Organic chemistry – Alkene and Alkyne crib sheet

In general

Alkene and alkyne chemistry is very similar as they are very similar in structure. The smallest alkene and alkyne contains 2 carbons. In this document, anything that is said for an alkene also occurs for an alkyne.

The main difference between the two is that the bond in an alkyne needs to be thought of as a “double-double” bond; it will react as if there are two double bonds. One set it broken, the other remains.

Structure and bonding

All alkenes and alkynes have more than one bond between the carbons.

When there are more than one bond between the carbons, the carbon atoms are pulled closer together. The carbons do not like to be close to each other. The bonds become strained but do not break. When a double or triple bond breaks, it releases a large amount of energy, but not the same amount as if the same number of single bonds were to break.

Alkenes and alkynes have “side on” single bonds (σ), but also have “overlapped” bonds called pi bonds (also known as π bonds – these give π orbitals in the same way that σ bonds give σ orbitals).

Alkenes

When an alkene is formed, three sp hybrid orbitals are formed from the combination of the 2s, $2p_x$ and $2p_y$ orbits. One single electron is left in the non-hybrid orbital. This electron occupies the π orbitals and gives the bond a negative charge.

As there is 1 σ bond and 1 π bond, the molecule is said to have a “double” bond.

Alkynes

When an alkyne is formed, two sp hybrid orbitals are formed from the 2s and 2px orbits. This leaves 2 unpaired electrons in the 2py and 2pz orbitals. These two electrons occupy the π orbitals giving a triple bond. It is a very electro-negative bond and is highly reactive.

Alkynes show a great deal of strain as the carbons are held very closely together.

Naming and formulae

The same naming rules for alkenes and alkynes apply as for alkanes. The formula of pure hydrocarbon alkenes is C_nH_{2n} (*for every carbon there are twice the number of hydrogens*) with alkynes being C_nH_n (*for every carbon there is the same number of hydrogens*).

All alkenes end with -ene, all alkynes end with -yne

e.g. C-C=C

Number of carbons = 3, skeletal name = prop

The hydrocarbon molecule has a double bond, it is an alkene. Ending is therefore -ene
Full name = propene

e.g. C-C≡C-C

Number of carbons = 4, skeletal name = but
The hydrocarbon has a triple bond, Ending is therefore -yne
As the triple bond is not on a terminal (end) C, it must be numbered. Counting from either side, the substitution is on the 2 carbons
Full name = but-2-yne

Isomerism - general

Alkynes do not have optical isomerism, but can have structural isomers. Alkenes and alkynes can not be a chiral centre (they cannot have 4 different groups coming from them by definition)

Alkene isomerism

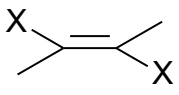
An alkene can have both structural and optical isomers at the same time. As has been seen with alkanes, a structural isomer will have the same formula, but different properties (for example boiling points). The combination of both structural and optical isomerisation doubles this change of properties (for example the compound “limonene” has two isomers – one smells of oranges, the other of lemons).

From a formula, the version of the isomer cannot be found. To tell which way around the isomer is, the cis / trans mechanism and E / Z mechanism are used.

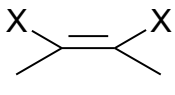
cis/trans

For cis/trans isomerisation, two groups must be the same.

If the groups (X) are diagonally opposite (a), the groups are said to be “trans” to each other. If the groups are horizontally opposite (b), the groups are said to be “cis” to each other. Note that the groups MUST be on either side of the double bond.



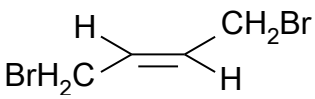
a



b

The naming rules still apply

1. Find the longest unbroken carbon chain
2. Find the highest priority group
3. Find the position of the double bond
4. Decide if the groups are cis or trans to each other



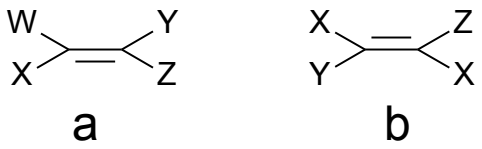
Longest carbon chain = 4, skeletal name = but
Highest priority (based on molecular weight) = Br
Position of groups = 1 and 4
Position of the double bond = 2
Double bond ending = -ene
Optical isomer type = diagonally opposite = trans

Full name trans-1,4-bromo-but-2-ene

This can also be called trans-1,4-bromo-2-butene; the 2-butene means the same as but-2-ene. Either way of naming the alkene is correct, though having the number in the middle is less confusing sometimes when naming.

