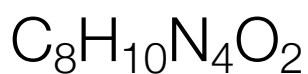
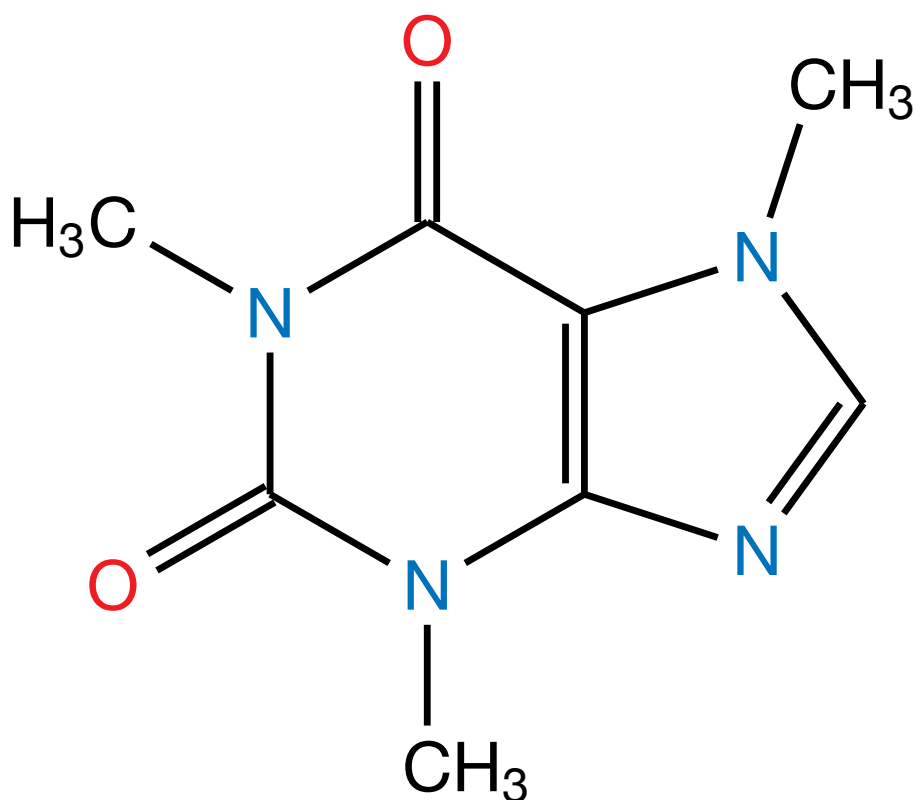


# Organic Chemistry



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

-

Caffeine

Chapters 8 to 12

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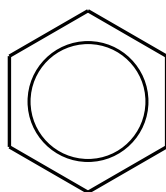
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# I Arenes

## 1 Benzene

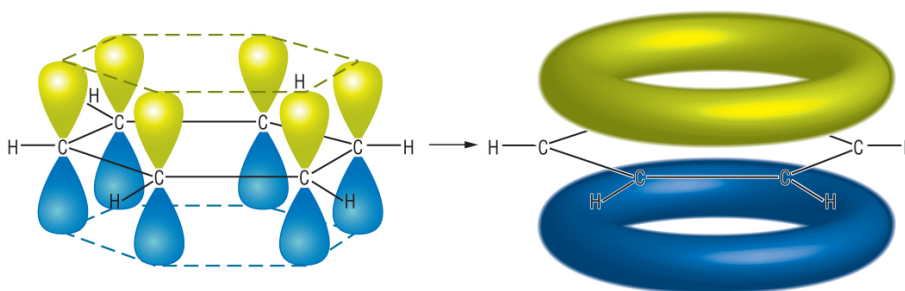
Benzene is simplest possible aromatic compound, or arene. The first known and isolated arene compounds had pleasant smells, such as benzaldehyde. Unfortunately, even though most known arenes now smell terrible and are carcinogenic, the name stuck.



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, the details of which can be found in the *addendum*.

### 2.1 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

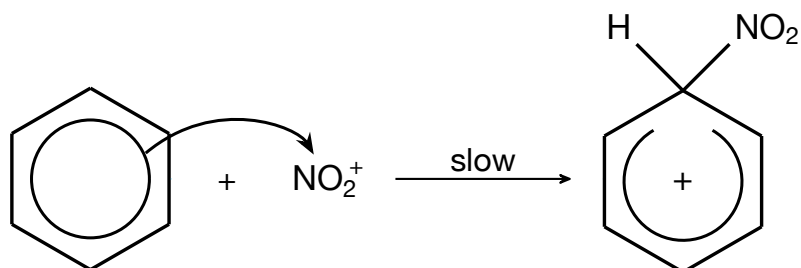
Since  $\text{H}_2\text{SO}_4$  is a stronger acid than  $\text{HNO}_3$ , it donates a proton to  $\text{HNO}_3$ , forming  $\text{H}_2\text{O}$ ,  $\text{HSO}_4^-$ , and  $\text{NO}_2^+$ , the electrophile. Next, another molecule of  $\text{H}_2\text{SO}_4$  then forms  $\text{H}^+$  (aq), or  $\text{H}_3\text{O}^+$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



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

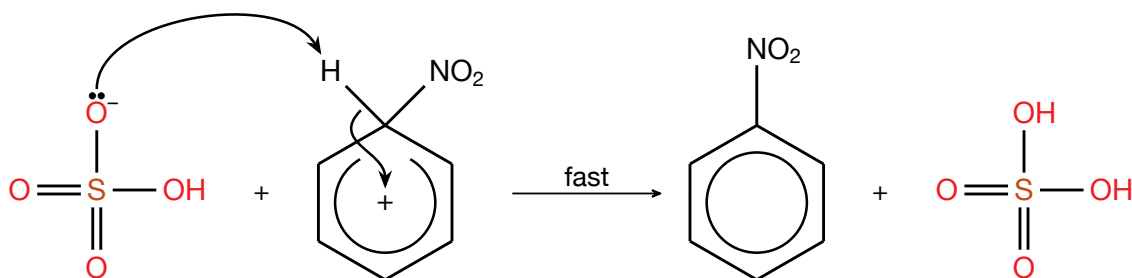
## V. The $\pi$ -Electrons Strike Back

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.

