2-ONO_2 \\ | \\ CH-ONO_2 \\ | \\ CH_2-ONO_2 \end{array} + 3H_2O$$

There is enough oxygen present in the molecule to convert all the carbon and hydrogen into the corresponding oxides with the liberation of elemental nitrogen.

$$\begin{array}{l} CH_2-ONO_2 \\ | \\ CH-ONO_2 \\ | \\ CH_2-ONO_2 \end{array} \longrightarrow \quad 3/2\ N_2\ +\ 3CO_2\ +\ 5/2\ H_2O\ +\ 1/4\ O_2$$

The sensitivity can be reduced by absorption on *kieselguhr*, a diatomaceous earth. It still retains its explosive power but a detonator is required. In this form it is called *dynamite*; discovered by Alfred Nobel in 1866. The endowments from his immense fortune provide the Nobel Prize money to various areas of Science, Medicine and the Arts each year.

Interestingly, nitroglycerine is used medicinally to dilate blood vessels and is taken to relieve angina. It is a source of NO, nitric oxide. The action of "*Viagra*" involves similar chemistry!
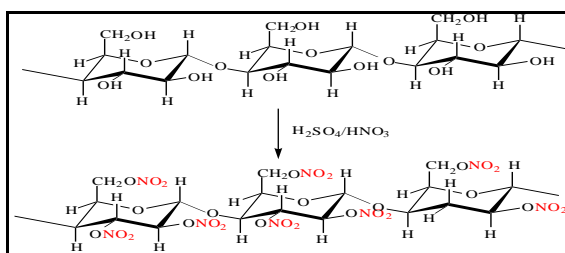

Nitrocellulose, or gun cotton, is used as a fuse and works on the same principles as nitroglycerine.

Under certain conditions, sulfuric acid converts alcohols into alkyl sulfates:

$$CH_3CH_2OH\ +\ H_2SO_4\ \longrightarrow\ CH_3CH_2OSO_3H\ +\ H_2O$$
$$\text{Ethyl sulfate}$$
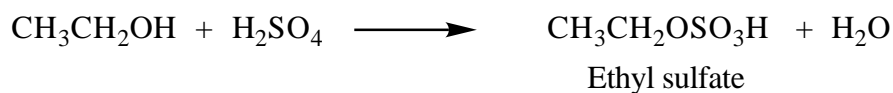
Some inorganic halides can also be used to convert alcohols to halides. The most commonly used are thionyl chloride, and the phosphorus trihalides.

$$R-OH + SOCl_2 \rightarrow RCl + HCl + SO_2$$
$$3ROH + PBr_3 \rightarrow 3RBr + H_3PO_3$$
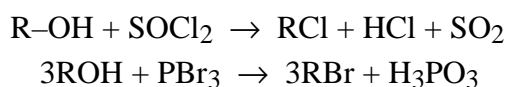
Similarly, phosphorus triiodide can be used to convert alcohols to alkyl iodides.

Self-Test Exercise 3.17

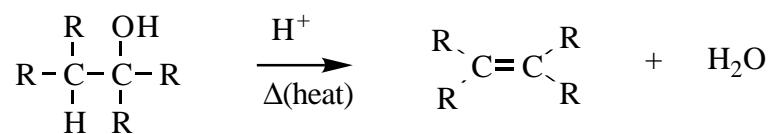Draw and name the products from the following reactions:

(a) 2-Propanol reacting with HBr

(b) Ethanol reacting with nitric acid

(c) Why is acid needed for both of these reactions?

Dehydration of alcohols - elimination reactions:

When alcohols are treated with acids, a competing reaction with substitution is elimination to give *alkenes*:

$$
\underset{\underset{\text{H}\quad\text{R}}{|\qquad|}}{\overset{\overset{\text{R}\quad\text{OH}}{|\qquad|}}{\text{R}-\text{C}-\text{C}-\text{R}}}
\quad\xrightarrow[\Delta(\text{heat})]{\text{H}^+}\quad
\underset{\text{R}}{\overset{\text{R}}{}}\text{C}=\text{C}\underset{\text{R}}{\overset{\text{R}}{}}
\quad+\quad \text{H}_2\text{O}
$$

Note that after conversion of the hydroxyl group to a good leaving group (water) by protonation, **loss of water** (*dehydration*) and regeneration of H^+

gives the alkene. Once again, alcohols, once protonated at oxygen, behave like alkyl halides.
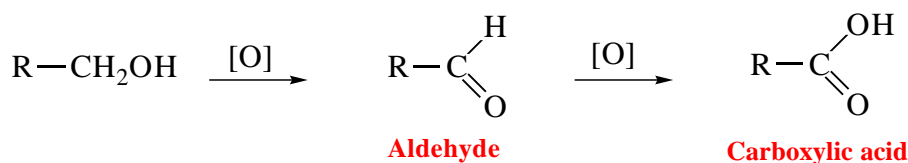
Ester formation:

A general and important reaction of alcohols, and one we will discuss in detail during CHEM120, is the formation of so-called *carboxylic esters* from carboxylic acids (see Topic3H).

carboxylic acid   **carboxylic ester**
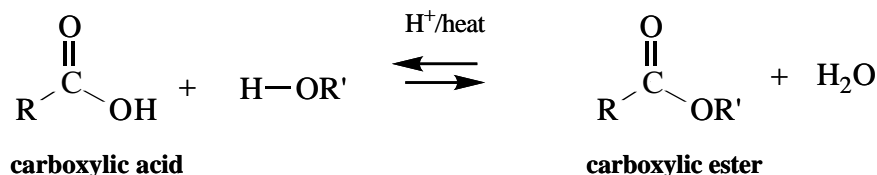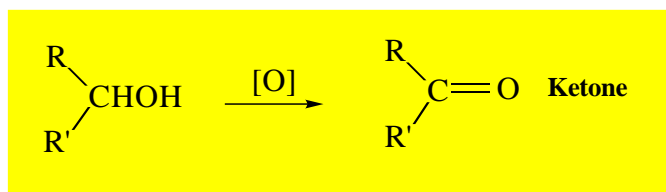
These important compounds are responsible for many fragrances and essences found in the manufacturing industry. They are also extensively used as feedstocks for the polymer industry.

Oxidation of alcohols:

Primary and secondary alcohols can be oxidised by many oxidising agents:

[O] means some oxidation reaction

Why do such reactions constitute an oxidation? They do so because in each case we are removing hydrogen and in the case of carboxylic acid formation we are also adding oxygen. Both processes are regarded as oxidation. Removal of hydrogen is the reverse of addition of hydrogen, which we know to be a reduction reaction.

Primary (1°) alcohols oxidise to **aldehydes**, which may oxidise further to **carboxylic acids.** Secondary (2°) alcohols yield **ketones**, while tertiary alcohols are unaffected. Aldehydes, ketones and carboxylic acids will be dealt with in Topics 3I and 3J of this course.

Commonly used oxidants are acidified aqueous sodium (or potassium) dichromate, chromium trioxide and potassium permanganate.

Although it is possible to write balanced equations for these reactions, it is sufficient for our purposes to depict the reactions as shown. Usually these oxidations are also accompanied by colour changes. The purple permanganate ion [manganese(VII)] is decolourised (it is reduced to the colourless manganese(II) cation) and the orange dichromate ion [Cr(VI)] (and the red chromium trioxide) turns green due to formation of chromium(III) ions. Some of you *may* (but we hope not) have encountered the latter colour change in your

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private life: in the breath analyzer where alcohol (i.e. ethanol) is tested for by oxidation.

Metal alkoxides and ether synthesis:

We have seen that alcohols, like water, are weak bases and are protonated by strong acids. Again like water, they can act as an acid and lose a proton to a **strong base**. A very strong base like sodium hydride is necessary (sodium hydroxide is not a powerful enough base to effect this deprotonation). Hydride ions are very unusual and are regarded as negatively charged hydrogen!! They are very, very strong bases.
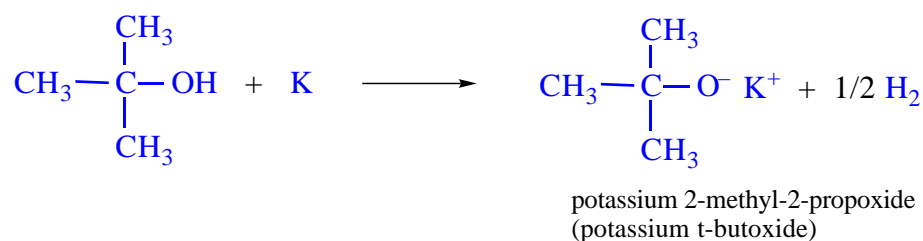
Thus:

$$R-O-H \quad \ ^-{:}H \ \ Na^+ \quad \longrightarrow \quad H_2\uparrow + R-O^- \ \ Na^+$$

a sodium alkoxide
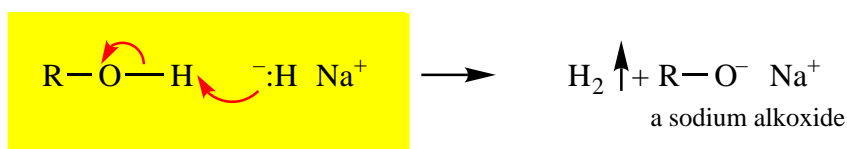
Experimentally it is usually more convenient to treat the alcohol with an alkali metal.

Thus:

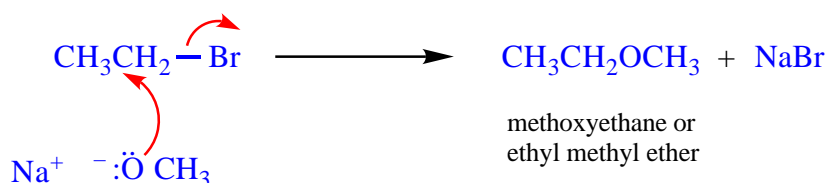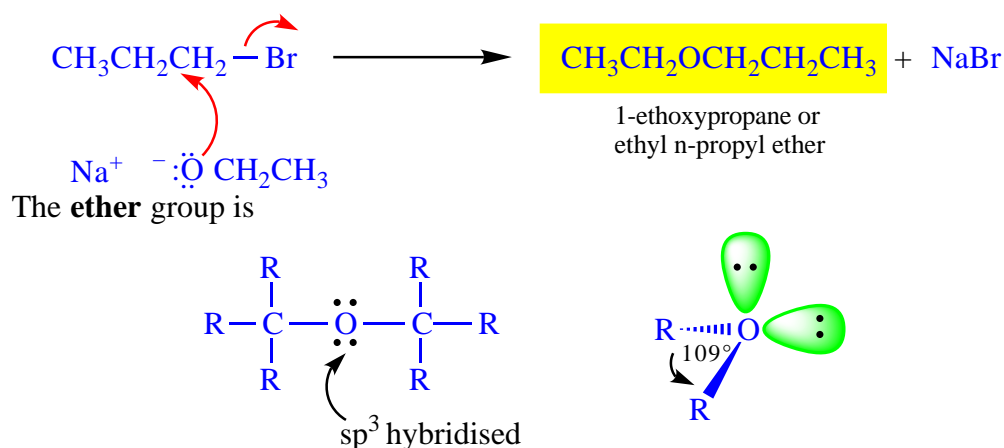$$CH_3CH_2OH + Na \ \rightarrow \ CH_3CH_2O^-Na^+ + \tfrac{1}{2} \ H_2 \uparrow$$

This reaction is a useful laboratory test for alcohols: bubbles of hydrogen gas are evolved which can be observed. With tertiary alcohols we may need to use the more reactive alkali metal, potassium. This is because the hydroxyl group is not so readily accessible to the metal: we call this effect *steric hindrance*.