E/Z naming

E/Z naming is used when the groups on the double bond are either not the same (a) or there is a cis/trans isomer and other non-hydrogen groups on the molecule (b)



To use the E/Z naming system, each carbon has to be taken by themselves (left of the double bond then right of the double bond).

(*using example a*)

First compare the molecular weight of the groups on the left carbon and decide if W weighs more than X. Second repeat for the right carbon, is Y heavier than Z.

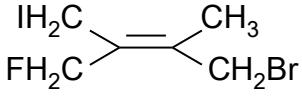
If W is heaver than X and Y is heaver than Z, it is Z
If W is heaver than X and Z is heaver than Y, it is E

In other words, if the heaviest group on both sides is at the top or the heaviest group on both sides is at the bottom, it's Z. Otherwise, it's E

(*using example b*)

Example b has two groups the same (X). This will give cis/trans isomerism. In this case, it is trans. Z and Y are other groups (but not the same as each other). To tell if this is E or Z, the same system is used. Compare the weights of the groups on each side and decide based on weight.

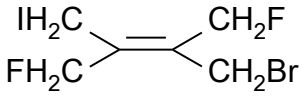
If Y and Z are both hydrogen, the E/Z system is not used.



Longest carbon chain = 4 = but
Has a double bond = ene

Double bond = 2nd carbon
Are the groups the same? No
Compare left side weight : $CH_2I > CH_2F$
Compare right side weight : $CH_3 < CH_2Br$
Heaviest groups are diagonally opposite = E
Naming priority : left CH_2I has I which is higher than other groups, lowest number from there

Full name : (E)-1 iodo, 1 fluoro, 2 bromo-but-2-ene



Longest carbon chain = 4 = but
Has a double bond = ene
Double bond = 2nd carbon
Are the groups the same? Yes
Are the groups cis / trans? trans
Are the other groups both H? No
Compare left side weight : $CH_2I > CH_2F$
Compare right side weight: $CH_2F < CH_2Br$
Heaviest groups are diagonally opposite = E
Naming priority : left CH_2I has I which is higher than other groups, lowest number from there

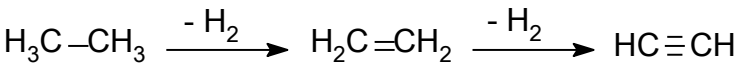
Full name : (E)-1 iodo, trans-1,4-fluoro, 2 bromo-but-2-ene

<u>Reactions of alkenes and alkynes</u>

All of these reactions work in the same way for alkenes and alkynes. The difference is that alkynes have a triple bond which means they can react again (triple bonds go to double bonds, double bonds are reactive due to the charge)

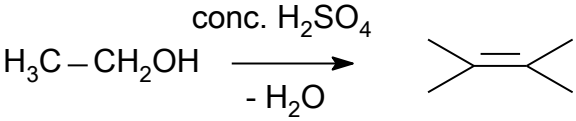
Producing an alkene or alkyne

This is done by dehydrating (or removal of H_2 from) an alkane



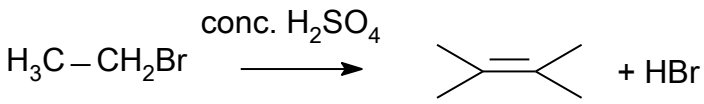
Dehydration is performed by reacting the oxidation with concentrated sulfuric acid or concentrated phosphoric acid. This is a very difficult process as alkanes are very unreactive.

As simpler method is to dehydrate an alcohol



If an alkane is used to produce the alkene, it is performed by dehydrating a haloalkane (an

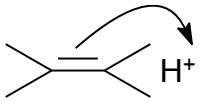
alkane with a halide group, eg CH_3CH_2Br). Here the hydrogen halide is also produced. This is known as an ELIMINATION reaction (the Br has been eliminated [removed] from the molecule)



Alkenes and alkynes are very useful starting materials for a large number of compounds.