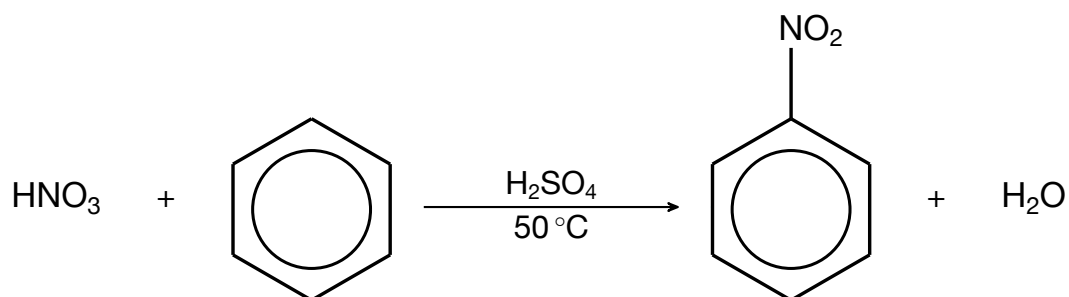


## VI. Return of the Aromaticity

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



## 2.2 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* ( $2 \text{ Fe (s)} + 3 \text{ Br}_2 \text{ (l)} \rightarrow 2 \text{ FeBr}_3$ ).

**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.

### 2.2.1 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.

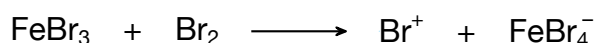
Indeed, this can be used to distinguish between alkenes and benzenes, since the former does not require a catalyst for addition of halogens.

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.

### 2.2.2 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.

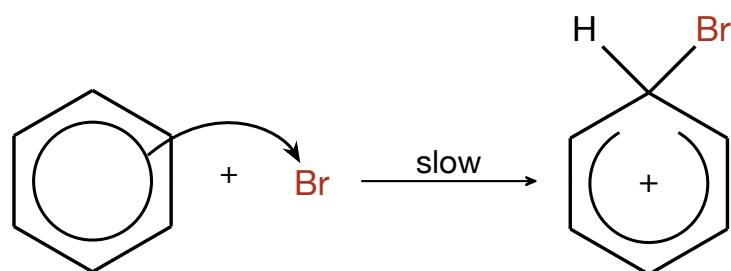


The catalyst is  $\text{FeBr}_4^-$ , and the *electrophile* is  $\text{Br}^+$



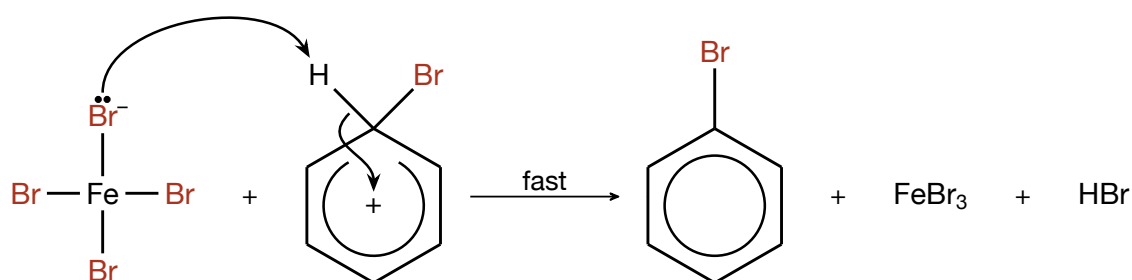
## Formation of Benzene Intermediate

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.

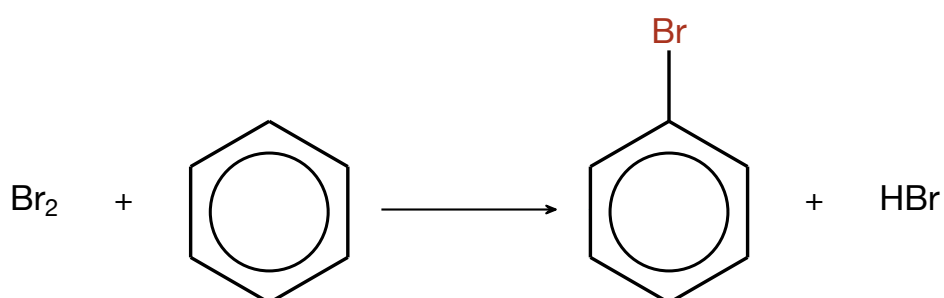


## Restoration of $\pi$ -system and Aromaticity

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

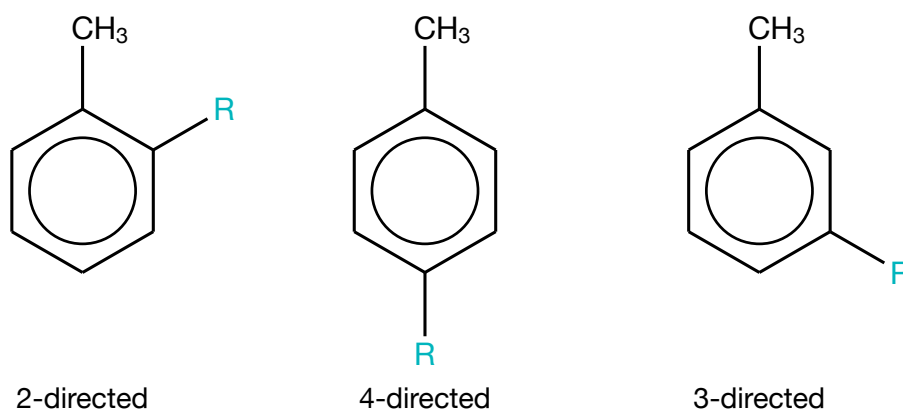
If a benzene has electron-donating substituents, (such as  $\text{CH}_3$ ) it will be more reactive, since it would increase the electron density of the  $\pi$ -system, making it a more appealing target for electrophiles. Thus, the ring is said to be *activated*. Conversely, electron-withdrawing substituents (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  $30^\circ\text{C}$ , whereas for *deactivated* rings, the required temperature is *above*  $50^\circ\text{C}$ .