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \ + \ K \quad \longrightarrow \quad CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O^- \ K^+ \ + \ 1/2 \ H_2$$

potassium 2-methyl-2-propoxide
(potassium t-butoxide)

The reaction of unhindered alcohols with sodium is usually vigorous and with potassium can often be violent.

Like hydroxide ions, alkoxides are strong nucleophiles and bases. They react with primary and secondary alkyl halides in substitution reactions giving **ethers**.

$$CH_3CH_2-Br \quad \longrightarrow \quad CH_3CH_2OCH_3 \ + \ NaBr$$

methoxyethane or
ethyl methyl ether

$$Na^+ \quad {}^-{:}\ddot{O} \ CH_3$$

$$CH_3CH_2CH_2 - Br \longrightarrow CH_3CH_2OCH_2CH_2CH_3 + NaBr$$

1-ethoxypropane or
ethyl n-propyl ether

$$Na^+ \quad {}^-\!:\!\ddot{O}\,CH_2CH_3$$

The **ether** group is

$$R - \underset{R}{\overset{R}{C}} - \ddot{O} - \underset{R}{\overset{R}{C}} - R$$

sp^3 hybridised

$$R\cdots O \atop 109°$$
$$R$$

and as indicated in the reaction products above, two methods of naming them are available. The alkoxyalkane name (which is correct systematically) is preferable, particularly for other than very simple structures.

The most important ether is *ethoxyethane* (*diethyl ether* or simply *ether*). Since ethers are inert to most reagents, and are reasonably polar liquids, they are excellent solvents for many reactions. The Grignard reaction of alkyl halides is usually performed in ether. They are, however, highly flammable so care is needed in their use.
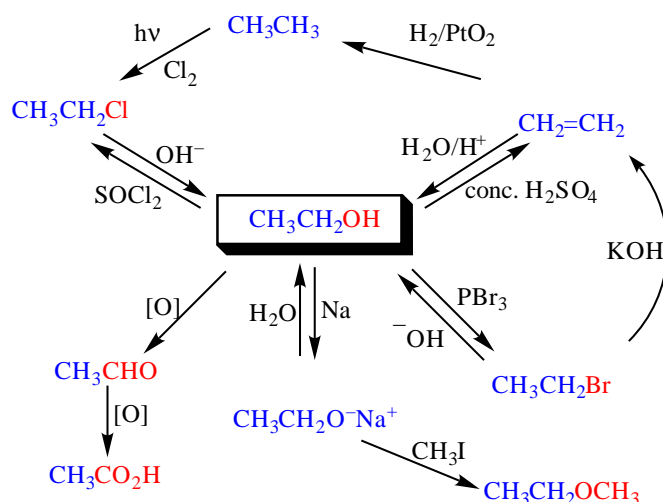
Reaction summaries

We are now well advanced into our discussion of the reactions of the various functional groups in organic chemistry. It should already be apparent to you that there is a high degree of inconvertability between them. For example, alkyl halides can be converted to alcohols by reaction with sodium hydroxide, and the reverse operation can be achieved by treatment of alcohols with hydrogen chloride or thionyl chloride. More examples of the same will appear as we proceed further.

This flexibility is of great importance to practising organic chemists: sometimes one type of compound will be available on their storeroom shelves (or readily available from a manufacturer) and at another time an alternative type of starting compound is more readily available.

Our number of reactions is steadily growing and so we need to **summarise our knowledge so that it can be readily accessed** (and revised in order to test our accumulation of this knowledge). A useful method is to produce a 'star diagram' in which a specific compound (or functionality) is at the centre of the star, with rays (conversion arrows) pointing inwards indicating methods of preparation and outwards indicating reactions.
For example with ethanol:

hv CH$_3$CH$_3$ H$_2$/PtO$_2$

Cl$_2$

CH$_3$CH$_2$Cl

OH$^-$

SOCl$_2$

CH$_3$CH$_2$OH

CH$_2$=CH$_2$

H$_2$O/H$^+$

conc. H$_2$SO$_4$

KOH

[O] H$_2$O | Na PBr$_3$

$^-$OH

CH$_3$CHO

CH$_3$CH$_2$Br

[O]

CH$_3$CH$_2$O$^-$Na$^+$

CH$_3$I

CH$_3$CO$_2$H

CH$_3$CH$_2$OCH$_3$

You will quite likely find this a very convenient method to summarise the reactions of each functionality. Why not now construct a similar diagram for the alkyl halides? Carry on the practise for each successive functional group as it is introduced.

This idea can be extended by using it as a method to test your knowledge, after completion of each chapter. Think of a compound (or a class of compound) and then without reference to these notes (or the textbook) write down the reactions you can remember. *Then* check your recollections against the text, to find out where you may have gone wrong or what you didn't remember. As the course progresses you will find that your reaction schemes will get bigger, and numerous branches and interconversions can be added to the overall picture. You may find that you want to use this idea as the base on which you build your revision.

Topic Highlights

You should be able to:

❏   draw and name the structures of straight-chain and branched alcohols;

❏   understand their properties in terms of the polarity of the oxygen-hydrogen bond;

❏   understand that they are weak acids but upon protonation they undergo substitution reactions;

❏   understand that they react with hydrohalic acids, nitric acid (forming nitrite esters) and sulfuric acid (forming sulfate esters) by this process;

❏   write down the elimination and oxidation products;

❏   show how, as alkoxides, they can form ethers.

Topic 3H - Amines

Key questions

What is an amine? How are amines covalently bonded together? Are they basic? How do they react?
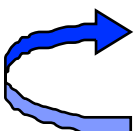
Outline

We will briefly look at properties of this very important class of molecules. The amine functionality is a part of every amino acid and as such is vital for protein formation and life.

What is an amine?

**Read
Brown Chapters 10.1, 10.2**

Topic 3F

In Topic 3F we dealt with nucleophilic substitution on alkyl halides. In one of these reactions we learnt that when the nucleophile is an amide anion NH_2^-, the halide is replaced by an amino group ($-NH_2$) and the product is called an **amine**.

Thus, with sodium amide, ethyl bromide yields sodium bromide and *ethanamine* or *ethylamine*:

$$Na^+\, H_2N^-\ +\ CH_3CH_2Br\quad \rightarrow\quad CH_3CH_2NH_2\ + Na^+\ Br^-$$
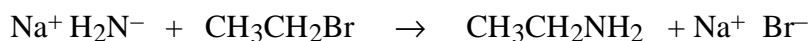
Amines are exceptionally important compounds because they can act as an organic base and, in addition, can participate in hydrogen bonding.
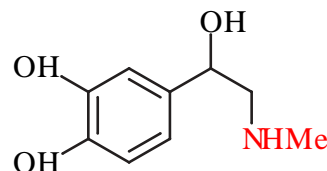
Seretonin is a derivative of *ethylamine*, which performs a vital role in the transmission of nerve impulses. Suppression of levels of this chemical in the brain is believed to be responsible for a very common ailment, mental depression. An elevation above normal levels is thought to cause anxiety.
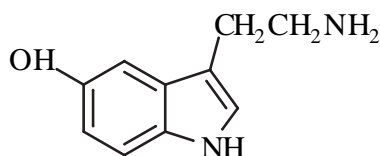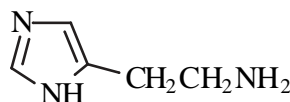
Seretonin   Histamine   Adrenalin

Histamine and adrenalin are two other examples of ethylamine derivatives that are biologically important; histidine is believed to be responsible for allergic symptoms while adrenalin is also a neurotransmitter. Amino acids, the constituents of proteins, all contain amine groups.

Structure and bonding in organic amines:

The nitrogen atom in amines is sp^3 hybridised and, like saturated carbon and oxygen in ethers or alcohols, it has a tetrahedral geometry. However since there are five valence electrons on nitrogen, two of the electrons are spin-paired in one of the sp^3 hybrid orbitals. The remaining three orbitals are singly occupied.
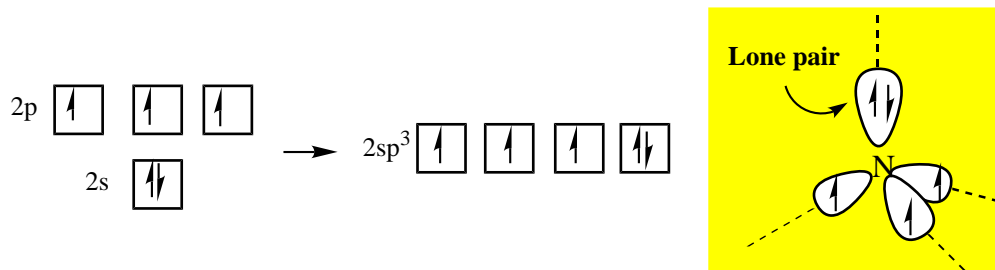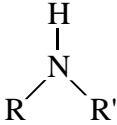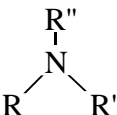

When these hybrid orbitals bond to three hydrogens the molecule is called ammonia. When carbon is bonded to one, two or all three semi-filled hybrid orbitals, amines are formed, e.g. methylamine:
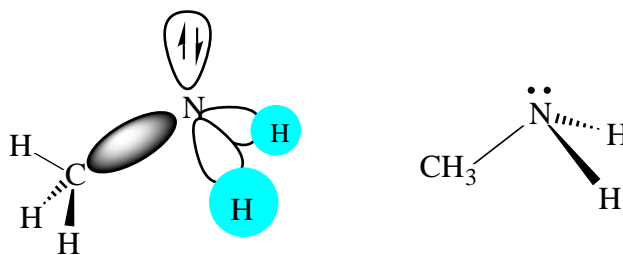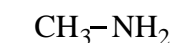

Methylamine (Methanamine)

We classify amines in a different way to alcohols or alkyl halides. The classification is based on how many of the hydrogens of ammonia are replaced by alkyl (and/or aromatic) groups.

Thus:

As is common in organic chemistry, the simplest members have trivial names derived by adding the suffix *amine* to the alkyl part.

Thus :

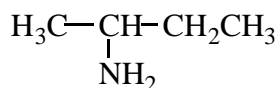$$CH_3-NH_2$$

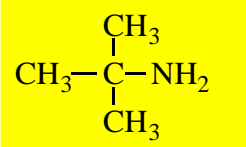Methylamine (1°)

$$CH_3CH_2-NH-CH(CH_3)_2$$

Ethylisopropylamine (2°)

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-NH_2$$

tert-Butylamine (1°)

$$H_3C-\underset{\underset{NH_2}{|}}{CH}-CH_2CH_3$$

sec-Butylamine (1°)

$$(CH_3CH_2)_3N$$

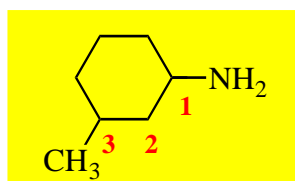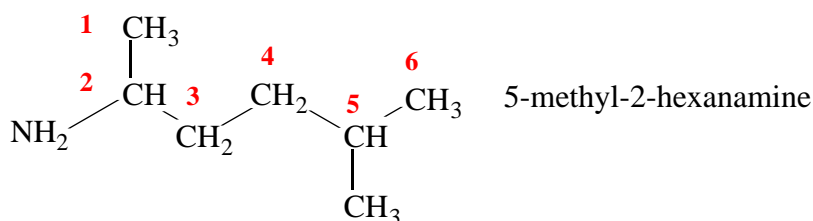Triethylamine (3°)

With more complex and larger amines, the systematic nomenclature becomes important. The systematic name is produced by adding the suffix *amine* to the alkane stem, together with appropriate numbering indicating its position.
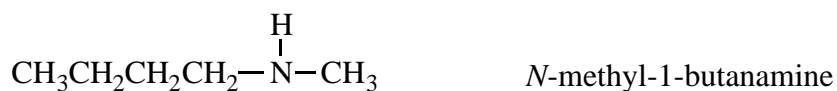
Thus:

5-methyl-2-hexanamine

3-methylcyclohexanamine

(Note that in the latter example the amino group is attached to C-1).

