

Organic Chemistry

(Brown & Le May, 3rd Ed.; Chapters 21 -26 & 28)

Organic Chemistry is based on the element carbon, so in this section we will look at the electronic configuration and bonding of carbon, including hybridization which is related to valence bond theory. (See Chapter 8 & 21.1)

Valence Bond Theory and Hybridisation

Carbon

Carbon is an element in group 14 (4A) of the periodic table, having an atomic number, Z, of 6.

Electron configuration: $1s^2 2s^2 2p^2$

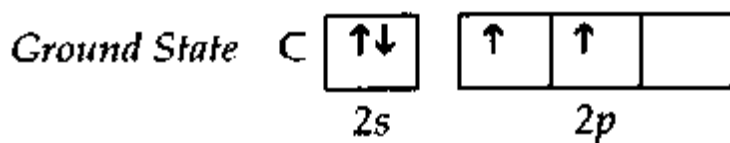
A characteristic property of carbon is that it is able to form multiple bonds, i.e. double and triple bonds, both with itself and other elements.

Valence Bond Theory

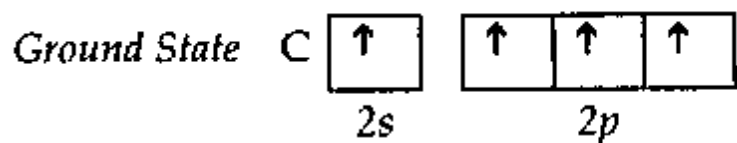
Valence bond theory (VBT) tries to explain how and why bonding occurs. According to VBT, covalent bonds form from the overlap of the atomic orbitals of the two involved, where each orbital contains a single e^- ; and the e^- 's must be spinning in opposite directions. The bonding electrons are localized in regions of orbital overlap between the nuclei of the bonded atoms. The driving force for bonding is that the Potential Energy of the molecule \ll Potential Energy of the individual atoms, i.e. the molecule is more stable, with the Potential Energy at minimum value when the intermolecular distance is such that electrostatic forces of repulsion & attraction are balanced.

Hybridisation

The problem with VBT is that according to the ground state electron configuration of carbon, only has TWO unpaired electrons, therefore should only form TWO covalent bonds but form FOUR bonds in most compounds.



In order to explain the bonding behaviour of carbon, VBT was adapted in hybridisation theory; the mixture/combination of "pure", non –equivalent atomic orbitals to generate new set of **hybrid** atomic orbitals. We can generate four equivalent hybrid orbitals for carbon by mixing the 2s orbital and the three 2p orbitals.



How many of the orbitals "mix" to give rise to the multiple bonding that exists with carbon.

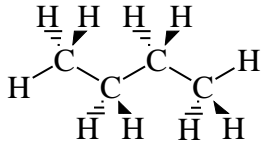
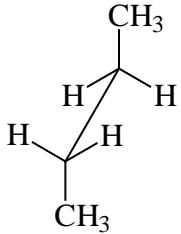

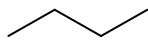
Complete the following table:

Hybridisation State	Bonds		Bond Angle	Molecular Geometry	Example
	σ Bonds	π Bonds			
sp^3	4	0	109.5°	Tetrahedral	C-C
sp^2					
sp					

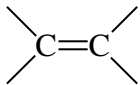
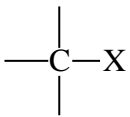
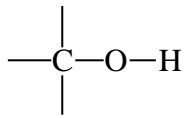
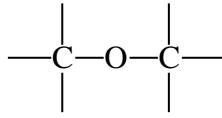
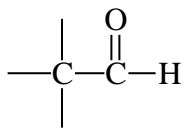
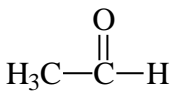
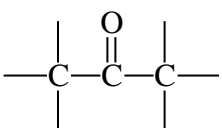
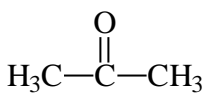
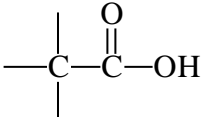
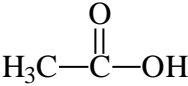
GENERAL BACKGROUND INFORMATION

1. Conventions for representing chemical formulae:

e.g. Formulae for *n*-butane:

empirical	C_2H_5
molecular	C_4H_{10}
structural	$CH_3CH_2CH_2CH_3$
Lewis	$ \begin{array}{cccc} H & H & H & H \\ & & & \\ H : & \overset{\cdot\cdot}{C} : & \overset{\cdot\cdot}{C} : & \overset{\cdot\cdot}{C} : & \overset{\cdot\cdot}{C} : & H \\ & & & \\ H & H & H & H \end{array} $
2-D structural	$ \begin{array}{cccc} H & H & H & H \\ & & & \\ H - C & - C & - C & - C - H \\ & & & \\ H & H & H & H \end{array} $
3-D structural	
Sawhorse projection	
Newman projection	
line	

Classification of Organic Compounds - List of organic functional groups

	<i>Family Name</i>	<i>Functional group structure</i>	<i>Simple example</i>	<i>Name ending</i>
Functional groups that are part of the molecular framework C & H only	Alkane	(Contains only C—H and C—C single bonds)	CH ₃ CH ₃	-ane Ethane
	Alkene		H ₂ C=CH ₂	-ene Ethene
	Alkyne	—C≡C—	H—C≡C—H	-yne Ethyne
C, H & X	Halide	 (X = F, Cl, Br, I)	H ₃ C—Cl	None Chloromethane
Functional Groups with oxygen 1. C-O single bond	Alcohol		H ₃ C—O—H	-ol Methanol
	Ether		H ₃ C—O—CH ₃	-ether Dimethyl ether
2. C-O double bond	Aldehyde			-al Ethanal
	Ketone			-one Propanone
3. single and double C-O bonds	Carboxylic acid			-oic acid Ethanoic acid

3. cont	Ester		$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_3$	<i>-oate</i> Methyl ethanoate
Functional groups containing nitrogen	Amide C, H, O & N		$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$	<i>-amide</i> Ethanamide
	Amine C, H, N		$\text{H}_3\text{C}-\text{NH}_2$	<i>-amine</i> Methylamine
	Nitrile C, H, N		$\text{H}_3\text{C}-\text{C}\equiv\text{N}$	<i>-nitrile</i> Ethanenitrile (Acetonitrile)

IUPAC Rules for Naming Compounds

1. The parent hydrocarbon is the longest continuous chain *containing the highest priority (see above list) functional group*.
2. The chain is numbered in the direction that gives the *highest priority functional group the lowest possible number*.
3. If there is a functional group and a substituent the functional group gets the lowest possible number.
4. If the same number for the functional group is obtained in both directions, the chain is numbered in the direction that gives a substituent the lowest possible number.
5. If there is more than one substituent, the substituents are cited in alphabetical order.

Nomenclature = the systematic naming of organic compounds**I) Alkanes** - suffix -ane

No. of C atoms	Formula	Name
1	CH ₄	Methane
2	C ₂ H ₆	Ethane
3	C ₃ H ₈	Propane
4	C ₄ H ₁₀	Butane
5	C ₅ H ₁₂	Pentane
6	C ₆ H ₁₄	Hexane
7	C ₇ H ₁₆	Heptane
8	C ₈ H ₁₈	Octane
9	C ₉ H ₂₀	Nonane
10	C ₁₀ H ₂₂	Decane
11	C ₁₁ H ₂₄	Undecane
12	C ₁₂ H ₂₆	Dodecane

Alkanes contain **only** carbon and hydrogen and are termed **hydrocarbons**. The important thing to remember about alkanes is that they contain only σ -bonds. The simplest alkane is methane.

A couple of important points arise from this table.

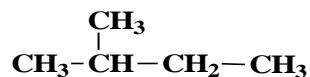
- 1) All the names end in **ane** - thus the **alkanes**. There is no other way around this-you must **learn** the names. It will make life a lot easier when naming other chemical species.

There is a definite trend in the formula of the alkanes. In fact they all have the general formula C_nH_{2n+2}.

Naming the Prefix – Substituents:

- Side chains have the ending -yl

e.g.



- If there is more than one of a particular substituent:

di = 2

penta = 5

octa = 8

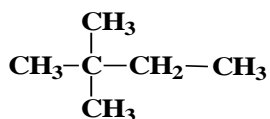
tri = 3






hexa = 6

nona = 9

tetra = 4

hepta = 7

**Hydrocarbon branches**

Group	Name
 -CH ₃	Methyl
 -CH ₂ CH ₃	Ethyl
 -CH ₂ CH ₂ CH ₃	Propyl
 -CH ₂ CH ₂ CH ₂ CH ₃	Butyl
 -CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	Pentyl

$\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\ \\ \text{~~~~~} \end{array}$	Isopropyl
$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\ \\ \text{~~~~~} \end{array}$	<i>sec</i> -butyl
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{~~~~~} \\ \\ \text{CH}_3 \end{array}$	<i>tert</i> -butyl
$\begin{array}{c} \text{CH}_3-\text{CHCH}_2\text{~~~~~} \\ \\ \text{CH}_3 \end{array}$	Isobutyl
$\begin{array}{c} \text{CH}_3-\text{CHCH}_2\text{CH}_2\text{~~~~~} \\ \\ \text{CH}_3 \end{array}$	Isopentyl
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2\text{~~~~~} \\ \\ \text{CH}_3 \end{array}$	Neopentyl
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2-\text{C}-\text{~~~~~} \\ \\ \text{CH}_3 \end{array}$	<i>tert</i> -pentyl (<i>tert</i> -amyl)

Naming Compounds with Functional Groups

The names of most organic compounds can be viewed as having three main parts.

Prefix-Parent-Suffix

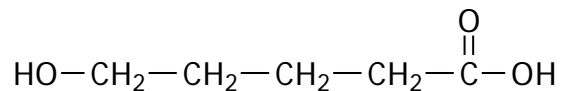
Prefix: identifies the where and what for the substituents.

Parent: this is the backbone of the molecule, the name of which depends upon the number of carbon atoms.


Suffix: this is particularly important as it describes the functional group present

Rule 1: The parent hydrocarbon chain is the longest continuous carbon chain containing the highest priority functional group.

Some compounds might contain more than one functional group and thus a priority list is required. For example, is the following compound named as an alcohol or as a carboxylic acid?



The answer is as a carboxylic acid as the $-\text{COOH}$ group has the highest priority. The full priority list is shown below.

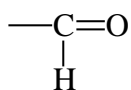
Functional Group	Name	Highest priority
$-\text{COOR}$	Ester	
$-\text{CONH}_2$	Amide	
$-\text{COX}$	Acid halide, X=Cl, Br	
$-\text{COOH}$	Carboxylic acid	
$-\text{CHO}$	Aldehyde	
RCOR	Ketone	
$-\text{OH}$	Alcohol	
$-\text{NH}_2$	Amine	
$\text{C}_n\text{H}_{2n-2}$	Alkyne	
C_nH_{2n}	Alkene	
$\text{C}_n\text{H}_{2n+2}$	Alkane	

An alkyl substituent (C_nH_{2n+1}) has the lowest priority. Halides are always named as substituents on the parent hydrocarbon. Common non-alkyl substituents are –

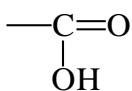
Substituent	Name
-F	Fluoro
-Cl	Chloro
-Br	Bromo
-I	Iodo
-NO ₂	Nitro

Rule 2: The chain is numbered in the direction that gives the highest priority functional group the lowest possible number.

