Chem Factsheet

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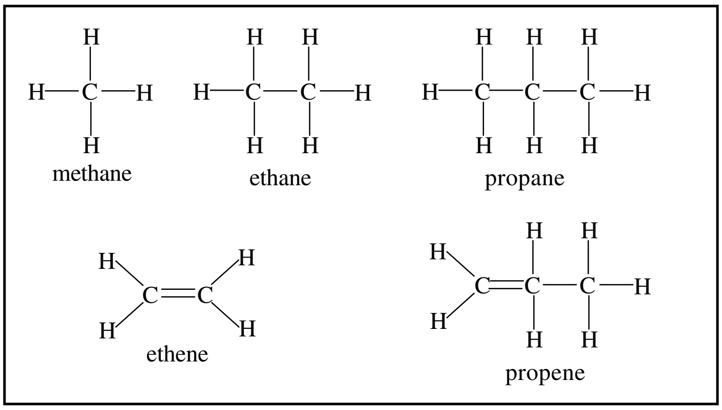
Organic Functionality and Structure – Part I (AS)

To succeed in this topic you need to:
- remember that carbon atoms form the backbone of all organic molecules
- understand why and how carbon atoms form four covalent bonds
- remember the structures and properties of simple organic compounds like alkanes, alkenes, alcohols etc.
- understand that the chemical and physical properties of a compound depend on the elements that the compound is made of and how they are bonded together

After working through this Factsheet you will:
- understand why functional groups are important features of organic molecules
- be able to recognise the key functional groups in AS Chemistry
- be able to predict chemical and physical properties of the key functional groups encountered in AS Chemistry

In your GCSE course you were introduced to organic chemistry through the study of two families of molecules, the alkanes and the alkenes (Fig 1). Like all organic molecules, these families of molecules (also called homologous series) are built around a framework of carbon atoms.

Fig 1. Some simple alkanes and alkenes



Alkanes and alkenes contain only carbon and hydrogen atoms, which is why they are known as hydrocarbons. Remember that each carbon atom forms four covalent bonds (a double bond counts as two), with hydrogen atoms hanging off the carbons wherever there is a free bond available.

Alkanes are relatively unreactive molecules. They don't do many interesting reactions apart from combustion – which they do very well (Fig 2) and the free radical substitution reaction described later.

Fig 2. The complete combustion of methane

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g)$$

Alkenes are a bit more interesting than alkanes because they contain a functional group. This is what we call the part of a molecule that makes it different from an alkane. In an alkene, the functional group is the carbon-carbon double bond.

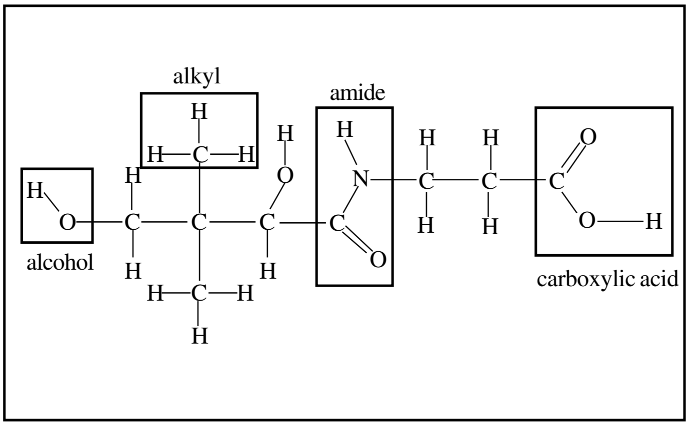
There are many other functional groups. Each of them imparts its own particular properties to the molecule it is part of. The organic molecules that you find in nature, in your body, your food, your shampoo or your medicine are built from a basic carbon backbone with all the functional groups hanging off it.

The carbon backbone gives the molecules their shape and structure (and if you think about enzymes, or DNA, you will understand why shape and structure are important), but the functional groups give them their reactivity and enable them to interact both physically and chemically with other substances.

In the picture of Vitamin B5 (Fig 3) some of the functional groups are labelled: alcohol (only one of the alcohol groups is labelled – can you spot the other one?), amide and carboxylic acid.

There is also an alkyl group. This is the name given to the bits of the molecule that resemble simple alkanes (in this example, the alkyl group is actually a methyl group, -CH_3). Alkyl groups are functional groups since they can also contribute their properties to a molecule, such as reducing the solubility of a drug in your bloodstream so that it stays in your body longer.