The naming of secondary and tertiary amines is much easier to handle using systematic nomenclature.

Thus:

$$CH_3CH_2CH_2CH_2-\underset{}{\overset{\overset{H}{|}}{N}}-CH_3$$

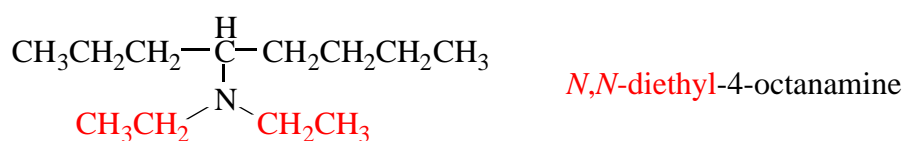*N*-methyl-1-butanamine

The italic upper case "*N*" indicates the methyl group is attached to the nitrogen atom.

Similarly:

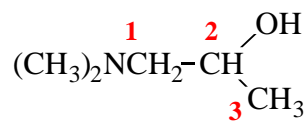$$CH_3CH_2CH_2-\underset{\underset{CH_3CH_2\diagup N \diagdown CH_2CH_3}{}}{\overset{\overset{H}{|}}{C}}-CH_2CH_2CH_2CH_3$$

N,N-diethyl-4-octanamine

We may also need to denote the presence of the functional group by use of the prefix *amino*:

$$H_2N\overset{\textbf{3}}{\diagdown}\underset{CH_3}{\overset{\textbf{2}\quad\textbf{1}}{CHCH_2CH_2OH}} \qquad (CH_3)_2N\overset{\textbf{1}}{CH_2}-\overset{\textbf{2}}{CH}\diagup^{OH}_{\underset{\textbf{3}}{CH_3}}$$
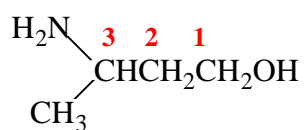
3-aminobutanol   1-(dimethylamino)-2-propanol

The alcohol group has priority over an amino group, meaning that the *compounds are named as alcohols rather than as amines*. The amino group is a substituent on the alcohol.

Self-Test Exercise 3.18

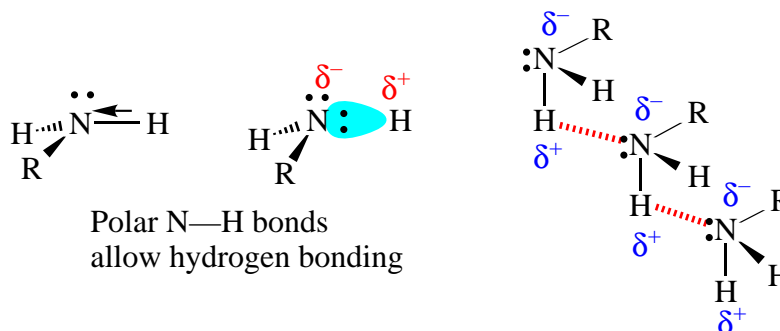Complete *Practice Problem 10.2* p. 282 Brown:

(a)

(b)

(c) [Ignore the (R)]
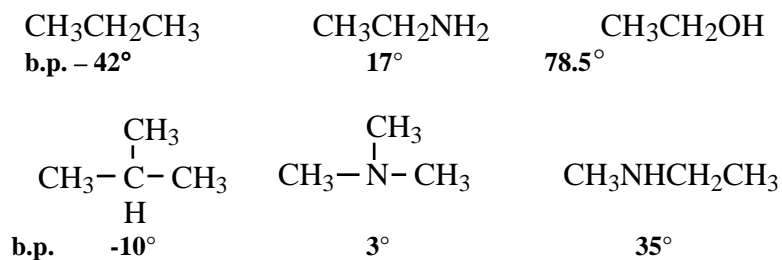
Physical properties of amines

Read
Brown Chapter 10.3

The physical properties of amines parallel those of alcohols, since amines can also form intramolecular hydrogen bonds:

Polar N—H bonds
allow hydrogen bonding

Amines have a relatively high boiling point, but not as high as the alcohols since the HN...H bond is much weaker than the HO...H bond. Tertiary amines bear no N—H bonds and cannot hydrogen bond to themselves, so their boiling points are lower.

Thus:

$CH_3CH_2CH_3$ $\qquad$ $CH_3CH_2NH_2$ $\qquad$ CH_3CH_2OH

b.p. – 42° $\qquad\qquad$ **17°** $\qquad$ **78.5°**

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_3 \qquad CH_3-\overset{\overset{\displaystyle CH_3}{|}}{N}-CH_3 \qquad CH_3NHCH_2CH_3$$

b.p. $\quad$ **-10°** $\qquad\qquad$ **3°** $\qquad\qquad$ **35°**

Lower members are completely soluble in water, as amines can readily hydrogen bond to water. Solubility decreases with increasing hydrophobic alkyl content.
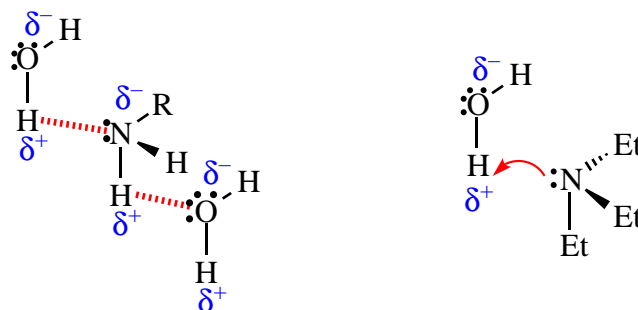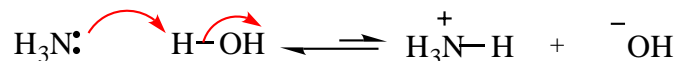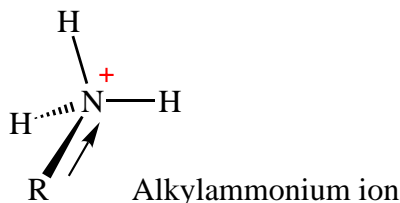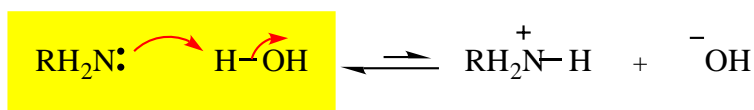
Basicity and nucleophilicity of amines

Ammonia is basic; it is a weak base.

$$H_3N\text{:} \quad H\text{—}OH \rightleftharpoons H_3\overset{+}{N}\text{—}H \quad + \quad \overset{-}{O}H$$

So are amines. Indeed, they are slightly stronger bases:

$$RH_2N\text{:} \quad H\text{—}OH \rightleftharpoons RH_2\overset{+}{N}\text{—}H \quad + \quad \overset{-}{O}H$$

Alkylammonium ion

Recall that alkyl groups are electron-donating? Well, the positive inductive (+**I**) effect helps to stabilize the positive charge on the nitrogen atom of the ammonium ion.

For a reaction of the type above, the equilibrium constant K_b, and pK_b are defined as:

$$K_b = \frac{[RNH_3^+]\,[OH^-]}{[RNH_2]}$$

$$pK_b = -\log K_b$$

Thus, the further the equilibrium is to the right, the greater is K_b, the stronger the base and the smaller is the pK_b value for the amine. It can therefore be seen that with increasing alkyl substitution, the basicity of the amine increases:
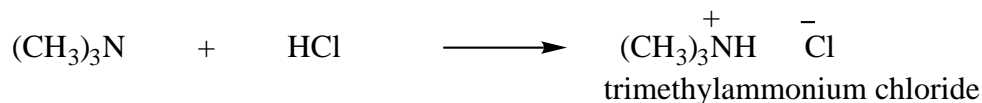
|	**NH_3**	**CH_3NH_2**	**CH_3NHCH_3**
K_b	1.79×10^{-5}	45×10^{-5}	54×10^{-5}
pK_b	4.75	3.35	3.27

Increasing base strength

Pyridine has a pK_b of 8.75 and this aromatic amine is a weaker base than alkylamines.

Weakly basic amines can be fully protonated by strong acids and this reaction is quite general. It results in the formation of *salts*, which are named as *alkyl ammonium salts*.

Thus:

$$CH_3CH_2NH_2 \quad + \quad HCl \quad \longrightarrow \quad CH_3CH_2\overset{+}{N}H_3 \quad \overset{-}{Cl}$$

ethylammonium chloride

$$(CH_3)_3N \quad + \quad HCl \quad \longrightarrow \quad (CH_3)_3\overset{+}{N}H \quad \overset{-}{Cl}$$

trimethylammonium chloride
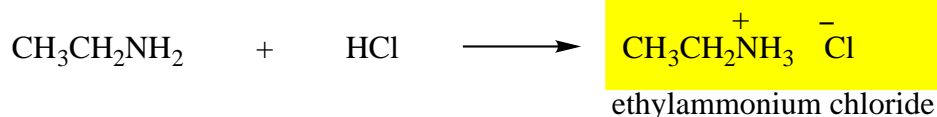
The salts are ionic and as such are soluble in water, and are generally crystalline solids with high melting points. Note that an amine can be regenerated from an ammonium salt in the presence of a base that is stronger than the amine itself:

$$R_3\overset{+}{N}-H \quad + \quad \overset{-}{O}H \quad \longrightarrow \quad R_3N{:} \quad + \quad H_2O$$
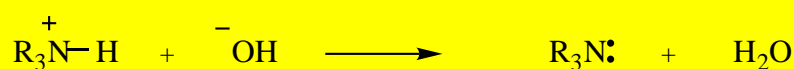
Amines are good nucleophiles and will react with alkyl halides forming N—C bonds in substitution reactions. For instance, ethlamine reacts with methylbromide to give the secondary amine, *N*-methylethylamine. Clearly a secondary amine can also be converted to a tertiary amine this way as well.

$$CH_3CH_2-NH-CH_3 \quad + \quad HBr$$

N-methylethylamine
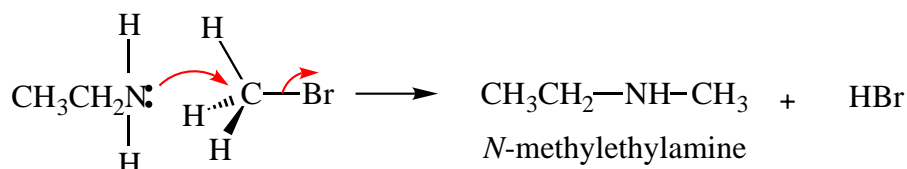
Self-Test Exercise 3.19

Based upon the last reaction, describe two ways in which you might make the following secondary amine:

N-ethyl-2-propanamine
(ethylisopropylamine)
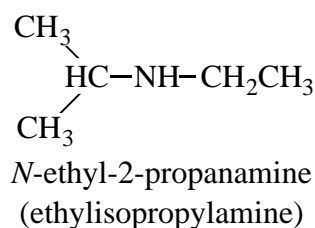
Topic Highlights

You should be able to:

❏ understand the nature of covalent bonding to form simple amines;

❏ write down the structure of primary, secondary and tertiary amines and be in a position to name simple amines;

❏ understand their properties in terms of the polarity of the nitrogen-hydrogen bond;

❏ understand that they are basic and react with acids to form salts as well as being excellent nucleophiles in substitution reactions.