### 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

For a quick-and-easy way to remember which groups are withdrawing and which are donating, electronegative atoms (O, N, halogens, etc.) are electron withdrawing (deactivating) when they are indirectly attached to the benzene ring, but are generally electron donating (activating) when directly attached to the benzene ring.

This can be explained by the fact that, when directly attached, there is the possibility of a p-orbital overlap with the  $\pi$ -electron cloud of the benzene, thus allowing for the electron density to be added to the benzene ring.

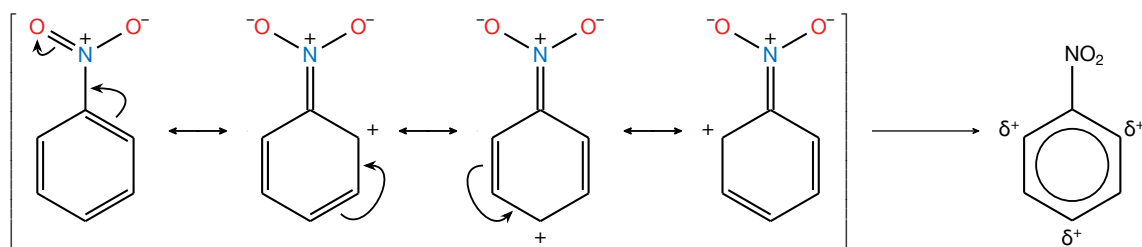
Conversely, when indirectly attached, the effect of electronegativity generally *pulls* the electron density through the  $\sigma$ -bonds. For example, even though N can have its p-orbital overlap with the  $\pi$ -electron cloud,  $-\text{NO}_2$  substituents are still strongly deactivating, as the two highly electronegative O atoms can still act to retract electron density away from the benzene ring, *through* the N atom.

### 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

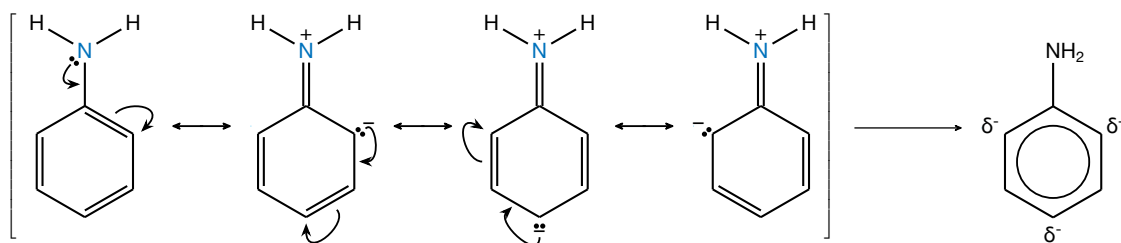
Taking nitrobenzene as an example, the attached  $\text{NO}_2$  group is electron-withdrawing. As such, based on the resonance structure of the  $\pi$ -system below, there will be three points with a partial positive charge ( $\delta^+$ ). Since the substitution requires the attack of an *electrophile*, 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

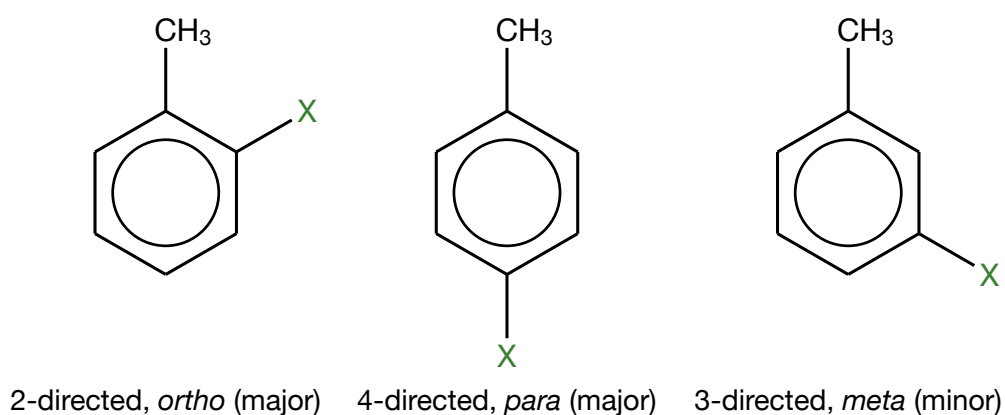
Halogens are a special case, since they can donate electrons through resonance, but can also withdraw electrons through the induction effect due to their substantial electronegativity difference, compared to carbon.

The overall effect is that halogens are *ortho/para* (2,4) directors, and are weakly electron-withdrawing.

## 3.4 Alkylbenzene Reactions

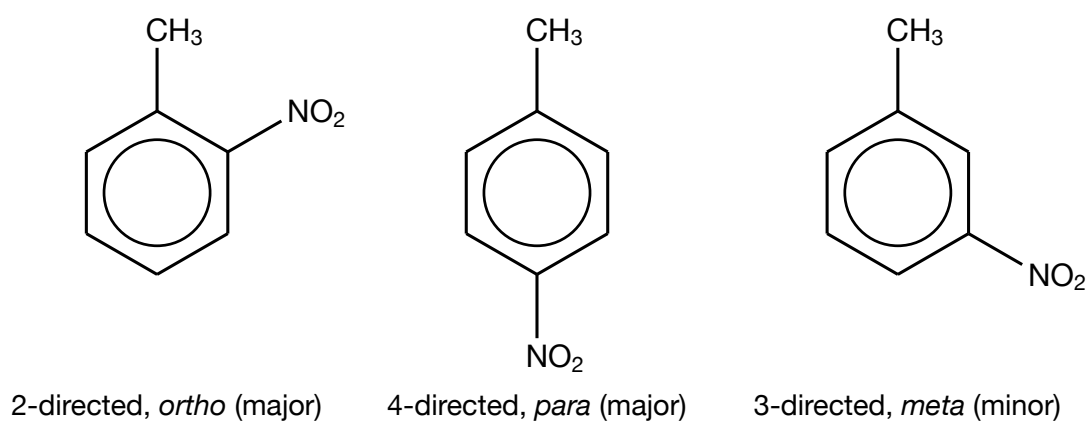
### 3.4.1 Halogenation

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.