Of course for some functional groups by their very nature have to come at the end of a chain. Examples of these are

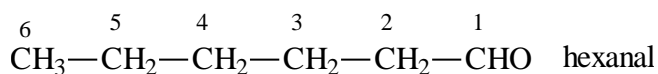
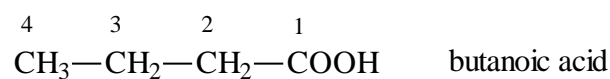


aldehydes



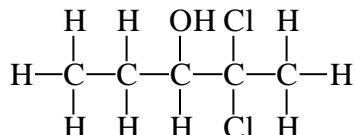
carboxylic acids

When numbering chains which include these functional groups start at the carbon attached to the heteroatoms. For example;



Rule 3: If the same number for the functional group is obtained in both directions the chain is numbered in the direction that gives the substituent the lowest number.

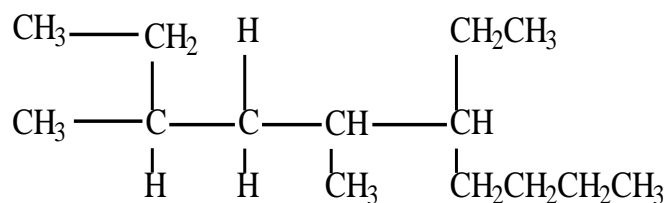
For example the following molecule.



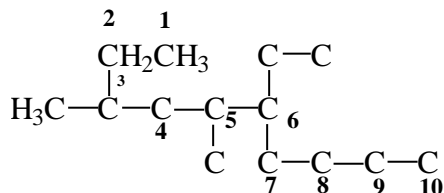
is 2,2-dichloropentan-3-ol (not 4,4-dichloropentan-3-ol).

Exercise

Name the following molecule.

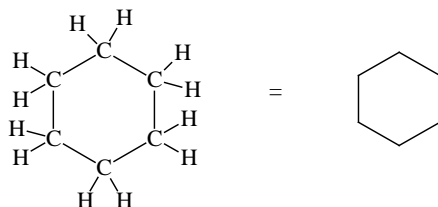


The longest carbon chain is ten carbons long, thus



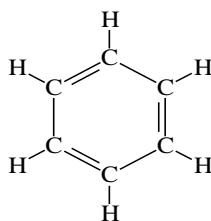
Naming Cycloalkanes

Alkanes, alkenes and alkynes are all linear molecules, where the carbon atoms are in a chain. There is however another way of joining carbons together and that is in rings. Consider for example the following molecule.

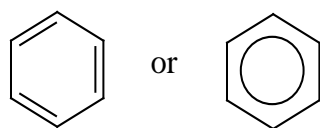


Here we have six carbon atoms joined in a ring. The naming of these compounds is still based upon the number of carbon atoms so this molecule is called **cyclohexane**. You will notice that the molecular formula for cyclohexane is C_6H_{12} . For all cycloalkanes the carbon:hydrogen ratio is $C_n:H_{2n}$. This is exactly the same ratio as for alkenes. However, cycloalkanes are saturated molecules and they will have a very different chemistry from alkenes with the same molecular formula, so beware!

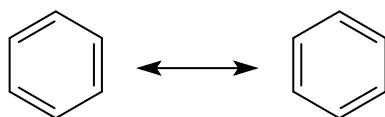
One can also get unsaturated rings such as the following molecule



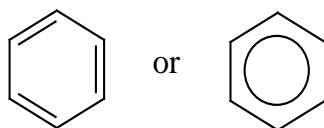
This pattern of a C-C single bond, C=C double bond, C-C single bond, C=C double bond, etc. is very important in organic chemistry. If this pattern exists, the molecule is said to be **conjugated**. If you have a conjugated ring, as in the above molecule, the molecule is described as being **aromatic**. We normally draw the above molecule as



The second structure is to show that the π -bonding in the molecule is de-localised, i.e., it is the average of the two resonance forms of the molecule.



This particular molecule is very important in organic chemistry and is called **benzene**.



Naming Cycloalkanes

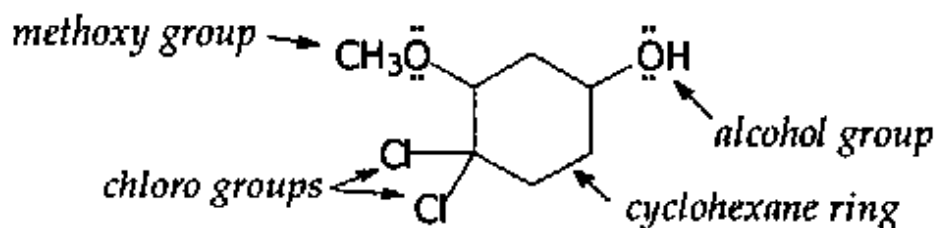
Count the number of carbon atoms in the ring and add the prefix *cyclo-* to the name of the corresponding alkane. For example



5 C \therefore cyclopentane

If substituents are present on the ring, the compound should be named as a substituted cyclo-compound, with the numbering of the ring starting at the carbon with the highest priority functional group.

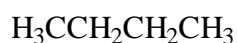
Example:



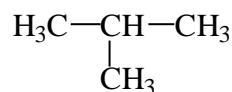
4,4-dichloro-3-methoxycyclohexanol

Isomers

Isomers are compounds that have the same numbers and kinds of atoms but differ in the way they are arranged. We have already seen that the molecular formula C_4H_{10} can give rise to two different molecules-



n-butane



isobutane

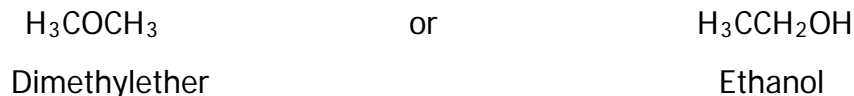
These two molecules are **isomers** of each other.

There are in fact many different types of isomerism that can occur in organic chemistry and this section will review them under two umbrella titles- **constitutional isomers** and **stereoisomers**.

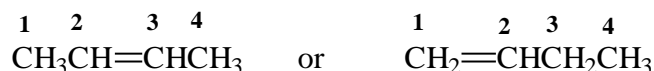
Constitutional Isomers

This type of isomerism occurs when the atoms are **connected differently**. Butane and isobutane have a different way of connecting the carbon atoms and are thus constitutional isomers. Another form of constitutional isomerism is when a molecular

formula can give rise to different functional groups. For example if we have a molecular formula of C_2H_6O , how many ways can we connect the atoms together? The answer is two, as shown below.



The presence of unsaturation in a molecule also introduces the possibility of isomerism. This is really just an extension of the idea of functional groups having different positions. Consider the molecule butene. Given only this description we can actually draw two possible structures.



We then need to specify the exact position of the double bond. The two molecules would therefore be but-2-ene and but-1-ene.

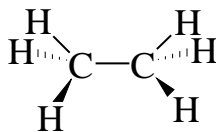
Stereoisomers

Stereoisomers are compounds where the atoms are connected in the same order but the molecules have different geometries. When talking of geometries, or shapes, we need to start thinking in three dimensions (3D). We will discuss three types of stereoisomer in this section: conformational isomers, geometric isomers and enantiomers. When thinking in 3D we need to remember the two very important concepts introduced in the CHEM110.

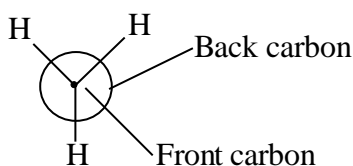
- There is rotation possible around a carbon-carbon single bond.
- There is no rotation possible around a carbon-carbon double-bond.

a. Conformational Isomers

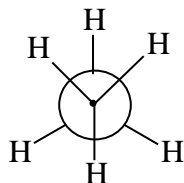
Organic chemists have various ways of drawing 3D structures on a 2D page. Thus for ethane we can draw the following structure.



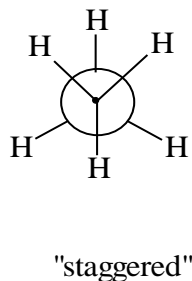
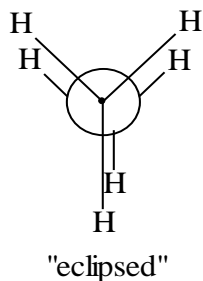
We can change our point of perspective when looking at the ethane molecule to an end-on view, looking directly along the C-C bonds. We now draw a circle to represent the other carbon atom (the one we can't see)-



and then we put into the diagram the three hydrogen attached to this carbon.



This type of representation is known as a Newman Projection. Newman projections are very useful when looking at what happens to the shape of a molecule when we rotate around a carbon-carbon bond. Upon rotation we can change the relative positions of the hydrogen on the back carbon with respect to the hydrogen on the front carbon. There are an infinite number of possibilities here but two extremes stand out. These are shown below.

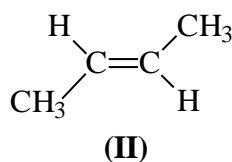
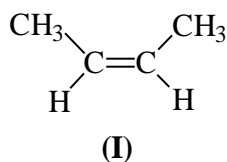


The eclipsed and staggered forms of ethane are said to be **conformational isomers** or **conformers**.

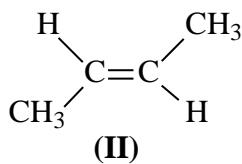
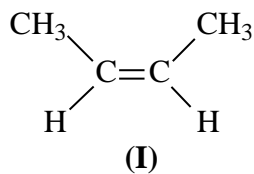
B. Geometric Isomers

To return to the second point we listed at the start of the section- there is no rotation possible around a double bond.

Ethene is a planar molecule. In fact the geometry immediately around an alkene functional group is always planar due to the fact that the carbons are sp^2 hybridised. If we now look at but-2-ene we can draw the molecule as



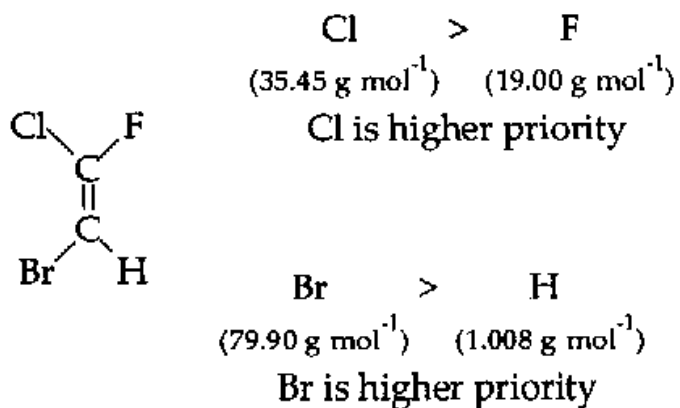
Molecule (I) has the two methyl groups on the same side of the double bond. This is called the *cis* – isomer or the *Z* – isomer. The other isomer has the methyl groups on the opposite sides of the double bond. This is known as the *trans* – isomer or the *E* – isomer.



cis-isomer } substituents on
Z-isomer } the **same** side
 cis-but-2-ene

trans-isomer } substituents on
E-isomer } **opposite** sides
 trans-but-2-ene

In the following example of 2-bromo-1-chloro-1-fluoroethane:

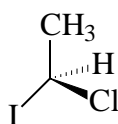


Since both Cl and Br are on the same side of the double bond, the structure has a *cis* (*Z*) confirmation:

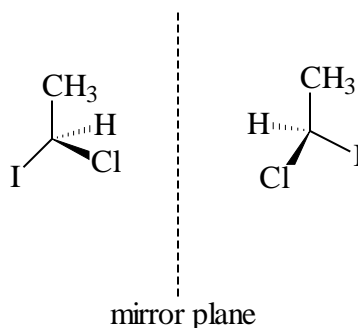
Z-2-bromo-1-chloro-1-fluoroethane

C. Enantiomers

Another form of stereoisomerism arises from molecules which contain a **chiral** centre. A chiral centre is an sp^3 hybridised carbon centre which is attached to four **different** substituents. An example would be the following molecule.



