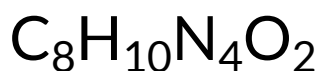
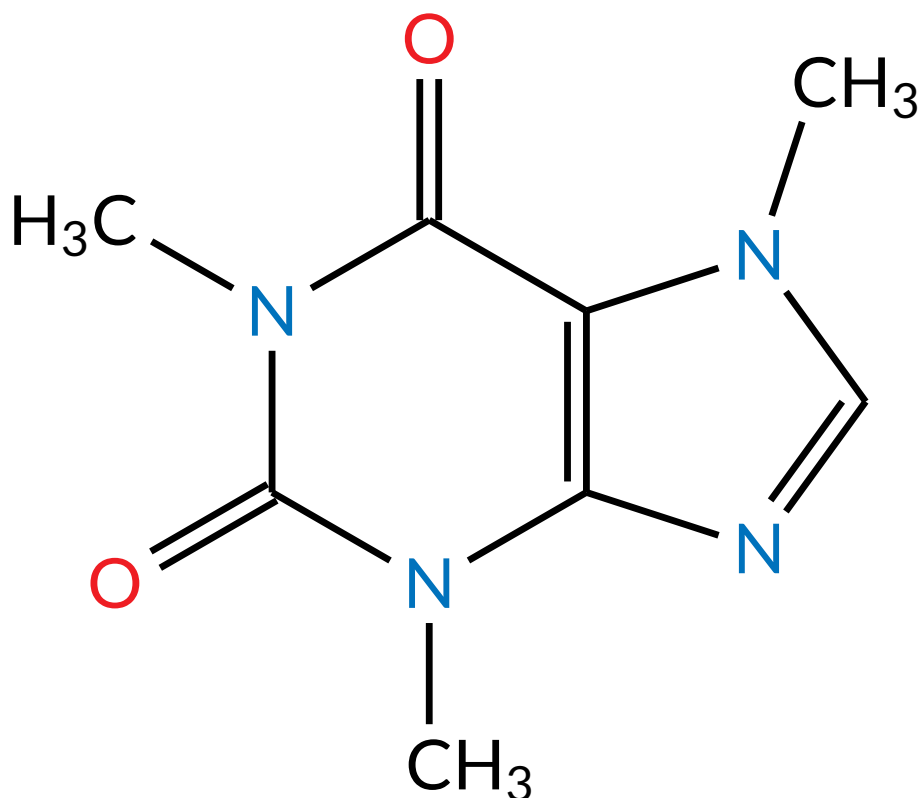


Organic Chemistry



1,3,7-trimethylpurine-2,6-dione

-

Caffeine

Chapters 8 to 12, 15 to 18

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I. Isomers

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I Isomers

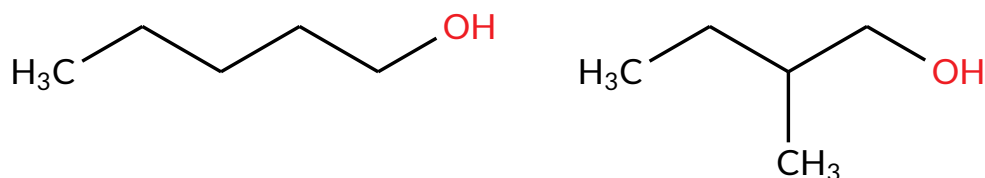
1 Overview

Isomers are molecules that share the same structural formula, yet exist in different forms. The two main forms of isomerism are structural isomerism and stereoisomerism. In both cases, the molecular formula of the compounds is the same, while the chemical and physical properties may differ greatly.

2 Structural Isomerism

2.1 Chain Isomerism

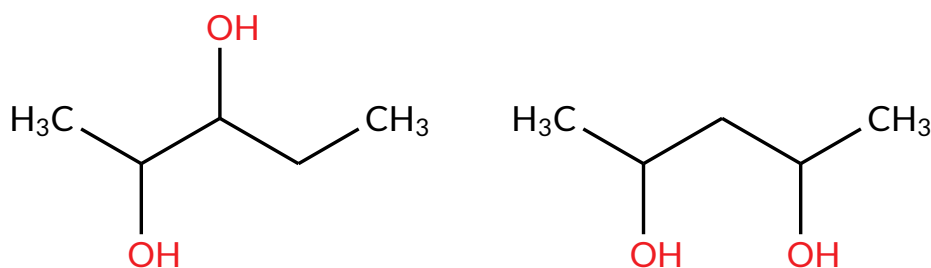
In chain isomerism, molecules have the same functional groups, except they are placed in different positions along the carbon chain. Chain isomers typically have similar chemical properties, but different physical properties (since the shape of the carbon chain can determine the strength of id-id interactions).