Topic 3I - Aldehydes and Ketones

Key questions

What is the nature of bonding in carbonyl groups? What is responsible for high boiling points and what is the solubility in water? How do we name aldehydes and ketones? What are typical reactions of both aldehydes and ketones?

Outline

These two classes of functional groups are very similar and are therefore treated together.
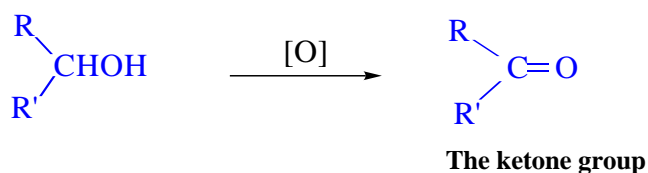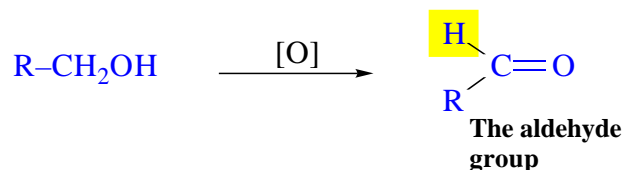
What are aldehydes and ketones?

Read
Brown Chapter 11.1

We proceed now to consider the chemistry of the oxidation products of alcohols, **aldehydes** and **ketones**. We have seen in Topic 3F that oxidation of primary alcohols gives aldehydes, and oxidation of secondary alcohols yields ketones.

Chemoffice Web (Brown)
CD-ROM
Model 11.1

$$R\text{–}CH_2OH \xrightarrow{[O]} \underset{R}{\overset{H}{>}}C=O \quad \text{The aldehyde group}$$

$$\underset{R'}{\overset{R}{>}}CHOH \xrightarrow{[O]} \underset{R'}{\overset{R}{>}}C=O \quad \text{The ketone group}$$

General Chemistry
CD-ROM
Screen 11.5

Both aldehydes and ketones contain the same functional group (–C=O, the carbonyl group) with the consequence that their chemistry is very similar. They differ in that in aldehydes, one of the substituents on the carbon atom is a hydrogen. The groups R or R' can be alkyl, alkenyl, alkynyl, aromatic rings or any other organic group bonded through a carbon atom.

Many naturally occurring compounds contain this functionality. Benzaldehyde (almond essence) and cinnamaldehyde (cinnamon) are two well-known flavours that are aldehydes. Acetone, a ketone, is a solvent and is used in nail-polish remover. The properties of carbonyls are vital to the functioning of many biological systems.

Nomenclature of aldehydes and ketones

Read
Brown Chapter 11.2

The suffixes for naming these carbonyl compounds are *-al* for *aldehyde* and *-one* for a *ketone*.
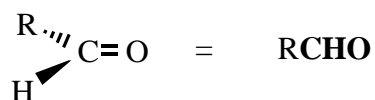
Thus:

CH_2O methanal (formaldehyde)

CH_3CHO ethanal (acetaldehyde)
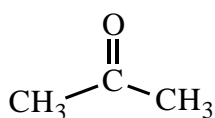
$CH_3CH(CH_3)CH_3CHO$ 3-methylbutanal

Note that the carbon atom of the carbonyl group in aldehydes is carbon *number 1*. It does not need to be ascribed a number in the compounds name - by its very nature it must be at the end of a chain, i.e. **C-1**. Also note that for convenience we often abbreviate the aldehyde structure to –CHO:
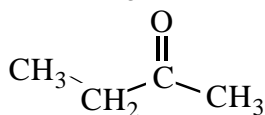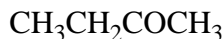
$$R\cdots C=O \quad = \quad R\mathbf{CHO}$$
$$H$$

And for ketones:

$$CH_3-\underset{\displaystyle O}{\overset{\displaystyle O}{C}}-CH_3 \quad \text{or} \quad CH_3COCH_3 \quad \text{propanone (acetone)}$$

$$CH_3-CH_2-\underset{}{\overset{\displaystyle O}{C}}-CH_3 \quad \text{or} \quad CH_3CH_2COCH_3 \quad \text{butanone (methyl ethyl ketone)}$$

The position of the carbonyl group does not need to be specified in the above compounds since the name is unambiguous, but with higher ketones where structural isomerism is possible, numbering becomes essential. For example:
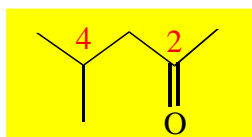
$CH_3COCH_2CH_2CH_3$ 2-pentanone

$CH_3CH_2COCH_2CH_3$ 3-pentanone

Note the conventional abbreviation for the C=O group in ketones, R**CO**R'.

And in more complex examples, the carbonyl carbon atom is given the lowest possible number (as with alcohols):

4-methyl-2-pentanone
(*not* 2-methyl-4-pentanone)

Finally, in discussion we often wish to specify the carbons along the chain adjacent to a carbonyl group. We can designate them with the Greek alphabet

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starting with the immediate neighbouring carbon as *alpha*(α), then *beta*(β), *gamma*(γ), *delta*(δ) and *epsilom*(ε):
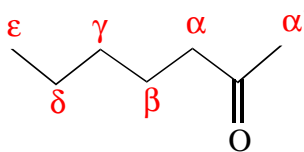
Self-Test Exercise 3.20

Complete *Practice Problem 11.1* p.305 Brown (ignore chirality):

(a)

(b)

(c)

Self-Test Exercise 3.21

Complete *Practice Problem 11.3* p.306 Brown:

(a)

(b)

(c)

## Bonding and physical properties in carbonyl compounds.

**Read
Brown Chapter 11.3**

The carbonyl group has much the same type of bonding as was found in alkenes, except one of the atoms contributing to the double-bond is an oxygen rather than another carbon atom. The term 'double bond' again stems from the formation of both a *sigma* and a *pi-*bond between the carbon and the oxygen.

Both atoms are sp^2 hybridised but in the case of oxygen, which has six valence electrons, hybrid formation from the 2s, $2p_x$ and $2p_y$ orbitals results in one half-filled and two filled sp^2 hybrid orbitals as well as a half filled, unhybridised $2p_z$ orbital.


An sp^2 hybridised oxygen atom.
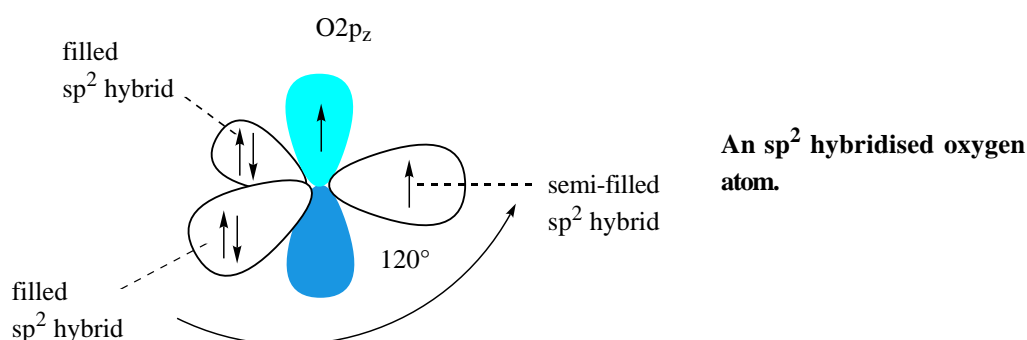
The half-filled sp^2 hybrid orbital and $2p_z$ orbitals form the *sigma* and *pi* covalent bonds with carbon. The two oxygen lone pairs can best be viewed as occupying the two unbonded sp^2 hybrid orbitals on the oxygen atom.
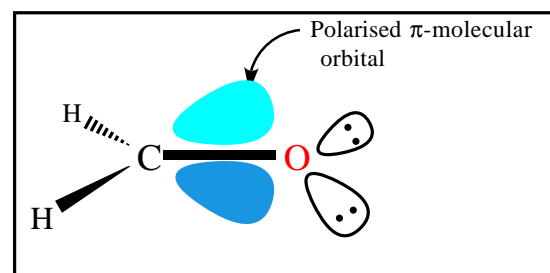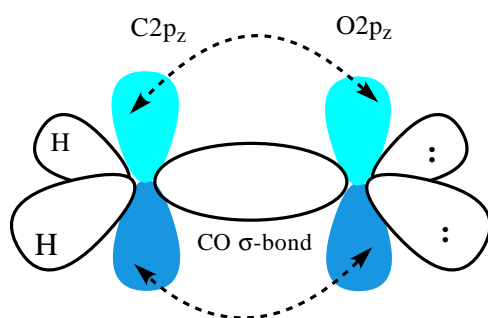
In aldehydes and ketones, the carbonyl bond is therefore similar to the carbon-carbon double bond in that it consists of a σ bond and a π bond, and is planar with bond angles between substituents at carbon (and between oxygen lone pairs) of about 120°. But it is also *polarised. Oxygen is more electronegative than carbon: consequently the bonding electrons in the pi molecular orbital* (and to some extent the *sigma* bonding orbital **are more associated with the oxygen atom than the carbon atom.**

We can designate this picture of electron charge dispersal as shown:
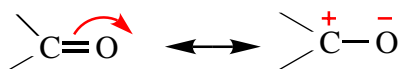

Each form of the carbonyl is termed a **resonance structure** and the pair of structures is termed a **resonance hybrid**. Neither form is truly representative of a carbonyl, but the polarised carbonyl is best represented by both forms. The charged structure contributes relatively little to the so-called **resonance hybrid**, but the effect is significant. Consequently aldehydes and ketones behave as if the carbonyl group has positive charge character on the carbon atom and negative charge character on the oxygen atom. The electron density surface of formaldehyde illustrates this polarisation towards oxygen.

