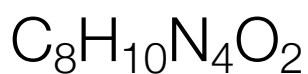
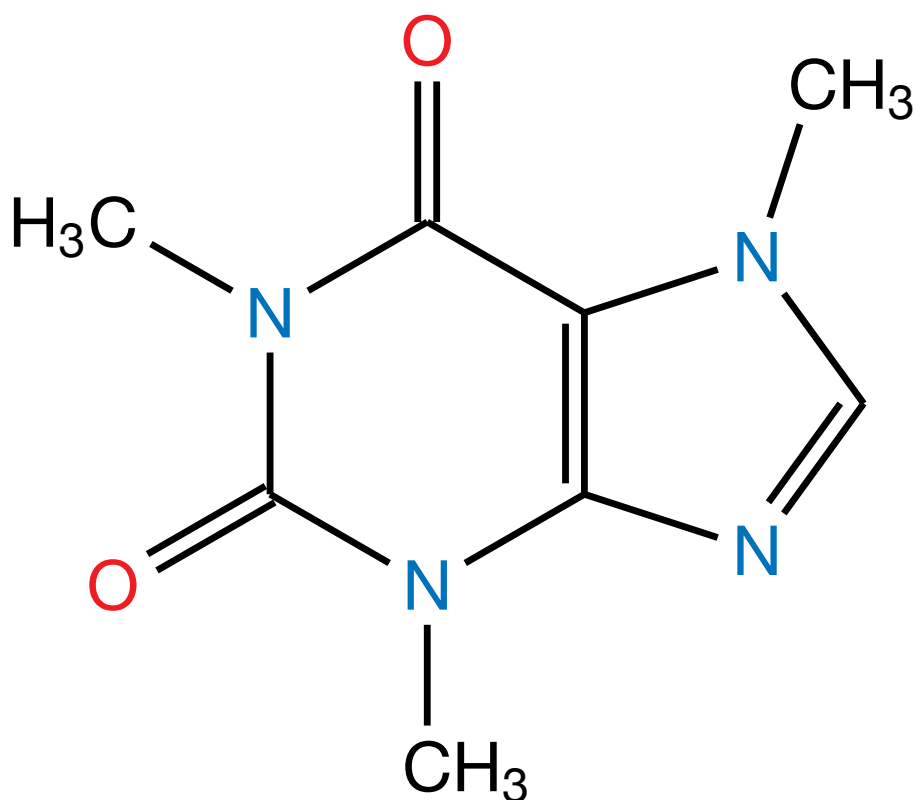


# Organic Chemistry



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

-

Caffeine

Chapters 8 to 12

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# Functional Groups

## Overview

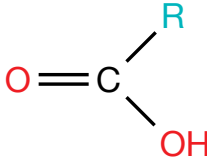
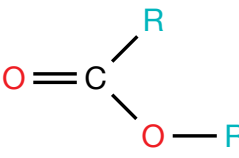
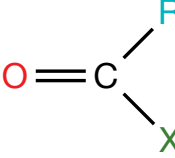
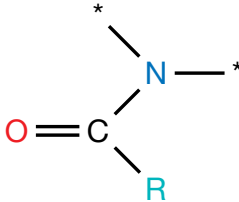
Functional groups are the main determinant of the chemical properties of a molecule. Molecules with the same functional group are of the same *family* and similar *chemical properties*.

Functional groups can be any size — the ketone functional group is just an oxygen double-bonded to a carbon atom in any position, while the carboxylic acid functional group has a more complex structure.

## Basic Functional Groups

Note that this table is ordered based on the *priority* of the functional group, in terms of where it appears in an IUPAC-named chemical compound.

*R*, as used below, represents a substituent alkyl or aryl group, the former being an arbitrary carbon chain, and the latter being some aromatic ring derivative.

Name	Prefix Form	Suffix Form	Structure
Carboxylic Acid	carboxy-*	*-oic acid	
Ester	-	*-oate	
Acyl Halide	halocarbonyl-*	*-oyl halide	
Amide	carbamoyl-*	*-amide	

Nitrile	cyano-*	*-nitrile	$\text{N} \equiv \text{C} - \text{R}$
Aldehyde	formyl-*	*-al	$\text{O} = \text{C} \begin{array}{l} \nearrow \text{R} \\ \searrow \text{H} \end{array}$
Ketone	oxo-*	*-one	$\text{O} = \text{C} \begin{array}{l} \nearrow \text{R} \\ \searrow \text{R} \end{array}$
Alcohol	hydroxy-*	*-ol	$\begin{array}{c} * \\   \\ * - \text{C} - \text{OH} \\   \\ * \end{array}$
Amine	amino-*	*-amine	$\text{R} - \text{N} \begin{array}{l} \nearrow * \\ \searrow * \end{array}$
Alkene	alkenyl-*	*-ene	$\begin{array}{c} * \quad * \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ * \quad * \end{array}$
Ether	alkoxy-*	-	$\text{R} - \text{O} - \text{R}$
Alkyl Halide	halogen-*	-	$\begin{array}{c} * \\   \\ * - \text{C} - \text{X} \\   \\ * \end{array}$

# Isomers

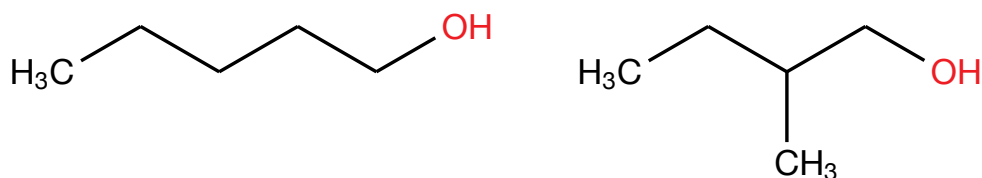
## Overview

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.

## Structural Isomerism

### Chain Isomerism

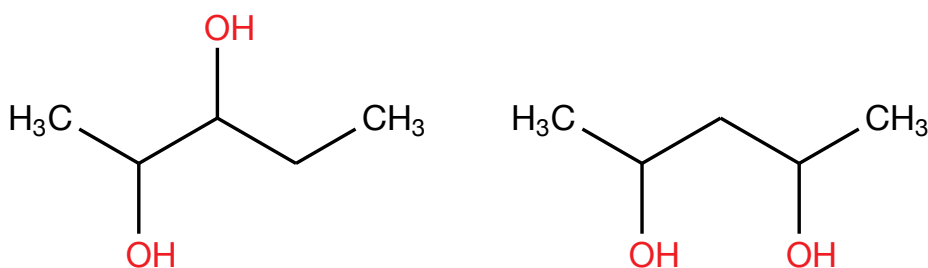
In chain isomerism, molecules have the same functional groups, except they are placed in different positions along the carbon chain. Chain isomers typically have similar chemical properties, but different physical properties (since the shape of the carbon chain can determine the strength of id-id interactions).



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

### 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.

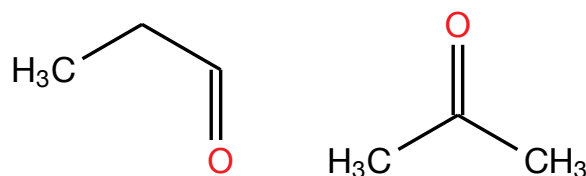


Butan-2,3-ol and butan-2,4-ol are positional isomers.



## 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

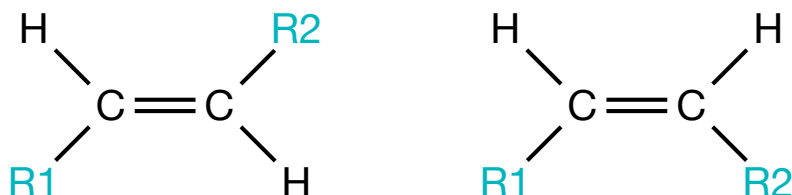
Stereoisomers of molecules have the same structure and functional groups, but those groups are arranged in a spatially differing way. The main forms of stereoisomerism are cis/trans (or E/Z) isomerism, and optical isomerism.

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  $\pi$ -bonds that only bond at 180° intervals. At these positions, it forms the cis and trans isomers.

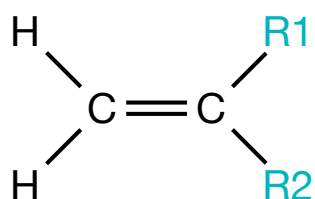


The molecule on the left is the *trans* isomer, while the one on the right is the *cis* isomer. *trans* is from Latin, meaning *other side*, while *cis* obviously means *same side*. In the former, the larger groups are on opposite sides of the alkene double bond, while in the latter, the larger groups 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 thought of as 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.

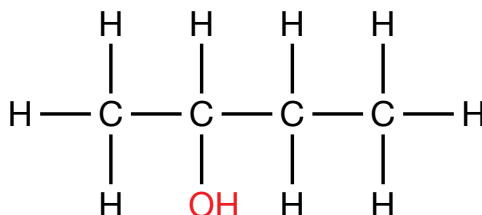
The above scheme should be used to find the two highest-priority groups attached to the alkene, after which, if the two groups are attached on the same side of the alkene, then the molecule is the *Z* isomer, and it is known as the *E* isomer if the reverse is true.

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

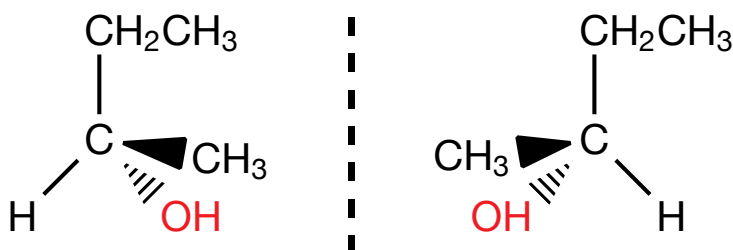
### 3.3 Optical Isomerism

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.

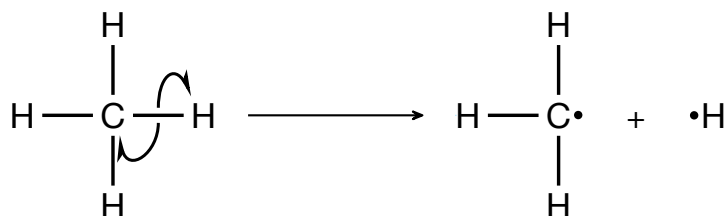
# III Reaction Mechanisms

## 1 Bond Breaking

### 1.1 Homolytic Fission

Homolytic fission involves the splitting of a single bond, with an equal (*homo*) distribution of the two electrons of the aforementioned bond. This results in the formation of radicals, since now both atoms from the bond will have unpaired electrons.

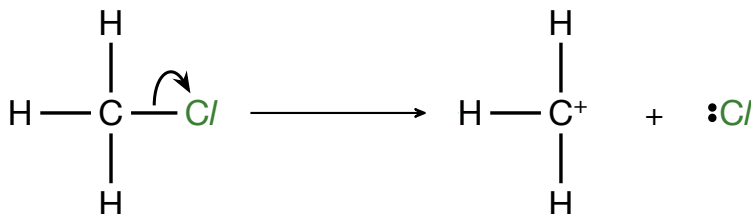
The movement of these single electrons is represented with single-hooked arrows. The arrow starts from the bond line, and points towards the target atom receiving the electron.



The homolytic fission of  $\text{CH}_4$ , forming  $\cdot\text{CH}_3$  and  $\cdot\text{H}$  radicals.

### 1.2 Heterolytic Fission

As the name implies, heterolytic fission is the opposite; it distributes both electrons of the bond to a single atom, which usually results in the formation of ions. The transfer here is represented using a full (double-hooked) arrow.



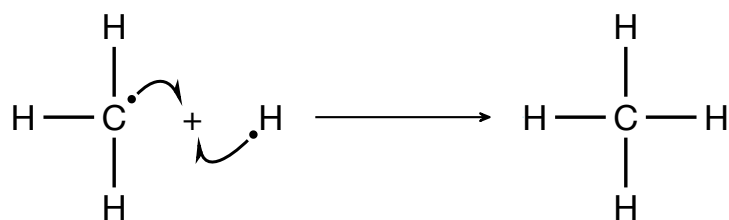
The heterolytic fission of  $\text{CH}_3\text{Cl}$ , resulting in  $\text{CH}_3^+$  and  $\text{Cl}^-$  ions

## 2 Bond Forming

### 2.1 Single Electrons

Bond forming is essentially the reverse of bond breaking, and hence the same notations apply — single-hooked arrow for the movement of single electrons, and double-hooked arrows for the movement of an electron pair.

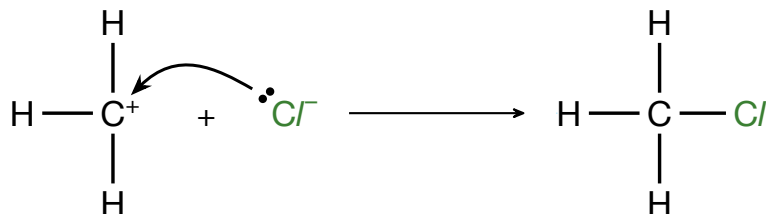
In this case, two single electrons from each atom contribute to the new bond.



The formation of a bond between  $\cdot\text{CH}_3$  and  $\cdot\text{H}$  radicals to form  $\text{CH}_4$ .

### 2.2 Electron Pairs

Electron pairs usually come from negatively charged radicals or lone pairs, although this is not a rule. Both electrons come from a single source to form a bond, but this is *not* a dative bond — it is simply a normal bond.



The formation of a bond between  $\cdot\text{CH}_3$  and  $\text{Cl}^-$  radicals, to form  $\text{CH}_3\text{Cl}$ .

## 3 Electrophiles and Nucleophiles

### 3.1 Electrophiles

Electrophiles are electron-deficient species that accept an electron pair from a nucleophile donor. Most electrophiles either have a positive charge, or contain an atom that is polarised and thus has a partial positive charge.

Examples of electrophiles include  $\text{CH}_3^+$ ,  $\text{Br}^+$ ,  $\text{NO}_2^+$ , polarised  $\text{Br}_2$ , and  $\text{HBr}$ .

### 3.2 Nucleophiles

Nucleophiles are electron-rich species that donate electron pairs to electrophiles. This process typically results in the formation of a new covalent bond. Nucleophiles usually contain atoms that are either negatively charged, or, more frequently, contain lone electron pairs that are not bonded.

Molecules with a  $\pi$ -bond, such as ethene or benzene, can also act as nucleophiles, due to the high electron density of the  $\pi$ -system.

Examples of nucleophiles include  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{OH}^-$ .

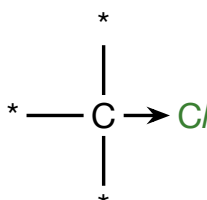
# IV Induction and Resonance

## 1 Inductive Effect

The inductive effect occurs through covalent bonds, where there is a significant difference in the electronegativity of participating atoms. Electrons are either withdrawn or donated through a  $\sigma$ -bond, due to the polarity of the molecule.

### 1.1 Withdrawal

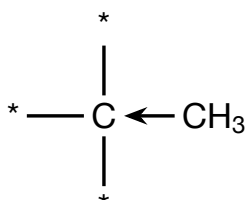
Below, *Cl* is more electronegative than the carbon it is bonded to. As such, it *inductively withdraws* electrons through the  $\sigma$ -bond.