Pentanol and 3-methylbutan-1-ol are chain isomers.

2.2 Positional Isomerism

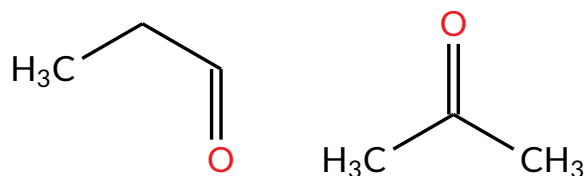
Positional isomers have the same arrangement of their carbon chains, and the same functional groups. However, said functional groups are placed at different positions.



Butan-2,3-ol and butan-2,4-ol are positional isomers.

2.3 Functional Group Isomerism

This is somewhat a misnomer since it is exactly the opposite of what it seems to intuit. Functional group isomers share only their molecular formulas; the carbon chain, the functional groups, etc. are all different.



Propanal and acetone are functional group isomers.

3 Stereoisomerism

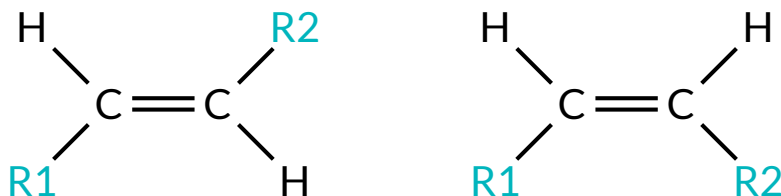
Stereoisomers of molecules have the same structure and functional groups, but those groups are arranged in a spatially differing way. The main forms of stereoisomerism are cis/trans (or E/Z) isomerism, and optical isomerism.

Note that for certain cis/trans (E/Z) isomers, the trans (or E) variant can 'pack' better, resulting in a higher melting point. This doesn't affect the boiling point since the molecules are too far apart in the gaseous phase for it to matter.

Additionally, the presence of *intramolecular* (within the same molecule) hydrogen bonds can also be a factor since it reduces the strength of *intermolecular* hydrogen bonds. Other than these, the chemical and physical properties of stereoisomers are mostly the same.

3.1 Cis/Trans Isomerism

Only alkenes can exhibit cis-trans isomerism, due to the C=C bond that restricts rotation along its axis. This is because of the π -bonds that only bond at 180° intervals. At these positions, it forms the cis and trans isomers.

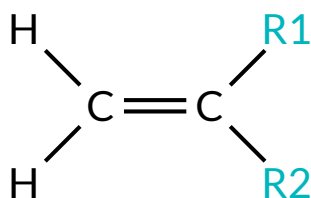


The molecule on the left is the *trans* isomer while the one on the right is the *cis* isomer. *trans* is from Latin, meaning *other side*, while *cis* obviously means *same side*. In the former, the larger groups are on opposite sides of the alkene double bond, while in the latter, the larger groups are on the same side. Note that these *groups* do not necessarily have to be functional groups — they can be as large or as simple as one wishes.

When naming cis/trans isomers, the qualifier *cis* or *trans* is placed before the stem name, like so:

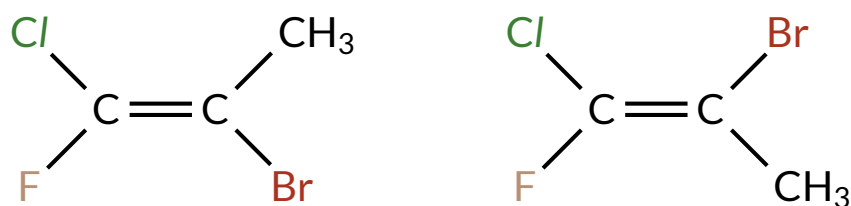
- cis-but-2-ene
- trans-but-2-ene

Note that cis/trans isomerism is not applicable to molecules where identical groups are attached to the any one carbon atom, since there is a line of symmetry going along the plane of the double bond.



3.2 E/Z Isomerism

E/Z is generally the more comprehensive, general form of cis/trans. Consider the alkene below, with two variants due to the lack of a plane of symmetry:



It has 4 distinct substituents, and thus a cis/trans designation cannot be used. Behold, E/Z isomerism. At its core, it is simply another method of handling alkene isomers that works for more general forms of molecules.