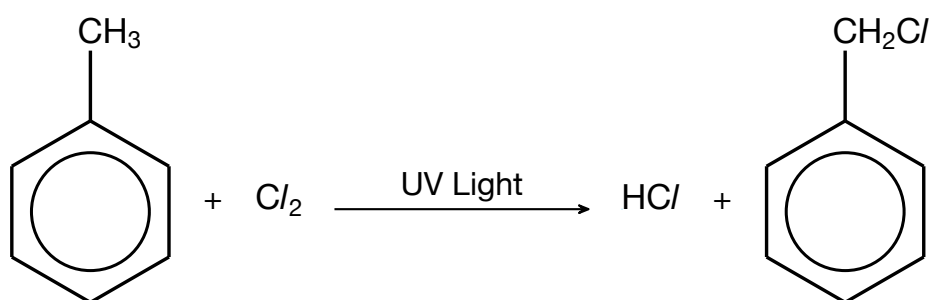


### 3.4.3 Free Radical Substitution

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.



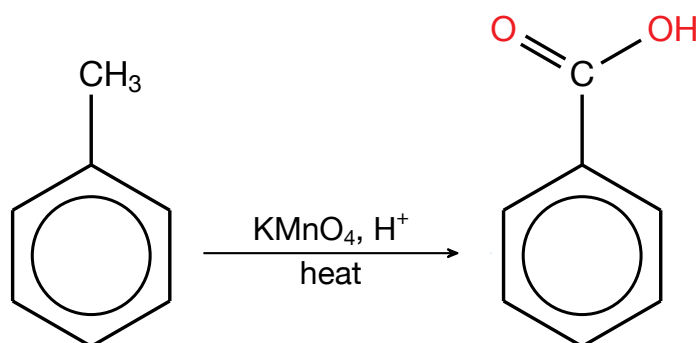
Naturally, the alkyl side-chain can also undergo multiple substitutions, giving a mix of products and isomers.

### 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.

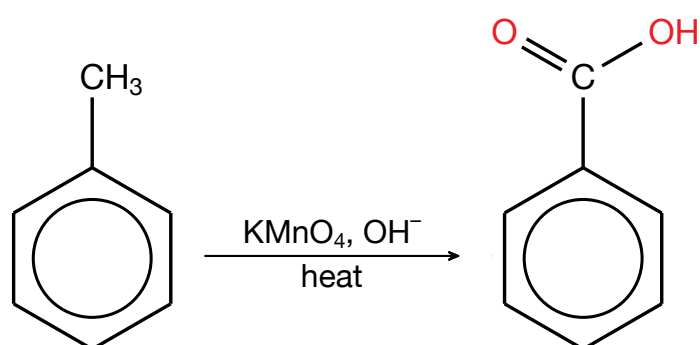
**Conditions:** Heat, KMnO<sub>4</sub>, dilute acid or alkali.

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

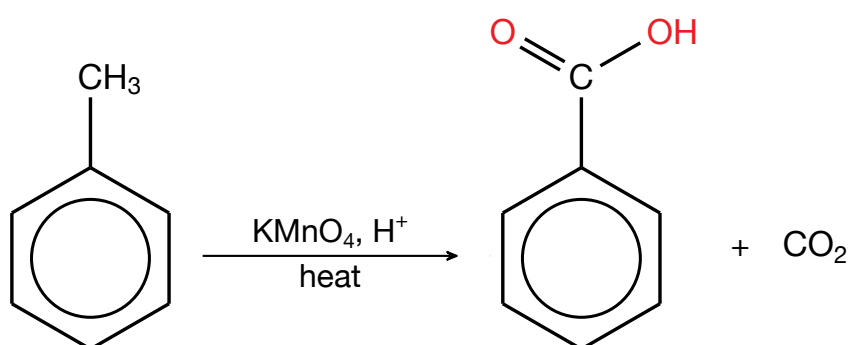


In this case, an acidic medium is used, hence H<sup>+</sup>.

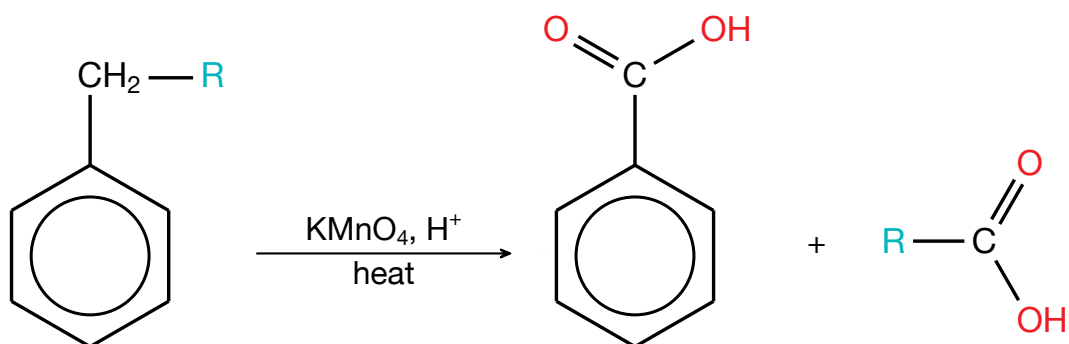
Alternatively, an alkali medium can be used, for instance with NaOH (aq). Instead of forming benzoic acid however, the benzoate ion is formed, which would form an ionic bond with Na.



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.



# Addendums

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



# A List of Reaction Mechanisms

## 1 Electrophilic Addition

Electrophilic Addition the main reaction mechanism for alkenes, and involves an electrophile attacking the electron-rich  $\pi$ -bond of the alkene.

