IITM MURTHAL
B.Sc 2nd sem
Organic Chemistry Notes
UNIT – 2 (ARENES AND AROMATICITY)

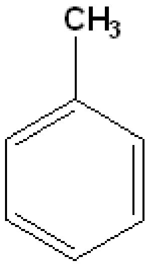
NOMENCLATURE OF BENZENE DERIVATIVES

Benzene is a hydrocarbon with the chemical formula C_6H_6. It has 6 carbon atoms joined in a ring and has 1 hydrogen atom attached to each of the carbon atoms. By replacing one or more of the hydrogen atoms with some functional group, we get several benzene compounds. While naming the substituted benzene compounds, we prefix the name of the substituent to the word benzene.

Mono-substituted Benzene Compounds

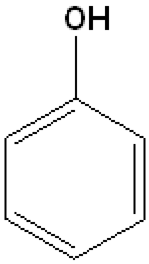
For the benzene compounds consisting of a single substituent, we simply prefix the name of the substituent to benzene. Some examples along with their common names are listed below.

- *Methylbenzene or Toluene*



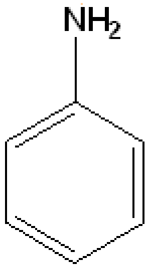
Toluene

- *Hydroxybenzene or Phenol*



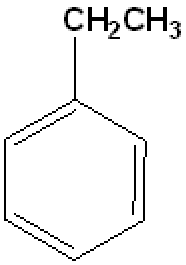
Phenol

- *Aminobenzene or Aniline*



Aniline

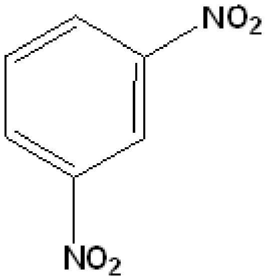
- *Ethylbenzene*



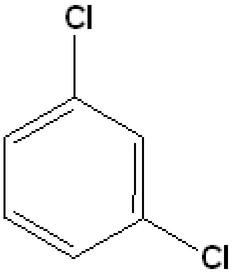
Di-substituted Benzene Compounds

When there are two substituents present in the compound, we number each of the carbon atoms in such a manner that the substituents are attached to the lowest possible numbered carbon atom.

- 1,3-dinitrobenzene is the name of the following compound. Naming it as 1,5-dinitrobenzene is incorrect because the carbon atom would not be numbered lowest.



- 1,3-dichlorobenzene

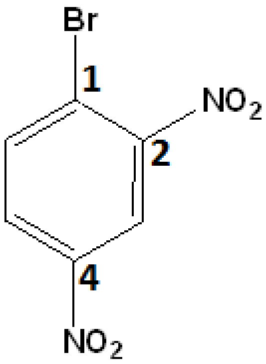


Moreover, when there is more than one substituent, we also name their positions as ortho- (*o*), meta- (*m*) and para- (*p*). They refer to the positions 1,2-;1,3- and 1,4- respectively. Thus, we can name the compound 1,3-dichlorobenzene as *m*-dichlorobenzene.

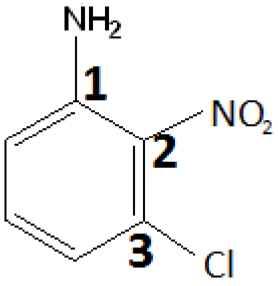
Poly-substituted Benzene Compounds

In case of poly-substituted compounds, if there is a base compound present, we assign it as the position 1. We then choose the next compound for numbering such that it gets the lowest number. However, if there is no special or base group present, we list them in the alphabetical order, giving them the lowest numbers.

- *1-Bromo-2,4-dinitrobenzene*



- For the following compound, aniline is the base compound. So, we name it as 3-Chloro-2-nitroaniline.



What is Huckel’s Rule?

Huckel’s Rule is used in order to estimate the aromatic qualities of any planar ring-shaped molecule in the field of organic chemistry. The supporting quantum mechanics required for the formulation of this rule was solved first by the German physical chemist and physicist Erich Armand Arthur Joseph Huckel in the year 1931.