Note that the arrow represents a withdrawal of electrons, *not* a dative bond.

### 1.2 Donation

Alkyl groups, or groups with the general formula  $C_nH_{2n+1}$ , *inductively donate* electrons. This behaviour is due to hyperconjugation, which lowers the total energy of the system, through an interaction between electrons in a  $\sigma$ -bond of the alkyl group, with a partially-filled or empty p-orbital in the adjacent atom.



Again, the arrow *does not* represent a dative bond.

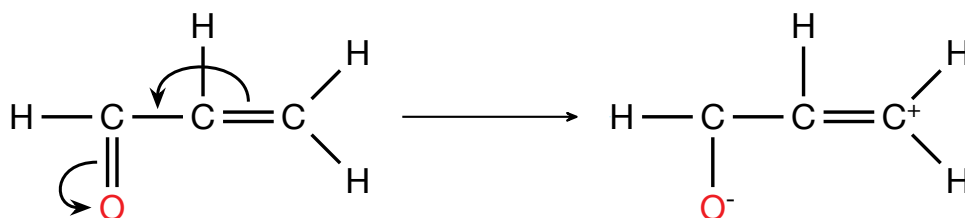


## 2 Resonance Effect

The resonance effect is the withdrawal or donation of electrons through the side-on overlap of *unhybridised* p-orbitals. Thus, the resonance effect can only occur when the substituent is bonded to an aromatic ring ( $\pi$ -system), or an alkene ( $C=C$ ).

### 2.1 Withdrawal

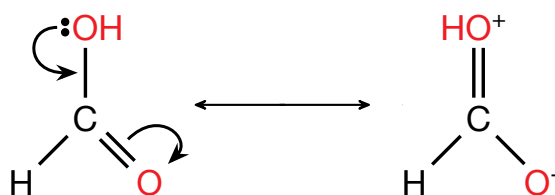
In the case below, electrons flow from the double-bonds to the substituent, via the resonance effect. In general, substituents that exhibit an electron-withdrawing resonance effect usually take the form of  $-Y=Z$ , where Z is more electronegative than Y. Examples include carbonyls and nitriles.



Electrons move from the electron-rich double-bonds, which have unhybridised p-orbitals, to an adjacent atom.

### 2.2 Donation

On the other hand, groups can donate electrons through resonance, flowing from the substituent to a single-bond, forming a double-bond. Substituents such as halogens (F, Cl, etc.), hydroxyls ( $-OH$ ), and amines ( $-NH_2$ ) are examples. They usually contain a lone pair of electrons that are free for donation.



This example shows both resonant withdrawal and donation.

## 2.3 Overall Effect

Since it is possible for a substituent group to simultaneously withdraw and donate electrons through different mechanisms, it can be difficult to determine whether the overall effect serves to withdraw or donate electrons.

Behold, the second ugly table.

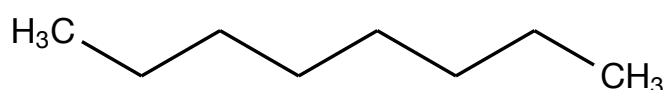
Substituent Group	Strength	Overall Effect
Alkyl/aryl groups (eg. $-\text{CH}_3$ )	Weak	Donating
$-\text{OH}$ , $-\text{NH}_2$ , $-\text{OCH}_3$	Strong	Donating
$-\text{Cl}$ , $-\text{Br}$	Weak	Withdrawing
$-\text{CHO}$ , $-\text{NO}_2$ , $-\text{CN}$ , $-\text{CO}_2\text{H}$	Strong	Withdrawing

# v Alkanes

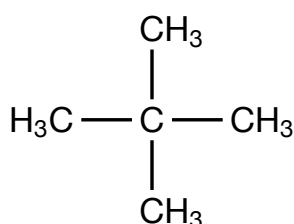
## 1 Open Chain

Open chain alkanes have the general formula of  $C_nH_{2n+2}$ . They are called 'open-chain' because the two ends of the chain are separate, in contrast with cycloalkanes.

Open chain alkanes can either be straight-chained or branch-chained. The terminology should be pretty much self explanatory.



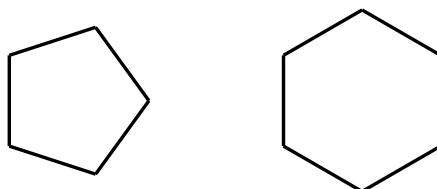
Octane is an example of a straight-chain alkane.



2,2-dimethylpropane is an example of a branched alkane.

## 2 Cycloalkanes

Cycloalkanes are alkanes where the carbon atoms at either end of the chain are bonded together, forming a closed loop. They are essentially 'closed-chain' alkanes. They take the shape of regular polygons — cyclopropane is just a triangle, and cyclobutane is a square.



Cyclopentane (left) and cyclohexane (right)

## 3 Physical Properties

### 3.1 Melting and Boiling Points

The melting and boiling points of alkanes follow a simple pattern. Due to the fact that they rely solely on induced dipole interactions for intermolecular bonding, both melting and boiling points increase with the length of the carbon chain, and by extension  $M_r$ . Note that small chains (eg.  $\text{CH}_4$ ) have very low boiling points.

However, because branched alkanes have a smaller surface area for a given number of carbon atoms than straight-chained alkanes, their melting and boiling points will be lower, due to a smaller area for polarisation.

### 3.2 Density

Most liquid alkanes, up to a certain point, are less dense than water. Additionally, since they are insoluble, they form an immiscible layer above water.

As the number of carbon atoms increases, the strength of the intermolecular interactions will increase as well — this forces each molecule ever so slightly closer together, marginally increasing density.

### 3.3 Solubility

As described before, alkanes rely only on induced-dipole interactions for intermolecular bonding; they are insoluble in polar solvents such as water. However, they are highly soluble in non-polar solvents like  $\text{CCl}_4$ . In fact, since solubility is dependent on the strength of solvent-solute bonds, larger alkanes will be more soluble in non-polar solvents.

## 4 Alkane Reactions

### 4.1 Free Radical Substitution of Alkanes

#### 4.1.1 Mechanism of Reaction

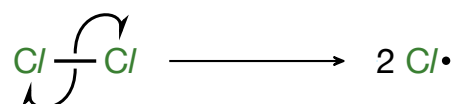
In the steps below, the free radical substitution of methane ( $\text{CH}_4$ ) by chlorine ( $\text{Cl}_2$ ) will be used. This applies for any alkane, and a sufficiently reactive halogen.

**Conditions:** UV Light,  $\text{Br}_2$  /  $\text{Cl}_2$  gas

**Observations:** *Reddish-brown*  $\text{Br}_2$  / *yellowish-green*  $\text{Cl}_2$  decolourises.

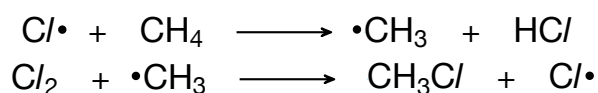
#### Stage I Initiation

The  $\text{Cl}-\text{Cl}$  bond is *homolytically* broken to form 2  $\text{Cl}\cdot$  radicals. The energy required to break this bond is provided by the UV light.



#### Stage II Propagation

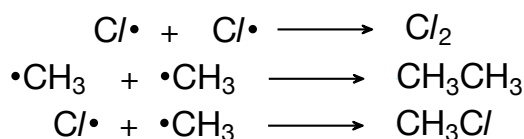
The highly reactive  $\text{Cl}\cdot$  radicals then react with the  $\text{CH}_4$  molecules, bonding with one of the hydrogen atoms to form  $\text{HCl}$  and a carbocation radical,  $\text{CH}_3\cdot$ .



This newly-minted  $\text{CH}_3\cdot$  radical can react with a  $\text{Cl}_2$  molecule to form  $\text{CH}_3\text{Cl}$  and another  $\text{Cl}\cdot$  radical, thus recreating the consumed radical. As long as the supply of  $\text{Cl}_2$  gas has not been exhausted, this reaction can continue, and no additional UV light is required to sustain it.

## Stage II Termination

In the termination stage, two radicals combine to form stable products, effectively terminating the chain reaction.

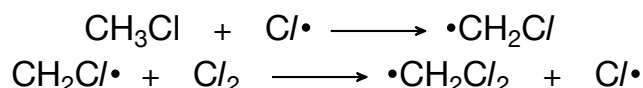


Once all the radicals have been consumed in this manner, the reaction will stop, unless more UV light is provided (along with more  $\text{Cl}_2$  gas).

### 4.1.2 Multi-substitution of Alkanes

Free radical substitution of alkanes is usually not the preferred way to produce halogenated alkanes, due to the random nature of the process and the possibility of multi-substitution, where more than one halogen atom has been substituted onto the alkane.

If there are still  $\text{Cl}\cdot$  radicals remaining, in the reaction chamber,  $\text{CH}_3\text{Cl}$  formed during the termination stage can still react with it, forming a  $\text{CH}_2\text{Cl}\cdot$  radical, which can continue to react.

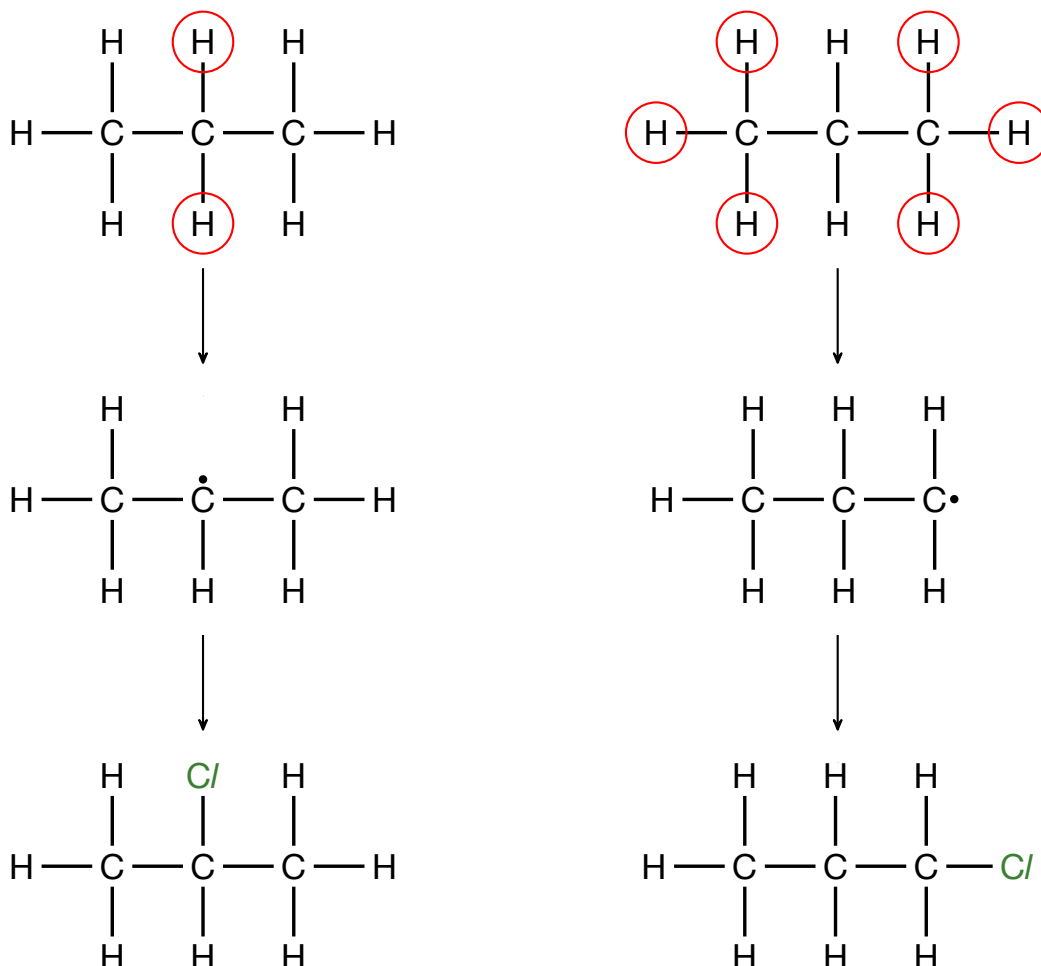


Indeed, this can continue *ad-infinitum*, so until all the hydrogen atoms on the alkane have been substituted. In the case of methane, this results in the formation of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$ .

In fact, there will also be a small amount of alkanes with more than 1 carbon in the chain; this is due to the possibility of two molecules of  $\cdot\text{CH}_2\text{Cl}$  reacting, which then has its hydrogens further substituted.

### 4.1.3 Isomerism of Substituted Alkanes

Because every hydrogen atom can be substituted by the halogen atom, alkanes with 3 or more carbon atoms in the chain can form isomers. The probability of the formation of each isomer depends on both the number of possible hydrogen atoms that can be substituted to result in it, as well as the stability of the carbon radical intermediate.



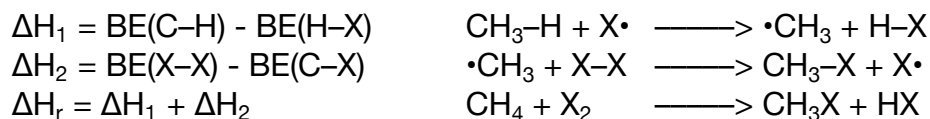
In the example above, propane can be substituted by Cl to form 2 different isomers, 2-chloropropane and 1-chloropropane. Only 2 hydrogens can be substituted to form the former, while 6 hydrogens can be substituted to form the latter. Thus, the *expected* ratio of products from the free radical substitution of propane with chlorine is 2 : 6 in favour of 1-chloromethane.

However, the stability of the carbon radical intermediate also plays a part in the ratio of products. For 1-chloropropane, it involves forming a carbon radical on carbon 1, which only has 1 electron-donating alkyl group (through the induction effect) to stabilise the positive charge. On the other hand, for 2-chloropropane, the positive charge is on carbon 2, which has 2 electron-donating alkyl groups to stabilise it. Thus, it is more likely to form, and hence 2-chloropropane is more likely to form. Therefore, the actual ratio of products is around 4 : 6, not 2 : 6.

#### 4.1.4 Free Radical Substitution Reactivity

The reactivity of the free radical substitution naturally depends on the species of halogen that is reacting. As is typical of halogens, the reactivity increases in this order:  $I_2 < Br_2 < Cl_2 < F_2$ . In fact, the substitution by fluorine is too reactive — even in the dark and at room temperature. On the other hand, the substitution of iodine is not feasible ( $\Delta G > 0$ ).

In the propagation steps of the reaction, several bonds are formed and broken. Using X as a halogen atom:



The values of the bond energies for H-X, X-X, and C-X are below:

$F_2$	H-F	= 562 kJ mol <sup>-1</sup>
	C-F	= 484 kJ mol <sup>-1</sup>
	F-F	= 158 kJ mol <sup>-1</sup>
	$\Delta H_r$	= -478 kJ mol <sup>-1</sup>
$Cl_2$	H-Cl	= 431 kJ mol <sup>-1</sup>
	C-Cl	= 340 kJ mol <sup>-1</sup>
	Cl-Cl	= 244 kJ mol <sup>-1</sup>
	$\Delta H_r$	= -117 kJ mol <sup>-1</sup>
$Br_2$	H-Br	= 366 kJ mol <sup>-1</sup>
	C-Br	= 280 kJ mol <sup>-1</sup>
	Br-Br	= 193 kJ mol <sup>-1</sup>
	$\Delta H_r$	= -43 kJ mol <sup>-1</sup>
$I_2$	H-I	= 299 kJ mol <sup>-1</sup>
	C-I	= 240 kJ mol <sup>-1</sup>
	I-I	= 151 kJ mol <sup>-1</sup>
	$\Delta H_r$	= +22 kJ mol <sup>-1</sup>

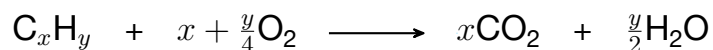
As can be seen, the reaction with  $F_2$  is highly exothermic; even the F-F bond energy is relatively small, hence the reaction is highly spontaneous — even at room temperature and without UV light, since the initiation stage requires little energy to progress.