### 1.1 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  $\text{Cl}_2$  or  $\text{Br}_2$ .

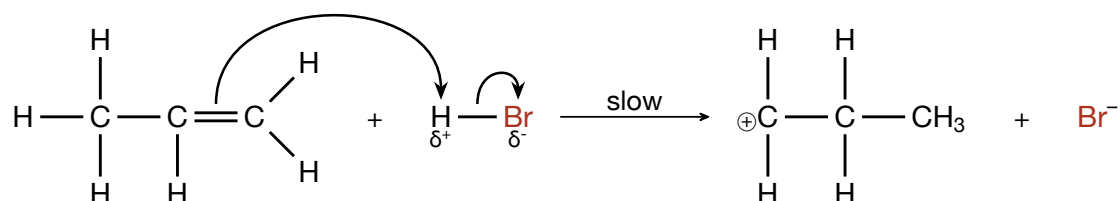
The rule states basically states that when a hydrogen compound with the general form  $\text{H-X}$  is added to an alkene that is asymmetrical about the double-bond, the hydrogen atom will be added to the carbon with *more* existing hydrogen atoms. Note that  $X$  can be a halogen, a hydroxide (ie.  $\text{H-X}$  is  $\text{H}_2\text{O}$ ) or some other electronegative species.

The mirror of the rule, used more with the cyclic halonium ion, is that the nucleophile will be added to the more substituted carbon atom.

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

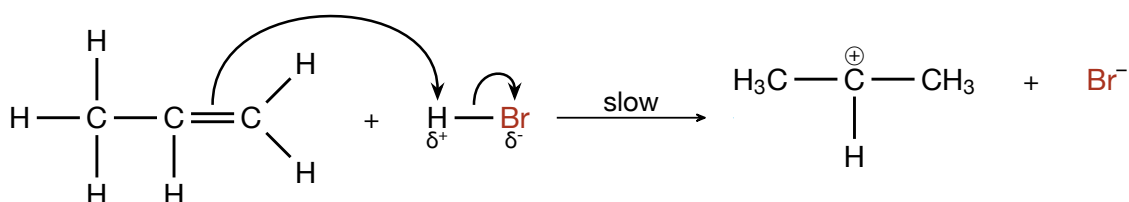
The behaviour that Markovnikov's rule predicts can be derived from the fact that adding the non-hydrogen species to the least substituted carbon would result in a less stable intermediate being formed. This can be illustrated using the electrophilic addition of HBr to prop-1-ene ( $\text{C}_3\text{H}_6$ ).

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.

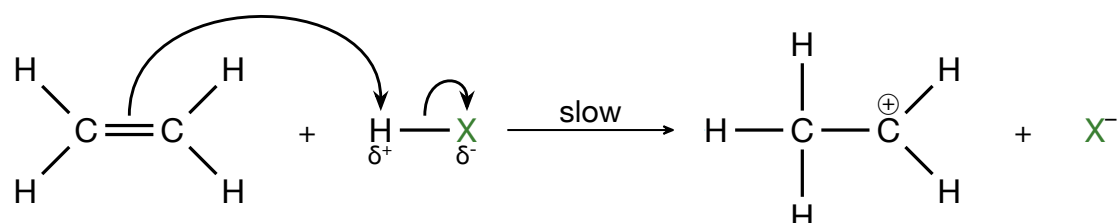
As such, it is more likely to form, and hence 2-bromopropane will be the *major product*, and 1-bromopropane will be the *minor product*.

## 1.2 Electrophilic Addition of HX

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).

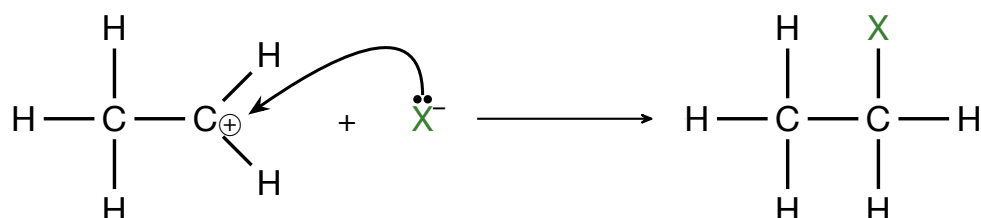
### Step 1



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, H $^{\delta+}$  atom.

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

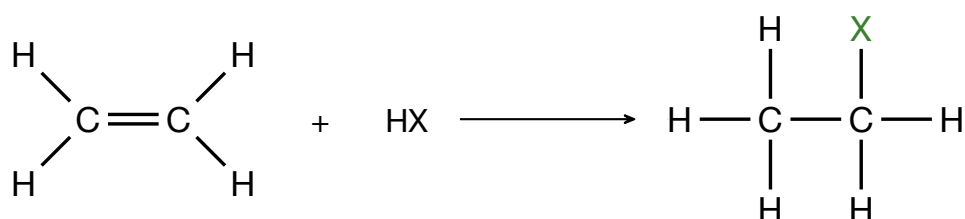
### Step 2



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.

### Overall Reaction



## 1.3 Electrophilic Addition of $X_2$

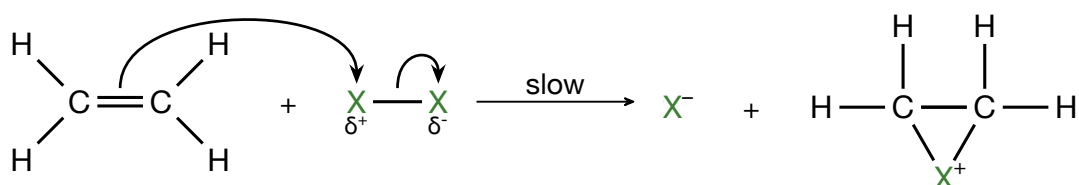
The electrophilic addition of halogens to alkenes does not involve Markovnikov's rule, since it is symmetrical. As the non-polar halogen molecule approaches the high-electron-density  $\pi$ -bond, it is polarised, forming  $\delta^+$  and  $\delta^-$  partial charges. The reaction mechanism involves the formation of a *cyclic halonium ion* — the double bond breaks, and each carbon forms a single bond with one positive halide ion.