Due to the negative charge on the bond, alkenes and alkynes are attacked by group containing a positive charge. These positively charged groups are known as ELECTROPHILES. Alkenes and alkynes are said to undergo “ELECTROPHILIC ATTACK”.

When drawing a “curly arrow” diagram, the direction always goes from the negative to positive charge (see right). It is important to remember this when drawing reaction mechanisms.



Reaction with oxygen

As with alkanes, alkenes and alkynes both under go combustion reactions with oxygen to produce water and carbon monoxide (incomplete combustion) or carbon dioxide (complete combustion).

Oxidation

Oxidation is defined as the loss of electrons from something. As there are additional electrons in the double and triple bonds, both alkenes and alkynes can undergo oxidation reactions.

There are two important reactions here

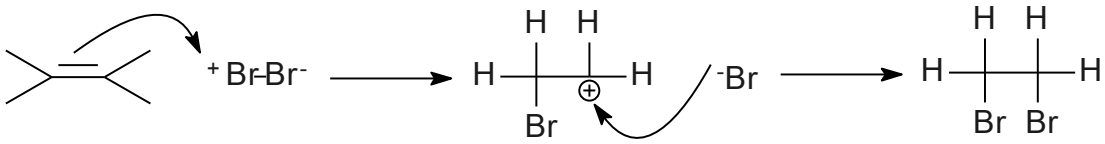
1. Reaction with Br_2
2. Reaction with $KMnO_4$

With bromine

Bromine is a dark brown liquid with a very unpleasant smell. As bromine is a group VII element, it has a p5 electronic structure (it requires an electron for a full outer shell and is therefore very reactive). In order for the p5 shell to be filled, it shares it's valent electron with another Br.

At any time though, that electron can be on one Br or the other Br giving a temporary charge on either side (one will be slightly negative [δ-], the other slightly positive [δ+]). This is known as a “dipole” (literally means 2 poles).

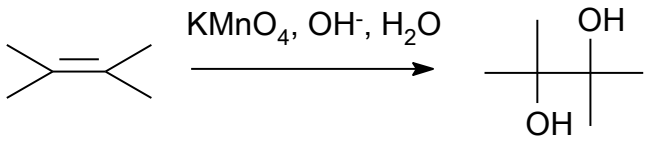
The charge on the double bond is attracted to this slight positive charge and the reaction begins. The Br_2 goes from a coloured liquid to a colourless liquid. It is a good test for either a double or triple bond.



With $KMnO_4$

This is another highly coloured liquid, most commonly used in the treatment of Athletes' Foot (a problem caused by a type of fungus which grows around the feet and toes causing dry skin and itching). This reaction is a “partial” oxidation.

When $KMnO_4$ is used to oxidise either the alkene or alkyne, it goes clear with a brown solid (MnO_2) being formed at the bottom of the flask. This also gives what is known as a “double alcohol”



<u>Other important reactions of alkenes and alkynes</u>

There are 5 other important reactions with alkenes and alkynes

1. Addition of hydrogen halides
2. Addition of acidified water
3. Addition of halogens
4. Catalytic addition of hydrogen
5. Polymerisation

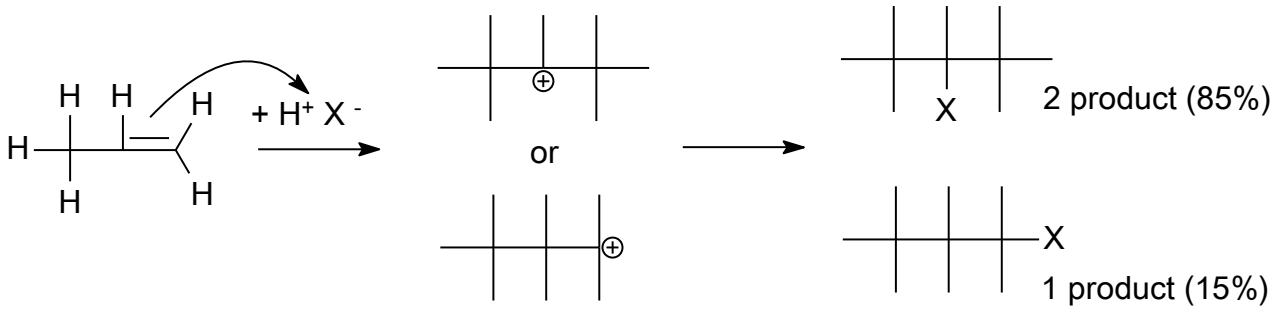
Addition of hydrogen halides

A hydrogen halide is a group VII element combined with hydrogen. It has a general chemical formula of HX (X = F, Cl, Br, I). It can be thought of as being an ionic bond giving the hydrogen a slight positive charge and the halide a negative charge.