Believe it or not there is another way of drawing this molecule! If we imagine a mirror beside the molecule then we can envisage what the molecule will look like in the mirror (or through the mirror plane).



These two molecules are not the same! If you try and superimpose the two molecules on top of each other you will find it impossible to do! The two different isomers are called **enantiomers**. It is sufficient to recognise that when a chiral centre is present in a molecule, the isomers are known as the R-isomer and the S-isomer.

Nomenclature of Enantiomers: R/S – Cahn-Ingold – Prelog system

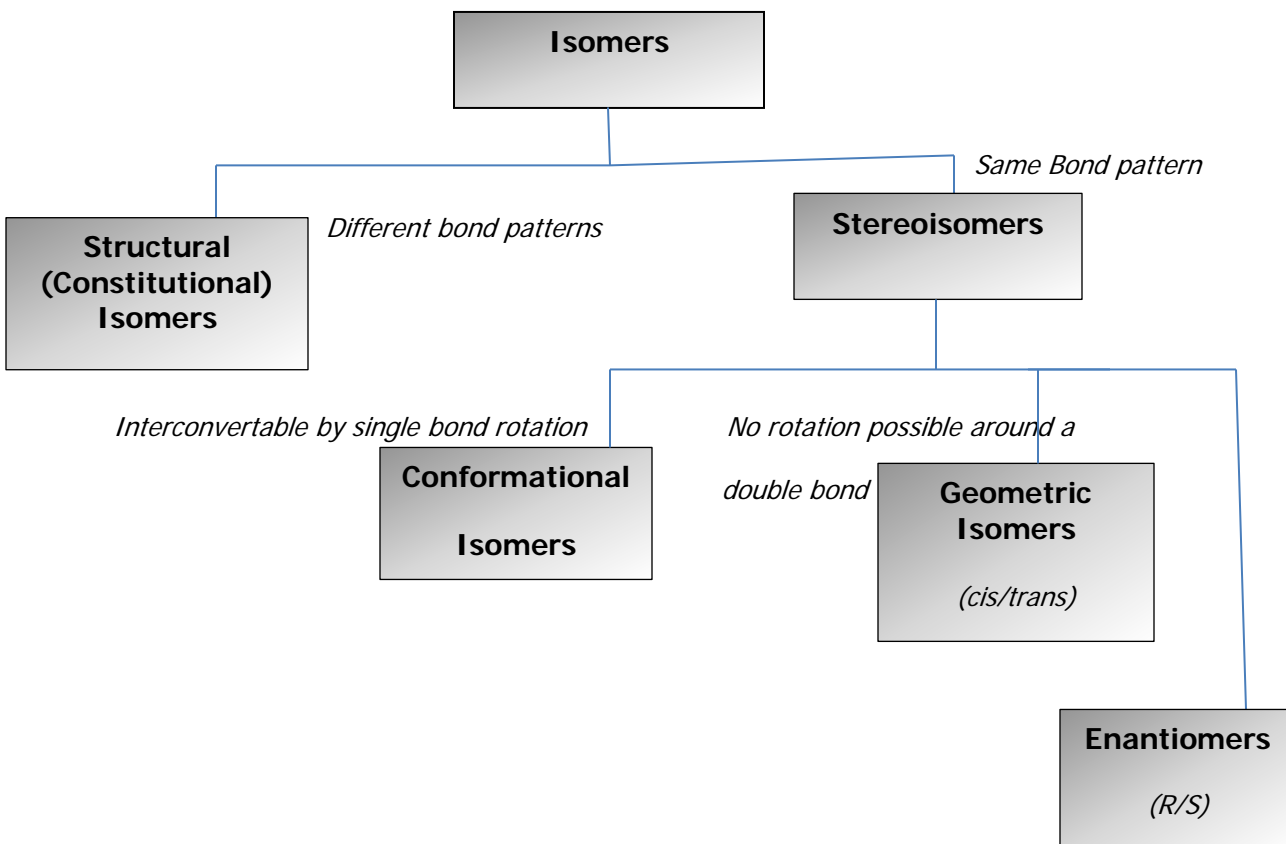
Optical Activity

Diastereoisomers

Newman Projections

Primary (1°), Secondary (2°), Tertiary (3°) & Quaternary (4°)

In Summary:



An Introduction to Reaction Mechanisms

Organic Chemistry is largely about making new carbon-containing compounds. To do this bonds in existing compounds must be broken and new bonds formed. In this section we will examine the major types of reactions that organic compounds undergo. These include:

1. Free radical halogenation of alkanes to form alkyl halides.
2. Electrophilic addition reactions of alkenes.
3. Ozonolysis of alkenes to form aldehydes and/or ketones.
4. Oxidation Reactions & Reduction reactions.
5. Elimination reactions to form alkenes.
6. Nucleophilic substitution reactions.

As well as learning the reactions, including the reagents and reaction conditions, we will study a number of reaction mechanisms.

Mechanisms

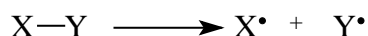
A mechanism attempts to show exactly **how** a reaction occurs in terms of bonds breaking and forming by means of single (Free radical mechanism) or double headed arrows (which apply to the rest of the mechanisms done).

1. Free radical halogenation of an alkane to an alkyl halide
2. Electrophilic addition to an alkene – Markovnikov & anti- Markovnikov addition
3. Elimination reactions to form alkenes – Saytzeff's rule
4. Nucleophilic substitution –SN1 & SN2

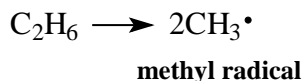
Bond Breaking (Fission) and Bond Formation

When a single covalent bond breaks, **two** different outcomes are possible.

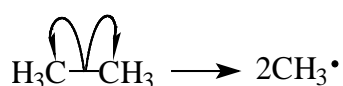
One way is for the two electrons in the bond to divide equally. This is known as **homolytic fission** and results in the formation of **free radicals**.



Each of X and Y now has an odd electron (as indicated by \bullet). For instance if we homolytically split the carbon-carbon bond in ethane then two methyl radicals will result.



We denote the movement of single electrons with a **single-headed** arrow \curvearrowright . Thus we can draw the reaction mechanism for the homolytic splitting thus



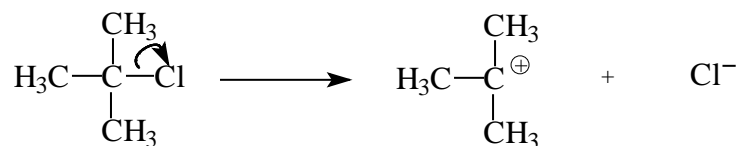
Radicals are, in general, **very reactive** species.

The other way to break a single covalent-bond is **heterolytic fission**, where the two electrons in the bond go to **one** of the atoms. The movement of two electrons is shown by a double-headed arrow \curvearrowleft .



Now we have a cation and an anion forming. If a carbon-carbon bond breaks in this fashion then we have a **carbocation** and a **carboanion** resulting.

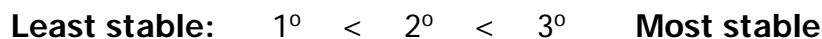
Consider the following reaction.



Generally,

- i) the more alkyl groups attached to the electron-deficient carbon, the greater the inductive effect (stability of the carbocation); and
- ii) the larger the alkyl group substituent the more electron-donating it will be and therefore the greater the inductive effect.

Thus, how easily the bond breaks depends on the stability of the carbocation (C^+) formed:

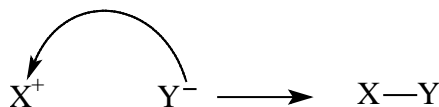


Bond Formation

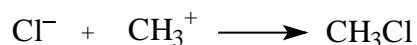
To form a single covalent bond we need two electrons. This can also happen in two ways.



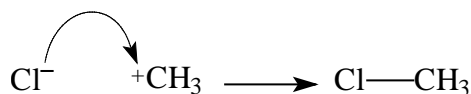
or



If we look at the following bond formation mechanism –



then we could draw the mechanism as



where the chloride ion has donated two electrons to carbon.

The chloride ion is termed a **nucleophile** and the carbocation is an **electrophile**. The formation of the bond comes from **nucleophilic attack on an electrophile**.

*A **nucleophile** is a “positive loving” species and will, itself, be negatively charged or electron rich. An **electrophile** is a “negative loving” species and will, itself, be positively charged or electron deficient.*

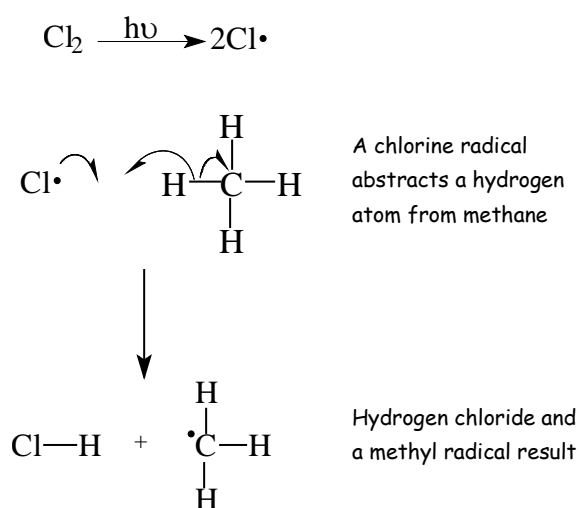
MECHANISMS

1. Free Radical Halogenation of Alkanes to form an Alkyl Halide

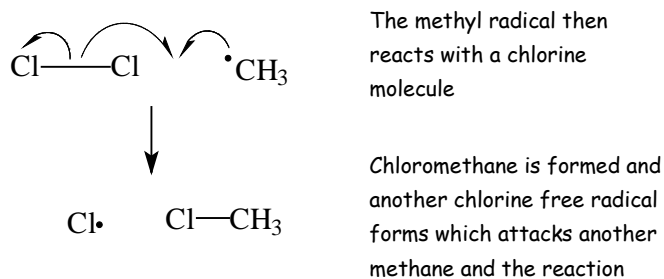
Alkanes are generally very unreactive (as they have no functional groups) but one particular reaction type is very important. This involves the substitution of a hydrogen within the alkane by a halide atom. The reaction between a halogen, such as Cl_2 , and an alkane, e.g. methane, proceeds via a **free-radical** mechanism. The reaction can be broken down into three steps; initiation, propagation and termination.