It follows a scheme of priorities (Cahn-Ingold-Prelog, or CIP), which are determined as such:

- i. The group with the largest atomic mass *directly attached* to the alkene's carbon has the highest priority.
- ii. In the event of a tie, look at the atoms directly attached to *that* offending atom. Use the previous rule, favouring higher priority atoms, to tiebreak. Double bonds are counted twice.
- iii. Recursively evaluate the previous rule with attached atoms, to continue the tiebreaking process.

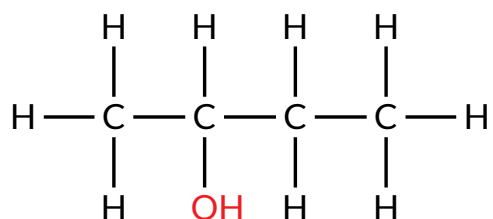
The above scheme should be used to find the two highest-priority groups attached to the alkene, after which, if the two groups are attached on the same side of the alkene, then the molecule is the Z isomer, and it is known as the E isomer if the reverse is true.

E and Z come from the German *entgegen* and *zusammen*, *opposite* and *together* respectively.

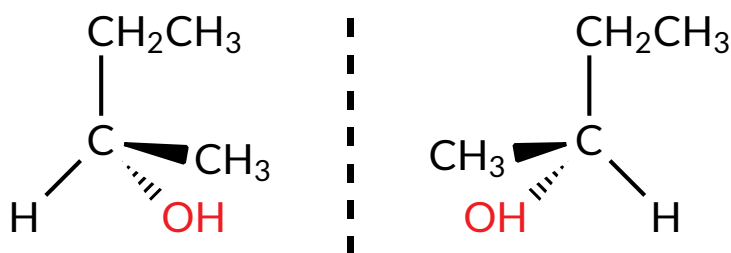
3.3 Optical Isomerism

Due to the 3-dimensional tetrahedral nature of a carbon atom, if there are 4 *distinct* substituents, two non-superimposable mirror images can exist, resulting from a lack of any plane of symmetry. Such carbons are called *chiral carbons*, and are the *chiral centres* of the molecule. A molecule can have multiple chiral centres.

Consider butan-2-ol below. Carbon 2, with the OH group, has 4 different groups attached to it. As such, it is a chiral carbon.



Indeed, it can take the form of 2 non-superimposable mirror images, that are differentiated by the adjacency of 2 of the 4 groups bonded to the chiral carbon. As can be seen, these two mirror images cannot be rearranged into the other, and are distinct — these are called *enantiomers*.



The solid wedge indicates a bond coming out of the plane of the paper, while the dashed wedge indicates a bond going into the plane.

Optical isomers have identical physical properties, except for their treatment of plane-polarised light (this is where the light wave is only oscillating along one plane). One of the isomers will rotate this light clockwise, while the other will rotate it counterclockwise. The magnitude of both rotations are the same.

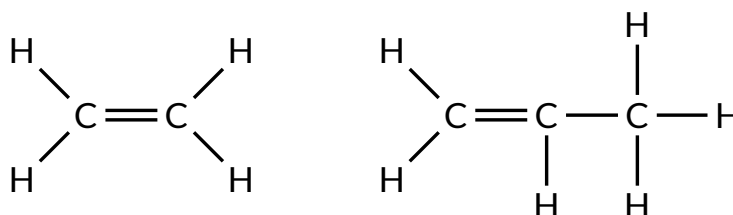
If equal amounts of each enantiomer are present in a solution, it is called a *racemic mixture*, and the net rotation of plane polarised light will be 0, for obvious reasons.

Enantiomers usually have identical chemical properties, except for certain interactions that require a certain spatial orientation to work, such as proteins, that can only work with one of the optical isomers.

II Alkenes

1 Open Chain

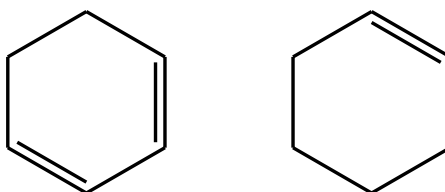
Alkenes are simply unsaturated hydrocarbons, with one or more double bonds. They have the general form of C_nH_{2n}



Ethene (C₂H₄) and propene (C₃H₆) are examples of alkenes.