For the addition of a hydrogen halide, it is important to recognise if the alkene or alkyne being added to has an even or uneven number of carbons on the chain. An even number is a number that can be divided by 2 without a remainder (e.g. 6 is even but 5 is not).

If the alkene or alkyne has an uneven number of carbons the reaction is different

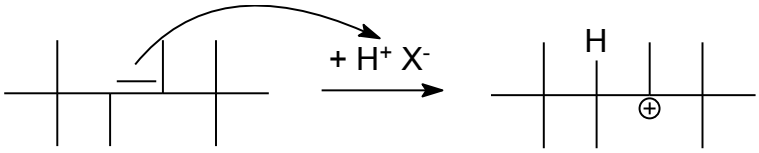
For example, the following alkene contains 3 carbons (= propene) and it is being reacted with any hydrogen halide (here it is given as HX)



The hydrogen is able to add to either the 1 or 2 carbon on the initial step. Which carbon it goes to depends on the number of hydrogens already on the carbon. Looking at the initial reactant, the 1 carbon has 2 hydrogens while the 2 carbon has 1. The 1 carbon is said to be “hydrogen rich”.

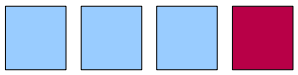
It is an easy way to think that “the rich get richer”, the hydrogen will go to the carbon with the most hydrogen on it. This was discovered by a Russian chemist called Markownikov, hence the name, Markownikov's Rule.

If the alkene or alkyne has an even number of carbons, there is only one product

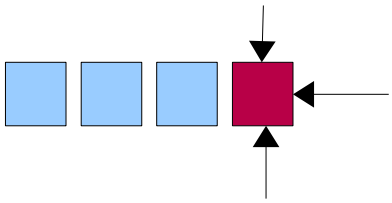


(the intermediate can be rotated by 180º to give a mirror image of itself)

A second reason for the production of the 2-product can be explained by the stability of the compound. To understand this, a compound must be thought of as a series of blocks (below – the purple block is a group, it has replaced one of the hydrogens)

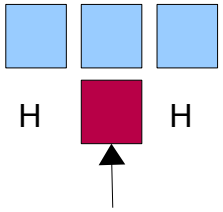


If the group is on the end, it is open for attack from three directions

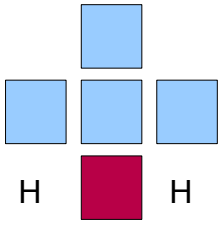


It is easy to remove and not very stable. This is known as a primary group (written as 1º)

If the group is in the middle (below), it is shielded from attack by the hydrogens on the neighbouring carbons and the carbon behind it. This is known as a secondary group (written as 2º). It is more stable that a primary carbon. The more stable a compound, the more likely it is to form.



A tertiary compound (3º, below) is more stable than a 2º compound. Tertiary compounds are unlikely to react unless under extreme chemical conditions.



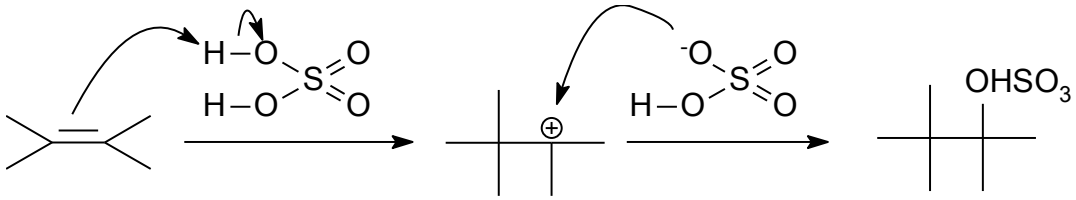
To summarise for stability : 3º > 2º > 1º