Step 1: Initiation: Generation of free radicals.

Photochemically induced homolytic fission results in two Cl radicals.

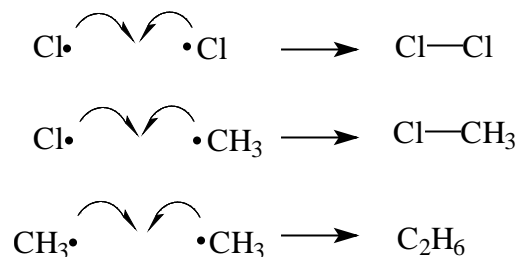


Step 2: Propagation



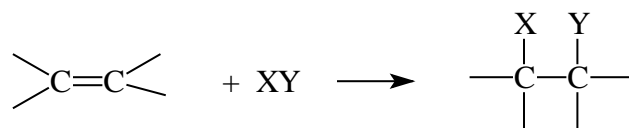
Step 3: Termination

For a free radical substitution to stop, free radicals must react with each other.



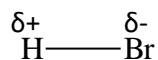
2. Electrophilic Addition to an Alkene – Markovnikov & Anti-Markovnikov Addition

An addition reaction is one in which the bond order between two carbon atoms **decreases**. For instance, we can **add** a species across a double bond.



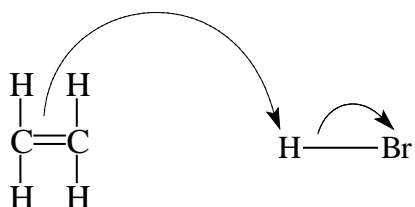
In the above reaction the bond order between the two carbon atoms has decreased from two to one. Addition reactions of alkenes proceed via a **carbocation intermediate**.

Alkenes are nucleophilic, that is, they have a centre of electron density in the double bond. We therefore require a positive centre to react with it. If we take a **polar molecule** such as HBr then we will have a positive centre on the H atom.

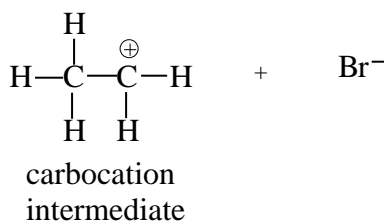


Thus the first step of the reaction will be a nucleophilic attack by the alkene at the hydrogen end of the HBr molecule.

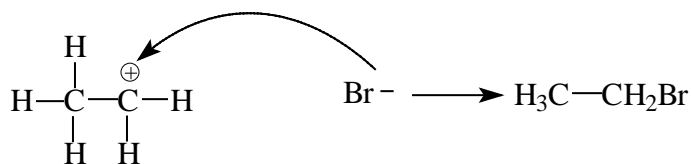
Taking ethane as an example –



As the carbon-hydrogen bond forms the hydrogen-bromine bond will simultaneously break to give –



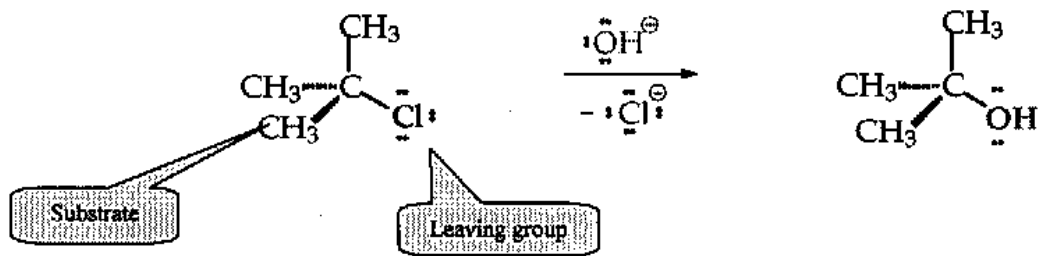
The bromide ion will now attack the carbocation thus



The sum total of the reaction is that we have converted an alkene into an alkyl halide.

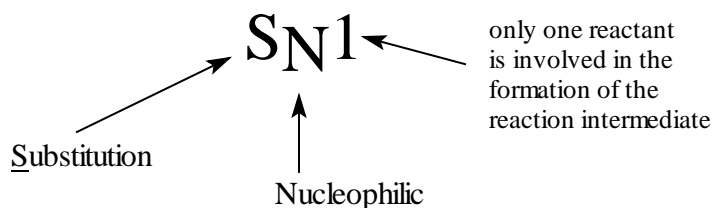
We need to be careful when dealing with larger alkenes. Consider for example the reaction between propene and HBr. Two carbocation intermediates are now possible depending on which carbon atom of the double bond uses the pi electrons to form a bond to the hydrogen atom.

This type of reaction is known as a substitution reaction as the halogen atom is merely being replaced by another group and the hybridization state and molecular geometry of the affected carbon does not change. Substituted is called In general for a substitution reaction, the electronegative atom (electron withdrawing group) is replaced by another group or atom. The atom or group that is substituted is called the leaving group.



Because the atom or group that is added to the carbon is a nucleophile, these reactions are known as **nucleophilic substitution reactions**.

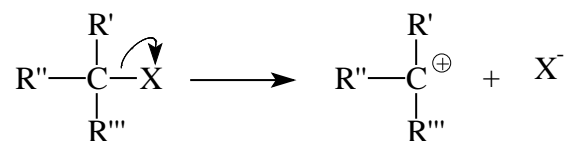
There are TWO mechanisms for the nucleophilic substitution reaction, namely SN1 and SN2 where



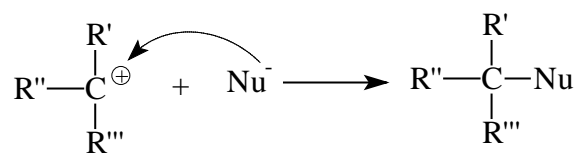
Which mechanism predominates depends on the following factors:

- the structure of the alkyl halide (substrate) 1° , 2° , or 3° i.e. $1^\circ \rightarrow \text{SN2}$, while $3^\circ \rightarrow \text{SN1}$
- the reactivity of the nucleophile – how strong a Lewis base it is: the stronger the base $\rightarrow \text{SN2}$
- the concentration of the nucleophile – the higher concentration $\rightarrow \text{SN2}$
- the solvent of the reaction – polar solvent $\rightarrow \text{SN1}$, while nonpolar solvent $\rightarrow \text{SN2}$

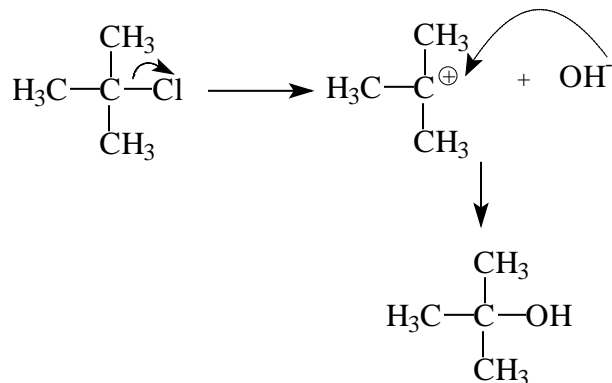
How do S_N1 reactions proceed? The answer is via a carbocation intermediate. The first step is therefore the breaking of the carbon-halogen bond.



The carbocation thus formed then undergoes nucleophilic attack.

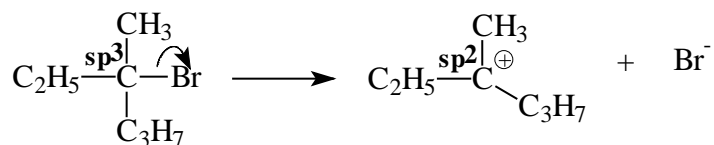


An example of S_N1 would be the following reaction.

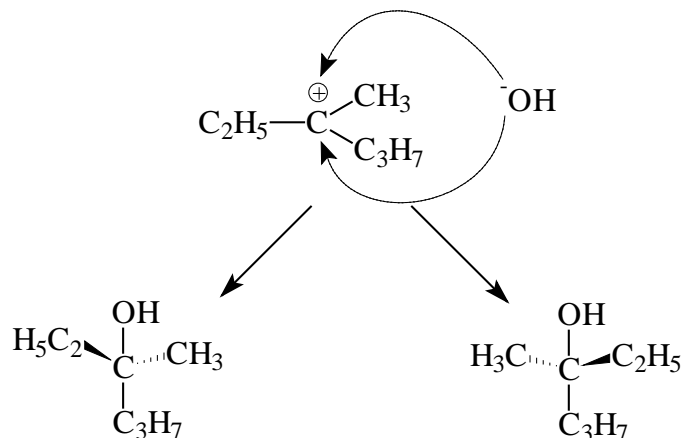


S_N1 reactions go via a carbocation intermediate.

Once again we need to consider the consequences of going through a carbocation intermediate. Consider the following reaction in a basic medium.



Once again we are forming an sp^2 hybridised carbon centre which is **trigonal planar**. We must recognise that the nucleophile, OH^- , now can either attack from below **or** above.



Two enantiomers will thus result and we will have a racemic mixture of products.

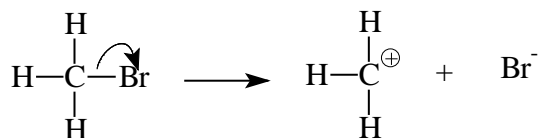
If the carbocation centre has three different substituents attached to it then a racemic mixture of the two enantiomers will result.

- Q. What type of alkyl halides will undergo S_N1 reactions?
 A. Those that can form stable carbocation intermediates.
 Q. Which alkyl halides will form the most stable carbocation intermediates?
 A. Tertiary alkyl halides as they will form 3° carbocations.

Tertiary alkyl halides undergo substitution via an S_N1 reaction mechanism.

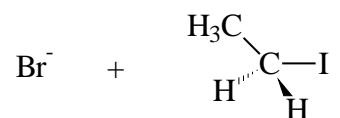
S_N2 Reactions

Would we expect CH_3Br to undergo an S_N1 type reaction? If it did then the first step would be



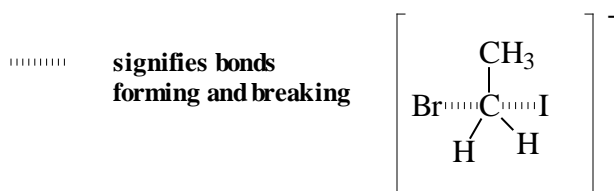
CH_3^\oplus is the least stable carbocation that can form as it has **no** stabilising inductive effect from alkyl substituents.