2 Cycloalkenes

Cycloalkenes are simply cycloalkanes where one or more of the C–C bonds have been replaced with a C=C double bond.



Cyclohex-1,3-diene and cyclohexene are examples of cycloalkenes.

3 Physical Properties

The physical properties of alkenes, including melting and boiling points, density and solubility follow the same trends as alkanes. Larger molecules have higher melting and boiling points, and higher densities, and alkenes are generally only soluble in non-polar solvents.

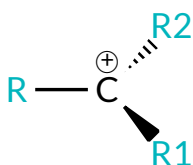
4 Stability of Carbocations

Before reactions and mechanisms of alkenes can be discussed, it is important to note the rules governing the formation of products, and the behaviour of molecules during the reaction.

All physical systems have a tendency to move to the lowest energy state — this state is characterised by the formation of the most stable molecules. As such, ions and radicals are inherently unstable.

4.1 Structure

One of the important intermediate products are carbocations, which are alkyl groups with an sp^2 hybridised central carbon atom, and carries a positive charge on that atom.



The 3 substituent groups are arranged in a trigonal planar fashion, with the p-orbitals above and below this plane. As such, nucleophiles can attack the carbocation from either the top or bottom.

4.2 Stability

Charged ions are inherently more unstable than their neutral molecule counterparts; any species that stabilises the charge on the carbon ion would in turn increase the stability of the entire molecule. The primary reason for this is that molecules that are created from a more stable intermediate product have a higher chance to form. Thus, the probability of formation of a given product of a reaction can be estimated by looking at the stability of the intermediate compound leading to its creation.

For carbocations, the carbon atom has a positive charge, thus electron-donating substituents such as alkyl groups ($-CH_3$), would stabilise the ion, as the donated electrons partially disperse the positive charge on the central atom.

Conversely, electron-withdrawing species such as halogens (F, Cl etc.) would further destabilise the carbocation, and as such products that involve the formation of these intermediates would have constitute much lower proportion of the final products.

5 Creation of Alkenes

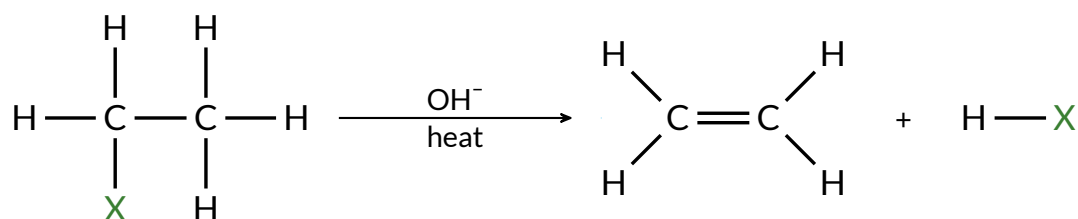
There are two methods of creating alkenes that are covered here, both of which involve elimination reactions, where a small molecule is *eliminated* along an alkane, and a double bond formed in its place.

For brevity, only the conditions and overall reaction will be covered.

5.1 Elimination of Hydrogen Halide

The main section that elaborates on this reaction can be found [here](#), in the chapter on halogenoalkanes.

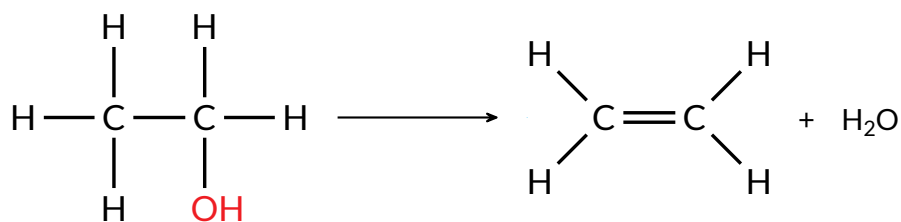
Conditions: Ethanolic KOH or NaOH, heat.



5.2 Dehydration (Elimination of Water)

Detail on this reaction, including the handling of isomers via Zaitsev's rule, can be found [here](#), in the chapter on alcohols.

Conditions: Excess concentrated H_2SO_4 , 170°C , OR
 Al_2O_3 , heat.



6 Alkene Reactions

6.1 Electrophilic Addition

The primary reaction mechanism of alkenes is electrophilic addition. Due to the high electron density of the π -bonds, electrophiles are readily attracted — thus alkenes are far more reactive than alkanes.