On the other hand, the  $\Delta H$  of the reaction with  $I_2$  is positive, hence the reaction is not as spontaneous, and it is not as likely to take place.



## 4.2 Combustion of Alkanes

Alkanes are a type of combustible fuel, and there exists a general formula describing the required amounts of  $O_2$  to combust a given hydrocarbon.

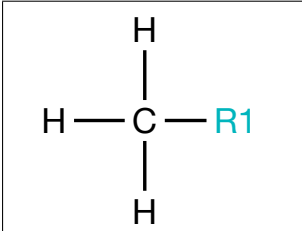
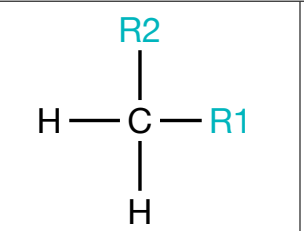
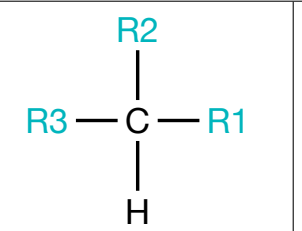
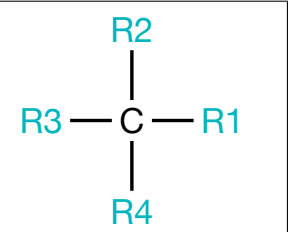


Note that while this combustion process is highly exothermic, it still has a high activation energy, and requires an energy input like a spark to begin the reaction.

## 5 Classification of Carbons

This applies to many things — carbons, halogenoalkanes, and alcohols. Essentially, the classification of an atom with substituent groups refers to the number of such groups attached to the carbon, and the number of hydrogens (ie. unfilled slots so to speak) attached to it.

As example, there are 4 possible classifications of carbons in an alkane: *primary*, *secondary*, *tertiary*, and *quaternary*.

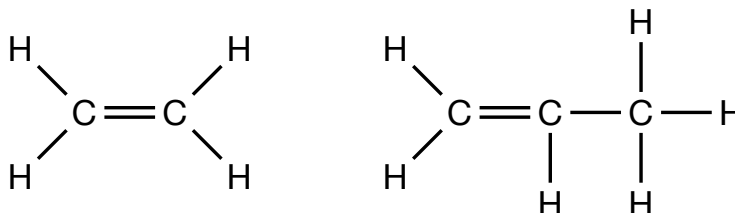
			
Primary (1°)	Secondary (2°)	Tertiary (3°)	Quaternary (4°)

The table (ew) above gives a visual representation. *R* represents an alkyl group substituent. This principle also applies when classifying alkyl radicals.

# vi Alkenes

## 1 Open Chain

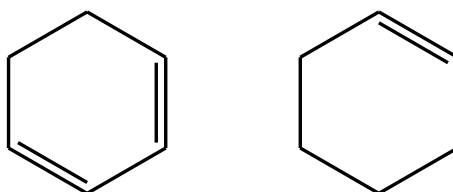
Alkenes are simply unsaturated hydrocarbons, with one or more double bonds. They have the general form of  $C_nH_{2n}$



Ethene (C<sub>2</sub>H<sub>4</sub>) and propene (C<sub>3</sub>H<sub>6</sub>) 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.

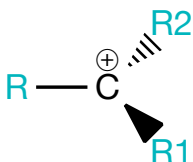
## 4 Stability of Carbocations

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 Alkene Reactions

### 5.1 Electrophilic Addition

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

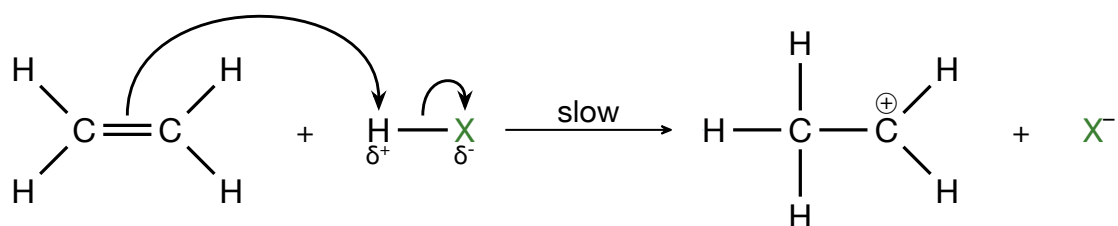
During a reaction, the comparatively weaker  $\pi$ -bond is preferentially broken over the stronger  $\sigma$ -bond; only a C–C bond remains, and atoms are *added* to the carbons, since they are now able to form an additional bond each. Hence, electrophilic *addition*.

#### 5.1.1 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).

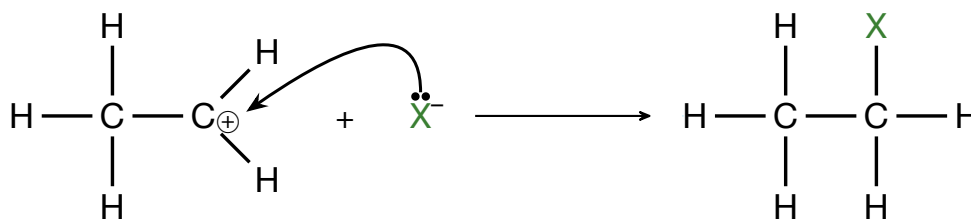
Step 1



This is the rate-determining step, which involves the breaking of the  $\pi$ -bond. The polar HX molecule has to approach the electron cloud of the  $\pi$ -bond in the correct orientation (hydrogen-facing), where the  $\pi$ -bond electrons attack the electron deficient,  $\text{H}^{\delta+}$  atom.

The H–X bond then undergoes heterolytic fission, producing a carbocation intermediate and a halide ion.

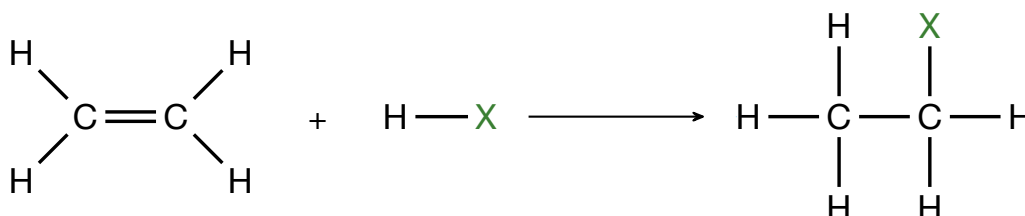
## Step 2



Note that the electron pair arrow points to the plus charge on the carbon, *not* the carbon atom itself.

This is the fast step; the bromide anion acts as a nucleophile, attacking the positively-charged carbocation. Since this step involves the reaction of two oppositely-charged species, it is a fast step.

## Overall Reaction



### 5.1.2 Markovnikov's Rule

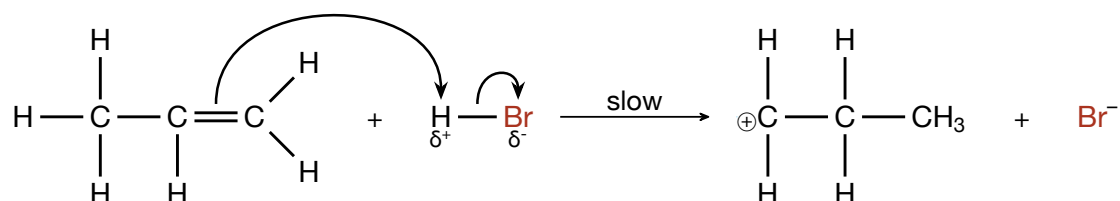
This rule governs the major product that is formed when asymmetrical compounds are electrophilically added to alkenes, such as hydrogen halides. It does not apply to symmetrical reactants like Cl<sub>2</sub> or Br<sub>2</sub>.

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<sub>2</sub>O) or some other electronegative species.

### 5.1.3 Addition of H-X to Unsymmetrical Alkenes

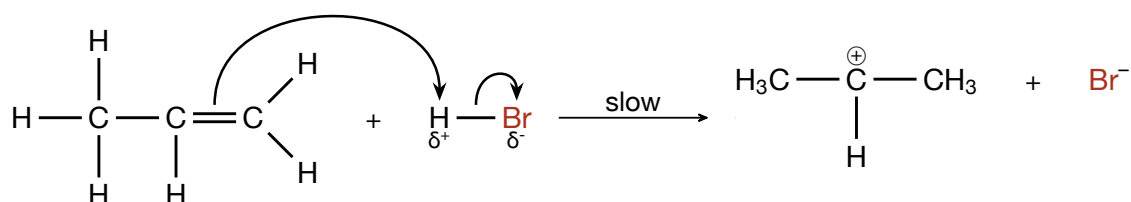
The behaviour that Markovnikov's rule predicts can be derived from the fact that adding the non-hydrogen species to the least substituted carbon would result in a less stable intermediate being formed. This can be illustrated using the electrophilic addition of HBr to prop-1-ene ( $C_3H_6$ ).

If the Markovnikov's rule is *not* followed, the following will take place:



The hydrogen was added to the centre carbon, in violation of Markovnikov's rule.

Notice that the positively-charged carbon on the intermediate only has 1 electron-donating alkyl group to stabilise its charge. Conversely, if Markovnikov's rule is followed below, the outcome would be different.



The hydrogen was added to the terminal carbon, following Markovnikov's rule.

In this case, the carbon atom containing the positive charge has 2 electron-donating alkyl groups attached to it, making this intermediate molecule more stable than the one above it.

As such, it is more likely to form, and hence 2-bromopropane will be the *major product*, and 1-bromopropane will be the *minor product*.

### 5.1.4 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 high-electron-density  $\pi$ -bond, it is polarised, forming  $\delta^+$  and  $\delta^-$  partial charges.

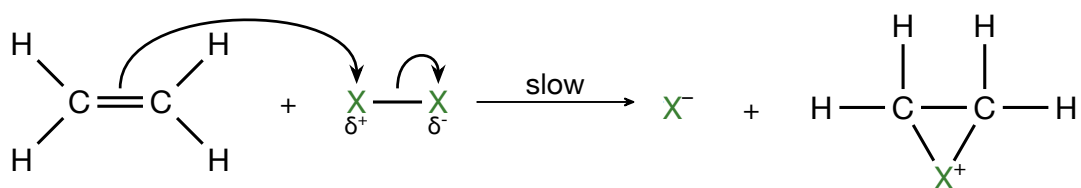
Note that the halogens used are usually either  $\text{Br}_2$  or  $\text{Cl}_2$ , since  $\text{F}_2$  is too reactive, and  $\text{I}_2$  is too *unreactive*. The reaction mechanism involves the formation of a *cyclic halonium ion* (bromonium or chloronium) — the double bond breaks, and each carbon forms a single bond with one positive halide ion (both carbons bond to the same atom).

**Conditions:** No UV Light, gaseous  $\text{X}_2$ .

**Observations:** *Reddish-brown*  $\text{Br}_2$  / *yellowish-green*  $\text{Cl}_2$  decolourises.

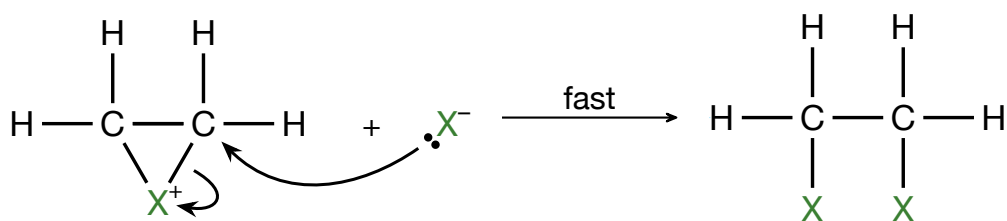
#### Step 1

This initial step is the slow, rate-determining one. It involves breaking of the  $\pi$ -bond, as well as the  $\text{X}-\text{X}$  bond. Note that the resulting cyclic halonium ion is highly unstable, due to the inherent strain of having a three-membered ring.

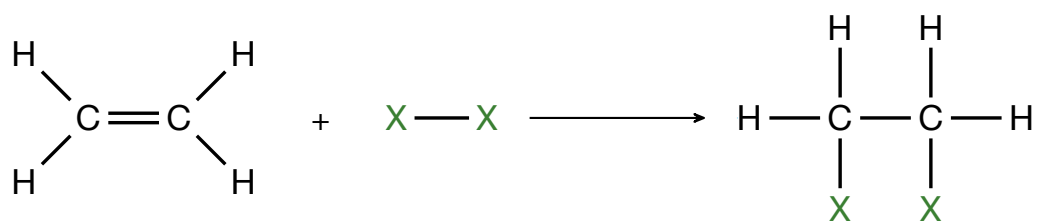


#### Step 2

In the second, fast step, the negatively-charged bromide ion from the first step attacks the overall positively-charged cyclic bromonium ion, resulting in the final product. Note that the bromide ion attacks one of the carbons attached to the positive bromide ion, breaking that bond. This is the fast step as it involves the reaction of two oppositely-charged species.



## Overall Reaction





### 5.1.5 Electrophilic Addition of Aqueous Br<sub>2</sub>

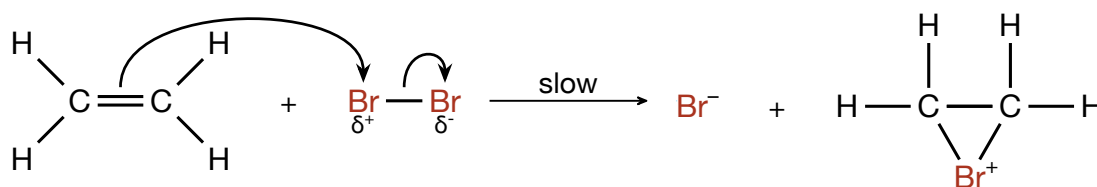
The mechanics of this reaction are basically the same as that of the electrophilic addition of Br<sub>2</sub>. The conditions and observations are fairly similar as well, except for the colour change — aqueous Br<sub>2</sub> is **yellow**, not reddish-brown.

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<sub>2</sub>.