Instead of forming carbocations 1° alkyl halides form a five-coordinate intermediate. If, for example, we look at the reaction of iodoethane with bromide ions–

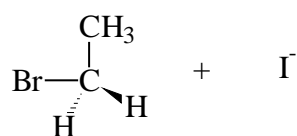


Firstly bromide approaches the central carbon atom **from the opposite side** to the iodide substituent.

What then happens is the carbon simultaneously starts to form a bond with the bromine and starts to break the bond with the iodine. We thus have a very short-lived pentavalent-carbon intermediate.



The iodide ion then leaves the intermediate to give –

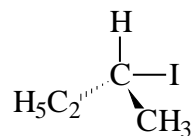


At **no** stage has a carbocation intermediate formed as in $\text{S}_\text{N}1$.

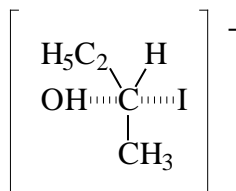
How many products form in $\text{S}_\text{N}2$ reactions? Well, again it will depend upon the starting alkyl halide. If we start with an alkyl halide that has three different substituents on the carbon **attached to the halide** (i.e a chiral centre) then we need to specify whether the starting material is a pure enantiomer or a racemic mixture. This is important, as during an $\text{S}_\text{N}2$ reaction the attack by the nucleophile is unidirectional i.e. it attacks from

one direction, the direction from **opposite** the leaving group. This will result in **inversion** at the chiral C-atom.

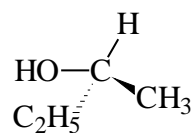
To help explain this, consider the following alkyl halide.



When this is attacked by a nucleophile, say OH^- , then the following intermediate will form –



and finally we will get –



If we therefore started with, say, the R-isomer of the alkyl halide we will get the S-isomer of the final alcohol, and **only** the S-isomer. This is called **inversion**. If instead we started with a racemate of the starting material then because all the starting material will be inverted to the other enantiomer a racemic mixture of the product will result.

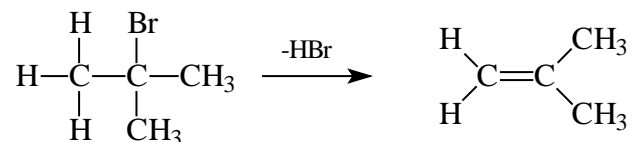
1° alkyl halides undergo $\text{S}_{\text{N}}2$ substitution pathways

3° alkyl halides undergo $\text{S}_{\text{N}}1$ substitution pathways

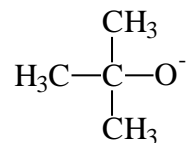
2° alkyl halides undergo either $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ substitution pathways

4. Elimination (Base catalyzed)

If addition reactions of alkenes are considered to be reductions then there must be an opposite reaction that will be considered an oxidation. The opposite of addition is **elimination**, where a small molecule is eliminated leaving behind an unsaturated alkene. For example –



In the above reaction HBr is eliminated to convert an alkyl halide into an alkene. This type of reaction is catalysed by a very strong base, namely tert-butoxide –

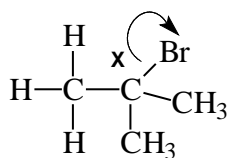


Mechanism:

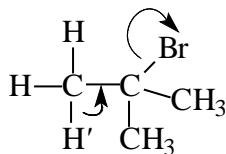
There are TWO possible mechanisms, **E1** or **E2** based on the same criteria as the SN1 and SN2 mechanisms i.e. the stability of the carbocation intermediate and the strength of the nucleophile.

The above reaction is typical of **E2 mechanism**:

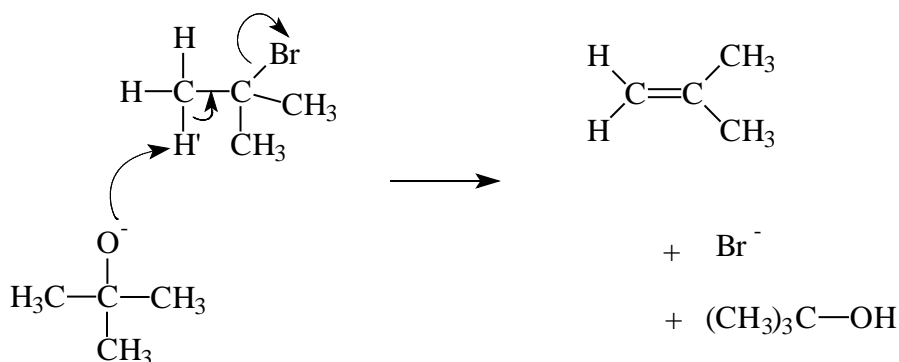
If we look at the alkyl halide we will notice that the bond most likely to be broken is the C-Br bond as it is the most polar, and Br⁻ will be the best leaving group.



If this happens then, of course the carbon marked with an **X** will be electron deficient. Therefore we require to move an electron pair towards it.



All we've got to do therefore is "encourage" the carbon-hydrogen, C-H' bond to break! How do we do this? By recognizing that if the H' atom gives up its two electrons then it will become H⁺, or an **acid**. What better therefore than to add a **base** such as our tert-butoxide ion! The full reaction mechanism can then be drawn as

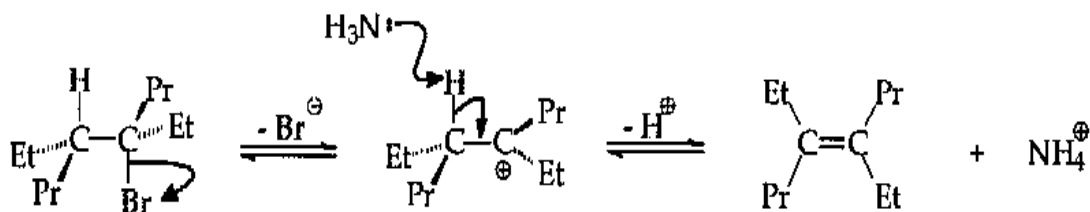


The overall order is bimolecular therefore (E2)

Therefore we end up eliminating H and Br from the alkyl halide and form an alkene. You'll note that we require a **very** strong base to do this as the hydrogen bonded to the carbon is **very** weakly acidic. Another strong base that can be used is NaOH.

E1 Mechanism

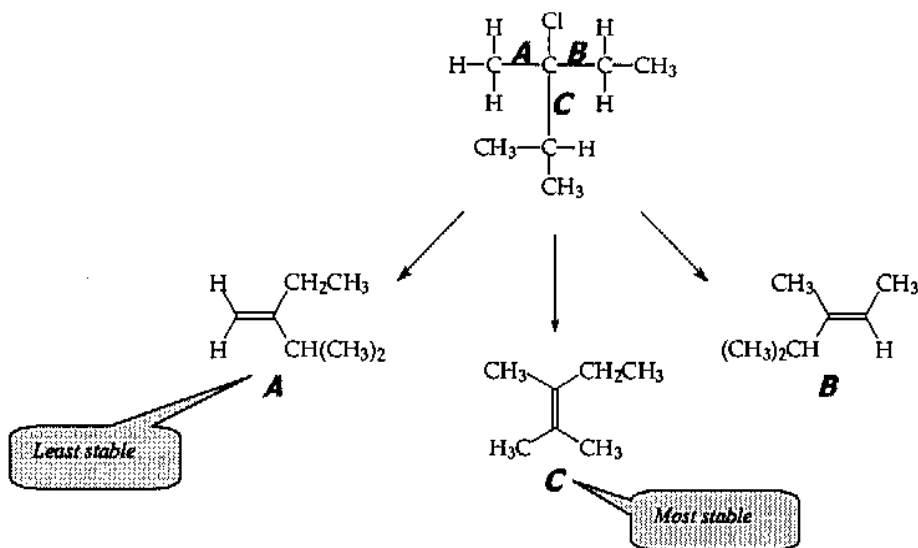
Consider the reaction between 4-bromo-4,5-diethyloctane and NH_3 to form 4,5-diethyloct-4-ene:



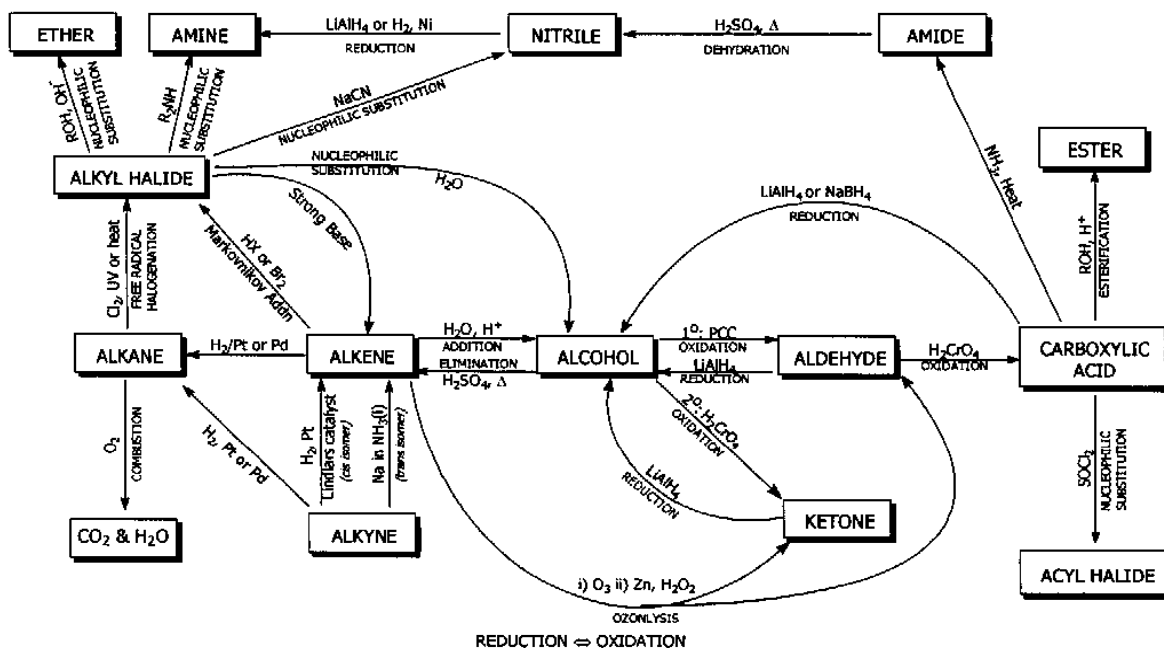
The overall order is unimolecular therefore E1.

Saltzeff's Rule:

The more substituted alkene product is obtained when a proton is removed from the β -carbon that is bonded to the fewest number of hydrogens.



SUMMARY OF ORGANIC CHEMICAL REACTIONS



ORGANIC REACTIONS

ALKANES

Alkanes contain **only** carbon and hydrogen and are termed **hydrocarbons**. The important thing to remember about alkanes is that they contain only σ -bonds. The simplest alkane is methane.

Methane contains four single carbon-hydrogen bonds. As it contains no π -bonds, methane is described as being **saturated**. In fact, **all alkanes are saturated**.

Paraffins- old name for alkanes

Source-alkanes are isolated by fractional distillation from fossil fuels.