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

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

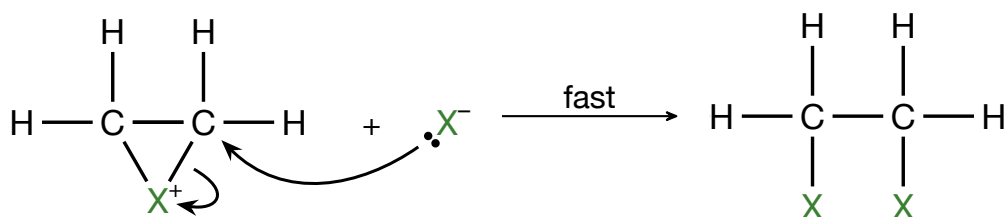
### Step 1

This initial step is the slow, rate-determining one. The resulting cyclic halonium ion is highly unstable, due to the geometric constraints of having a three-membered ring.

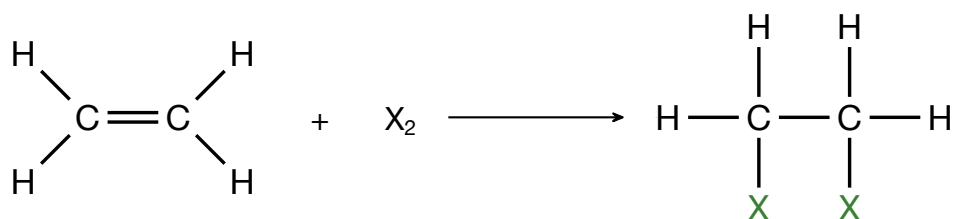


### Step 2

In the second, fast step, the negatively-charged bromide ion from the first step attacks the overall positively-charged cyclic bromonium ion. The bromide ion attacks one of the carbons attached to the positive bromide ion, breaking that bond.



### Overall Reaction



## 1.4 Electrophilic Addition of Aqueous $X_2$

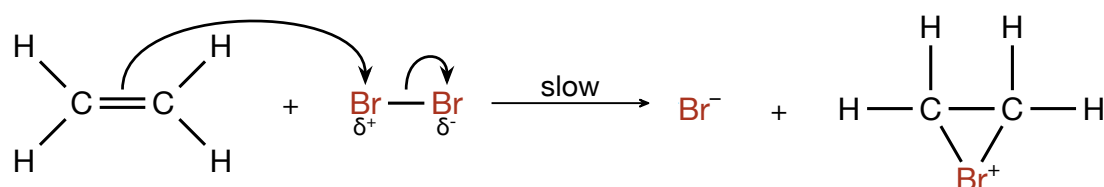
The mechanics of this reaction are basically the same as that of the electrophilic addition of  $Br_2$ , and the conditions and observations are fairly similar as well.

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

**Conditions:** No UV Light, aqueous  $Br_2$ .

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

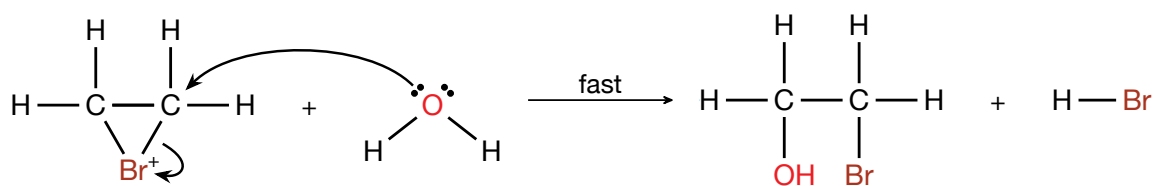
### Step 1



The cyclic bromonium ion is formed.

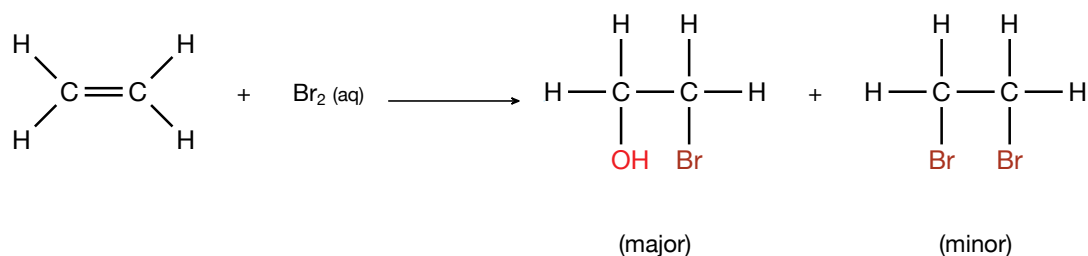
### Step 2

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  $Br^-$ . Since it is in much higher concentrations than  $Br^-$ , the primary product will now have an OH group.



Following Markovnikov's Rule, the  $OH^-$  group will attach to the more substituted carbon.

### Overall Reaction



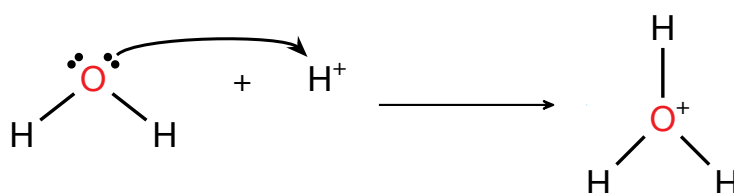
## 1.5 Electrophilic Addition of Steam (Hydration)

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

**Conditions:** 300 °C, at 70 atm,  $\text{H}_3\text{PO}_4$  catalyst, *OR*  
Concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , warming.