This has consequences for both the physical and chemical properties of aldehydes and ketones. There is an electrostatic interaction between carbonyl groups.
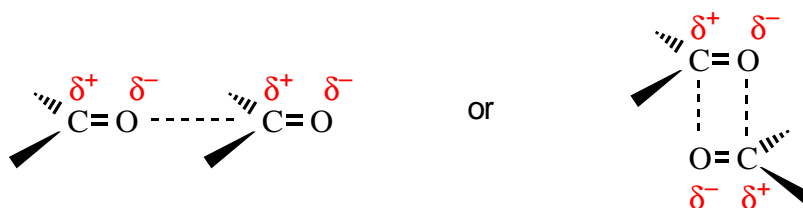
This effect results in an elevation in the boiling points of aldehydes and ketones compared with those of alkanes of similar molecular weight. Table 11.2 p. 307 illustrates this fact. Remember that methane—butane are all gases at room temperature so you can see that the boiling points of carbonyl analogues are much higher. The interaction is weaker than hydrogen bonding, so aldehydes and ketones have lower boiling points than the corresponding alcohols. However the polarisation *does* mean that the carbonyl oxygen can participate in hydrogen bonding with water (and alcohols). Hence, the lower molecular weight aldehydes and ketones are water soluble.
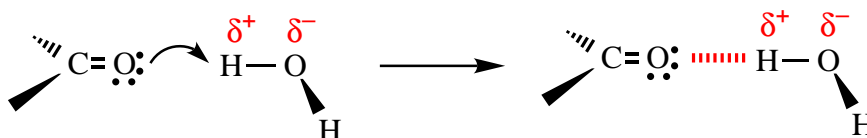
Note that the hydrogen atom of the aldehyde group is not acidic - aldehydes do not hydrogen bond with themselves.
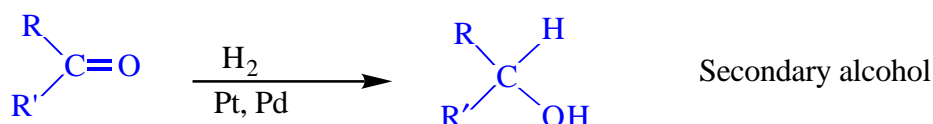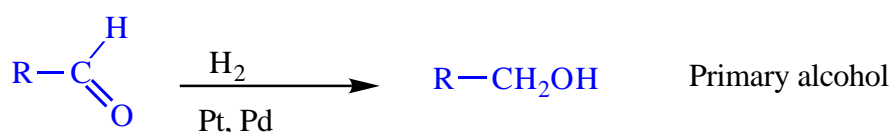
Reactions of aldehydes and ketones

> **Read**
> **Brown Chapters 11.4, 11.5, 11.9**

Reduction of the carbonyl group (addition of hydrogen):

The presence of a π bond in the functional group leads us to expect the chemistry of aldehydes and ketones, like that of alkenes, to be dominated by addition reactions. This is indeed so, and like alkenes they can be catalytically hydrogenated, using the same catalysts as are employed in alkene hydrogenation.

$$R-C\overset{H}{\underset{O}{\big\|}} \quad \xrightarrow[\text{Pt, Pd}]{H_2} \quad R-CH_2OH \qquad \text{Primary alcohol}$$

$$\overset{R}{\underset{R'}{>}}C=O \quad \xrightarrow[\text{Pt, Pd}]{H_2} \quad \overset{R}{\underset{R'}{>}}C\overset{H}{\underset{OH}{<}} \qquad \text{Secondary alcohol}$$

The reaction may be seen as the reversal of the oxidation of alcohols (if a carbon-carbon double or triple bond is also present in the molecule this will also be reduced, i.e. hydrogenated).

Another well-known reduction reaction uses sodiumborohydride ($NaBH_4$) or, the more reactive lithium aluminium hydride ($LiAlH_4$). These substances provide hydrogen in the form of H^-! Yes, negatively charged hydrogen. H^- is strongly attracted to the positively polarised carbon of carbonyls and, after treatment with acid, the product is once again the corresponding alcohol.

$$\overset{R}{\underset{R'}{>}}C=O \quad \xrightarrow[\text{2. } H_2O,\, H^+]{\text{1. } NaBH_4 (LiAlH_4)} \quad \overset{R}{\underset{R'}{>}}CH-OH$$
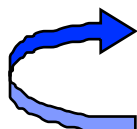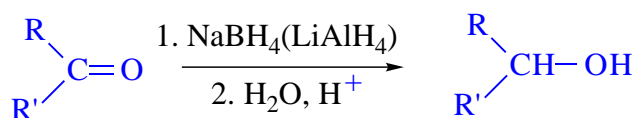
Mechanistically this can be viewed as taking place as follows:

Topic 3G

$$H\!:\!^- \quad \overset{R}{\underset{R'}{>}}C=O \quad H^+ \quad \longrightarrow \quad \overset{R}{\underset{R'}{>}}CH-OH$$
$$\delta+ \quad \delta-$$
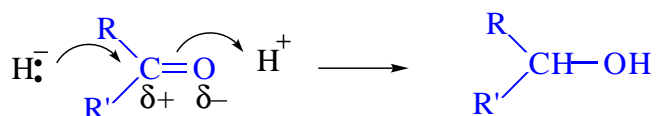
Hydride behaves here as a **nucleophile** (recall these were defined in Topic 3G).

Addition of Grignard reagents:

A similar reaction occurs with Grignard reagents. Remember these are formed from alkyl halides and magnesium (Topic 3F) and the carbon atom attached to the magnesium has some negative character, i.e. it is also **nucleophilic**.
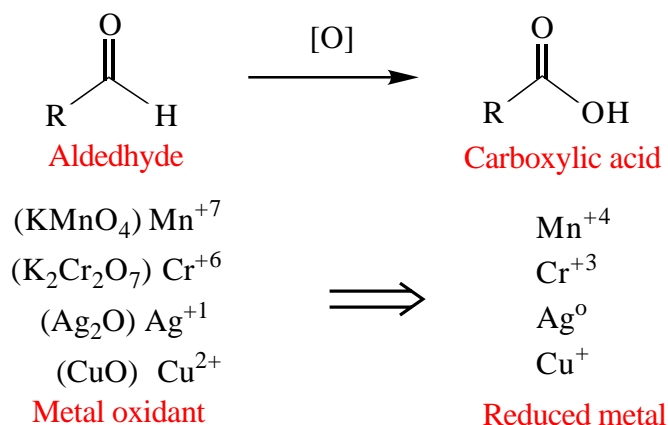
$$R–X \;+\; Mg \longrightarrow \overset{\delta^-\;\;\delta^+}{R–Mg–X}$$
$$\text{(Grignard reagent)}$$
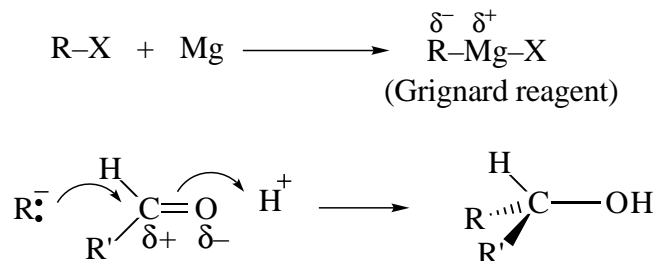
The product with an aldehyde is a secondary alcohol: with the simplest aldehyde methanal (formaldehyde), the product is a primary alcohol.

Oxidation of aldehydes:

Aldehydes are readily oxidised to **carboxylic acids** (next Topic 3J). We have already briefly noted this in the discussion of the reactions of alcohols where we saw that with primary alcohols, further oxidation of aldehydes is possible.

$$R–CH_2OH \;\xrightarrow{[O]}\; R–CHO \;\xrightarrow{[O]}\; R–CO_2H$$

Various metals will oxidise aldehydes under appropriate conditions and in the process they are reduced. Some examples are:

Metal oxidant	Reduced metal
$(KMnO_4)\; Mn^{+7}$	Mn^{+4}
$(K_2Cr_2O_7)\; Cr^{+6}$	Cr^{+3}
$(Ag_2O)\; Ag^{+1}$	Ag^{o}
$(CuO)\; Cu^{2+}$	Cu^{+}

This ease of oxidation of aldehydes and the relative resistance to oxidation of ketones is the most significant difference between aldehydes and ketones and gives rise to simple laboratory tests to distinguish between them. These are the **Tollens** test and the **Fehlings (Benedict)** test.

In the **Tollens test** an aqueous ammoniacal solution of silver nitrate is reduced (as the aldehyde is oxidised) to metallic silver. If the test tube is scrupulously clean a silver mirror is deposited on the glass (because of this, the test is also called the **Silver Mirror test).**

$$R–CHO + 2Ag(NH_3)_2 + 3OH^- \rightarrow RCO_2^- + 2Ag° \downarrow + 4NH_3 + 2H_2O$$
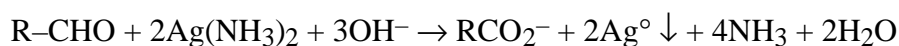
In the Fehling's or Benedict tests a deep blue colour of complex copper(II) ions is lost and a red precipitate of copper(I) oxide is formed.

$$R–CHO + 2Cu^{2+} + 5OH^- \rightarrow \quad RCO_2^- + Cu_2O \downarrow + 3H_2O$$
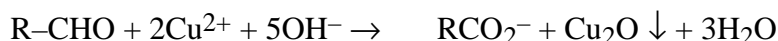
Aldehydes are even slowly oxidised by atmospheric oxygen: once a container of an aldehyde has been opened a few times it will usually be contaminated with carboxylic acid. For example, most bottles of benzaldehyde (a liquid) will contain a solid deposit of benzoic acid.

Self-Test Exercise 3.22

Complete *Practive problem 11.9* p.322 Brown:

(a)

(b)

Topic Highlights

You should be able to:

❏ show how a carbon—oxygen pi-bond is formed;

❏ understand that carbonyls are polar bonds and be able to explain their properties in terms of the polarity of the carbonyl bond;

❏ draw the structures and name simple aldehydes and ketones;

❏ recognise that they undergo addition of hydrogen and undergo nucleophilic addition reactions with hydride and Grignard reagents;

❏ recognise that aldehydes but not ketones can be oxidised to carboxylic acids.

Topic 3J - Carboxylic acids and their derivatives

Key questions

What are the structures and properties of the carboxylic acids, carboxylic esters, carboxylic acid chlorides and carboxamides? How do we name these? How acidic are carboxylic acids? How are esters formed from acids and alcohols and what are the reactions of acid chlorides?

Outline

In this final topic we will be concerned with carboxylic acids and some of their derivatives. They form a vital class of organic compounds — the carboxylic acid group forms the other half of amino acids and amino acids link up in proteins through amide bonds. The texbook deas with carboxylic acids, esters and amides. We will also look at the synthetically versatile acid chloride derivatives.
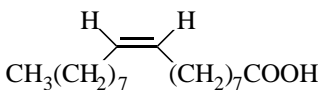
What is a carboxylic acid?

Read
Brown Chapter 12.1

The alkanoic acids (systematic name) are more commonly called **carboxylic acids**, and occasionally by the old trivial name of fatty acids. They are characterised by the carboxyl group:
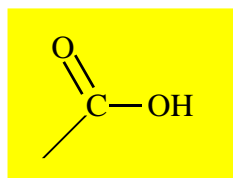
The carboxyl group is usually abbreviated to $-CO_2H$ or $-COOH$. They are widely found in nature and in our everyday life. Some recognisable examples are shown below, and others are to be found in Table 12.1:

|		
$H-COOH$	CH_3-CO_2H	$CH_3CH_2CH_2-CO_2H$
Formic acid is found in the sting of ants	**Acetic acid is found in vinegar and is produced from glucose by fermentation**	**Butanoic acid (Butyric acid) is responsible for the rancid smell in sour butter**
$CH_3(CH_2)_4-CO_2H$		
Hexanoic acid (Caproic acid) is responsible for the unmistakable aroma of goats (latin 'caper')	$CH_3(CH_2)_7 \quad (CH_2)_7COOH$ with H, H cis double bond **Oleic acid is a biological precursor of fats and lipids.**	

Structure and bonding in organic acids

Read
Brown Chapters 12.2, 12.3, 12.4

The carbon of a carboxylic acid group is sp^2 hybridised and the group as a whole is **planar**. The difference between the electronegativities of carbon and oxygen make this a polar double bond, as was indicated for aldehydes and ketones in Topic 3I.