**Observations:** **Yellow** Br<sub>2(aq)</sub> decolourises.

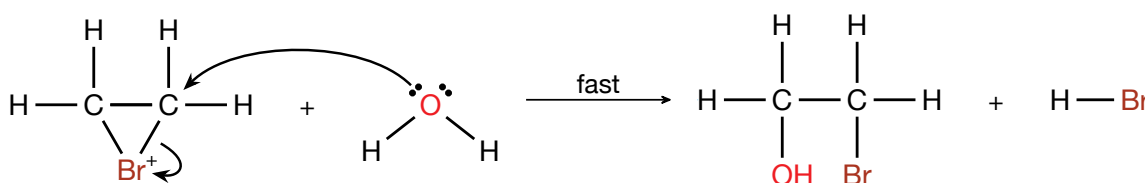
#### Step 1



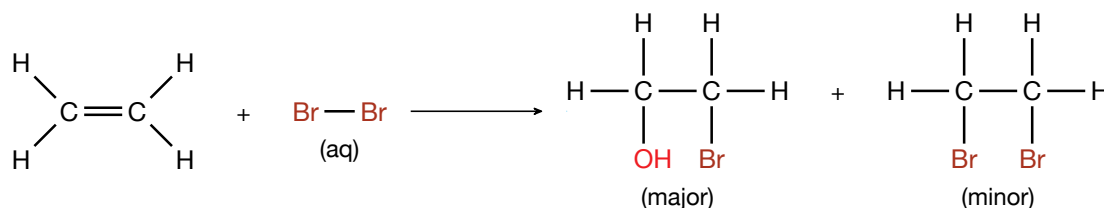
The cyclic bromonium ion is formed.

#### Step 2

Once the cyclic bromonium ion is formed however, it is susceptible to attack from any and all nucleophiles — including water, which has lone pairs and is a stronger nucleophile Br<sup>-</sup>. Since it is in much higher concentrations than Br<sup>-</sup>, the primary product will now have an OH group.



#### Overall Reaction



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

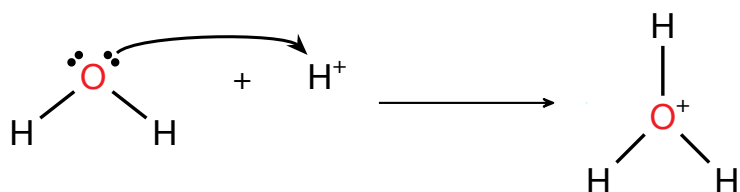
### 5.1.6 Electrophilic Addition of Steam (Hydration)

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,  $\text{H}_3\text{PO}_4$  catalyst.

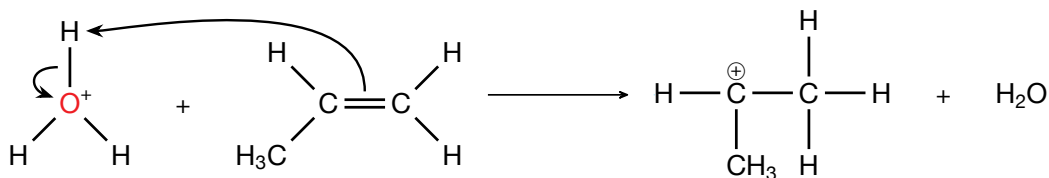
#### Step 0

The first step is to form  $\text{H}_3\text{O}^+_{(\text{aq})}$ . Simply put, it is aqueous  $\text{H}^+$ .



#### Step 1

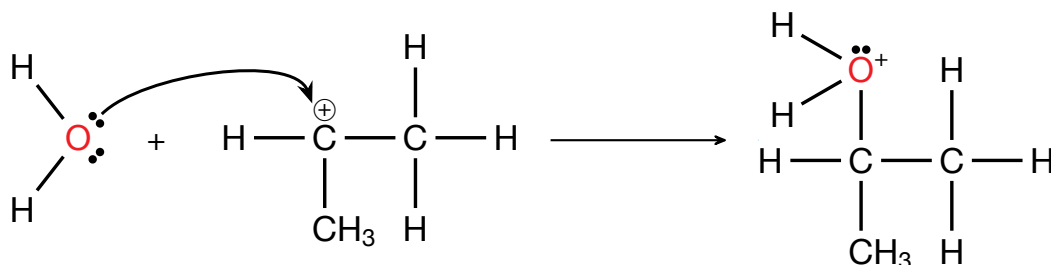
The electron-rich double-bond ( $\text{C}=\text{C}$ ) is then attacked by one of the H atoms on the  $\text{H}_3\text{O}^+$ , acting as an electrophile.



Since the alkene is not symmetrical, there are two product possibilities; hence, the positive charge will be on the carbon atom with more electron donating alkyl groups, in this case carbon 2.

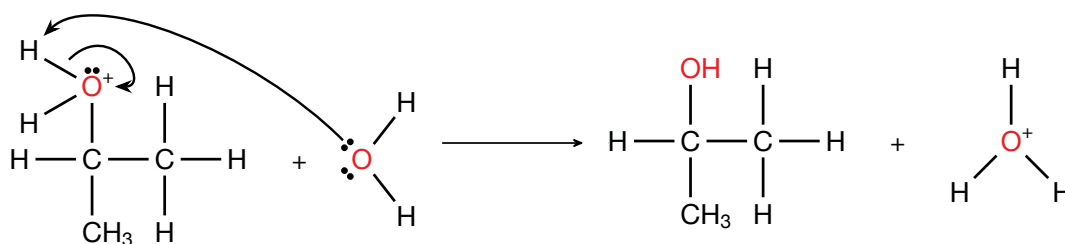
## Step 2

One of the lone pairs on the oxygen atom of a water molecule acts as a nucleophile, attacking the newly-formed carbocation. This results in a protonated alcohol, which is basically an alcohol with an extra H atom on the OH group.

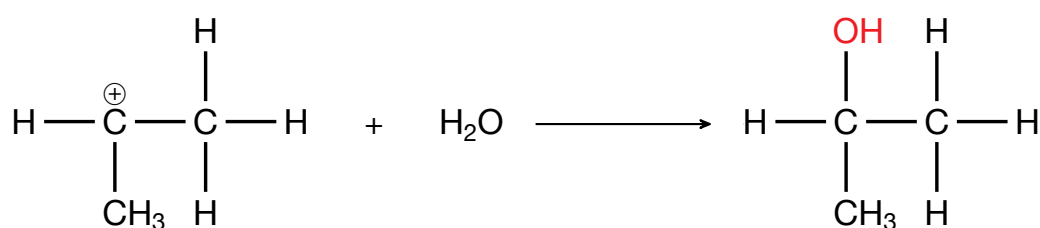


## Step 3

The acid catalyst is regenerated as a lone pair on another water molecule's O atom attacks the extra H of the OH group. This forms the alcohol proper, and the H<sub>3</sub>O<sup>+</sup> ion.



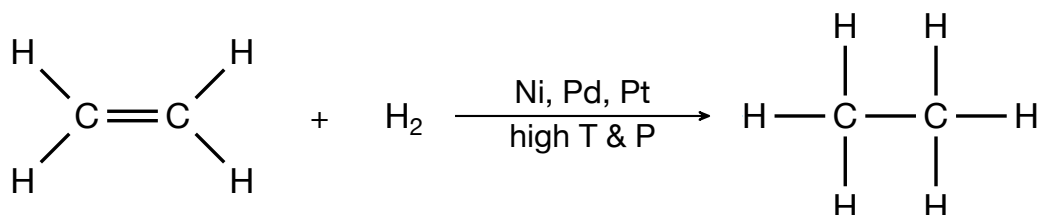
## Overall Reaction



## 5.2 Hydrogenation of Alkenes

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.



## 5.3 Mild Oxidation of Alkenes

Alkenes can be mildly oxidised with potassium manganate (VII),  $\text{KMnO}_4$ , forming *diols*. This requires a cold environment, and either an acidic or alkaline medium (for  $\text{MnO}_4^-$  to function).

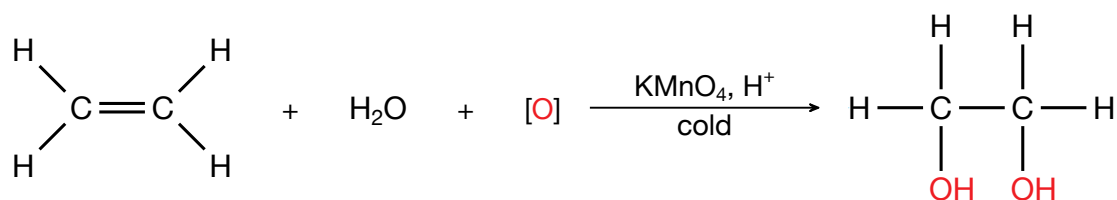
On a side note, balancing redox reactions involving organic molecules simply involves adding  $\text{H}_2\text{O}$  to balance the H or O (for oxidation and reduction respectively), and adding an appropriate number of  $[\text{O}]$  or  $[\text{H}]$  to balance the remaining oxygen or water.

### 5.3.1 Acidic Medium

A dilute acid is used to provide the acidic medium, in the form of  $\text{H}^+$  ions. Typically, this is  $\text{H}_2\text{SO}_4$ . The oxidising agent,  $\text{MnO}_4^-$ , is reduced, forming  $\text{Mn}^{2+}$ .

**Conditions:** Cold  $\text{KMnO}_4$ , acid ( $\text{H}_2\text{SO}_4$ ).

**Observations:** *Purple*  $\text{KMnO}_4$  decolourises.

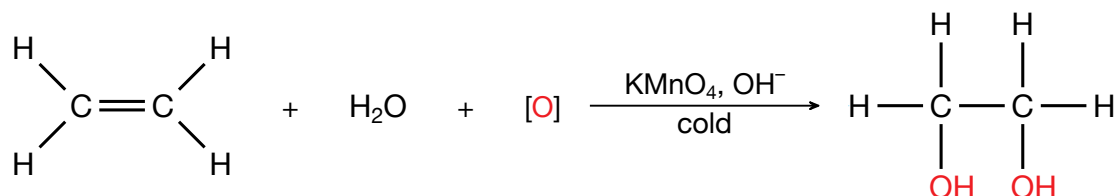


### 5.3.2 Alkaline Medium

An aqueous base, such as  $\text{NaOH}$ , is used to provide the  $\text{OH}^-$  ions. The oxidising agent  $\text{MnO}_4^-$  is reduced to  $\text{MnO}_2$ .

**Conditions:** Cold  $\text{KMnO}_4$ , aqueous base ( $\text{NaOH}$ ).

**Observations:** *Purple*  $\text{KMnO}_4$  decolourises, forming a *brown* precipitate of  $\text{MnO}_2$ .

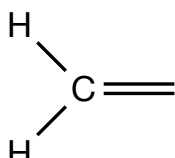
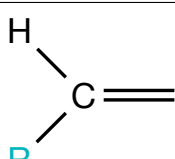
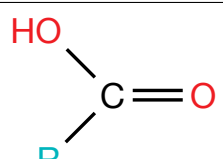
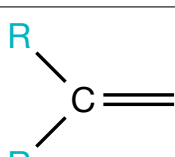
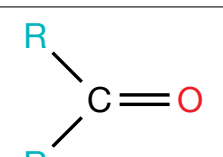


## 5.4 Oxidative Cleavage (Strong Oxidation) of Alkenes

When the  $\text{KMnO}_4$  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.

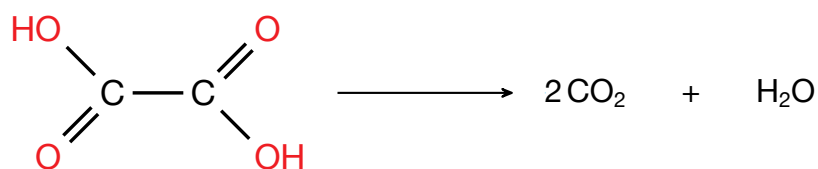
Furthermore, only a strong oxidising agent like  $\text{MnO}_4^-$  can be used. The difference between mild and strong oxidation also depends *only* on the temperature of the reacting solution. Only heated solutions will result in oxidative cleavage.

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		$\text{CO}_2 + \text{H}_2\text{O}$
1		
2		

### 5.4.1 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  $2\text{CO}_2$  and  $\text{H}_2\text{O}$ .



Ethanedioic acid, or oxalic acid.

### 5.4.2 Uses of Oxidative Cleavage

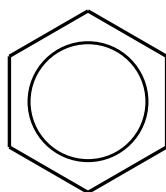
Oxidative cleavage can be used to determine the position of the double bond in carbon chains and cycloalkenes, given the products (fragments) of the cleavage reaction.

Most importantly, if  $\text{CO}_2$  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  $\text{CO}_2$ .

## vii Arenes

### 1 Benzene

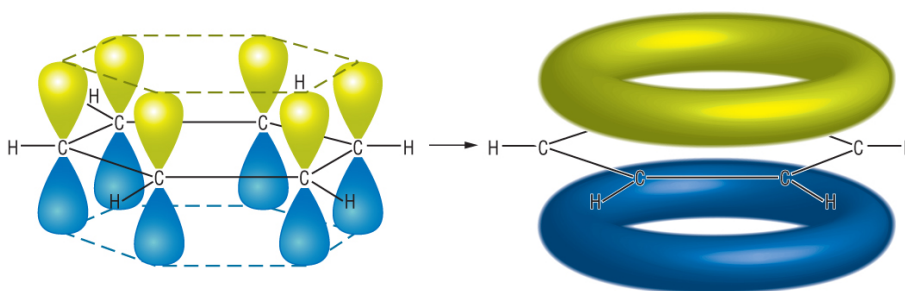
Benzene is simplest possible aromatic compound, or arene. The first known and isolated arene compounds had pleasant smells, such as benzaldehyde. Unfortunately, even though most known arenes now smell terrible and are carcinogenic, the name stuck.



The structural representation of benzene.

The most common form of arene is the benzene ring, or phenyl functional group. Note that aromatic rings with other configurations and structures can also form, such as with nitrogen.

Its basic structure consists of 6 carbon atoms, arranged in a hexagonal fashion. However, unlike cyclohexane, benzene is a flat, planar molecule. All 6 carbon atoms are  $sp^2$  hybridised, forming the following structure:



The trigonal structure of the  $sp^2$  hybrid orbitals dictates this structure, since the angle between each orbital is  $120^\circ$ , which is the internal angle of a regular hexagon. Note that there is one H atom bonded to each carbon, making the molecular formula of benzene  $C_6H_6$ .

The carbon atoms are bonded to each other through  $\pi$ -bonds with their unhybridised p-orbitals, while the bonds with the hydrogen atoms (or other substituents if substituted) are done with the  $sp^2$  orbitals.



Furthermore, the 6  $\pi$ -bond electrons are delocalised, and move freely within the ring. This increases the stability of the benzene ring, which increases the amount of energy needed to modify it by fiddling with bonds.

## 1.1 Physical Properties

Since benzene is a regular hexagon, each C=C bond is the same length. However, it is shorter than a C–C bond, but longer than a C $\equiv$ C bond.

Benzene is a volatile, flammable and carcinogenic. Don't drink it. Don't eat it. Don't touch it. It also happens to be colourless, with a distinct "aromatic" odour.

As a non-polar molecule, it has relatively low melting and boiling points (5.5 °C and 80.1 °C), as well as low solubility in water. Of course, it is soluble in non-polar solvents, and in fact can be used as a solvent in its own right.

## 2 Arene Reactions

Benzene undergoes substitution reactions rather than addition reactions, since adding atoms to the ring would destroy the delocalised  $\pi$ -system of the ring, which is energetically unfavourable. Instead, the H atoms on the ring are substituted.