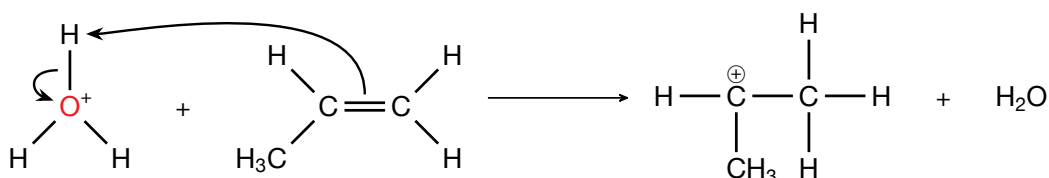
### Step 0

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



### Step 1

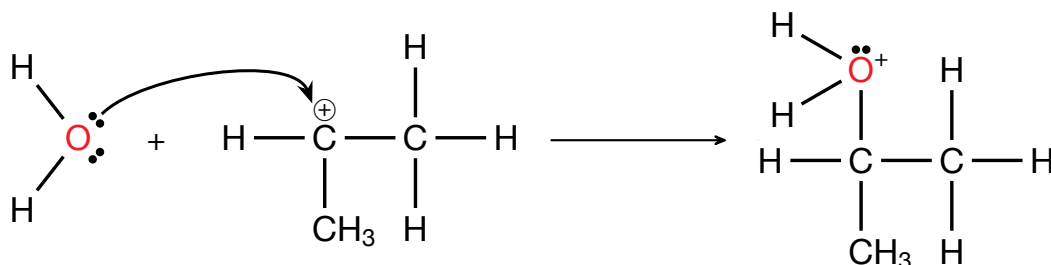
The electron-rich double-bond ( $\text{C}=\text{C}$ ) is then attacked by one of the H atoms on the  $\text{H}_3\text{O}^+$ , acting as an electrophile.



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.

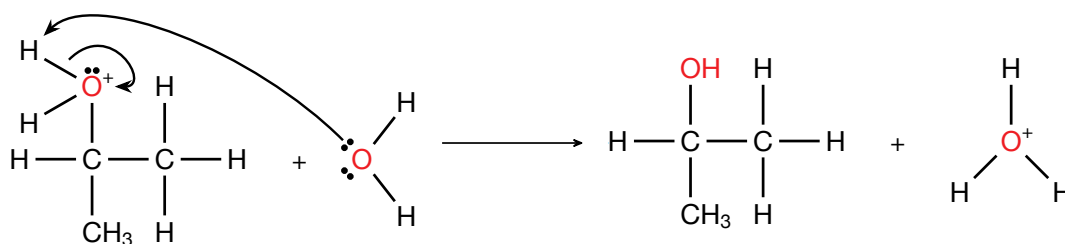
## Step 2

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.

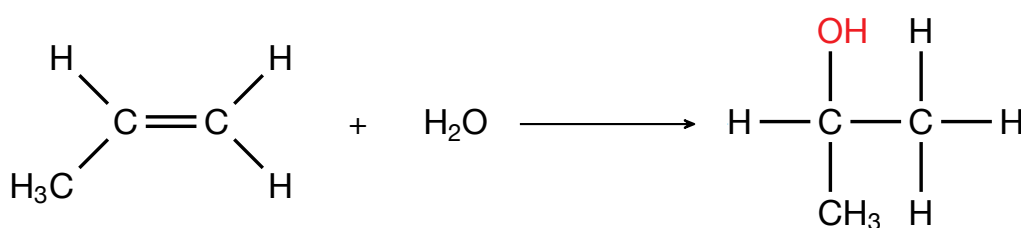


## Step 3

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



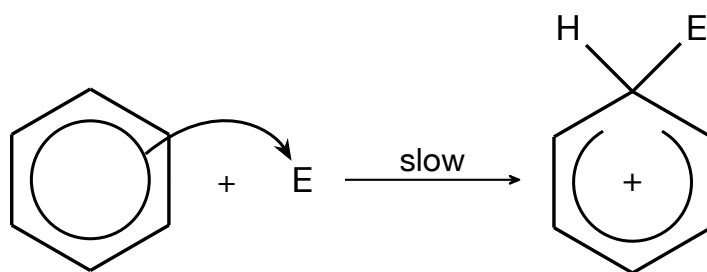
## 2 Electrophilic Substitution

In general, benzene rings undergo electrophilic substitution, since it is not possible for more bonds to be formed.

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.

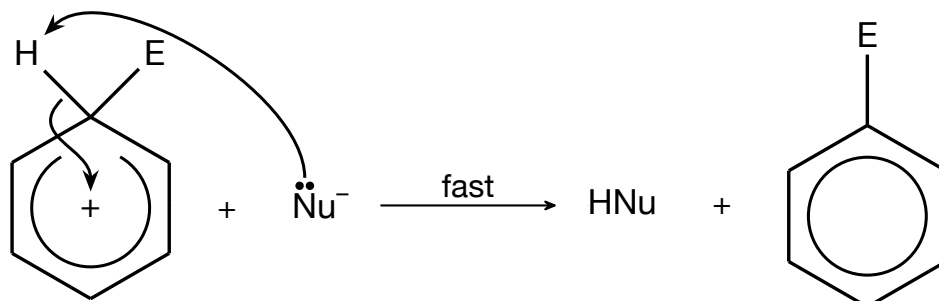
Two electrons out of six from the delocalised  $\pi$ -system are used to form the bond between the electrophile, E, and the carbon. Thus, there is a positive charge on the carbon; due to the delocalised nature of the  $\pi$ -system however, this positive charge is delocalised across *all 6 carbons*,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

## 2.1 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.

### A New Electrophile

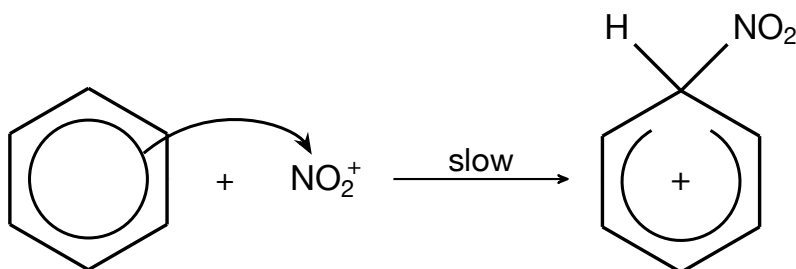
Since  $\text{H}_2\text{SO}_4$  is a stronger acid than  $\text{HNO}_3$ , it donates a proton to  $\text{HNO}_3$ , forming  $\text{H}_2\text{O}$ ,  $\text{HSO}_4^-$ , and  $\text{NO}_2^+$ , the electrophile. Next, another molecule of  $\text{H}_2\text{SO}_4$  then forms  $\text{H}^+$  (aq), or  $\text{H}_3\text{O}^+$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