General Chemistry CD-ROM Screen 11.5

However, carboxylic acids are very much more polar than aldehydes and ketones - the O—H bond is strongly polarised as indicated below. In Screen 11.5 of the *General Chemistry* CD-ROM you can check out the geometry of a simple acid, propanoic acid.
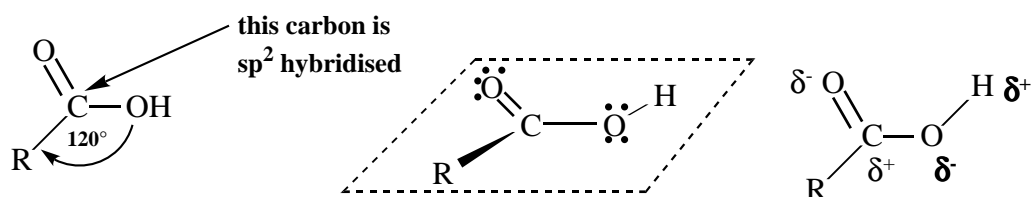

Carboxylic acids are sharp-smelling (and are often unpleasant smelling liquids). They have boiling points that are higher than any of the other classes of compounds we have considered so far. This is a consequence of the polar O—H bonds which facilitate strong hydrogen bonding between two carboxylic acid molecules.
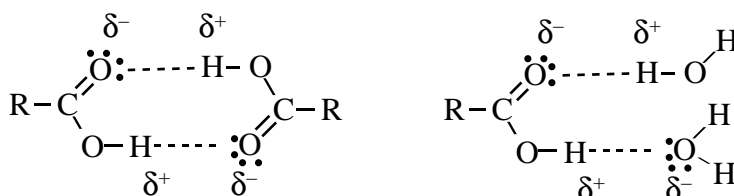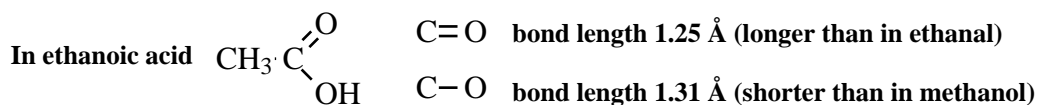

Hydrogen bonding between carboxylic acids and water also confers water solubility on the carboxylic acids with low molecular weight.

Note that the structure of the carboxyl group formally consists of a carbonyl group and a hydroxyl group. However the chemistry of the acids does not parallel that of alcohols or ketones. The two functionalities interact electronically: *the carbonyl group is electron-withdrawing and the alcohol group electron-donating*.
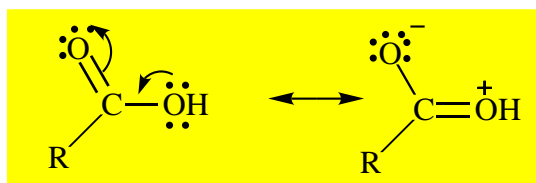
This resonance interaction modifies the reactivity considerably and is also reflected in the carbon-oxygen bond lengths in carboxylic acids.
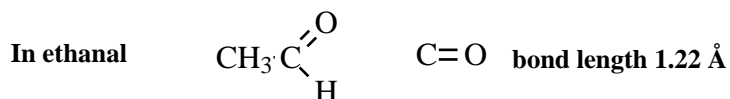
| In ethanal	$CH_3\cdot C\!\!\overset{O}{\underset{H}{\diagup}}$	$C=O$ bond length 1.22 Å
In methanol	CH_3-OH	$C-O$ bond length 1.43 Å
In ethanoic acid	$CH_3\cdot C\!\!\overset{O}{\underset{OH}{\diagup}}$	$C=O$ bond length 1.25 Å (longer than in ethanal)
		$C-O$ bond length 1.31 Å (shorter than in methanol)

As in the case of aldehydes, the carbon atom of the carboxyl group is included in the carbons of the systematic name. Since the carboxyl group must be at the end of a carbon chain the carbon atom of the group is carbon number 1. The *-ane* ending in the parent alkane is changed to *-anoic acid*.

Thus:
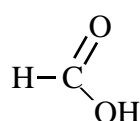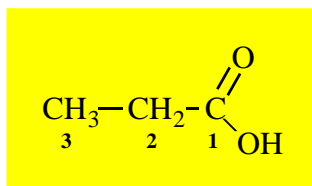
methanoic acid   **propanoic acid**   **3-methylpentanoic acid**
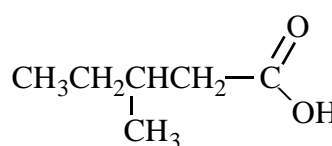
But when the carboxyl group is attached to a ring we have
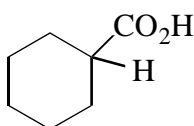
cyclohexane carboxylic acid

Many have trivial names, usually indicative of the natural sources from which they were first isolated:

Methanoic	Formic	Ants
Ethanoic	Acetic	Vinegar
Butanoic	Butyric	Butter
Hexanoic	Caproic	Goats
Octadecanoic	Stearic	Fat

Derivatives of carboxylic acids are compounds that yield the carboxylic acids on reaction with water, and will be considered after a discussion of the parent acids.

Preparation of carboxylic acids:

We have already encountered one method by which the acids can be made:

That is by the oxidation of primary alcohols (or aldehydes which are intermediate on the oxidation pathway).

$$R-CH_2OH \xrightarrow{[O]} R-CHO \xrightarrow{[O]} RCO_2H$$

Another method is similar to a reaction we saw in Topic 3I in which a Grignard reagent reacts with carbonyl compounds. Carbon dioxide also has a carbonyl group, and the analogous reaction takes place.

$$R\text{---}X + Mg \longrightarrow \overset{\delta^-\;\;\;\delta^+}{R\text{--}MgX}$$

Grignard reagent

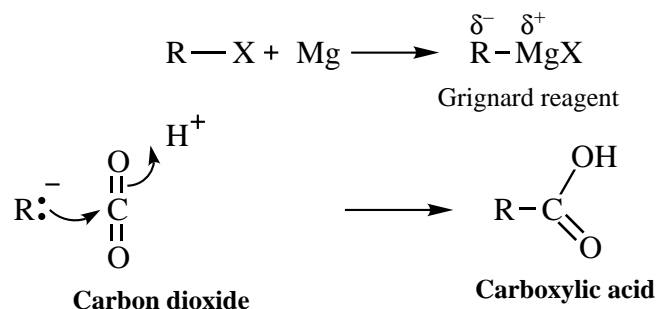**Carbon dioxide**   **Carboxylic acid**

In practice an ethereal solution of the Grignard reagent is added dropwise to dry ice (solid CO_2).

As will be seen later in this Topic, carboxylic acids can be generated by hydrolysis of carboxylic acid derivatives such as esters, amides and anhydrides.

Acidity of carboxylic acids:

As their name indicates, carboxylic acids are acidic. Thus, in water ionization of the acid occurs:

Carboxylate anion
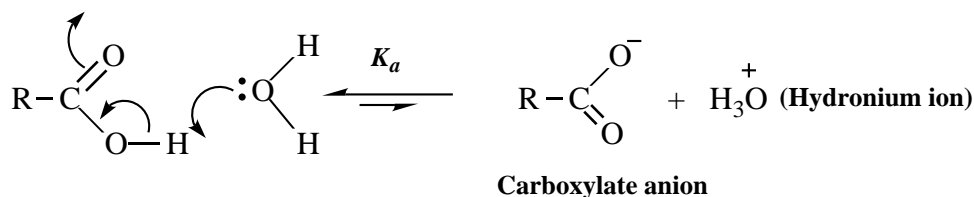
Not surprisingly, the low molecular weight carboxylic acids are water soluble.

The acid strengths of carboxylic acids are measured by the **acidity constant, K_a**, the equilibrium constant for this ionisation, or the **pK_a** value.

$$K_a = \frac{[RCO_2^-][H_3O^+]}{[RCO_2H]}$$

$$pK_a = -\log K_a$$

The smaller the pK_a value, the stronger the acid and *vice versa*. With carboxylic acids, the equilibrium lies far to the left and K_a is small; pK_a is correspondingly large. pK_a values for many carboxylic acids are given in your SI data book and are in the range of 2-5. Thus K_a values are typically 10^{-2}—10^{-5}. Acidity can be expected to increase (lower pK_a) with electron-withdrawing groups on the acid sidechain.

Compare the values for formic, acetic, chloroacetic and dichloroacetic acids in the table below:

formic acid — H–C(=O)OH	pK_a 3.8	
acetic acid — H_3C–C(=O)OH	pK_a 4.8	$CH_3 \rightarrow C(O^-)(O)$ **electron donation by the +I methyl group destabilising the anion**
chloroacetic acid — $ClCH_2$–C(=O)OH	pK_a 2.9	$ClCH_2 \leftarrow C(O^-)(O)$ **electron withdrawal by the -I chlorine atom stabilising the anion**
dichloroacetic acid — Cl_2CH–C(=O)OH	pK_a 0.7	$Cl_2CH \leftarrow C(O^-)(O)$ **increased stabilisation of the anion (two -I chlorines)**
3-chloropropanoic acid — $ClCH_2CH_3$–C(=O)OH	pK_a 4.1	$ClCH_2CH_2 - C(O^-)(O)$ **inductive effects only operate over short distances so the acidity differs little from that of of ethanoic acid**

This can be understood from a consideration of the structure of the carboxylate anion, where we see that charge delocalisation in the resonance hybrid stabilises the anion.

Resonance hybrid
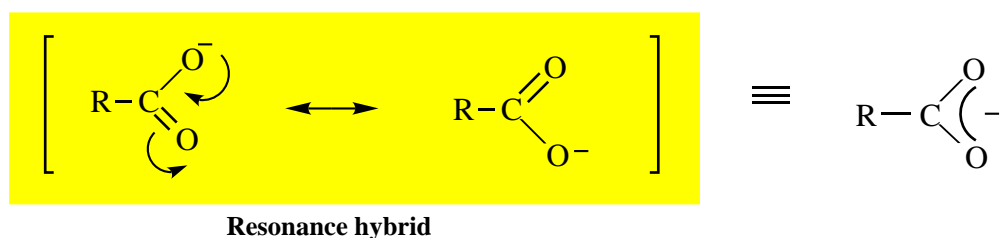
This resonance stabilisation is reflected in the carbon-oxygen bond lengths of the alkanoate salt where we find that the *bonds are of equal length* (1.27 Å): compare the bond lengths in the parent acid. Furthermore we note that the negative charge is spread over two electronegative oxygen atoms.

Since in the anionic form there is a buildup of negative charge in the O—C—O system, electronic effects in the alkyl group will influence the relative acidity of the parent acid. Stabilisation of the anion through electron withdrawal facilitates its formation and hence increases the acidity of the parent acid. Chlorine atoms, being very *electronegative* are strongly negatively inductive (**–I**). Methyl, on the other hand is **+I** and decreases acidity by destabilising the carboxylate form.

(a) The pK_a's for Acetic acid, bromoacetic acid and fluoroacetic acid are given below:

H_3C—$\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagdown}}$ $BrCH_2$—$\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagdown}}$ FCH_2—$\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagdown}}$
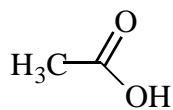
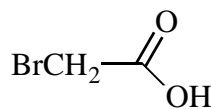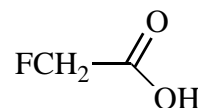**acetic acid**   **bromoacetic acid**   **Fluoroacetic acid**
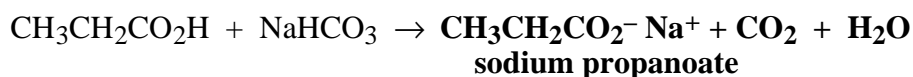
pK_a 4.8   pK_a 2.9   pK_a 2.2

(a) Which acid is most acidic?