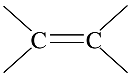
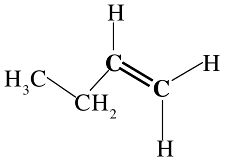
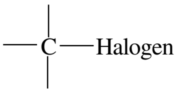
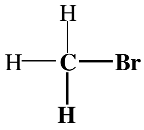
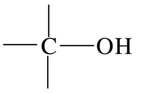
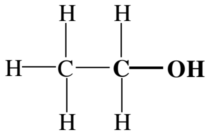
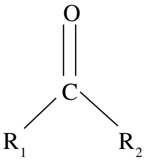
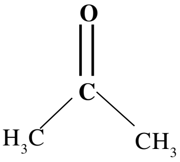
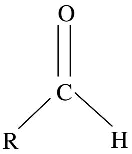
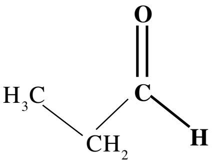
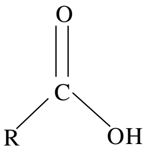
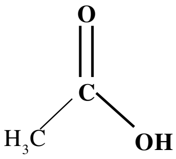
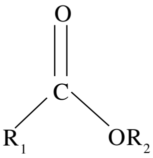
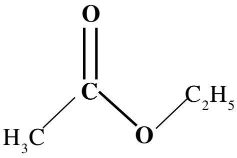
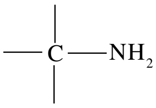
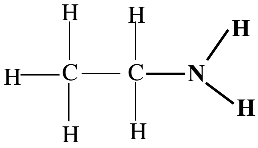
Fig 3. Vitamin B5 (pantothenic acid)



Functional groups can contain many different elements – sulphur, phosphorus or magnesium, for example – but the most common ones contain oxygen, nitrogen and halogen atoms. Table 1. shows the ones that you will encounter most commonly, along with the suffix or prefix used in the systematic naming of the group.

The functional groups are highlighted in the examples. Notice that in some of the structures the abbreviation R is used. This is the conventional way to show that a carbon-containing group, linking to the rest of the molecule, is attached to the atom we are interested in.

Table 1. Some common functional groups

Name	Suffix or prefix*	Structure	Example
Alkene	-ene		 But-1-ene
Halogenoalkane	fluoro-, chloro-, bromo- or iodo-		 Bromomethane
Alcohol	-ol or hydroxy-		 Ethanol
Ketone**	-one		 Propanone
Aldehyde**	-al		 Propanal
Carboxylic acid**	-oic acid		 Ethanoic acid
Ester**	-oate		 Ethyl ethanoate
Amine	amino- or –amine		 Aminoethane or ethylamine

***Naming of functional groups is covered in detail in Factsheet 15.**
**** Note that these compounds all contain C=O, called the carbonyl group.**

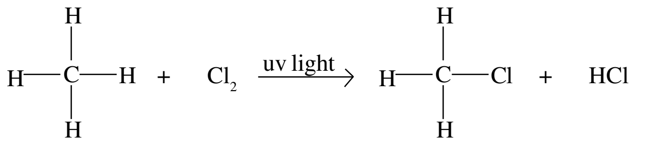
Reactions and properties of functional groups

Below we look at the key properties of these functional groups. This should enable you to predict their behaviour even in more unusual molecules. For practice in this, try the questions at the end of the Factsheet.

Free Radical Substitution of Alkanes

Alkanes are non-polar, saturated molecules, so they tend not to interact with most reagents. However, they will react with halogens by the free radical substitution reaction (Fig 4).This reaction takes place through a chain reaction involving highly reactive free radicals (species with a single unpaired electron). It is initiated by ultra-violet light, which provides the energy to split the chlorine molecule into two free radical chlorine atoms. These atoms are so reactive that they can break the strong C-H bonds and thereby react with the alkane (see Factsheet 16 for more information).

Fig 4. Free Radical Substiution of Methane by Chlorine



Although this reaction can be difficult to control because multiple substitutions will occur, it is important because it provides a route from an alkane to a halogenoalkane and thereby provides access to the whole range of functional groups, using some of the transformations described below.