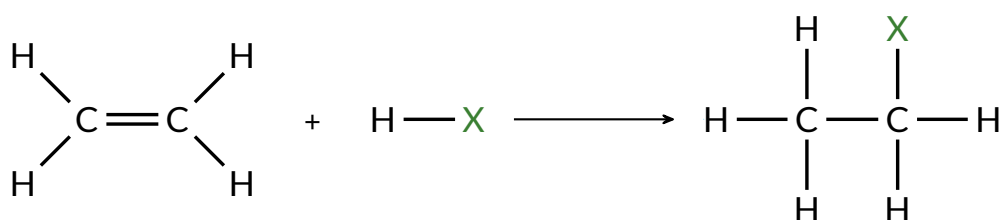
During a reaction, the comparatively weaker π -bond is preferentially broken over the stronger σ -bond; only a C–C bond remains, and atoms are *added* to the carbons, since they are now able to form an additional bond each. Hence, electrophilic *addition*.

The detailed mechanisms for each type of electrophilic addition, which are *required knowledge*, can be found in *the appendix*.

6.1.1 Electrophilic Addition of Hydrogen Halides

In this reaction, the hydrogen and halogen atom are added across the double bond of the alkene. The hydrogen halide should be in a gaseous state for this reaction.

Conditions: Gaseous HX (usually HCl or HBr).



6.1.2 Markovnikov's Rule

This rule governs the major product that is formed when asymmetrical compounds are electrophilically added to alkenes, such as hydrogen halides. It does not apply to symmetrical reactants like Cl_2 or Br_2 .

The rule states basically states that when a hydrogen compound with the general form H–X is added to an alkene that is asymmetrical about the double-bond, the hydrogen atom will be added to the carbon with *more* existing hydrogen atoms. Note that X can be a halogen, a hydroxide (ie. H–X is H_2O) or some other electronegative species.

A detailed illustration of the rule can be found in *the appendix*.

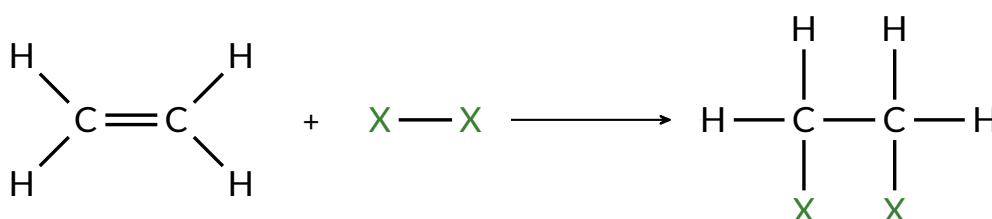
6.1.3 Electrophilic Addition of Halogens

The electrophilic addition of halogens to alkenes does not involve Markovnikov's rule, since it is symmetrical. As the non-polar halogen molecule approaches the electron-rich π -bond, it is polarised, forming $^+$ and $^-$ partial charges.

Note that the halogens used are usually either Br_2 or Cl_2 , since F_2 is too reactive, and I_2 is too *unreactive*. The reaction mechanism involves the formation of a *cyclic halonium ion* (bromonium or chloronium) – the double bond breaks, and each carbon forms a single bond with one positive halide ion (both carbons bond to the same atom).

Conditions: No UV Light, gaseous X_2 .

Observations: **Reddish-brown** Br_2 / **yellowish-green** Cl_2 decolourises.



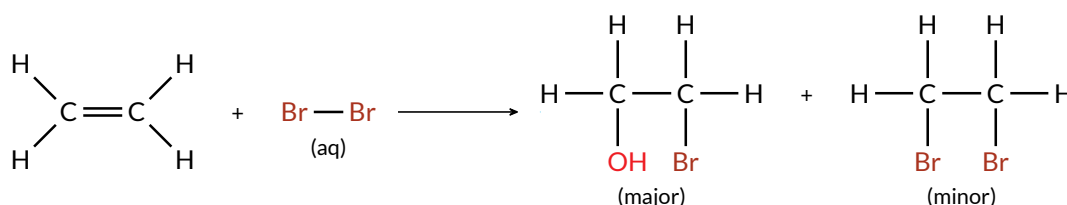
6.1.4 Electrophilic Addition of Aqueous Br_2

The mechanics of this reaction are basically the same as that of the electrophilic addition of Br_2 . The conditions and observations are fairly similar as well, except for the colour change – aqueous Br_2 is **yellow**, not reddish-brown.