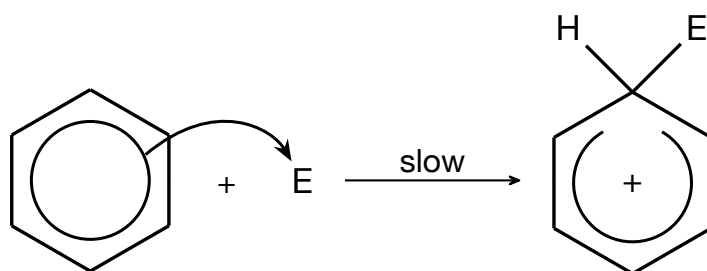
The main mechanism for this is electrophilic substitution, as seen below.

### 2.1 Electrophilic Substitution

The delocalised  $\pi$ -system of benzene has a very high electron density, and thus is a prime target for electrophiles, which will substitute the H atoms on the ring. Thus, the most common form of reaction involving benzenes is electrophilic substitution, barring special conditions and requirements.

#### Step 1

In the first, rate-determining step, the aromaticity of the benzene ring is partially and temporarily broken, disrupted by the attacking electrophile.



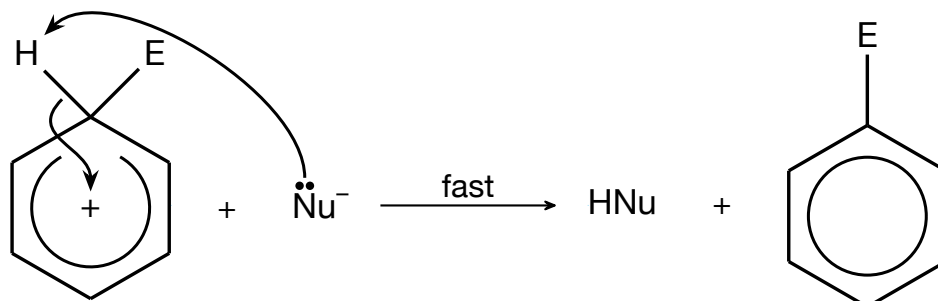
Note that the '+' is drawn in the centre of the ring, not on any one carbon.

Two electrons out of six from the delocalised  $\pi$ -system are used to form the bond between the electrophile, E, and the carbon. Thus, there is a positive charge on the carbon; due to the delocalised nature of the  $\pi$ -system however, this positive charge is delocalised across *all 6 carbons*, making it much more stable than a simple carbocation.

However, the activation energy for this step is still large, and only strong electrophiles are able to attack the benzene ring without catalysts.

## Step 2

Next, a nucleophile ( $\text{:Nu}^-$  in this example) attacks the hydrogen attached to the carbon atom, restoring the aromaticity of the benzene ring. The new substituent is now in place, and the two electrons in the C–H bond are returned to the  $\pi$ -system.



Note that the arenium ion (which is the partially delocalised benzene) has 5  $\text{sp}^2$  carbons, and one  $\text{sp}^3$  carbon. This results in a disruption of the planar structure of benzene — it is restored once the substitution is completed.

## 2.2 Nitration of Benzene

The nitration of benzene involves the substitution of one of the H atoms on the benzene with a nitro ( $-\text{NO}_2$ ) group. It has a number of specific requirements:

**Conditions:** Concentrated  $\text{HNO}_3$ , concentrated  $\text{H}_2\text{SO}_4$  catalyst.  
*Constant* temperature of  $50^\circ\text{C}$ .

**Observations:** *Pale yellow* oily liquid, nitrobenzene.

### IV. A New Electrophile

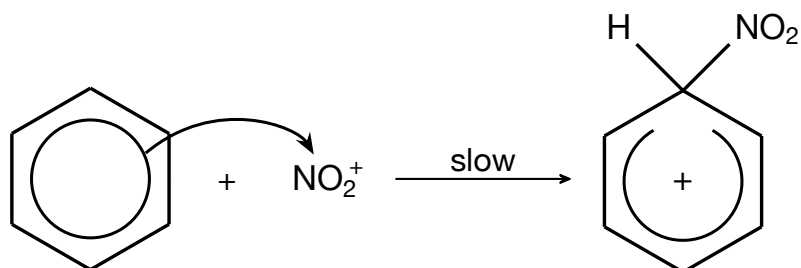
Since  $\text{H}_2\text{SO}_4$  is a stronger acid than  $\text{HNO}_3$ , it donates a proton to  $\text{HNO}_3$ , forming  $\text{H}_2\text{O}$ ,  $\text{HSO}_4^-$ , and  $\text{NO}_2^+$ , the electrophile. Next, another molecule of  $\text{H}_2\text{SO}_4$  then forms  $\text{H}^+_{(\text{aq})}$ , or  $\text{H}_3\text{O}^+$ . The overall equation is as such:



The catalyst  $\text{H}_2\text{SO}_4$  is restored in a later step.

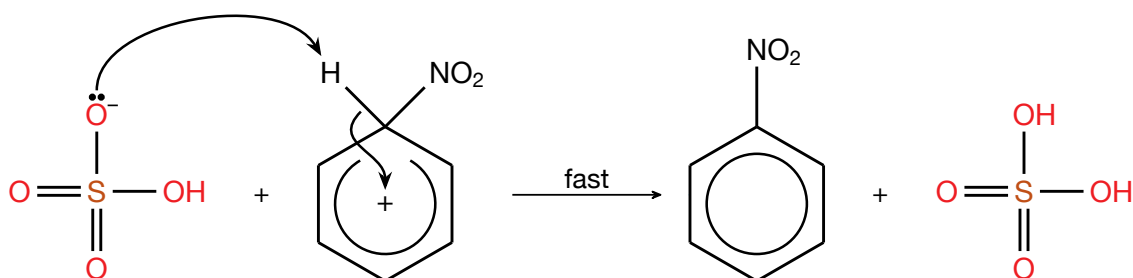
## V. The $\pi$ -Electrons Strike Back

Now that the electrophile  $\text{NO}_2^+$  has been formed, it is attacked by the  $\pi$ -system. As with all electrophilic substitutions, this involves the breaking of the aromatic system, and is the slow step. The mechanism follows the general mechanism outlined above.

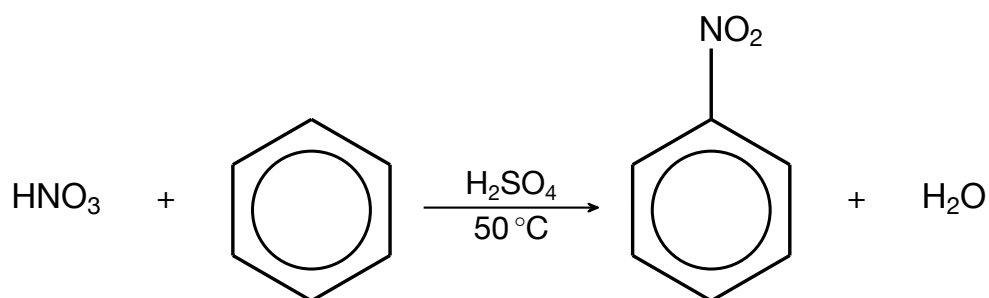


## VI. Return of the Aromaticity

The  $\text{HSO}_4^-$  intermediate acts as a nucleophile and attacks the H atom bonded to the benzene intermediate. This restores both the  $\pi$ -system of the benzene ring, as well as the catalyst,  $\text{H}_2\text{SO}_4$ .



## VII. Overall Reaction



## 2.3 Halogenation of Benzene

Halogenation of benzene requires rather specific conditions, such as anhydrous  $\text{FeBr}_3$  or  $\text{FeCl}_2$  (for a reaction with bromine and chlorine respectively), and a warm environment.

Aluminium-based analogues of these catalysts ( $\text{AlBr}_3$ ,  $\text{AlCl}_3$ ) can also be used, as can pure filings of the metal, in which case the catalyst will be generated *in-situ* ( $2\text{Fe}_{(\text{s})} + 3\text{Br}_{2(\text{l})} \longrightarrow 2\text{FeBr}_3$ ).

**Conditions:** Warm, anhydrous  $\text{FeBr}_3$ ,  $\text{AlBr}_3$ , or Fe / Al filings (for bromine),  
Anhydrous  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ , or Fe / Al filings (for chlorine)

**Observations:** *Reddish-brown*  $\text{Br}_2$  / *yellowish-green*  $\text{Cl}_2$  decolourises.  
Formation of white fumes of HX gas.

### 2.3.1 Conditions for Reaction

Lewis acid catalysts must be used, since the  $\text{Br}-\text{Br}$  and  $\text{Cl}-\text{Cl}$  are only instantaneously polar (instantaneous dipole moments). As such, they are nowhere near strong enough to attack the benzene system on their own.

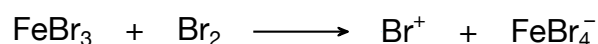
Indeed, this can be used to distinguish between alkenes and benzenes, since the former does not require a catalyst for addition of halogens.

Furthermore, the entire reaction must be conducted in the absence of water; the reaction mechanism for the lewis-acid catalyst involves accepting a lone pair, the lone pair on water can, and will, in sufficient concentrations, destroy the catalyst.

### 2.3.2 Reaction Mechanism

#### Generation of Electrophile

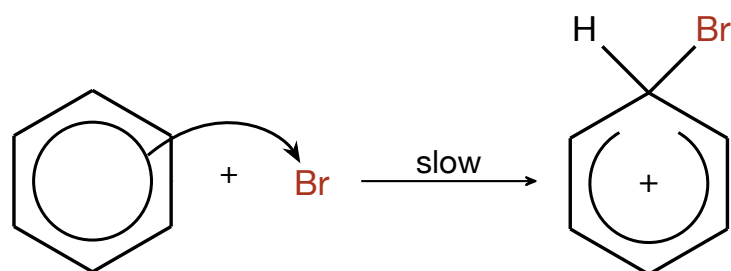
The reaction below uses Iron (III) chloride ( $\text{FeCl}_3$ ) as an example, adding  $\text{Cl}$  to benzene, and this reaction mechanism applies to aluminium-based catalysts as well.



The catalyst is  $\text{FeBr}_4^-$  — the *electrophile* is  $\text{Br}^+$

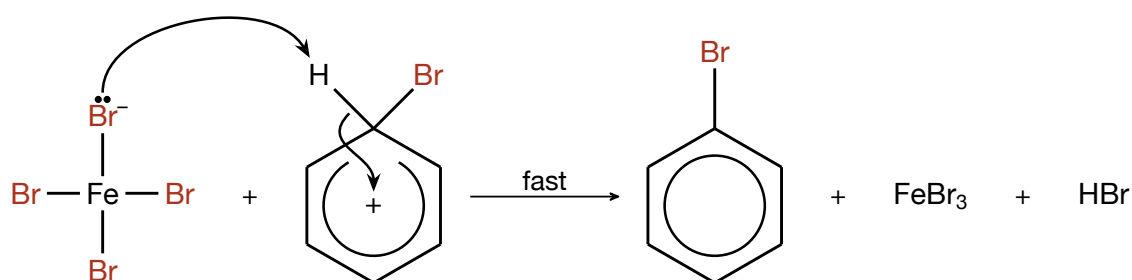
## Formation of Benzene Intermediate

Again, this mechanism is similar in nature to electrophilic substitution in general. Now, the electrophile ( $\text{Br}^+$ ) attacks the  $\pi$ -system, forming the arenium ion.

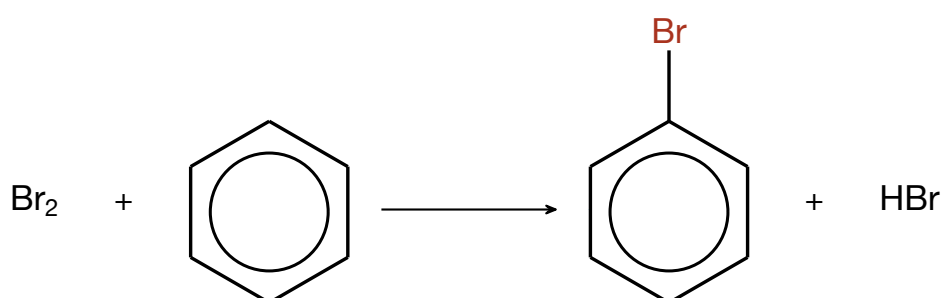


## Restoration of $\pi$ -system and Aromaticity

In the final step, the  $\text{FeBr}_4^-$  acts as a nucleophile, attacking the H atom attached to the benzene intermediate. This regenerates the catalyst  $\text{FeBr}_3$ , and also forms  $\text{HBr}$ .



## Overall Reaction



## 3 Substituted Benzenes

The primary reaction mechanism of benzenes is electrophilic substitution, which involves the electrophiles attacking the electron-rich  $\pi$ -system of the benzene ring. As mentioned in Chapter 4 on Induction and Resonance, certain groups and atoms have the ability to withdraw or donate electrons, which affects the characteristics of the benzene ring.

### 3.1 Effect of Reactivity

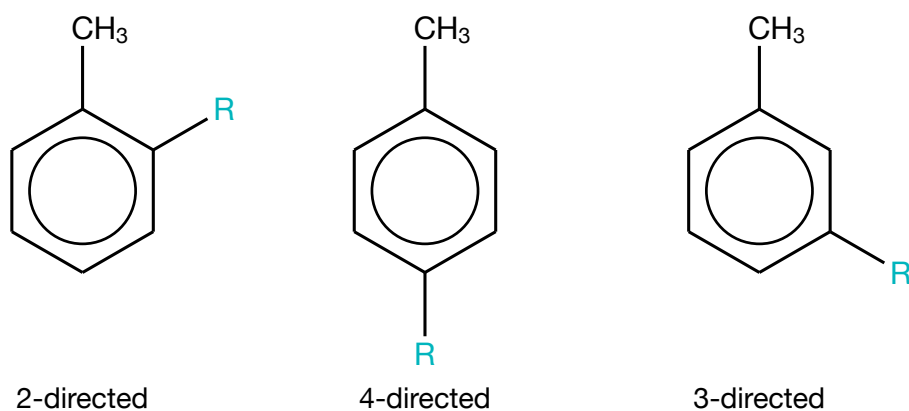
If a benzene has electron-donating substituents, (such as  $\text{CH}_3$ ) it will be more reactive, since it would increase the electron density of the  $\pi$ -system, making it a more appealing target for electrophiles. Thus, the ring is said to be *activated*. Conversely, electron-withdrawing substituents (such as  $-\text{NO}_2$  or  $-\text{CO}_2\text{H}$ ) *deactivate* the benzene, which decreases the reactivity of the benzene ring by making it less susceptible to electrophilic attacks.

Importantly, it *must be noted* that for the nitration of benzene, when the benzene ring is *activated*, the required temperature for reaction is only **30 °C**, whereas for *deactivated* rings, the required temperature is **above 50 °C**.

### 3.2 Effect on Positions of Further Substituents

Since the main way substituents affect the benzene ring is through the distortion of its  $\pi$ -system electrons, naturally this distortion can affect the positions of additional substituents on the ring.

For instance, an electrophilic substitution, of an electrophile R on methylbenzene can produce 3 possible products:



In this case, the  $\text{CH}_3$  is considered to be attached to carbon 1.

The exact reasoning for this directing behaviour is complex, and has to deal with the resonance structures of the intermediate benzene, and the distribution of electrons

within the  $\pi$ -system. Furthermore, there are only two types of substituents: *2,4-directing* and *3-directing*. Also note that this is similar in concept to major and minor products; both will be produced, except one in much larger quantities.