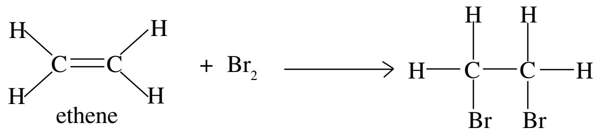
Electrophilic Addition to Alkenes

Double bonds are areas of high electron density (four electrons shared between just two atoms). This means that they react readily with electrophiles, species which seek out electron density. Some commonly used electrophiles are H^+ ions (from hydrogen halides and acids) and Br^+(from Br_2). When the electrophile reacts it accepts an electron pair from the alkene. Since an alkene is unsaturated, it is most likely to react by addition to form a more stable saturated compound. These reactions are therefore called electrophilic additions (Fig 5).

Fig 5. Electrophilic addition of HBr to an alkene

The test for an alkene, where orange-brown bromine solution is shaken with the alkene, producing a colourless product, is similarly an electrophilic addition reaction (Fig 6).

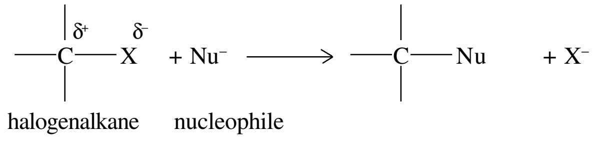
Fig 6. Electrophilic addition of bromine to ethane



Nucleophilic Substitution of Halogenoalkanes

The halogen atom is more electronegative than the carbon atom. This means that the carbon-halogen bond is polar, with the carbon holding a partial positive charge (δ+). The carbon atom is therefore open to attack by nucleophiles such as hydroxide ions, ammonia and water. These nucleophiles donate electron pairs to the electron-deficient carbon atom. Since halogenoalkanes are already saturated, they usually react by substitution to make another saturated molecule. These reactions are therefore called nucleophilic substitutions (Fig. 7).

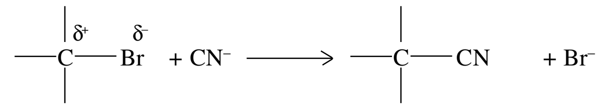
Fig 7. Nucleophilic substitution of halogenoalkanes



The reactivity of the halogenoalkanes in these reactions varies with the halogen in the following order; **C-I > C-Br > C-Cl > C-F**. This is due to the increasing bond strength of the carbon-halogen bonds, with carbon-iodine being the weakest and carbon-fluorine the strongest. The weakest bond is broken most easily resulting in the greatest reactivity.

If the cyanide ion CN^- (found in HCN and KCN, for example) is used as the nucleophile, the product is a nitrile which contains an additional carbon atom (Fig 8). This is an important process in organic synthesis since it allows us to increase the length of the carbon chain. The nitrile group can be easily converted to other functional groups such as carboxylic acids and amines.

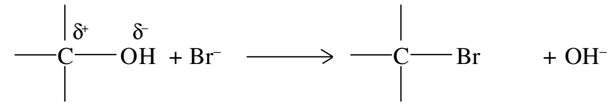
Fig 8. Nucleophilic substitution of a bromoalkane by CN^-



Nucleophilic Substitution of Alcohols

The polar nature of the C-O bond in alcohols, combined with the fact that they are saturated molecules, suggests that they are also likely to react by nucleophilic substitution. As seen in Figure 10, alcohols can react with the nucleophilic Br^- ion from HBr to form the corresponding bromoalkane.

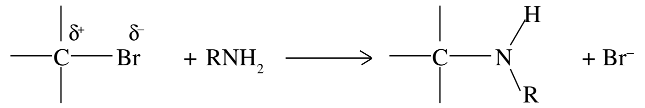
Fig 9. Nucleophilic substitution of an alcohol by Br^-



Nucleophilic behaviour of alcohol and amines

As discussed above, alcohols can undergo nucleophilic substitution of their OH group, but the lone pairs of electrons on the O of alcohols, and also on the N of amines, mean that they can behave as nucleophiles themselves and take part in nucleophilic substitution reactions *as the nucleophile*. Alcohols can make esters by reacting with carboxylic acids (see Fig 15 below) and amines make secondary amines by substitution of halogenoalkanes (Fig 10).