Addition of water

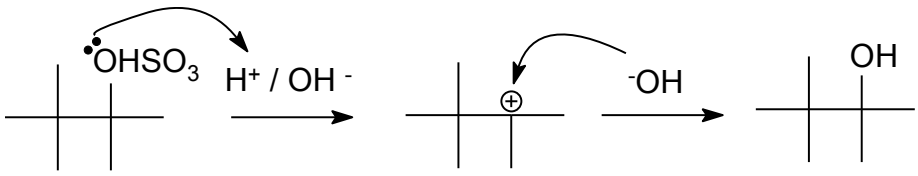
Water, while being an ionic compound, does not readily form ions (this is known as dissociation. A mole of water will produce $1x10^{-14}$ ions of H^+ and OH^-. This can effectively be ignored).

In order for water to be added across a double bond, a source of H+ must be introduced. This readily comes from the likes of acids, in particular sulfuric acid.

Sulfuric acid has a formula H_2SO_4. This gives two H^+ ions when dissociation occurs, however, it is more usual to think of the dissociation product being H^+ HSO_3O^-. The positive H^+ is attacked by the negative charge on the double bond (this is a slow process) leaving a carbocation. The remaining dissociation product has a negative charge and adds to the carbocation.



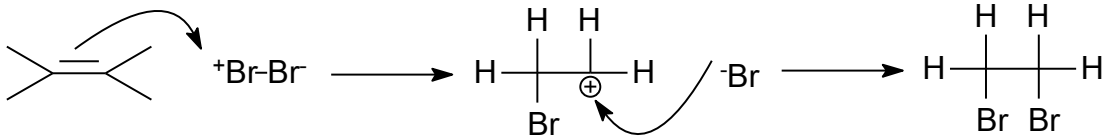
The second stage of the reaction is to add water. The HSO_3O^- group will react with the ionised water to reform the sulfuric acid leaving a carbocation which is free to react with the remaining OH to form an alcohol.



Water cannot directly add across a double (or triple) bond. The negative charge on the carbon carbon bond is not strong enough to polarise the water molecule to react.

Addition of halides

Halides are group VII elements. As has been previously discussed, these all have a single electron in the p5 orbit which is shared with another halide to give effectively a complete outer orbital. The negative charge on the double (or triple) bond polarises the halide molecule (forms a dipole)



The above reaction applies to any halide molecule.

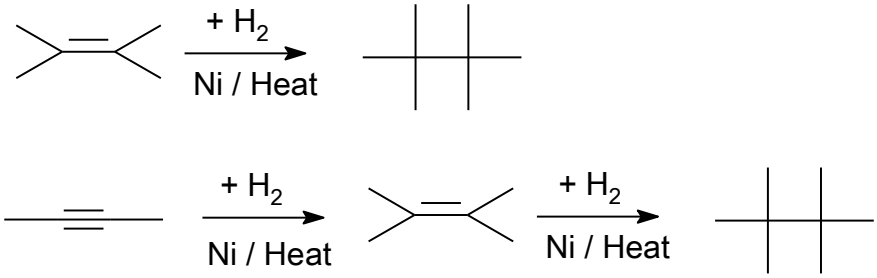
Catalytic addition of hydrogen.

At room temperature, an alkene or alkyne will react with hydrogen gas, but the rate is very slow (too slow for any practical purpose). H_2 is a very stable molecule and does not break easily.

For the reaction to occur at a “chemically useful” rate, a catalyst has to be used.

A catalyst is a compound which normally increases the speed of a reaction. It may take part in the reaction, but at the end comes out unchanged.

For the conversion of an alkene/alkyne to an alkane, Ni, Rh or Pt are normally used as catalysts.



Polymerisation

A polymer is a repeating unit of a molecule and are used in every day life (their uses range from the plastics covering a USB pen to ladies tights to artificial limbs).

Normally a polymer is formed by reacting the alkene with another agent to form a carbocation. This cation is used to react with the negative charge on another alkene. This reaction carries on until there is no more alkene left.

The initial starting unit is called a monomer. When this changes to the carbocation, it is known as the “monomeric unit”. When a large number of these monomeric units add together, they form the polymer.

While an alkyne may take part in a polymerisation, it is very unlikely to happen due to the potential for unwanted polymers to be produced.