The directing effects of various groups are summarised below.

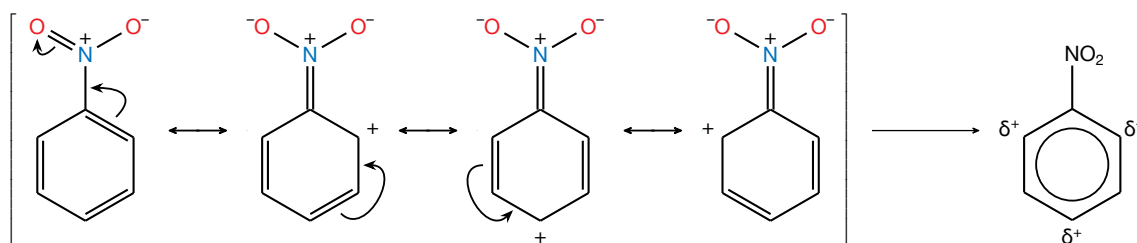
Substituent	Electron Effect	Directing Effect
Alkyl/aryl groups (eg. $-\text{CH}_3$ )	Weakly Activating	2,4-directing
$-\text{OH}$ , $-\text{NH}_2$ , $-\text{OCH}_3$	Strongly Activating	2,4-directing
$-\text{Cl}$ , $-\text{Br}$	Weakly Deactivating	2,4-directing
$-\text{CHO}$ , $-\text{NO}_2$ , $-\text{CN}$ , $-\text{CO}_2\text{H}$	Strongly Deactivating	3-directing

### 3.3 Directing Mechanism

The exact mechanism behind the directing effects of substituents can be explored through the resonance structure of the substituted ring. Technically, the 2, 3, and 4 positions are called *ortho*, *meta*, and *para* respectively. It's just a naming thing.

#### 3.3.1 Electron-withdrawing Groups

Taking nitrobenzene as an example, the attached  $\text{NO}_2$  group is electron-withdrawing. As such, based on the resonance structure of the  $\pi$ -system below, there will be three points with a partial positive charge ( $\delta^+$ ). Since the substitution requires the attack of an *electrophile*, these positions are *less favourable*. Hence, the electrophile will tend to target the meta (or 3-directed) position, and the  $\text{NO}_2$  group is said to be meta-directing, or 3-directing.

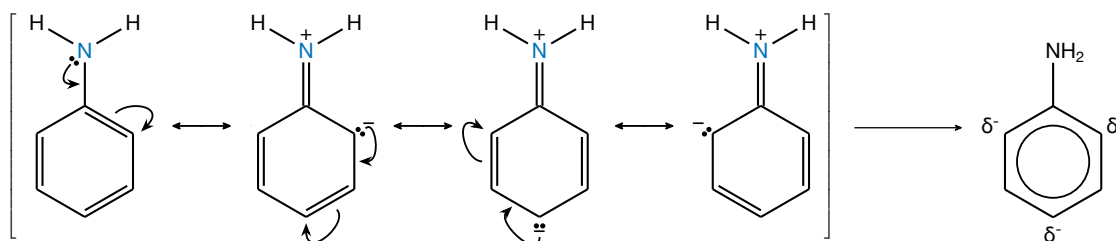


The  $\delta^+$  positions represent areas of low electron density.



### 3.3.2 Electron-donating Groups

On the other hand, for an electron-donating group such as  $\text{NH}_2$ , the reverse is true; there will be 3 areas of *high electron density* (actually the same 3 positions), which *attracts* electrophiles, and as such favours substituting further groups on the ortho/para positions, or 2,4 positions. Thus,  $\text{NH}_2$  is said to be ortho/para-directing, or 2,4-directing.



The  $\delta^-$  positions represent areas of high electron density.

### 3.3.3 Halogen Substituents

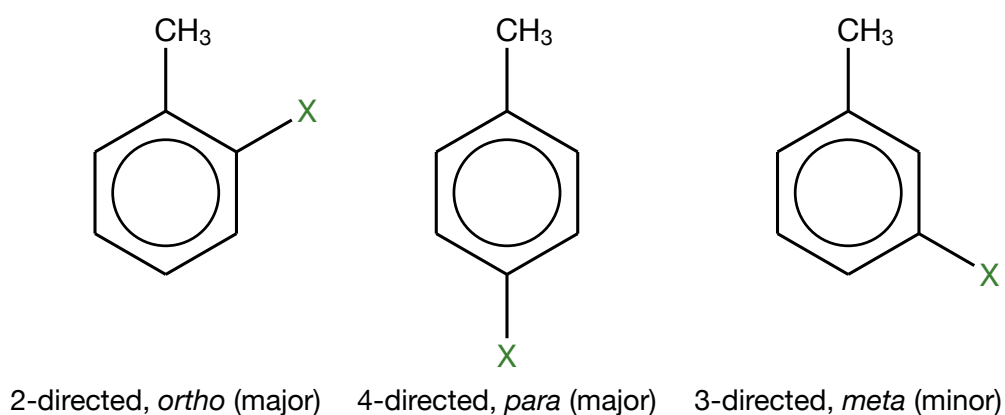
Halogens are a special case, since they can donate electrons through induction, but can also withdraw electrons through the resonance effect due to their substantial electronegativity difference, compared to carbon.

The overall effect is that halogens are *ortho/para* directors.

## 3.4 Alkylbenzene Reactions

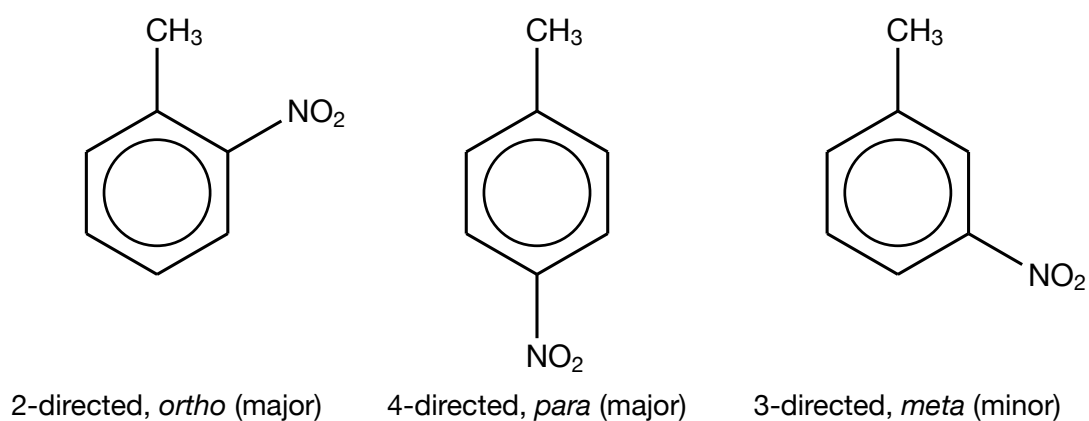
### 3.4.1 Halogenation

The reagents and conditions for the halogenation of alkylbenzenes is similar to that of normal, unsubstituted benzenes. This time, however, there are two major products, and one minor product, due to the 2,4-directing nature of alkyl groups.



### 3.4.2 Nitration

Similarly, the nitration of alkylbenzenes also gives two major products, and one minor product.

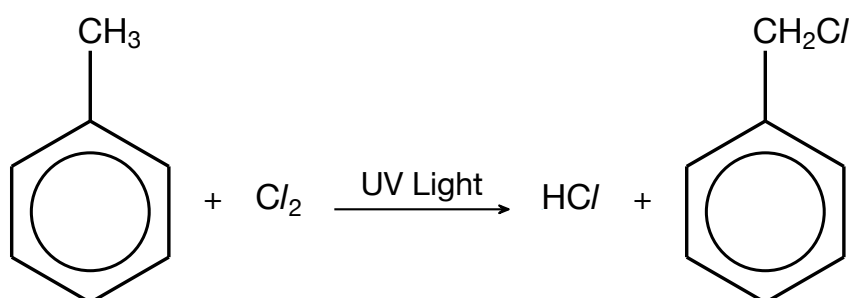


### 3.4.3 Free Radical Substitution

In the absence of Lewis-acid catalysts, halogens will not react with the benzene ring, due to the high unfavourability of that reaction. However, remember that reactants can, and will, react with *any* functional group on the molecule. In this case, the halogens will react with the alkyl side-chain of the alkylbenzene. The conditions are identical to that of regular free radical substitution.

**Conditions:** UV Light, Br<sub>2</sub> / Cl<sub>2</sub> gas

**Observations:** *Reddish-brown* Br<sub>2</sub> / *yellowish-green* Cl<sub>2</sub> decolourises.



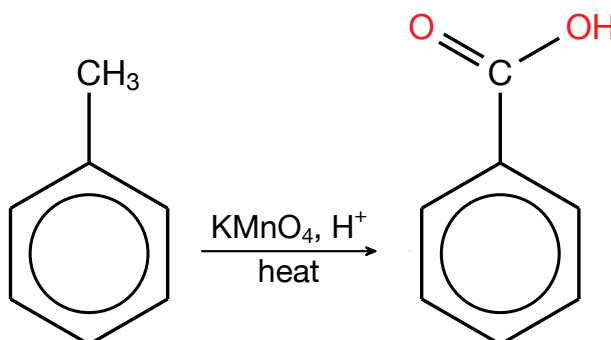
Naturally, the alkyl side-chain can also undergo multiple substitutions, giving a mix of products and isomers.

### 3.4.4 Side-chain Oxidation

When reacted with the strong oxidising agent, KMnO<sub>4</sub>, and heated, the alkyl chain attached to the benzene will be oxidised. Regardless of the length of the chain, benzoic acid is always formed.

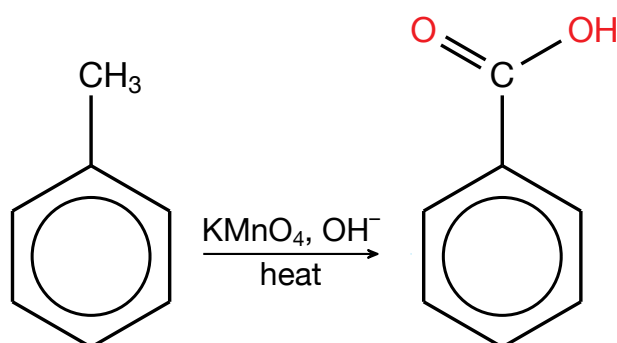
**Conditions:** Heat, KMnO<sub>4</sub>, dilute acid or alkali.

**Observations:** *Purple* KMnO<sub>4</sub> decolourises (*acid*), or forms *brown* precipitate of MnO<sub>2</sub> (*alkali*).

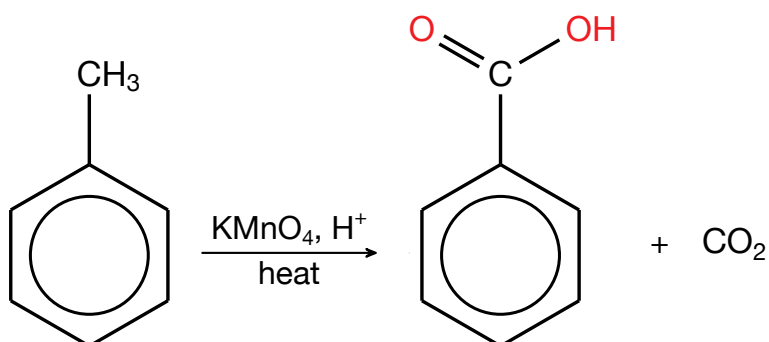


In this case, an acidic medium is used, hence H<sup>+</sup>.

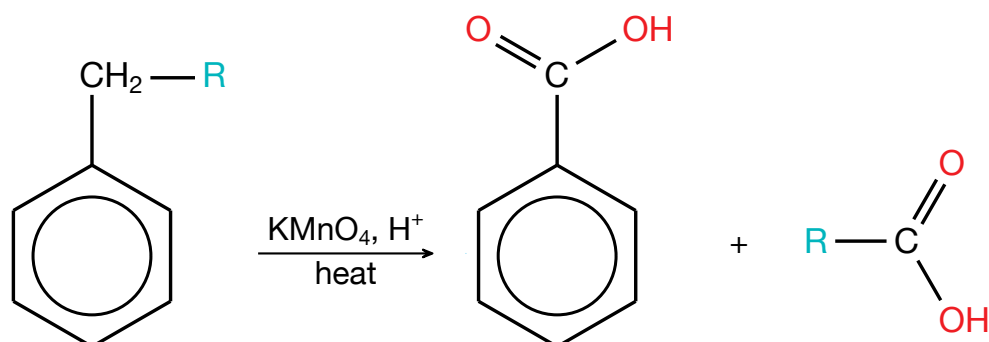
Alternatively, an alkali medium can be used, for instance with  $\text{NaOH}_{(\text{aq})}$ . Instead of forming benzoic acid however, the benzoate ion is formed, which would form an ionic bond with Na.



If the alkyl chain is 2-long, (ie. ethylbenzene), then  $\text{CO}_2$  will be formed from the oxidation of the second carbon, in addition to benzoic acid.



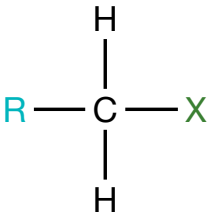
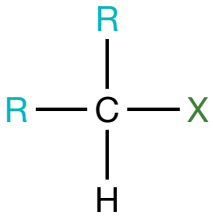
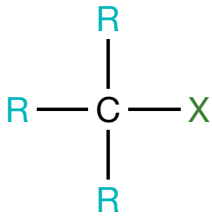
If the chain is 3 or longer, then the rest of the chain (apart from the first) will be oxidised to form a carboxylic acid.



# viii Halogen Derivatives

## 1 Halogenoalkanes (Alkyl Halides)

Halogenoalkanes are simply alkanes, with one or more halogen atoms taking the place of a hydrogen atom. They are classified in a similar way to alkanes and alcohols.

		
Primary (1°)	Secondary (2°)	Tertiary (3°)

### 1.1 Physical Properties

Halogenoalkanes are generally colourless like their alkane counterparts, and might have a sweetish smell.

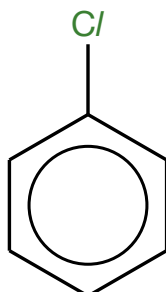
Compared to their alkane counterparts, halogenoalkanes have a higher boiling point for the same carbon chain length, mainly due to the increased size of the halogen atom. The primary method of intermolecular bonding is still via instantaneous dipole-induced dipole interactions, which is strengthened by the larger electron cloud, and thus results in a higher *polarisability* of the molecule.

However, permanent-dipole interactions are still present, and contribute slightly to the increase in melting and boiling points. This is of more significance for chloroalkanes, since *Cl* is more negative than both *Br* and *I*, hence creating a larger dipole moment.

When comparing between different halogens with otherwise identical carbon chains, the melting and boiling points increases as the halogen atom's size increases — the instantaneous dipole-induced dipole interaction plays a larger role in determining that.

## 2 Halogenoarenes

Halogenoarenes are simply molecules where the halogen atom is *directly attached* to the benzene ring.



Chlorobenzene is a halogenoarene.