Crude oil/petroleum, a dark viscous liquid, is composed of a mixture of several hydrocarbons. Methane contains four single carbon-hydrogen bonds. As it contains no π -bonds, methane is described as being **saturated**. In fact, **all alkanes are saturated**.

There are different hydrocarbons particularly straight chain alkanes, some branched alkanes and varying quantities of aromatic hydrocarbons. The composition of the petroleum depends upon where it is formed. The name 'petroleum' means 'rock oil' and is also called 'black gold'.

Table Product distribution in a typical distillation of crude petroleum & its uses

%V	Sp /°C	C Atoms	PRODUCTS	USES
1-2	< 30	C ₁ - C ₄	Natural gas	Fuel, Carbon black, polymerised petrol
15-30	30-90	C ₅ - C ₇	Petroleum ether(C _{5,6}), ligroin(C ₇)	Solvent, dry cleaning, refrigerant
	40-200	C ₅ - C ₁₂	Straight-run petrol*	Motor fuel
5-20	200-300	C ₁₂ - C ₁₅	Kerosene, heater oil	Furnace oils
10-40	300-400	C ₁₅ - C ₂₅	Gas oil, diesel fuel, lubricating oils, greases, waxes, asphalt	Lubrication, diesel fuel, medicine ingredient
8-69	> 400	> C ₂₅	Residual oil, paraffin waxes, pitch, asphalt(tar)	Candles, waterproofing fabrics, roofing, protective paints, mfr rubber

* refers to petrol straight from petroleum, without having being treated in any way.

Boiling Points

The larger chain alkanes are used as petrol, kerosene fuel, oils, greases, waxes and asphalt (tar for roads). The longer chain alkanes obtained from crude petroleum are broken down into smaller fragments in a process called "cracking".

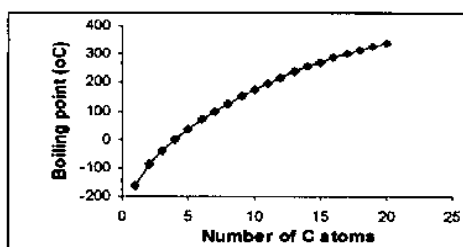
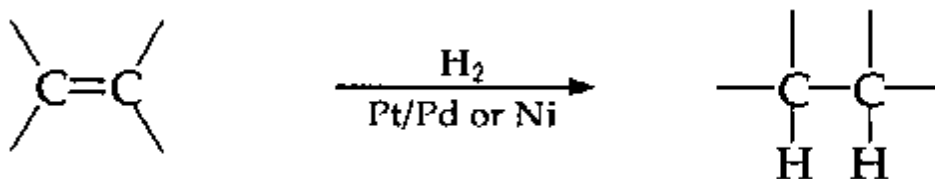


Figure: Plot of Boiling points of alkanes versus chain length.

Preparation:

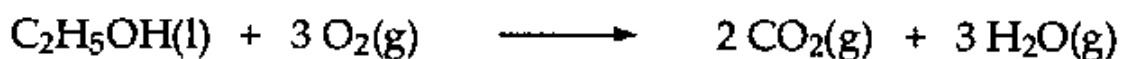
1. Hydrogenation of Alkenes/ Alkynes using $\text{H}_2(\text{g})$ over a Pt/Pd//Ni Catalyst



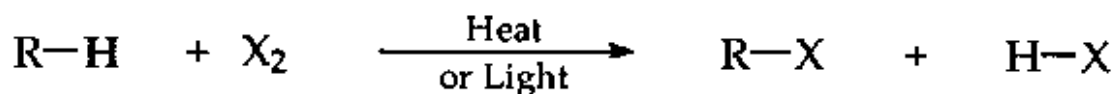
Addition occurs on the surface of the metal and always results in *cis* addition.

Reactions:

1. Combustion in the Presence of Excess $\text{O}_2(\text{g})$



2. Free Radical Halogenation of Alkanes to form Alkyl Halides

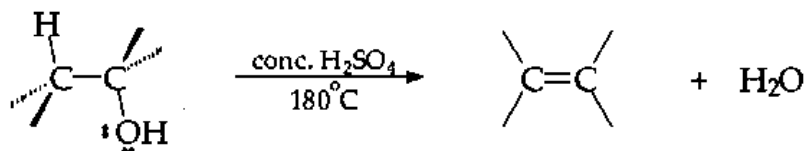


Where X = chlorine or bromine

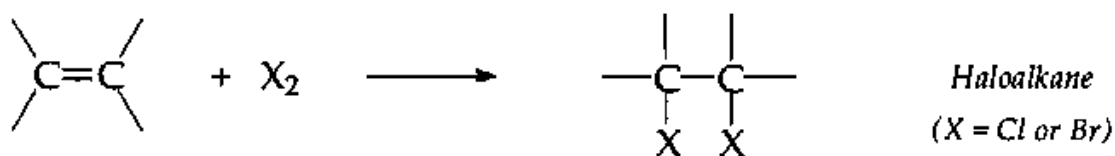
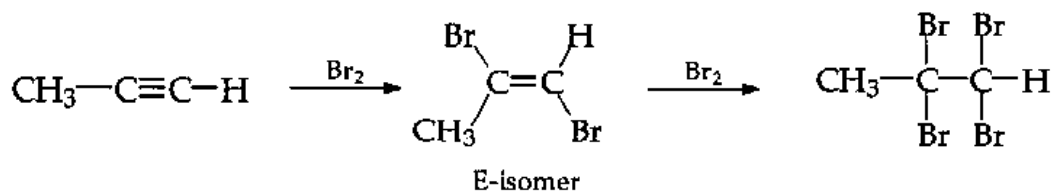
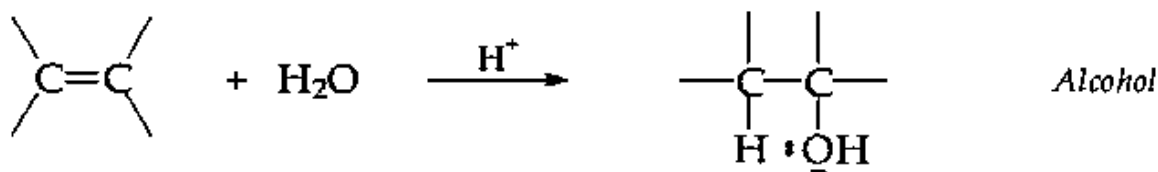
ALKENES & ALKYNES**Introduction:**

Unsaturated Hydrocarbons – C & H only, but contain double and triple bonds, as a result they could accommodate more hydrogen atoms. Compounds with more than one double or triple bond are called “polyunsaturated”. Many natural fats and oils are polyunsaturated (margarines).

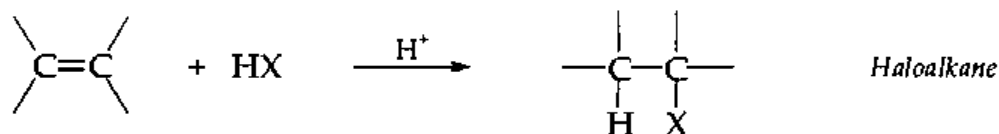
Olefins –old name

Preparation:**1. Dehydration of an Alcohol**

NB: Saytzeff's rule when deciding the major product

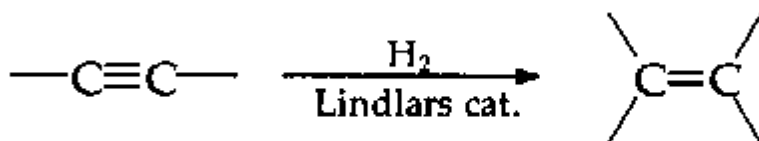
Reactions:**1. Electrophilic Addition Reactions of Alkenes****a) Addition of Halogens****Halogenation of an Alkyne to form an Alkyl Halide****b) Addition of Polar Reagents****Hydration of an Alkene to form an Alcohol**

Hydrohalogenation of an Alkene to form an Alkyl Halide



2. Catalytic Reduction – Hydrogenation

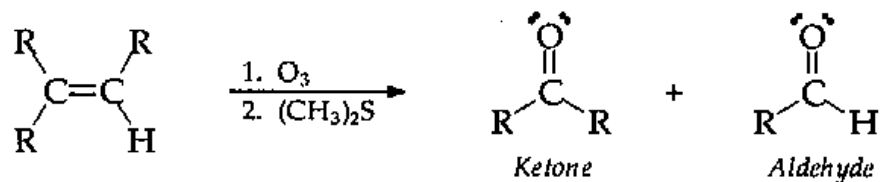
a) Alkenes



b) **Alkynes**- If H_2 is added in the presence of Pt/Pd or Ni catalyst, the reaction will continue until the alkane is formed. If you wish to stop the hydrogenation at an alkene, a "poisoned" catalyst must be used, i.e. Lindlars catalyst.

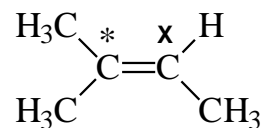
3. Ozonolysis

One particularly important oxidation reaction of alkenes is their reaction with ozone, O_3 . This reaction cleaves the double bond in the alkene to form a **carbonyl species** i.e. a species containing the $\text{C}=\text{O}$ group. The reaction can be summarised as shown below.

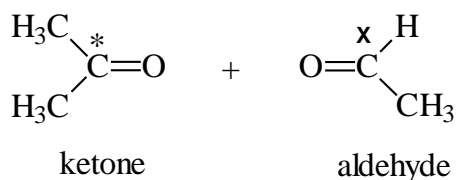


where $\text{R} = \text{any alkyl group}$

The exact identity of the products of this reaction will depend upon the nature of the R groups. If for instance we start with the following alkene



then the products will be



Why is this reaction so important? Well it allows us to identify the alkene starting material if its structure is unknown.

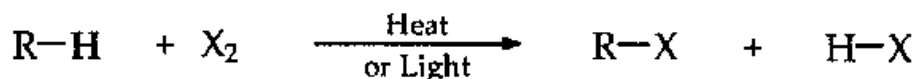
ALKYL HALIDES

Introduction

Although chlorine and bromine containing natural products have been isolated in marine species, most alkyl halides have been synthesized in laboratories. It is relatively easy to introduce halogens into various organic compounds. They are useful compounds with a variety of uses, namely, as synthetic reagents, solvents (CCl_4 , CH_2Cl_2), insecticides and herbicides (DDT), fire retardants, cleaning fluids ($\text{Cl}_2\text{C} \cdot \text{CCl}_2$), refrigerants and the coatings used on non-stick cookware (Teflon).