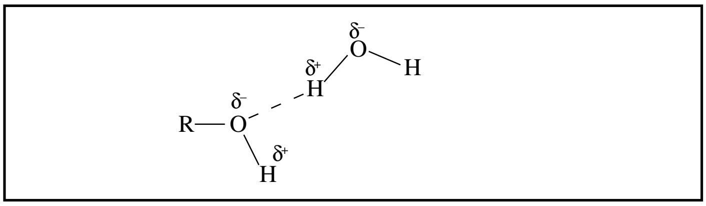
Fig 10. Nucleophilic substitution of a bromoalkane by an amine



Hydrogen Bonding in Alcohols, Amines and Carboxylic Acids

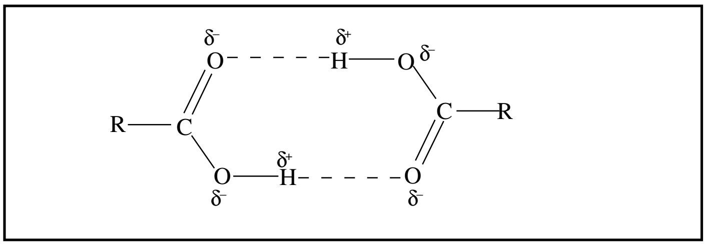
The polar nature of the bonds in these functional groups means that they tend to be more soluble in water than similar sized alkanes since they can form hydrogen bonds to water molecules (Fig 11).

Fig 11. Hydrogen bonds between water and an alcohol



These compounds can also form intermolecular hydrogen bonds, which strengthen the forces between molecules, leading to relatively higher boiling points. This is especially true of carboxylic acids, which can form dimeric structures (Fig 12) consisting of two molecules hydrogen bonded together. Carboxylic acids thus have even higher boiling points.

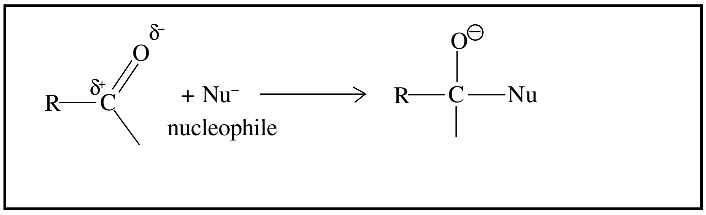
Fig 12. Intermolecular hydrogen bonds in carboxylic acids



Nucleophilic Addition to Carbonyl Groups

The carbonyl group, C=O, is found in a number of functional groups – aldehydes, carboxylic acids, ketones and esters are the ones you are most likely to encounter in AS Chemistry. Like an alkene, the carbonyl group is unsaturated, with a high electron density. Its functionality, though, is usually determined by the polarity of the C=O bond (although this can be modified by the other part of the functional group). Oxygen is more electronegative than carbon, so the carbon is δ+. As in a halogenoalkane, this makes it susceptible to attack by nucleophiles (Fig 13), giving rise to nucleophilic addition reactions.

Fig 13. Nucleophilic addition to the carbonyl group



This is a reaction that you will come across in many guises: reduction of aldehydes by hydride ions (H^-, provided by $NaBH_4$ and $LiAlH_4$) (Fig 14), interconversion of carboxylic acids and esters (Fig 15), and testing for aldehydes and ketones with 2,4-dinitrophenylhydrazine (Fig 16), for example. It may not always be easy, at first glance, to recognise the nucleophilic addition, but if you draw out the mechanism it should become clear.

Fig 14. Reduction of an aldehyde

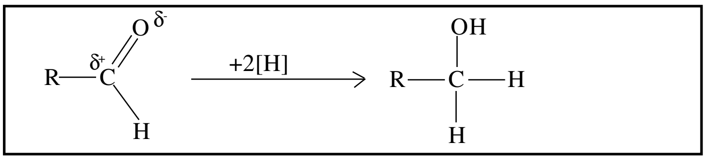


Fig 15. Conversion of carboxylic acid to methyl ester by addition-elimination

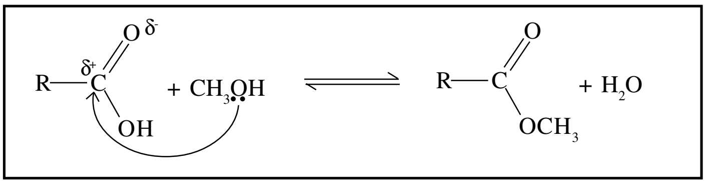
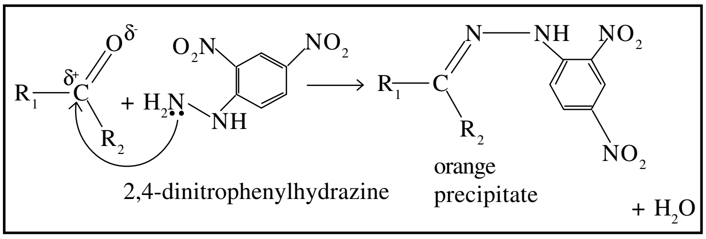