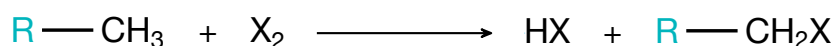
## 3 Creation of Halogenated Molecules

### 3.1 Free Radical Substitution of Alkanes

As covered above, alkanes can undergo free radical substitution, replacing one or more of their hydrogen atoms with halogen atoms.

**Conditions:** UV Light, Br<sub>2</sub> / Cl<sub>2</sub> gas

**Observations:** *Reddish-brown* Br<sub>2</sub> / *yellowish-green* Cl<sub>2</sub> decolourises.



However, this is usually a *bad* way to prepare halogenoalkanes, due to the mix of products that will be formed, including isomers and multisubstituted molecules. It is difficult (or nigh impossible) to control the extent or position of substitution, but to decrease the chances of multisubstitution, the alkane should be used in excess, as a last resort.

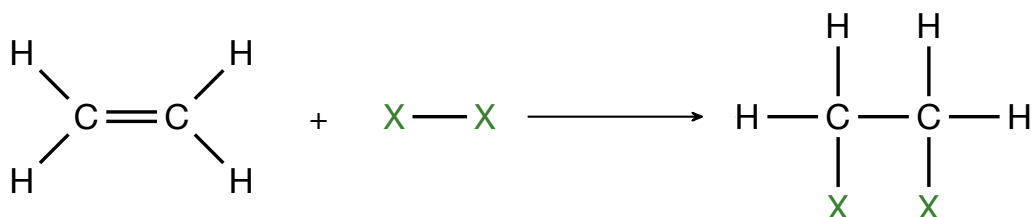
## 3.2 Electrophilic Addition to Alkenes

### 3.2.1 Addition of $X_2$

Halogen molecules ( $X_2$ ) can be added to alkenes to form halogenoalkanes, as covered above. Naturally, this results in having two halogen atoms in the molecule, or a *dihalide*.

**Conditions:** No UV Light, gaseous  $X_2$ .

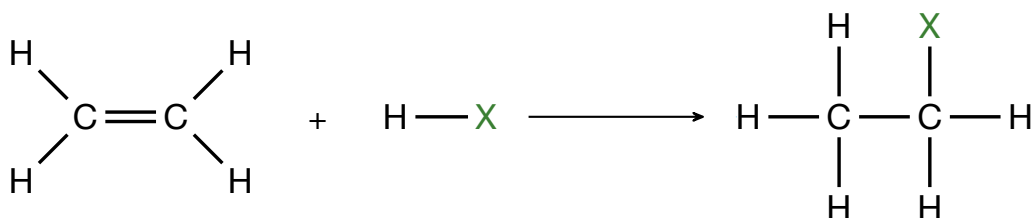
**Observations:** *Reddish-brown*  $Br_2$  / *yellowish-green*  $Cl_2$  decolourises.



### 3.2.2 Addition of HX

Gaseous HX can also be added, resulting in a monohalogenated molecule.

**Conditions:** Gaseous HX (usually HCl or HBr).

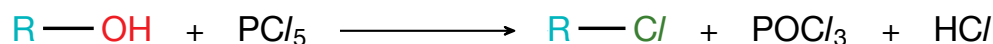


### 3.3 Substitution of OH groups (Chloroalkanes)

#### 3.3.1 Phosphorous Pentachloride ( $\text{PCl}_5$ )

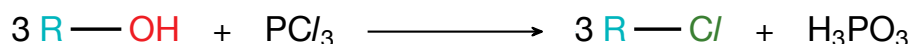
**Conditions:** Solid  $\text{PCl}_5$ , room temperature.

**Observations:** Formation of white fumes of  $\text{HCl}$  gas.



#### 3.3.2 Phosphorous Trichloride ( $\text{PCl}_3$ )

**Conditions:** Solid  $\text{PCl}_3$ , room temperature.

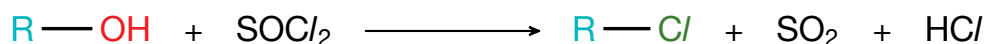


#### 3.3.3 Thionyl Chloride ( $\text{SOCl}_2$ )

This reaction is slightly preferred over the others, since both by-products ( $\text{SO}_2$  and  $\text{HCl}$ ) are gaseous, and would bubble out of the solution, leaving mainly the halogenoalkane in the reaction mixture.

**Conditions:** Warm, liquid  $\text{SOCl}_2$ .

**Observations:** Formation of colourless, pungent  $\text{SO}_2$  gas, and white fumes of  $\text{HCl}$  gas.

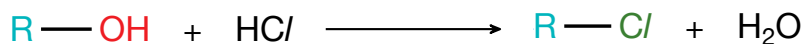




### 3.3.4 Hydrogen Chloride (HCl)

Here, a distinction must be made between *primary*, *secondary*, and *tertiary* alcohols; tertiary alcohols will react fine with simply concentrated HCl.

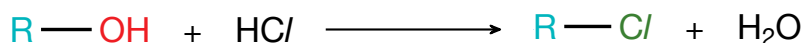
**Conditions:** Concentrated  $\text{HCl}_{(\text{aq})}$  / gaseous HCl OR  
Solid NaCl, concentrated  $\text{H}_2\text{SO}_4$ , heat.



HCl can be prepared *in-situ* with NaCl and  $\text{H}_2\text{SO}_4$ .

For primary and secondary alcohols, anhydrous  $\text{ZnCl}_2$  catalyst must be used, and the reaction mixture must be heated. Apart from that, the reaction is similar.

**Conditions:** Concentrated  $\text{HCl}_{(\text{aq})}$  / gaseous HCl.  
Anhydrous  $\text{ZnCl}_2$  catalyst, heat.

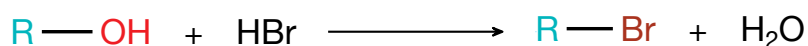


### 3.4 Substitution of OH groups (Bromoalkanes)

#### 3.4.1 Hydrogen Bromide (HBr)

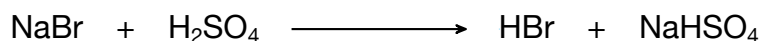
Gaseous hydrogen bromide (HBr) can be reacted with alcohols to give bromoalkanes.

**Conditions:** Gaseous HBr.



HBr can be prepared by reacting concentrated  $\text{H}_2\text{SO}_4$  with solid NaBr.

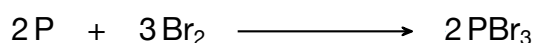
**Conditions:** Solid NaBr, concentrated  $\text{H}_2\text{SO}_4$ , heat.



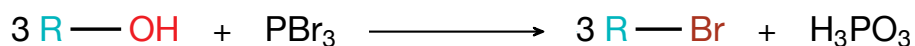
#### 3.4.2 Phosphorous Tribromide ( $\text{PBr}_3$ )

$\text{PBr}_3$  is typically prepared *in-situ* by heating red phosphorous with liquid bromine. It then proceeds to react with the alcohol, in a manner similar to that of  $\text{PCl}_3$ .

**Conditions:** Liquid  $\text{PBr}_3$ , OR  
Liquid  $\text{Br}_2$ , red phosphorous, heat.



*In-situ* formation of  $\text{PBr}_3$ .

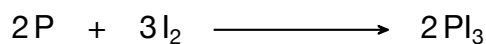


## 3.5 Substitution of OH groups (Iodoalkanes)

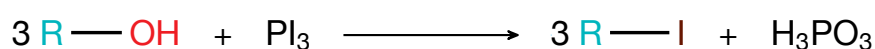
### 3.5.1 Phosphorous Triiodide (PI<sub>3</sub>)

This reaction is identical to the reaction involving PBr<sub>3</sub>, above.

**Conditions:** Liquid PI<sub>3</sub>, *OR*  
Solid I<sub>2</sub>, **red** phosphorous, heat.



*In-situ* formation of PI<sub>3</sub>.

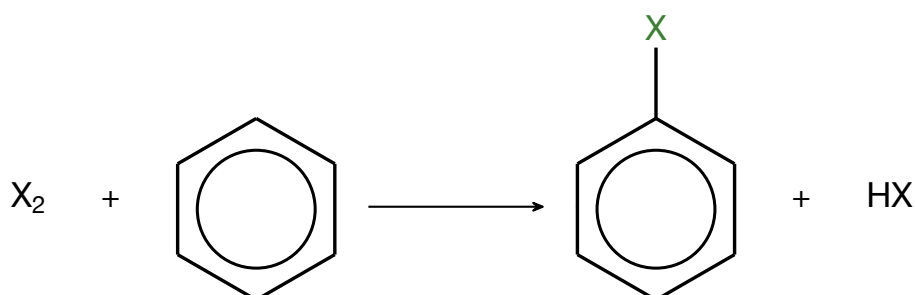


## 3.6 Electrophilic Substitution of Arenes

Halogens can be substituted onto a benzene ring through the use of a catalyst, in an electrophilic substitution reaction.

**Conditions:** Warm, anhydrous FeBr<sub>3</sub>, AlBr<sub>3</sub>, or Fe / Al filings (for bromine),  
Anhydrous FeCl<sub>3</sub>, AlCl<sub>3</sub>, or Fe / Al filings (for chlorine)

**Observations:** **Reddish-brown** Br<sub>2</sub> / **yellowish-green** Cl<sub>2</sub> decolourises.  
Formation of white fumes of HX gas.



## 4 Halogenoalkane Reactions

### 4.1 Nucleophilic Substitution

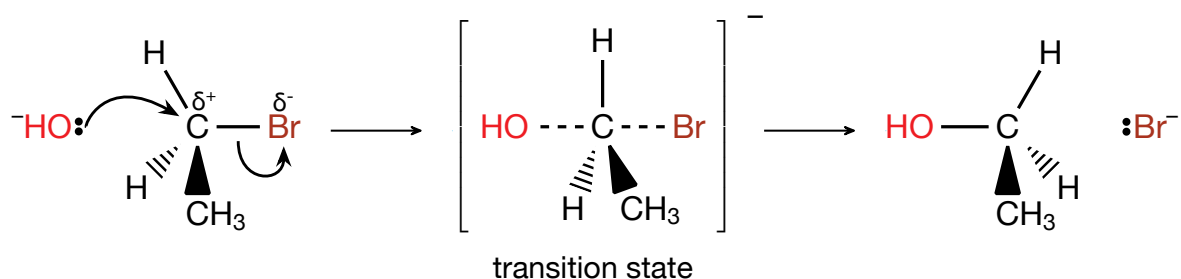
Due to the high relative electronegativity of the halogen atom attached to the carbon atom, the carbon atom is *electron-deficient*, which makes it more susceptible to attacks from nucleophiles (*electron-rich*), and as such halogenoalkanes are fairly reactive.

There are two primary mechanisms of nucleophilic substitution — single-step and two-step reactions. Generally, primary halogenoalkanes (molecules with 1 or 0 alkyl groups attached to the halogen-containing carbon) react via a one-step mechanism, while tertiary halogenoalkanes react via a two-step mechanism. Secondary halogenoalkanes can react via either mechanism, depending on the specific molecule.

The primary differentiating factor is the size of the substituents on the central carbon — larger groups will hinder  $S_N2$  substitution, forcing an  $S_N1$  reaction.

#### 4.1.1 $S_N2$ Mechanism (one-step, bimolecular)

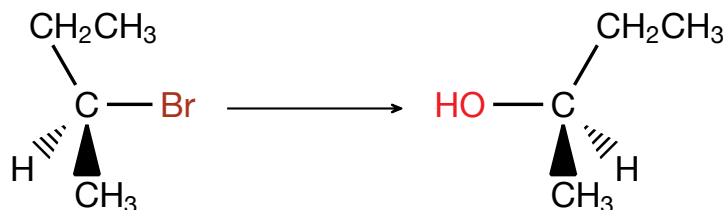
The nucleophilic substitution of  $\text{CH}_3\text{CH}_2\text{Br}$  by  $\text{OH}^-$  is a one-step reaction. Take note that  $S_N2$  is a *one*-step reaction — it is  $S_N2$  because *two* molecules are involved in the slow (only) step.



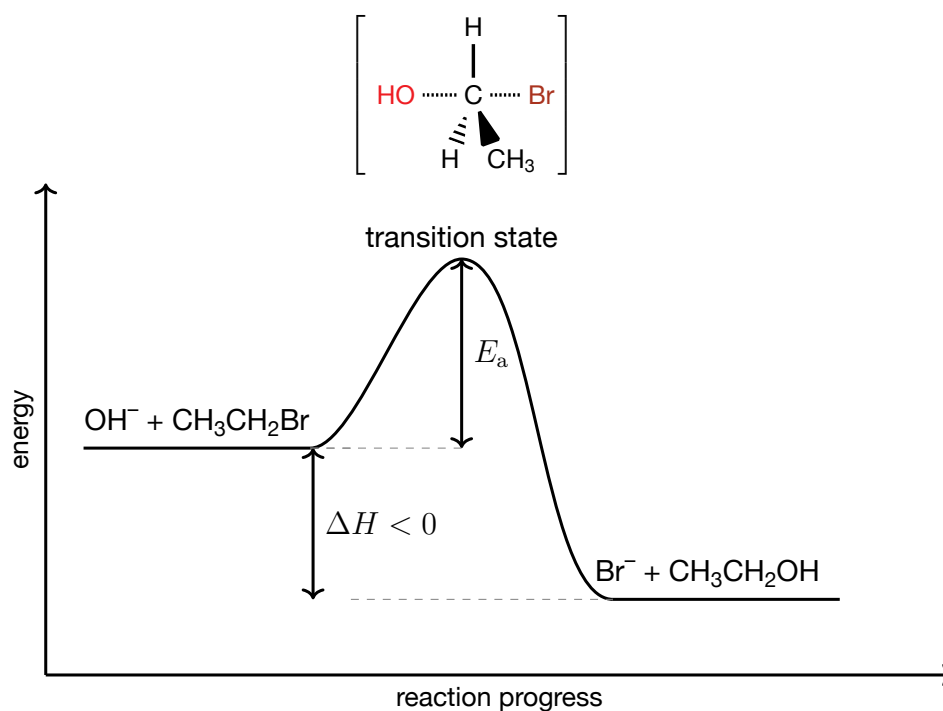
Due to the difference in electronegativity between the C and Br atoms, the  $\text{C}-\text{Br}$  bond is polar. Thus, nucleophiles will be attracted towards the partially-positive carbon atom. They attack from the side opposite the leaving atom (Br in this case) due to spatial constraints.

As the nucleophile attacks, it donates a lone pair to the carbon atom to stabilise it, forming a bond. At the same time, this weakens the  $\text{C}-\text{Br}$  bond, and it begins to break. At this stage, the *transition state* is formed, which is an unstable, activated complex where bond-breaking and bond-forming occur simultaneously — this is a *one-step* mechanism.

Note that the chirality of the molecule will be *inverted*, if it is chiral. Imagine the attacking nucleophile 'pushing' the other groups away from itself.