Preparation:

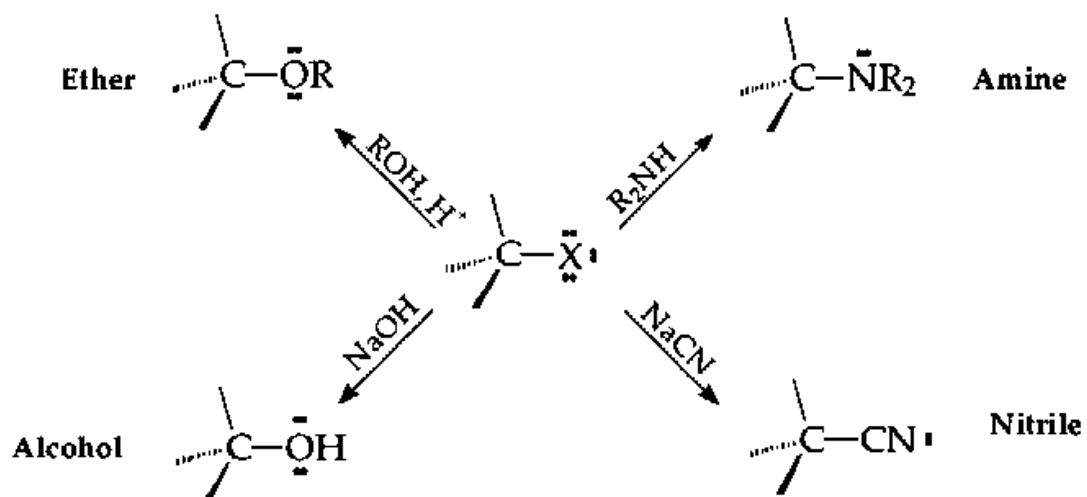
1. Free Radical Halogenation of Alkanes



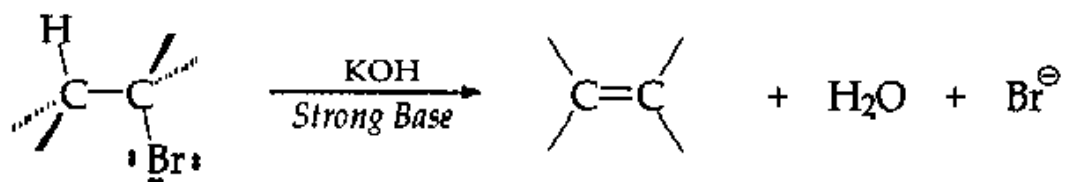
where $\text{X}_2 = \text{chlorine or bromine}$

Reactions

1. Nucleophilic Substitution Reactions



2. Dehydrohalogenation to form an Alkene



ALCOHOLS & ETHERS

Introduction

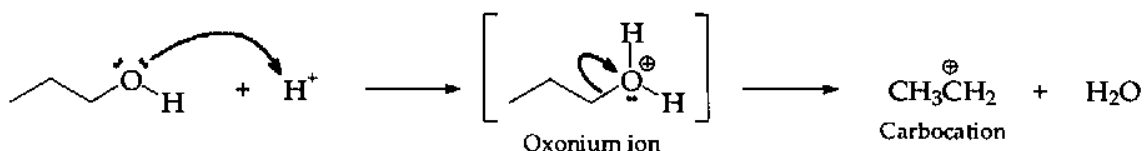
Alcohols – compounds that have hydroxyl groups bonded to saturated sp^3 hybridised carbon atoms. These compounds occur widely in nature and have many industrial and pharmaceutical applications. Two examples: ethanol is a fuel additive, an industrial solvent, and a beverage and menthol, an alcohol isolated from peppermint oil, is a flavouring agent.

Hydrogen Bonding in Alcohols

Alcohols are able to hydrogen bond which means that the intermolecular forces are stronger, therefore the melting and boiling points of the alcohols are higher than the corresponding alkanes and ethers. In addition to higher melting and boiling points, the polar $-OH$ group makes alcohols more soluble in water. The longer the nonpolar alkyl chain, the more insoluble it becomes.

Acid-Base Properties of Alcohols

Due to the lone pairs of electrons on the oxygen atom, an alcohol can act as a Lewis base:



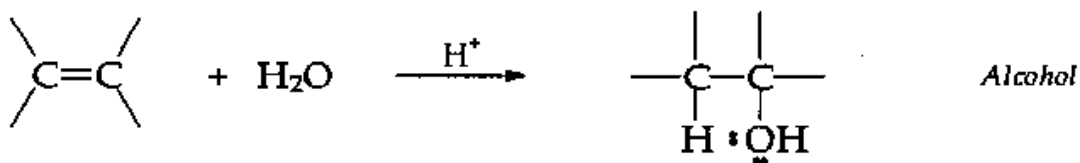
The stability of the resulting carbocation is a major driving force in the reaction.

Preparation

1. Hydration of an Alkyl Halide (Nucleophilic Substitution)

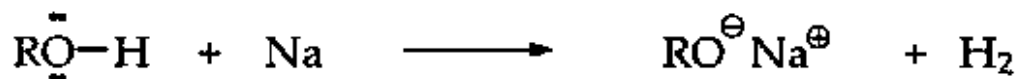


2. Addition of Water to an Alkene

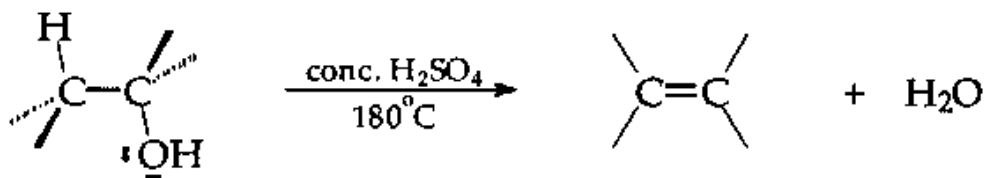
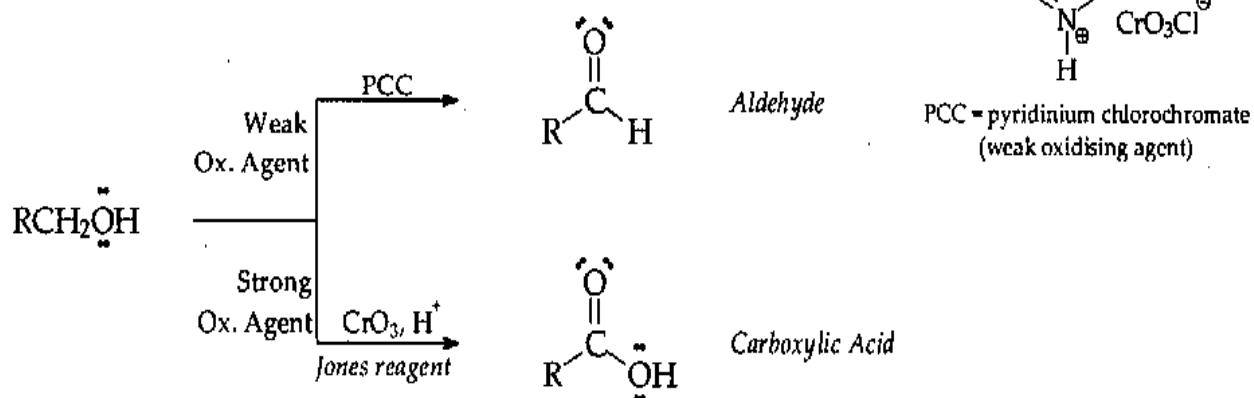


Reaction

1. Formation of Alkoxides Ion

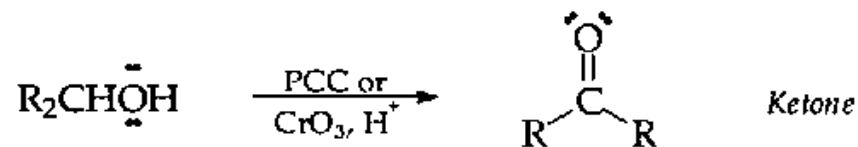


2. Dehydration of an Alcohol to form an Alkene

3. Oxidation of an Alcohol to form an Aldehyde or Ketonea) Primary Alcohols

Other strong oxidising agents include: $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , H_2CrO_4 .

a) Secondary Alcohols



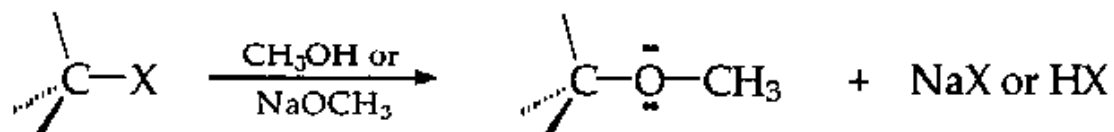
b) Tertiary Alcohols – NO REACTION

Ethers – compounds with two organic groups connected to a single oxygen atom.

Ethers occur in nature and have industrial applications for example, diethyl ether, the familiar 'ether' of medicinal use, was once a popular anesthetic agent but is now mainly used as industrial solvent.

Preparation

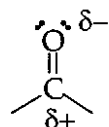
1. Nucleophilic Substitution of an Alkyl Halide



ALDEHYDES & KETONES

Introduction

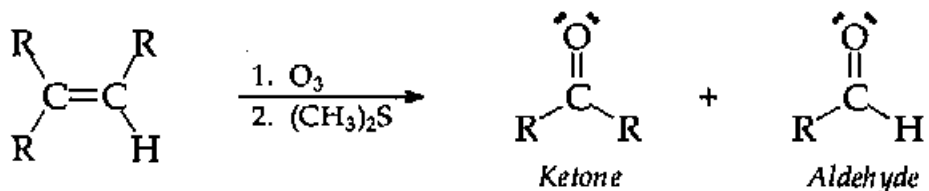
Aldehydes and ketones occur widely in nature. Many have pleasant flavours and aromas, and are therefore used extensively in perfumes and consumer products, i.e. Soaps, bleaches, air freshener's, etc.



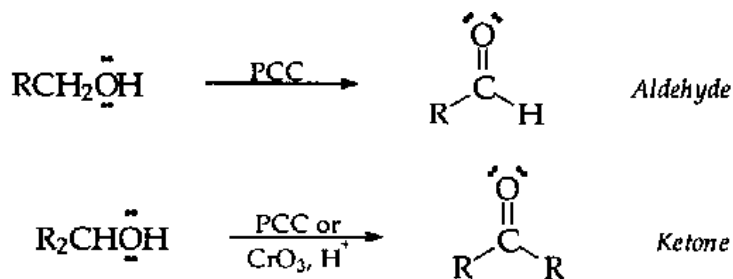
The functional group of aldehydes and ketones is the carbonyl group, in aldehydes this is always terminal, while in ketones it occurs within the parent chain. The reactions that aldehydes and ketones undergo are due to the nature of the carbonyl group. As a consequence of the bond polarity most carbonyl reactions involve nucleophilic attack at the carbonyl carbon, accompanied by addition of a proton to the oxygen.