Also, since the Br atoms are not both added across the double bond in a symmetrical manner, Markovnikov's Rule applies – the OH group will preferentially attack the carbon that has more stabilising alkyl groups.

Conditions: No UV Light, aqueous Br_2 .

Observations: **Yellow** Br_2 (aq) decolourises.

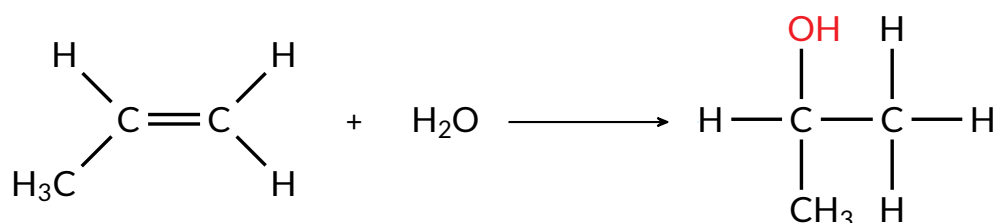


Both products are formed, except 1,2-dibromoethane is in much lower proportions.

6.1.5 Electrophilic Addition of Steam (Hydration)

Under certain (usually industrial) conditions, alkenes can react with steam to form alcohols. Since this reaction involves the formation of a carbocation intermediate, the proportion of products will be governed by Markovnikov's Rule.

Conditions: 300 °C, at 70 atm, H₃PO₄ catalyst, OR
Concentrated H₂SO₄, H₂O, warming.



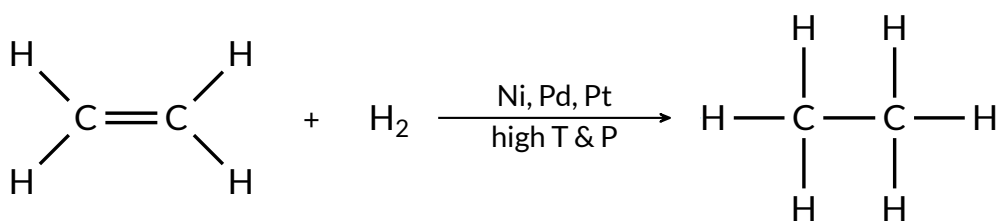
6.2 Reduction of Alkenes (Hydrogenation)

Hydrogen gas can be used to saturate alkenes, through the use of an insoluble metal catalyst such as nickel, palladium or platinum, as well as sufficiently high temperatures and pressures.

It was commonly used in the food industry to produce margarine from unsaturated plant oils. However, the resulting dense fats were found to be hazardous to human health, and subsequent usage was discontinued.

Note that although hydrogen atoms are added across the double bond, this is *not* an electrophilic addition reaction; it is actually a reduction-addition reaction.

Conditions: H₂ (g), high temperature and pressure, Ni, Pd or Pt catalyst.



6.3 Mild Oxidation of Alkenes

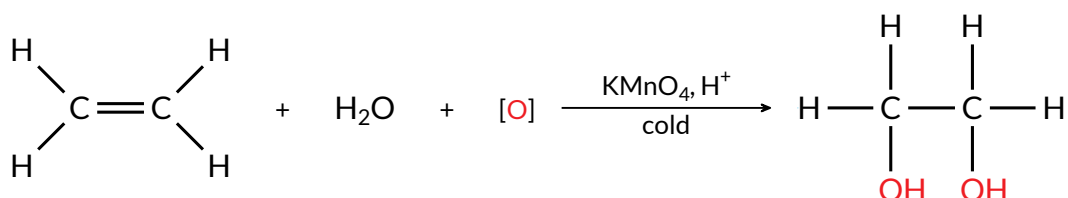
Alkenes can be mildly oxidised with potassium manganate (VII), KMnO_4 , forming *diols*. This requires a cold environment, and either an acidic or alkaline medium (for MnO_4^- to function).

On a side note, balancing redox reactions involving organic molecules simply involves adding H_2O to balance the H or O (for oxidation and reduction respectively), and adding an appropriate number of [O] or [H] to balance the remaining oxygen or water.

6.3.1 Acidic Medium

A dilute acid is used to provide the acidic medium, in the form of H^+ ions. Typically, this is H_2SO_4 . The oxidising agent, MnO_4^- , is reduced, forming Mn^{2+} .