Fig 16. Testing for a ketone with 2,4-dnp

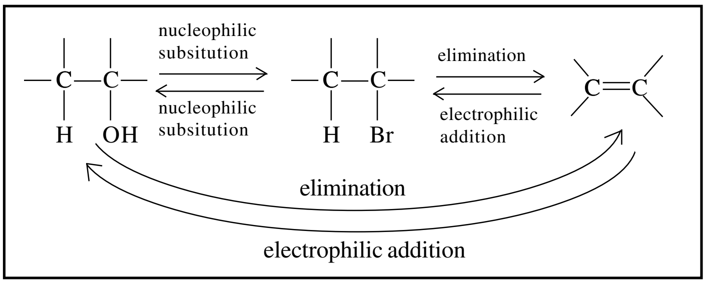


Interconversion of Functional Groups

Perhaps the most significant reactions of functional groups are those which allow conversion of one to another. This is a powerful tool for organic chemists since it allows them to manipulate the functionality of a molecule, firstly to reach their target molecule, and secondly to adapt it, thereby enabling the testing of new functional groups in a particular position of the molecule. This is often vital in the development of new therapeutic drugs.

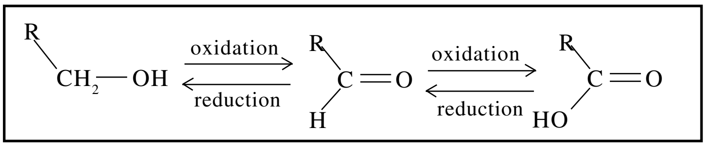
By combining the reactions of functional groups it is possible to convert, either directly or indirectly, any functional group to any other. For example, a halogenoalkane can be converted to an alcohol or an amine by nucleophilic substitution, as described above, or to an alkene by elimination of a hydrogen halide (HX). These reactions can also be reversed, or bypassed by direct conversion of alkene to alcohol (Fig 17).

Fig 17. Interconversion of halogenoalkanes, halides and alkenes



Alcohols, aldehydes and carboxylic acids can be interconverted by oxidation and reduction (Fig 18).

Fig 18. Interconversion of alcohols, aldehydes and carboxylic

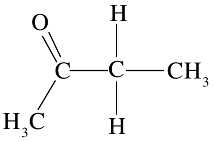
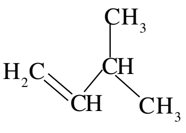
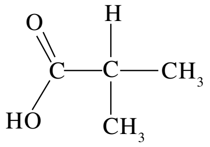
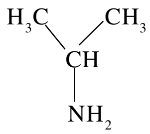
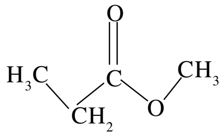
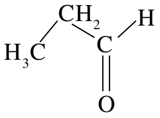


Acids

There are many other functional group reactions, and you will need to learn them to succeed in A Level Chemistry, including the reagents and conditions necessary to make them work well. However, the principles behind them are the same and you should get into the habit of looking at a molecule and making predictions about its reactions and properties based on the structure, degree of saturation and polarity of the functional groups it contains.

Practice Questions

1. Name the functional group in each of these organic molecules

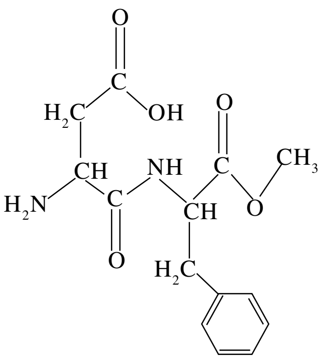
2. Name the functional group in each of these compounds:
   (a) Propan-2-ol
   (b) 2-Methylpropene
   (c) Propanone
   (d) Butanal
   (e) Ethyl ethanoate
   (f) Hexanoic acid

3. Ethanol, C_2H_5OH, chloromethane, CH_3Cl, and propane, C_3H_8, have similar molecular masses (46, 51 and 44 respectively), but their boiling points are very different (79, -24 and -42°C respectively). Explain why.

4. Amines are more soluble in water than alkanes. Why is this?

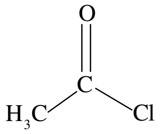
5. (a). The test for an alkene is the addition of bromine solution. What would you observe in this reaction?
   (b). What type of reaction is this?
   (c). What functional group does the product of this reaction contain?

6. The diagram shows the structure of aspartame, a controversial synthetic sweetener that is nearly 200 times sweeter than sugar. Name four functional groups in the molecule.