(b) Explain the relative magnitudes of the three pK_a's?

Carboxylic acids are weaker acids than mineral acids such as hydrochloric acids. They are, however, stronger acids than carbonic acid. Consequently, they will liberate carbon dioxide from sodium carbonate or sodium hydrogen carbonate, forming the sodium salt of the carboxylic acid:

$$2CH_3CO_2H + Na_2CO_3 \rightarrow \mathbf{2CH_3CO_2^- \, Na^+ + CO_2 + H_2O}$$
$$\mathbf{sodium\ ethanoate}$$

$$CH_3CH_2CO_2H + NaHCO_3 \rightarrow \mathbf{CH_3CH_2CO_2^- \, Na^+ + CO_2 + H_2O}$$
$$\mathbf{sodium\ propanoate}$$
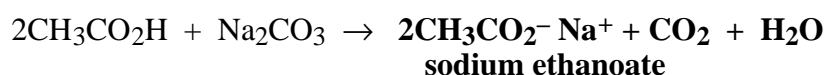
The same reaction with **citric acid** is the commercial basis for most antacids used to remove excess stomach acid.

The evolution of carbon dioxide from aqueous sodium carbonate (or hydrogen carbonate) represents a useful qualitative test for carboxylic acids. Furthermore the ionic salts are water soluble. Salt formation can be reversed by reaction with a stronger acid.

$$R–CO_2^- \, Na^+ + HCl \rightarrow RCO_2H + Na^+ \, Cl^-$$
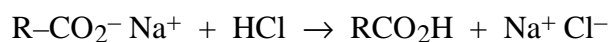
Obviously, carboxylic acids will also form salts with sodium hydroxide.
$$R–CO_2H + NaOH \rightarrow RCO_2^- \, Na^+ + H_2O$$
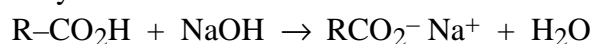
Finally, carboxylic acids will also form ammonium salts with ammonia and the organic bases, amines.

$$R–CO_2H + NH_3 \rightarrow \mathbf{RCO_2^- \ NH_4^+}$$
$$R–CO_2H + R'NH_2 \rightarrow \mathbf{RCO_2^- \ NR'H_3^+}$$
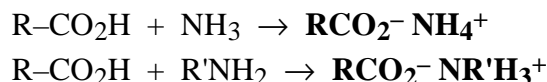
Derivatives of carboxylic acids

**Read
Brown Chapter 12.6**

Formation and reaction of carboxylic esters:

When carboxylic acids react with alcohols under acid catalysis (concentrated sulfuric acid) esters are formed.

$$R-CO_2H \ + \ R'OH \ \underset{\longleftarrow}{\overset{H^+}{\rightleftharpoons}} \ R-\overset{\overset{O}{\|}}{C}-O-R' \ + \ H_2O$$

Ester or alkyl alkanoate

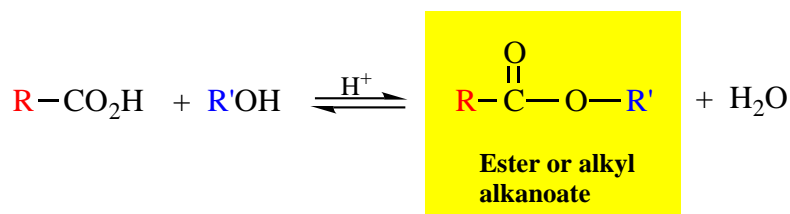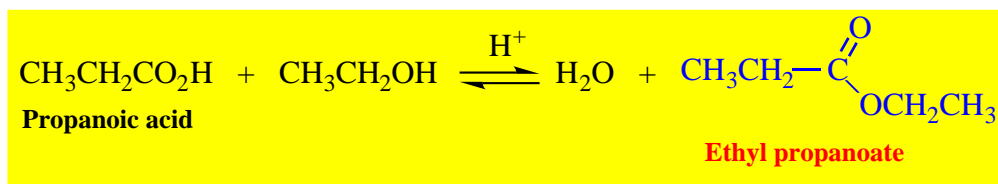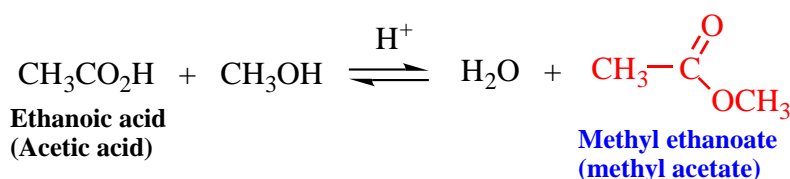Note that the reaction is reversible (it can be forced to completion by, for example, removal of the water formed in the reaction), and is frequently quite slow. We will shortly see better methods for the preparation of esters. In actual fact the overall transformation, which is called Fischer esterification, consists of a series of reversible reactions we will encounter again in CHEM120.

Some examples of esterification:

$$CH_3CO_2H \ + \ CH_3OH \ \underset{\longleftarrow}{\overset{H^+}{\rightleftharpoons}} \ H_2O \ + \ CH_3-C\overset{O}{\underset{OCH_3}{\diagdown}}$$

**Ethanoic acid
(Acetic acid)**

**Methyl ethanoate
(methyl acetate)**

$$CH_3CH_2CO_2H \ + \ CH_3CH_2OH \ \underset{\longleftarrow}{\overset{H^+}{\rightleftharpoons}} \ H_2O \ + \ CH_3CH_2-C\overset{O}{\underset{OCH_2CH_3}{\diagdown}}$$

Propanoic acid

Ethyl propanoate

Many simple esters have fruity smells (they occur naturally in fruits and are used as flavouring agents). For example:

$CH_3CH_2CH_2CO_2CH_3$ methyl butanoate   apple
$CH_3CO_2CH_2CH_2CH(CH_3)_2$ 3-methylbutyl ethanoate   pear
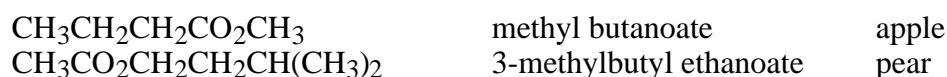
The propanoate ester of 3-methyl-1-butanol smells of apricots and the butanoate ester smells of plums. *Chemical Connections* p.351 Brown illustrates some other fragrant esters and *Chemical Connections* p.348-349 describes

aspirin, an ester of salicylic acid. Oil of wintergreen, a common component of many sports linaments (*Dencorub*, *Deep Heat*) is a source of the analgesic salicylic acid, also formed from aspirin (Topic 3E). Both aspirin and oil of wintergreen are hydrolysed back to the free acid in the body releasing the active constituent into the bloodstream.

| aspirin | salicylic acid | oil of wintergreen |
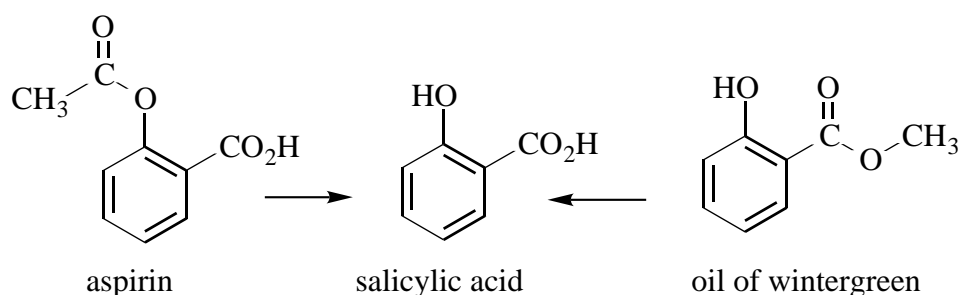
Note how we name esters: as **alkyl alkanoates** where the alkyl part indicates the parent alcohol and the alkanoate part the acid.

When esters are treated with dilute acid or base, they are converted back to carboxylic acids. This conversion is known as *hydrolysis*, as the ester group is replaced by a hydroxyl group.

Acid catalyzed hydrolysis is the reverse of Fischer esterification.
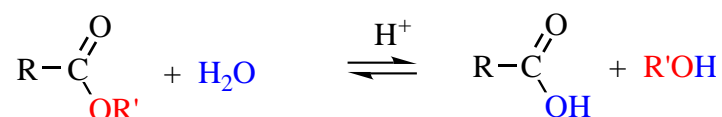
Self-Test Exercise 3.24

Complete *Practice Problem 12.4* p.350 Brown:

Fats and Oils

General Chemistry CD-ROM Screen 11.7

This interesting section highlights just how important esters are. As triglycerides, esters of glycerol (1,2,3-propanetriol), are the main source of ingestion of fats. The body hydrolyses these esters back to fatty acids and glycerol. The acids are further degraded to acetyl units (catabolism of fats), which are utilised in different ways.

It is interesting to see the difference between saturated and unsaturated fats. This section of the textbook explains why saturated fats with no double bonds in the chain are generally solids while unsaturated fats are oils. Margerine is hydrogenated vegetable oil and is generally monounsaturated. Polyunsaturated oils (e.g. from linolenic acid) are too runny to be used this way. Removing double bonds in a process called "hardening" makes them more solid so that they can be spread in a manner similar to butter (comprised mainly of esters of saturated fats). Unsaturated fats are better for us because they are more readily metabolized, as the double bonds are more reactive than the single bonds that make up the hydrocarbon chains of saturated fats.

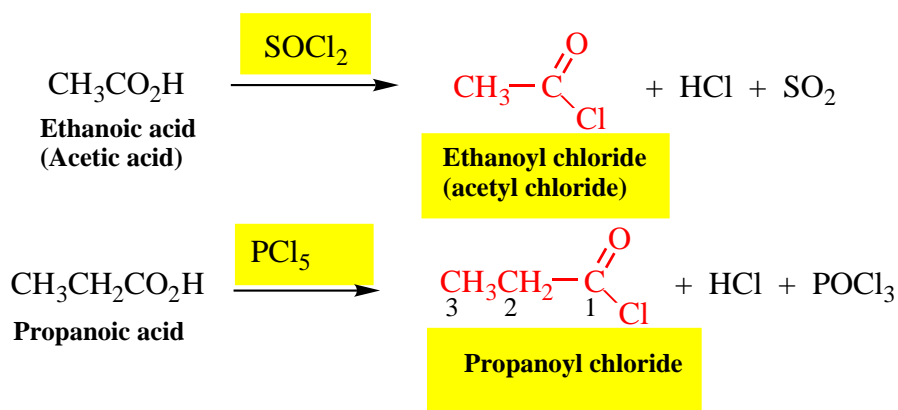## Preparation and reactions of carboxylic acid chlorides

Carboxylic acids react with thionyl chloride or phosphorus pentachloride to give acid chlorides (acyl chlorides).

Chemoffice Web (Brown) CD-ROM Model 13.1

$$CH_3CO_2H \xrightarrow{\text{SOCl}_2} CH_3-\overset{\displaystyle O}{\underset{\displaystyle Cl}{C}} + HCl + SO_2$$

Ethanoic acid (Acetic acid)

Ethanoyl chloride (acetyl chloride)

$$CH_3CH_2CO_2H \xrightarrow{\text{PCl}_5} \underset{3\quad 2\quad 1}{CH_3CH_2}-\overset{\displaystyle O}{\underset{\displaystyle Cl}{C}} + HCl + POCl_3$$

Propanoic acid

Propanoyl chloride

The first method is usually more convenient since both by-products of the reaction are gases.