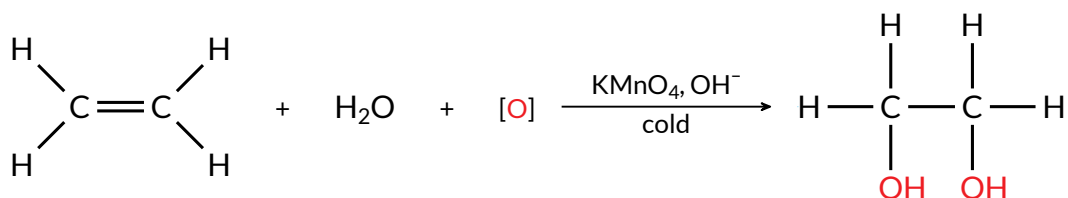
Conditions: Cold KMnO_4 , acid (H_2SO_4).
 Observations: **Purple** KMnO_4 decolourises, forming Mn^{2+} .



6.3.2 Alkaline Medium

An aqueous base, such as NaOH , is used to provide the OH^- ions. The oxidising agent MnO_4^- is reduced to MnO_2 .

Conditions: Cold KMnO_4 , aqueous base (NaOH).
 Observations: **Purple** KMnO_4 decolourises, forming a **brown** precipitate of MnO_2 .



6.4 Oxidative Cleavage (Strong Oxidation) of Alkenes

When the KMnO_4 solution containing an alkene is heated, *strong oxidation* will take place. The double bond is *cleaved* instead of added to, and each side of the double bond forms its own fragment. In the case of cycloalkenes however, the end product might still only be one molecule.

Furthermore, only a strong oxidising agent like MnO_4^- can be used. The difference between mild and strong oxidation also depends *only* on the temperature of the reacting solution. Only heated solutions will result in oxidative cleavage.

Conditions: KMnO_4 , dilute H_2SO_4 , heat.

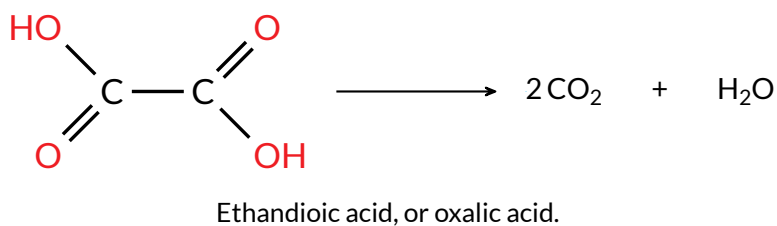
Observations: *Purple* KMnO_4 decolourises, forming Mn^{2+} .

Depending on the number of substituents (or inversely, the number of hydrogen atoms) attached to the carbon with the double bond, there are 3 possible products. Again, a table is the best way to present this, unfortunately.

| Substituents | Structure | Product |
|--------------|---|---|
| 0 | $\begin{array}{c} \text{H} \\ \diagdown \\ \text{C} = \\ \diagup \\ \text{H} \end{array}$ | $\text{CO}_2 + \text{H}_2\text{O}$ |
| 1 | $\begin{array}{c} \text{H} \\ \diagdown \\ \text{C} = \\ \diagup \\ \text{R} \end{array}$ | $\begin{array}{c} \text{HO} \\ \diagdown \\ \text{C} = \text{O} \\ \diagup \\ \text{R} \end{array}$ |
| 2 | $\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} = \\ \diagup \\ \text{R} \end{array}$ | $\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} = \text{O} \\ \diagup \\ \text{R} \end{array}$ |

6.4.1 Further Oxidation of Ethanedioic Acid

The sole special case that must be noted is that if the oxidative cleavage results in the formation of ethanedioic acid ($\text{C}_2\text{H}_2\text{O}_4$), it is further oxidised to form 2CO_2 and H_2O .



6.4.2 Uses of Oxidative Cleavage

Oxidative cleavage can be used to determine the position of the double bond in carbon chains and cycloalkenes, given the products (fragments) of the cleavage reaction.

Most importantly, if CO_2 is one of the products (gas evolved), then there are 2 possibilities — either the original molecule has a terminal $\text{C}=\text{C}$ double bond, or the cleavage involved the formation of ethanedioic acid that further decomposed to form CO_2 .

Appendices

Herein lie things that *must* be known, but for brevity are excluded from the main text.