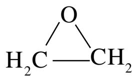


Aspartame

7. The molecules below contain some other functional groups. Predict whether you think they will react predominantly with nucleophiles or electrophiles.



Acyl chloride

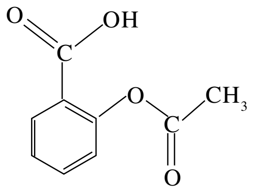


Epoxide

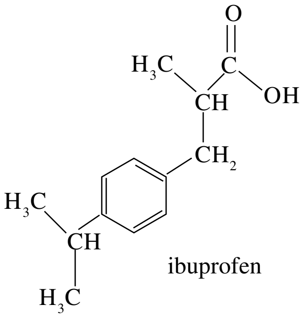
$H_3C-C\equiv N$

Nitrile

8. The diagram below shows the structure of two commonly used analgesics (pain killers), aspirin and ibuprofen.



aspirin

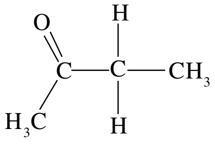


ibuprofen

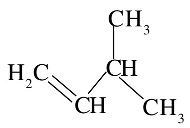
   (a) Name one functional group found in ***both*** molecules.
   (b) Name one functional group found in aspirin but not in ibuprofen.
   (c) Ibuprofen is a drug that was designed and synthesised in the research labs of Boots the chemists. Suggest a reason why the research chemists included the alkyl chain labelled in the molecule, rather than an alcohol group in the same position.

Answers

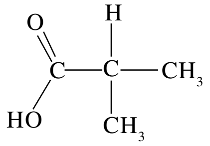
1.



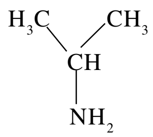
Ketone



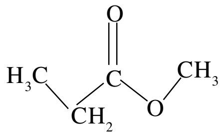
Alkene



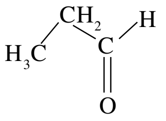
Carboxylic acid



Amine



Ester



Aldehyde

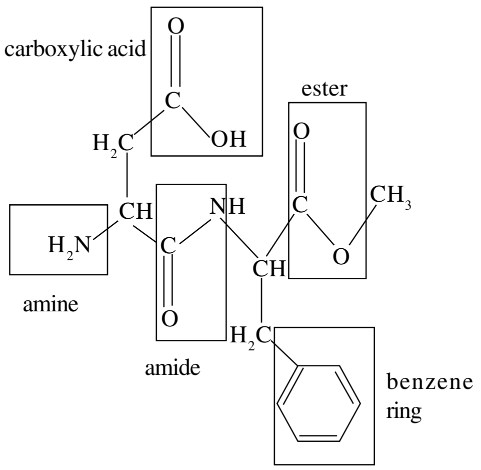
2. (a) Alcohol (secondary)
   (b) Alkene
   (c) Ketone
   (d) Aldehyde
   (e) Ester
   (f) Carboxylic acid

3. Ethanol contains intermolecular hydrogen bonds, due to the polar nature of the O-H bond, which increase the strength of their intermolecular forces. Remember that ethanol will also have permanent dipole and van der Waal's interactions as well. Chloroethane contains polar C-Cl bonds, which lead to permanent dipole-dipole interactions between molecules (as well as van der Waal's), making intermolecular forces stronger than in non-polar molecules. Propane is an alkane, a non-polar molecule, with only weak van der Waal's forces holding the molecules together.

4. Amines can form hydrogen bonds with water molecules due to the polar N-H bonds. Alkanes cannot since they do not contain polar bonds.

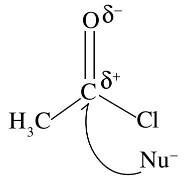
5. (a) The brown/orange bromine solution would turn colourless
   (b) An electrophilic addition reaction
   (c) The product is a (di)bromoalkane

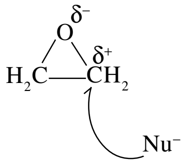
6.

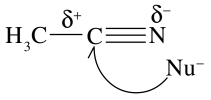


Aspartame

7. All these molecules will be susceptible to nucleophilic attack on the δ^+carbon atoms.







8. (a) Carboxylic acid
   (b) Ester
   (c) To reduce water solubility of the drug. Using an alcohol group here would make the molecule much more water-soluble. This would lead to it staying dissolved in the bloodstream and passing straight through the body, rather than passing into cells where it can work as a painkiller.

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