Since this is a single-step reaction, there is one activation energy step, and the energy profile diagram looks like this:

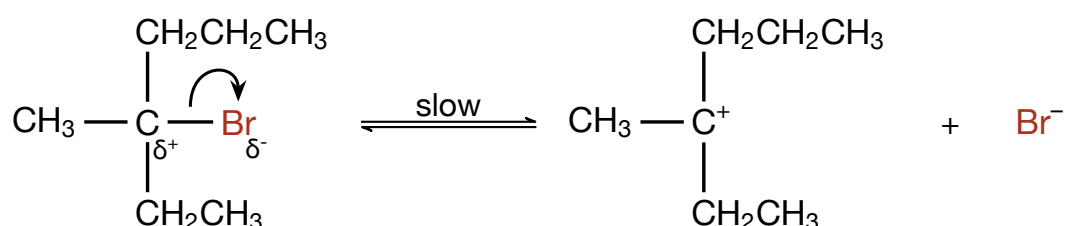


### 4.1.2 S<sub>N</sub>1 Mechanism (two-step, unimolecular)

The S<sub>N</sub>1 reaction is a *two-step* reaction, because larger groups attached to the central carbon often hinder the direct attack of nucleophiles, and thus require the formation of a carbocation. Only one molecule is involved in the slow (first) step, hence it is a unimolecular reaction.

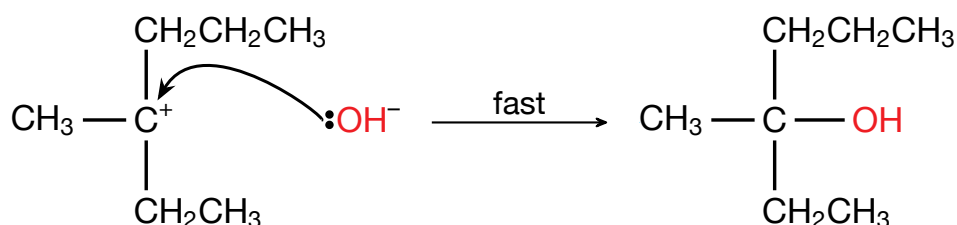
Again, the reaction hinges on the polar C–Br bond, due to the differences in electronegativity.

#### Step 1



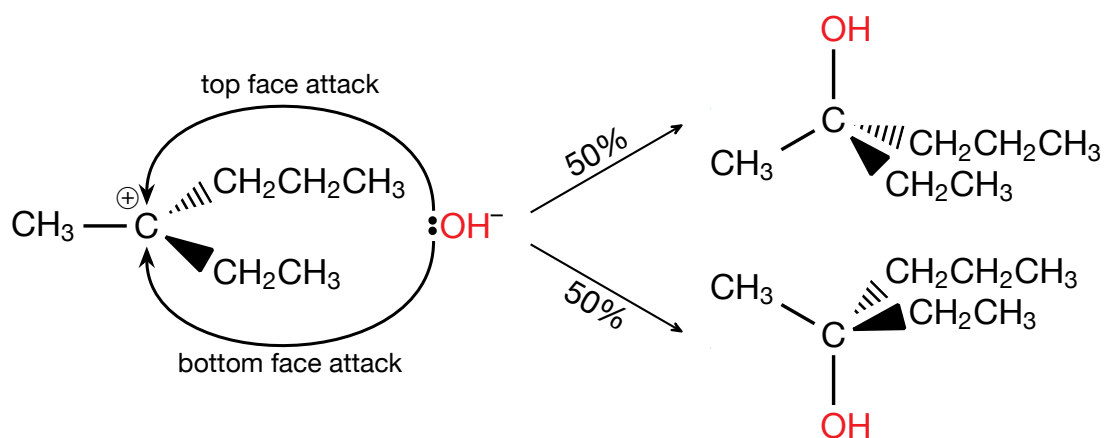
The C–Br bond undergoes heterolytic fission, giving a carbocation intermediate, and a bromide ion. The reaction is more feasible due to the 3 electron-donating alkyl groups that stabilise the positive charge on the carbocation intermediate, which would not be possible in a primary alcohol.

#### Step 2

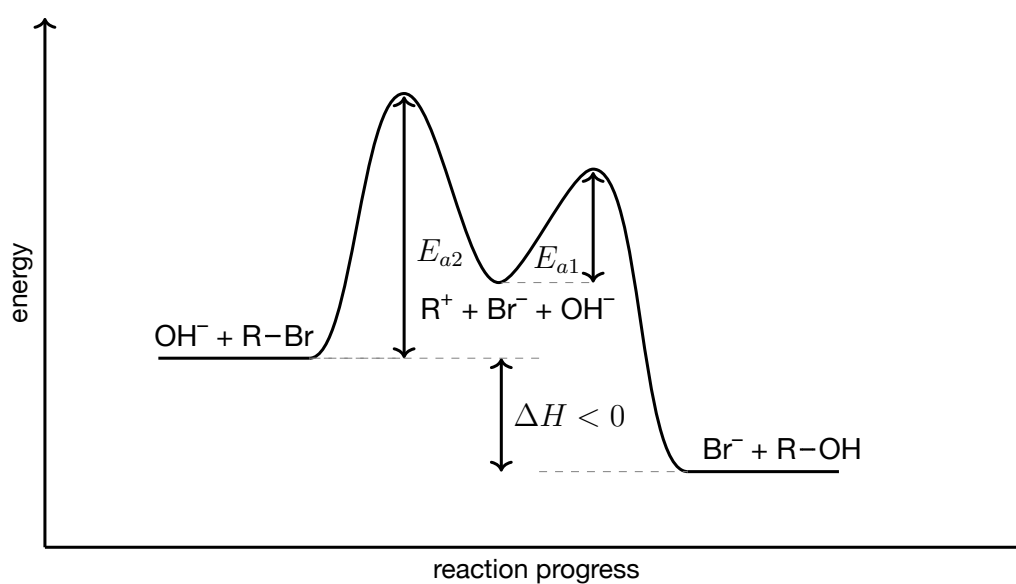


The carbocation intermediate is now attacked by the OH<sup>−</sup> ion, forming the product.

Since the carbocation is trigonal planar (wrt. the central carbon), the nucleophile can attack from both sides of the carbocation, with equal probability. Hence, if the product formed is chiral, the resulting solution will be a *racemic mixture*.



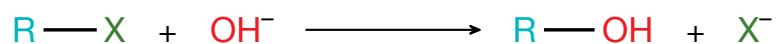
Since this is a two-step reaction, there are two activation energies that must be overcome, and isolatable intermediates (the carbocation and bromide ion).



### 4.1.3 Formation of Alcohols

The  $\text{OH}^-$  ion acts as a nucleophile, substituting the attached halogen atom.

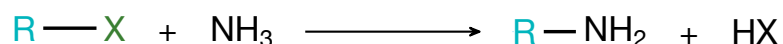
**Conditions:** Aqueous NaOH or KOH, heat.



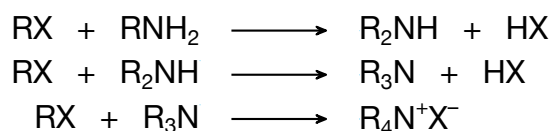
### 4.1.4 Formation of Amines

This reaction forms a primary amine. Ethanolic  $\text{NH}_3$  is simply a solution of  $\text{NH}_3$  in ethanol. Also, the reaction mixture must be heated in a sealed tube, to prevent the  $\text{NH}_3$  from escaping.

**Conditions:** Ethanolic concentrated  $\text{NH}_3$ , heat in sealed tube.



However, this amine turns out to be a *stronger* nucleophile than  $\text{NH}_3$ , which opens the possibility for multiply-substituted amines, forming secondary amines, tertiary amines, and even quaternary ammonium salts.



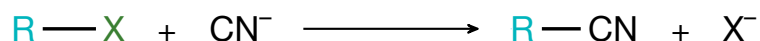
Thus, to prevent this from happening,  $\text{NH}_3$  should be used in excess, in essence 'crowding-out' the amines formed from reacting further.



### 4.1.5 Formation of Nitriles

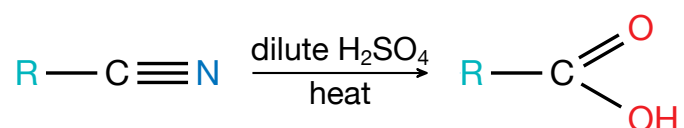
In this reaction, the lone pair is donated not by the nitrogen atom, but by the *carbon* atom. This reaction is important, as it serves to increase the length of the carbon chain — a *step-up* reaction — which is useful in the synthesis of organic molecules.

**Conditions:**      Ethanolic KCN, heat.



Indeed, the nitrile that is formed can be hydrolysed to form carboxylic acids.

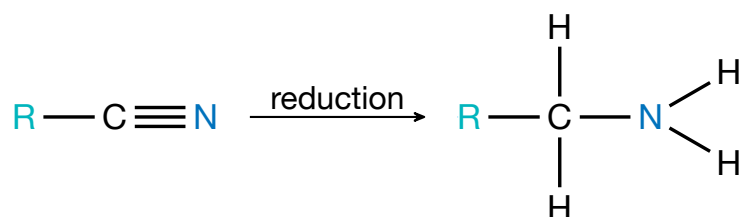
**Conditions:**      Dilute  $\text{H}_2\text{SO}_4$ , heat.



If NaOH is used instead of  $\text{H}_2\text{SO}_4$ , a carboxylate salt is formed instead.

Furthermore, it can also be reduced to form amines, either through the very strong reducing agent  $\text{LiAlH}_4$  (dissolved in dry, diethyl ether due to its high reactivity with water), the slightly weaker  $\text{NaBH}_4$  dissolved in methanol, or the traditional, copious application of  $\text{H}_2$  gas with a metal catalyst at high temperatures and pressures.

**Conditions:**       $\text{LiAlH}_4$  in dry ether (diethyl ether), *OR*  
                          $\text{NaBH}_4$  in methanol, *OR*  
                          $\text{H}_{2(\text{g})}$ , Ni catalyst, high temperature and pressure.

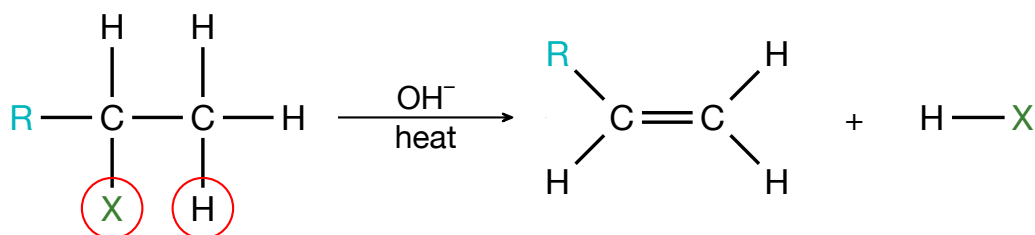


If NaOH is used instead of  $\text{H}_2\text{SO}_4$ , a carboxylate salt is formed instead.

## 4.2 Elimination

$\text{OH}^-$  behaves as a Brønsted-Lowry base, accepting, or in this case removing, an  $\text{H}^+$  ion from the halogenoalkane. At the same time that this  $\text{C-H}$  bond breaks, the  $\text{C-X}$  bond in the adjacent carbon atom breaks, thus forming  $\text{HX}$ , and an alkene.

**Conditions:**      Ethanolic  $\text{KOH}$  or  $\text{NaOH}$ , heat.



The alkane can be of any length, the important bit happens here. The circled atoms are the ones forming the  $\text{HX}$  molecule.

Naturally, isomerism, either optical or cis/trans ( $\text{E/Z}$ ), may occur, and a mix of products can be formed.

One might notice that these reaction conditions are similar to that for the nucleophilic substitution of alcohols. Indeed, both reactions will occur at the same time, forming both alcohols and alkenes.

To favour one reaction over the other, there are a number of factors that can be controlled

- Type of halogenoalkane (primary, secondary or tertiary)
- Temperature of reaction mixture
- Concentration of  $\text{KOH}$  or  $\text{NaOH}$
- Solvent used (ethanol or water)

Primary halogenoalkanes tend to mainly favour nucleophilic substitution, while tertiary halogenoalkanes tend to favour the elimination reaction — secondary halogenoalkanes favour either reaction.

Furthermore, the higher the temperature of the mixture, the more likely it is that the elimination reaction will take place. A higher concentration of  $\text{NaOH}$  or  $\text{KOH}$  will also increase the likelihood of the elimination reaction occurring. Finally, using ethanol as a solvent for the hydroxide, versus water, will also favour elimination.

## 5 Halogenoarene Reactions

Since the halogen atom is directly bonded to the benzene ring, its p-orbitals overlap in a parallel manner to the  $\pi$ -system of the benzene ring, and thus get delocalised.



This makes the bond stronger than a typical C–X bond, and also reduces the effect of the electronegativity of the halogen atom. Thus, it is less susceptible to nucleophile attacks, and is fairly unreactive. The high electron density also tends to repel the electron-rich nucleophiles.

### 5.1 Electrophilic Substitution

Of course, being attached to a benzene ring, halogenoarenes can undergo electrophilic substitution — this is really a reaction of the benzene ring, not specific to the halogen.

However, it must be noted that since halogens are deactivating, the conditions for some reactions become slightly harsher; nitration would require temperatures *above* 50 °C. Also, it is *ortho/para*, or 2,4-directing.

## 6 Distinguishing Tests

### 6.1 Comparing Colour of Precipitate

The primary means of determining the identity of the attached halogen is by looking at the colour of the precipitate formed, when reacted with  $\text{AgNO}_3$  — silver halides are insoluble.

1. Aqueous  $\text{NaOH}$  or  $\text{KOH}$  is added with heat, to substitute the halogen with an  $\text{OH}^-$  group, forming the  $\text{X}^-$  ion.
2. Excess, dilute  $\text{HNO}_3$  is added to neutralise unreacted  $\text{OH}^-$ .
3. Aqueous  $\text{AgNO}_3$  is added, to form the  $\text{AgX}$  precipitate.

**Conditions:** Aqueous  $\text{NaOH}$  or  $\text{KOH}$ , dilute  $\text{HNO}_3$ , aqueous  $\text{AgNO}_3$ .

<b>Observations:</b>	Chlorine	White precipitate of $\text{AgCl}$ .
	Bromine	Cream precipitate of $\text{AgBr}$ .
	Iodine	Yellow precipitate of $\text{AgI}$ .

### 6.2 Comparing Rate of Formation of Precipitate

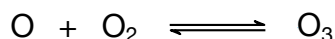
The steps are identical to that above, but instead of comparing the colour, the rate of formation is measured instead. Since the rate-determining step in nucleophilic substitution involves breaking the  $\text{C-X}$  bond, the weaker this bond, the faster the precipitate will form.

Hence, iodoalkanes will form the precipitate the fastest, followed by bromoalkanes, then chloroalkanes.

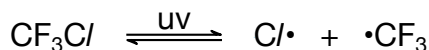
## 7 Chlorofluorocarbons (CFCs)

CFCs were commonly used as refrigerants and aerosol propellants, due to their inert, odourless, and non-toxic properties. Indeed, Teflon is a fluoroalkane, and is typically used to coat non-stick surfaces.

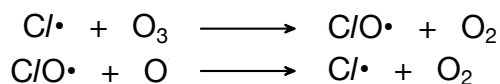
However, under the Montreal Protocol, the use of CFCs were banned due to their harmful effect on the ozone layer. Naturally, there is the following equilibrium in the ozone layer:



Also, in the presence of UV light in the stratosphere, the previously inert chlorofluorocarbons undergo photodecomposition.



When the ozone equilibrium is exposed to these chlorine radicals, they are disrupted, since the radicals can act as a homogeneous catalyst, reforming afterwards.



Thus, the ozone molecules are destroyed, and depletes the free oxygen atoms required in the formation of ozone.