Preparation

1. Ozonolysis of an Alkene to form an Aldehyde &/or a Ketone

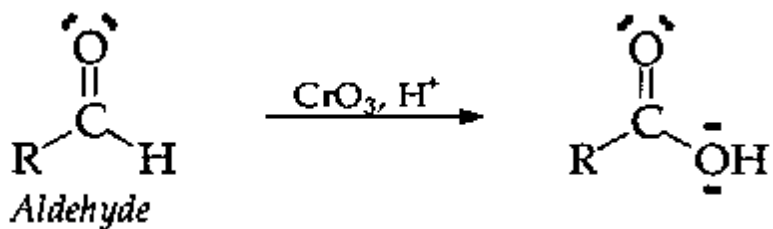


2. Oxidation of an Alcohol to form an Aldehyde or Ketone

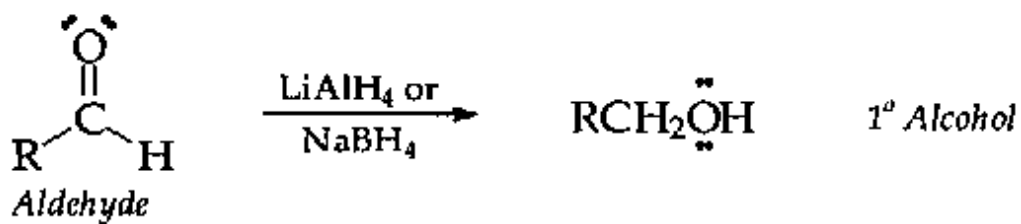
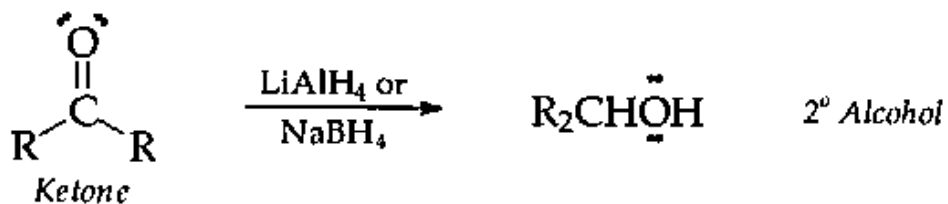


Reactions

1. Oxidation of an Aldehyde to form a Carboxylic Acid



2. Reduction to form an Alcohol

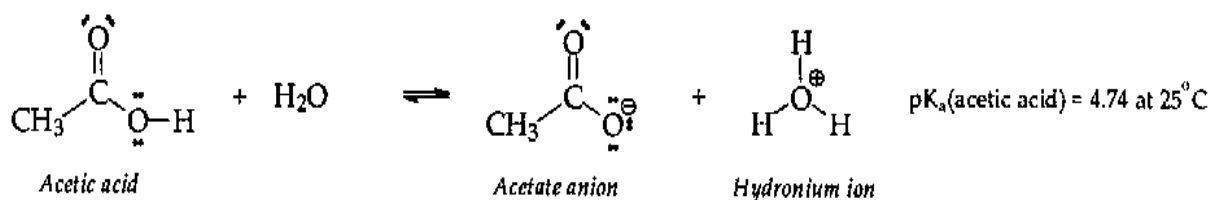
a) Aldehyde \rightarrow 1° Alcoholb) Ketones \rightarrow 2° Alcohol

CARBOXYLIC ACID

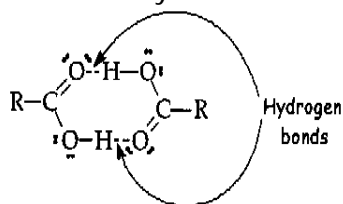
Introduction

Carboxylic acids are the most important acyl derivatives in both nature and the laboratory. Vinegar, formed by the spoilage of wine, is a dilute solution of ethanoic acid; butanoic acid is responsible for the rancid odour of butter and hexanoic acid is partially responsible for the unmistakable odour of goats.

Acidic Properties

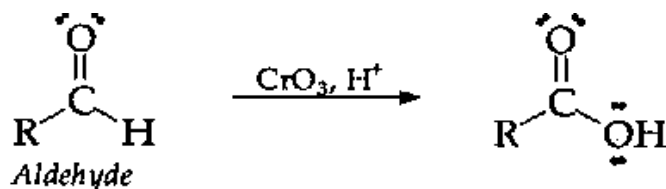


Carboxylic acids are polar molecules which are hydrogen bond with themselves (to form a dimer) or with other molecules, therefore they have high boiling points for their molar masses. Most carboxylic acids exist as dimers held together by hydrogen bonds.



Preparation

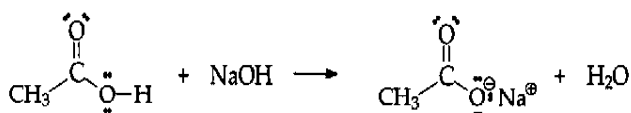
1. Oxidation of an Aldehyde to form a Carboxylic Acid



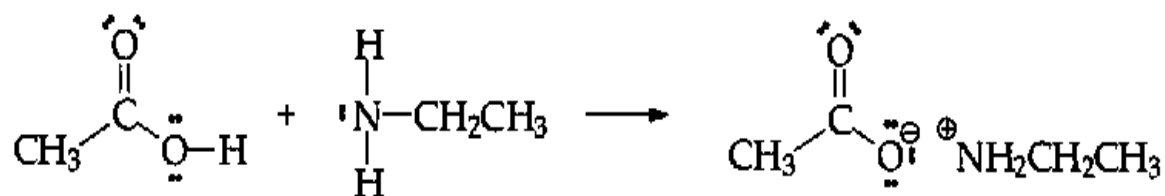
Reactions

1. Acid-Base Reactions to form a Salt

a) Hydroxide base e.g. sodium hydroxide



b) Nitrogen base e.g. ammonia or ethylamine, etc.

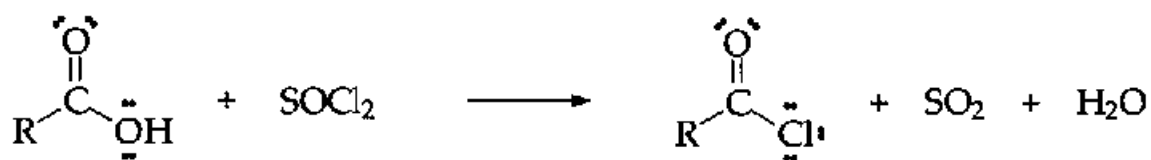


2. Substitution Reaction

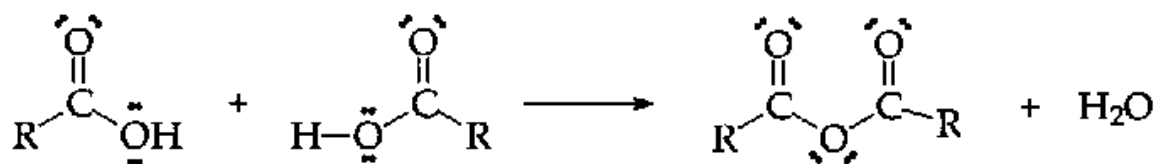
a) Esterification



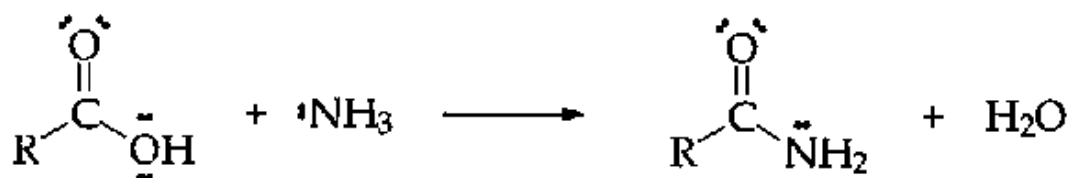
b) Acid Chlorides



c) Acid Anhydrides



d) Amides



CARBOXYLIC ACID DERIVATIVES

Introduction

The carboxylic acid derivatives are formed from the corresponding carboxylic acid by a nucleophilic substitution reaction. In comparing the acyl derivatives the more polar a compound is, the more reactive it is. Reactivity decreases from Acyl halides, acid anhydrides, esters to the least reactive, amides. The most naturally occurring of the derivatives are esters, which are pleasant smelling liquids responsible for the fragrant odours in fruits and plants.

Nomenclature

The IUPAC system for naming carboxylic acid derivatives is summarized in the following table:

DERIVATIVE	IUPAC NAME
Esters RCO ₂ R'	First give the name of the alkyl group attached to the oxygen and then identify the carboxylic acid from which it is derived. Suffix: replace <i>-ic acid</i> with <i>-oate</i>
Acyl Halides RCOX	Identify the acyl group and then the halide Suffix: replace <i>-ic acid</i> with <i>-yl halide</i> or <i>-carboxylic acid</i> with <i>-carbonyl</i>
Acid Anhydrides RCO ₂ COR'	Replace the word <i>acid</i> with <i>anhydride</i>
Amides RCONH ₂	Unsubstituted (-NH ₂) replace the <i>-oic acid</i> or <i>-ic acid</i> with <i>-amide</i> , or by replacing the <i>-carboxylic acid</i> with <i>-carboxamide</i> .

Preparation

1. Nucleophilic Substitution of Carboxylic Acid

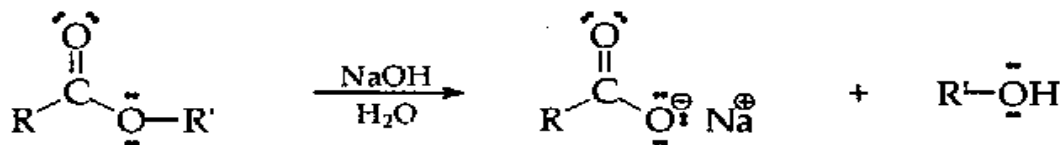
See reactions section in Carboxylic acids

2. Synthesis of an Amide from an Acyl Chloride and an Amine



Reactions

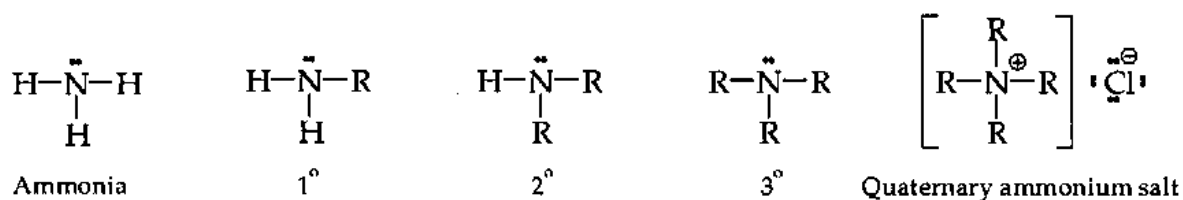
1. Hydrolysis of an Ester



AMINES

Introduction

Amines are organic derivatives of ammonia. Amines may be classified as either **primary** (RNH_2), **secondary** (R_2NH) or **tertiary** (R_3N), depending upon the number of organic groups attached to the nitrogen atom. Compounds with four groups attached to the nitrogen atom are called **quaternary ammonium salts**, salts since the nitrogen must carry a positive charge.



Amines can be either alkyl-substituted (**alkylamines**) or aryl-substituted (**arylamines**), which exhibit some important differences in their chemistry.

Because of the lone pair of electrons on the nitrogen, amines like ammonia, can act as bases.

Preparation

1. Nucleophilic Substitution of an Alkyl Halide

Reaction

1. Synthesis of an Amide from both a Carboxylic Acid or an Acyl Chloride.

References:

1. *Brown & Le May, Chemistry the Central Science. 2nd Ed.*
2. *PMB Campus Tutorial Book*
3. *Naidoo S, Organic Chemistry Notes*
4. *Chem 196 Organic Chemistry Notes*