The Huckel 4n + 2 Pi Electron Rule

A ring-shaped cyclic molecule is said to follow the Huckel rule when the total number of pi electrons belonging to the molecule can be equated to the formula ‘4n + 2’ where n can be any integer with a positive value (including zero).

Examples of molecules following Huckel’s rule have only been established for values of ‘n’ ranging from zero to six. The total number of pi electrons in the benzene molecule depicted below can be found to be 6, obeying the 4n+2 π electron rule where n=1.

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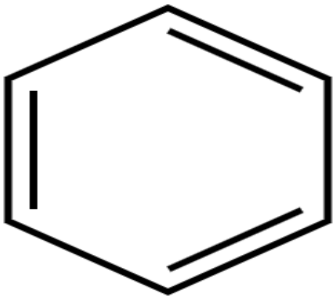

Thus, the aromaticity of the benzene molecule is established since it obeys the Huckel rule.

Generally, aromatic compounds are quite stable due to the resonance energy or the delocalized electron cloud. For a molecule to exhibit aromatic qualities, the following conditions must be met by it:

- There must be 4n + 2 **π** electrons present in a system of connected p orbitals (where the electrons are delocalized) belonging to the molecule.
- In order to meet the first condition, the molecule must have an approximately planar structure wherein the p orbitals are more or less parallel and have the ability to interact with each other.
- The molecule must have a cyclic structure and must have a ring of p orbitals which doesn't have any sp^3 hybridized atoms.

Other examples of aromatic compounds that comply with Huckel's Rule include pyrrole, pyridine, and furan. All three of these examples have 6 pi electrons each, so the value of n for them would be one.

AROMATIC IONS

Aromatic molecules need not be neutral molecules. Ions that satisfy Huckel's rule of $4n + 2$ π-electrons in a planar, cyclic, conjugated molecule are considered to be aromatic ions. For example, the cyclopentadienyl anion and the cycloheptatrienylium cation are both considered to be aromatic ions, and the azulene molecule can be approximated as a combination of both.

In order to convert the atom from sp^3 to sp^2, a carbocation, carbanion, or carbon radical must be formed. These leave sp^2-hybridized carbons that can partake in the π system of an aromatic molecule. Like neutral aromatic compounds, these compounds are stable and form easily. The cyclopentadienyl anion is formed very easily and thus 1,3-cyclopentadiene is a very acidic hydrocarbon with a pK_a of 16. Other examples of aromatic ions include the cyclopropenium cation (2 π-electrons) and cyclooctatetraenyl dianion (10 π electrons).

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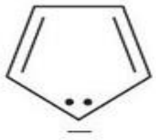
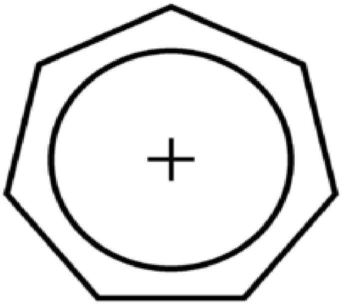
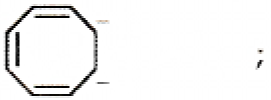


cyclopentadienyl anion



cycloheptatrienylium cation

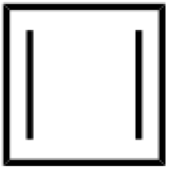


Cyclooctatetraenyl dianion
[$n = 2$, 10π-electrons, aromatic]

Annulenes

- **Annulenes** are the family of completely conjugated, monocyclic hydrocarbons.
- The annulenes are named as [n]-annulene where n is an even number that represents the number of C atoms in the ring.
- We have already met the first 3 members of the series, [4]-, [6]-, and [8]-annulene but we called them 1,3-cyclobutadiene, benzene 1, and 3,5,7-cyclooctatetraene respectively.
- Higher members of the annulene series have also been synthesized and investigated in relation their aromaticity.

Remember that according to the Huckel rule, (4n + 2) π electrons systems are expected to aromatic whereas 4n π electrons systems are not.
[10]-annulene is not particularly stable due to geometric factors
1,3-cyclobutadiene



The compound is the prototypical antiaromatic hydrocarbon with 4 π-electrons. It is the smallest [*n*]-annulene ([4]-annulene).