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

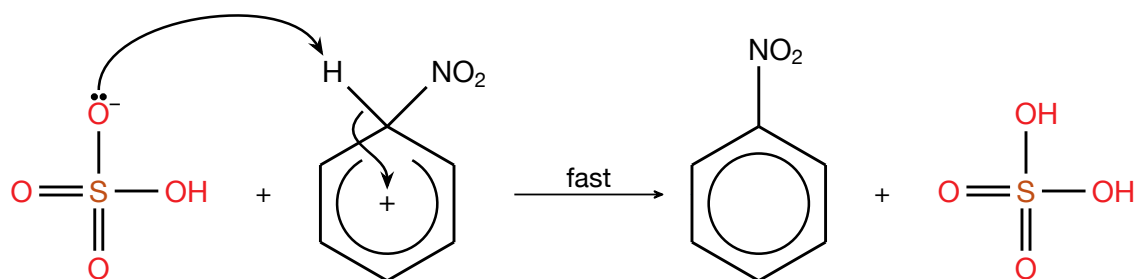
### The $\pi$ -Electrons Strike Back

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.

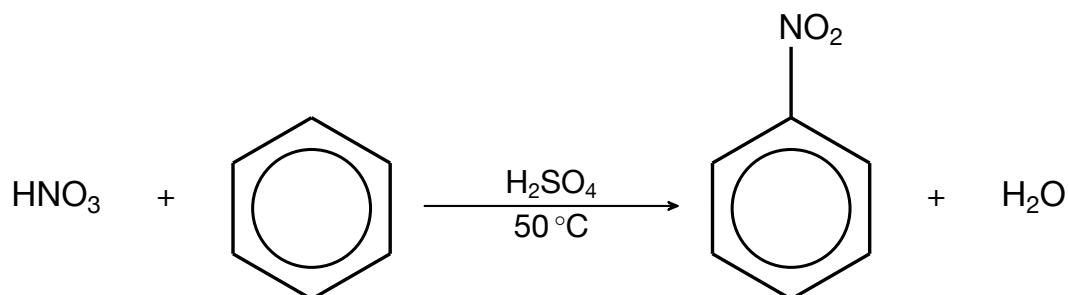


## Return of the Aromaticity

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,  $\text{H}_2\text{SO}_4$ .



## The Product Awakens



## 2.2 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* ( $2 \text{ Fe (s)} + 3 \text{ Br}_2 \text{ (l)} \rightarrow 2 \text{ FeBr}_3$ ).

**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.

### 2.2.1 Catalysts

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.

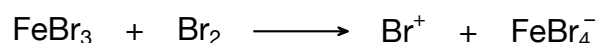
Indeed, this can be used to distinguish between alkenes and benzenes, since the former does not require a catalyst for addition of halogens.

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.

### 2.2.2 Reaction Mechanism

#### Generation of Electrophile

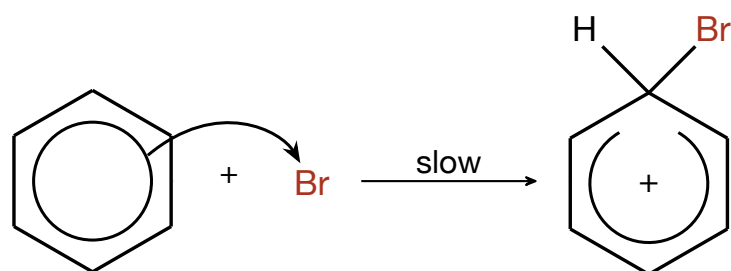
The reaction below uses Iron (III) chloride ( $\text{FeCl}_3$ ) as an example, adding  $\text{Cl}$  to benzene, and this reaction mechanism applies to aluminium-based catalysts as well.



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

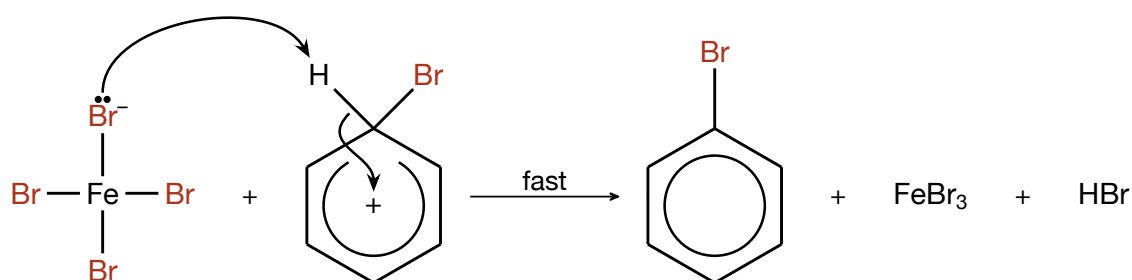
## Formation of Benzene Intermediate

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.

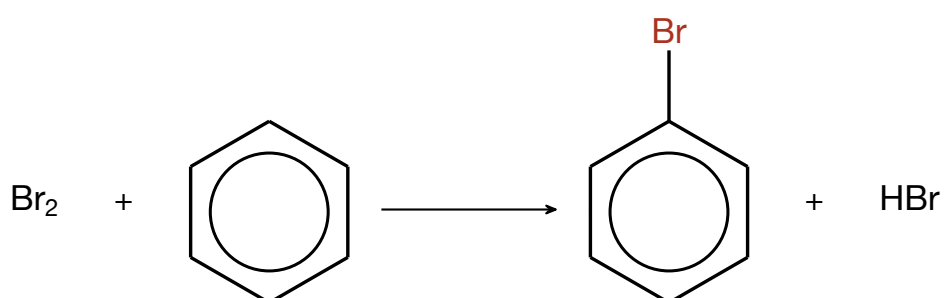


## Restoration of $\pi$ -system and Aromaticity

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 Nucleophilic Addition

## 4 Nucleophilic Substitution ( $S_N1$ )

## 5 Nucleophilic Substitution ( $S_N2$ )