Note the systematic naming of acid chlorides: as ***alkanoyl chlorides*** where the carbon count in the alkanoyl stem includes the carbon of the carbonyl group.

The acid chlorides represent the starting point for the preparation of several new acid derivatives. Although acid fluorides, bromides and iodides are well

known, and show similar chemical properties to the acid chlorides, our discussion will focus on the latter which are the reagents of choice in essentially all acid halide reactions.

Nucleophiles attack at positive carbon

Chlorine is a good leaving group
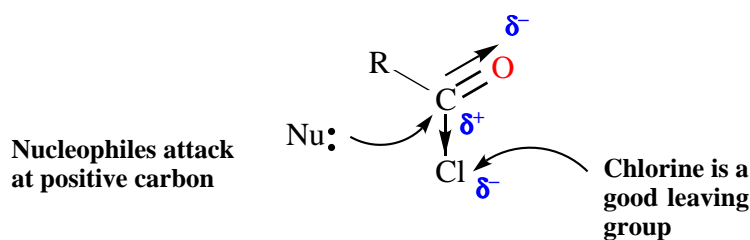
The electronegativity of the halogen generates positive character on the carbon atom. But in the acid halide, the carbon is also doubly bonded to the electronegative oxygen atom and so we have two electron-withdrawing effects operating in tandem, imparting even more positive character to the carbon of the carbonyl group. Not surprisingly then, acid chlorides are **very readily attacked by nucleophiles**. Chlorine is also a good leaving group as it can depart as chloride (Cl^-).
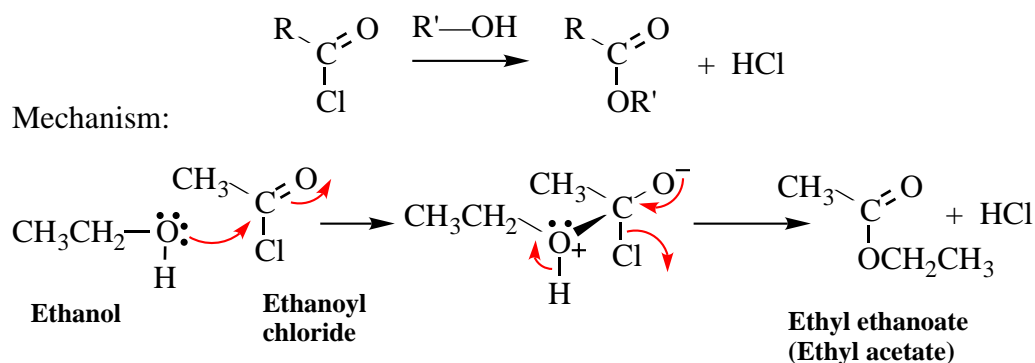
Formation of carboxylic acids with water:

With water as nucleophiles, acid halides re-form carboxylic acids:
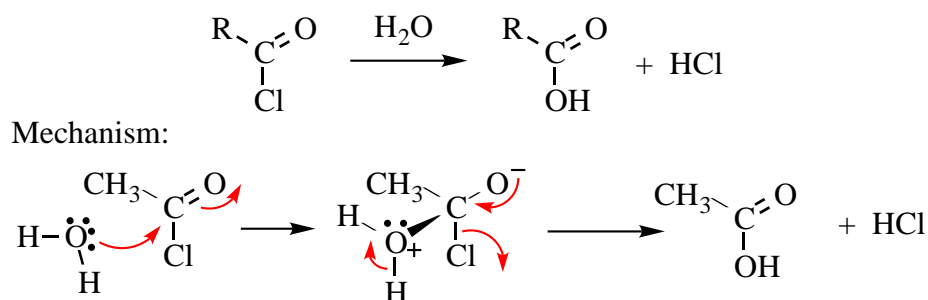
Mechanism:

The mechanism (not for examination) is illustrated to show nucleophilic attack and departure of the chloride leaving group. The reaction is vigorous: the low molecular weight acid halides, being quite volatile, fume in moist air liberating hydrogen chloride.

Formation of esters with alcohols:

There is a similar reaction with alcohols to yield esters by a second method:

Mechanism:

Ethanol

Ethanoyl chloride

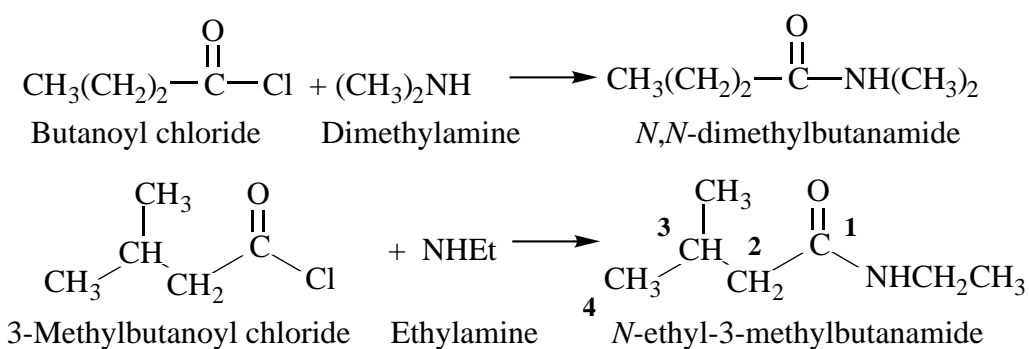**Ethyl ethanoate (Ethyl acetate)**

This is a much superior route to esters than the acid catalysed reaction between carboxylic acids and alcohols. Again the reaction is vigorous and usually needs to be moderated by being performed in an inert solvent.

Formation of amides with amines:

Acid halides react with ammonia and amines in a similar manner to yield *amides*, an important class of carboxylic acid derivatives:

$$CH_3-C(=O)-Cl \xrightarrow{NH_3} CH_3-C(=O)-NH_2 + HCl$$

Ammonia   **Ethanoyl chloride**   **Ethanamide (Acetamide)**
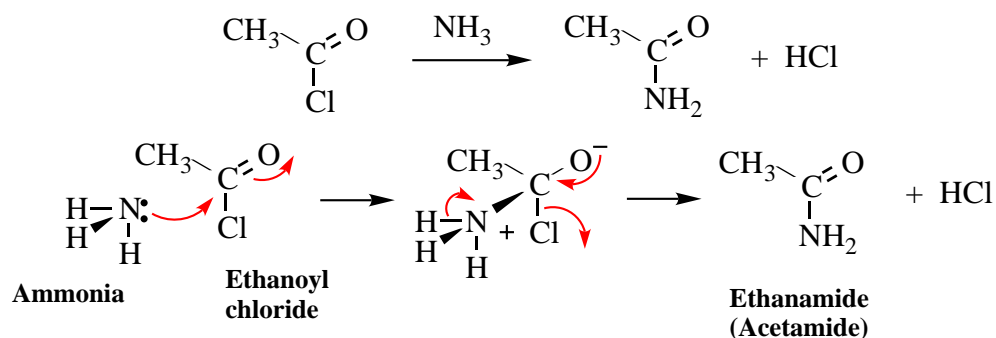
Similarly, primary and secondary amines react with acid halides to give secondary and tertiary amides respectively. Secondary amides have one, and tertiary amides have two substituents on nitrogen.

$$CH_3(CH_2)_2-\overset{O}{\overset{\|}{C}}-Cl + (CH_3)_2NH \longrightarrow CH_3(CH_2)_2-\overset{O}{\overset{\|}{C}}-NH(CH_3)_2$$

Butanoyl chloride   Dimethylamine   *N,N*-dimethylbutanamide

3-Methylbutanoyl chloride   Ethylamine   *N*-ethyl-3-methylbutanamide

Some comments on nomenclature of amides: the carbonyl group (as in aldehydes, carboxylic acids and esters) is carbon number one, and the capital "*N*" precedes a group that is a substituent on nitrogen.

Self-Test Exercise 3.25

(a) Draw the structures and name the acid chloride and amine you would use to make *N*-pentyl-2-methylbutanamide.


The amide functional group is best represented (again) by a resonance hybrid:
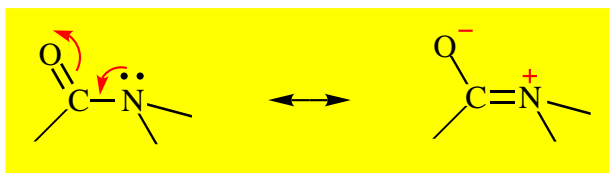
There is therefore substantial double bond character between the nitrogen and the carbon and this usually imparts restricted rotation about the N—C bond. Screen 11.5 of the *General Chemistry* CD-ROM depicts the structure of both an amine and an amide. Note the difference between the hybridisation at nitrogen in both of these. In the amine the nitrogen is sp^3 hybridised, while in the amide the nitrogen is sp^2 hybridised and the lone pair is in the nitrogen $2p_z$ orbital, which can overlap with the neighbouring $2p_z$ orbital of the carbonyl carbon to facilitate resonance. As a consequence of their planarity, amides can form strong hydrogen bonds between one another:

General Chemistry
CD-ROM
Screen 11.5
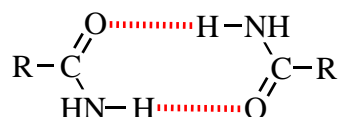
Similar hydrogen bonding is vital to the synthesis of proteins and the structure and replication of DNA. Amide linkages also join amino acids together to form peptides and proteins (see below).

Most amides are solids but because of hydrogen bonding, many are water soluble.

Polyamides—nylon and proteins

Read
Brown p. 421 – 423, 502, 510

General Chemistry
CD-ROM
Screens 11.8,
11.10

Condensation polymers such as nylon are made from a diacid chloride (adipoyl chloride) and a diamine (hexamethylenediamine). The resultant long chain polymer is comprised of a series of four and six carbon alkane chains bonded together through the amide group. Not only is the condensation reaction a typical acid chloride amine reaction, but the strength of the nylon polymer is due to the hydrogen bonding that can occur between chains, as depicted in Figure 15.2. Screen 11.10 of the *General Chemistry* CD-ROM illustrates the actual polymerisation reaction and is well worth viewing.

Pages 502 and 510 of Brown introduces us to amino acids and proteins, the natural polymers. Naturally occurring amino acids are metabolically linked by amide bonds to give peptides and ultimately long chains known as proteins (view Screen 11.8 of the *General Chemistry* CD-ROM). These are coiled in an α-helix form, the structure of which is controlled by two features of the amide linkage - the amide groups are planar owing to the restricted rotation about the amide N—C bonds; and the helix is held together by hydrogen bonds between amide carbonyl oxygens and amide N—H bonds on amino acids some distance along the chain. Amides constitute a remarkably important functional group.

Topic Highlights

You should be able to:

❏   draw and name simple carboxylic acids;

❏   understand that carbonyls are polar entities and be able to explain their properties and hydrogen bonding in terms of the polarity of the carbonyl and hydroxyl bonds;

❏   understand that they are acidic and the factors that affect the acidity constants or pK_a values;

❏   draw and name the structure of esters as well as know how they are made by Fischer esterification

❏   understand the difference between saturated and unsaturated fats;

❏   write reactions for conversion of acids to acid chlorides and understand the extreme polarity in acid chlorides;

❏   show how acid chlorides can be used to make acids, esters and amides by acyl substitution reactions with water, alcohols and ammonia or amines;

❏   interpret the reasons why amides are planar and why they can form strong hydrogen bonds;

❏   understand the important role that amides play in protein formation;

❏   understand condensation polymer formation, e.g. the synthesis of nylon.