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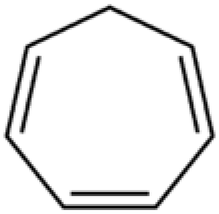
Cyclopropene

Cyclopropene is an organic compound with the formula C_3H_4. It is the simplest cycloalkene. Because the ring is highly strained, cyclopropene is difficult to prepare and highly reactive.

Cyclopentadiene

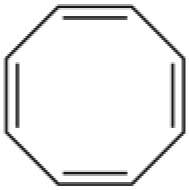
Another odd member of annulene family

Cycloheptatriene



Cycloheptatriene (CHT) is an organic compound with the formula C_7H_8. This colourless liquid has been of recurring theoretical interest in organic chemistry

3,5,7-cyclooctatetraene



1,3,5,7-Cyclooctatetraene (**COT**) is an unsaturated derivative of cyclooctane, with the formula C_8H_8. It is also known as [8]-annulene. Unlike benzene, C_6H_6, cyclooctatetraene, C_8H_8, is not aromatic.

Cyclononatetraene

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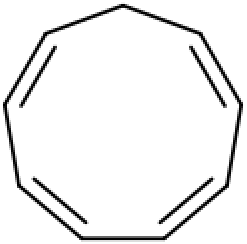
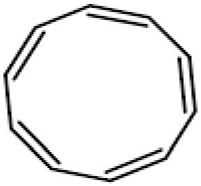


Cyclononatetraene is an organic compound with the formula C_9H_{10}. It was first prepared in 1969 by protonation of the corresponding aromatic anion.

Cyclodecapentaene or **[10]annulene**



All cis
[10]-Annulene

Cyclodecapentaene or **[10]-annulene** is an annulene with molecular formula $C_{10}H_{10}$. This organic compound is a conjugated 10 pi electron cyclic system and according to Huckel's rule it should display aromaticity. It is not aromatic, however, because various types of ring strain destabilize an all-planar geometry.

What are Aromatic Compounds?

Aromatic compounds are chemical compounds that consist of conjugated planar ring systems accompanied by delocalized pi-electron clouds in place of individual alternating double and single bonds.

Aromatic Compounds Examples

Aromatic hydrocarbon, are hydrocarbons containing sigma bonds and delocalized pi electrons between carbon atoms in a ring. For example, benzene. They are known as aromatic due to their pleasant smell.

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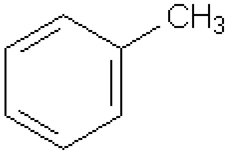
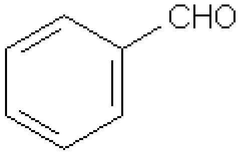
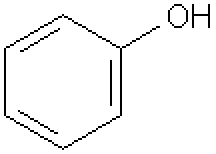
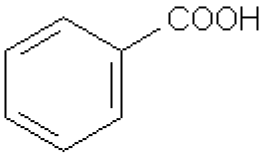
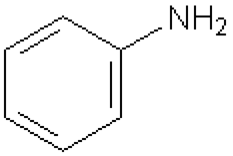
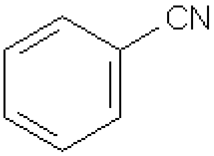

toluene

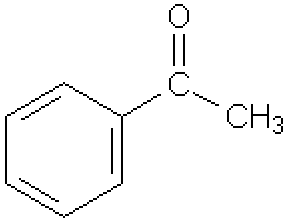

benzaldehyde

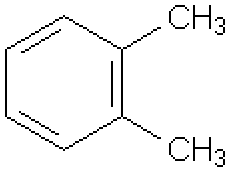

phenol

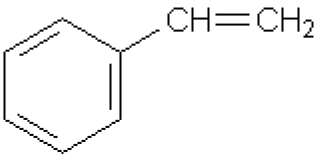

benzoic acid


aniline


benzonitrile


acetophenone


***ortho*-xylene**


styrene

Aromatic compounds are broadly divided into two categories: benzenoids (one containing benzene ring) and non-benzenoids (those not containing a benzene ring) for example, furan. Any hydrocarbon can be classified as an aromatic compound provided they follow the Huckel rule. According to Huckel rule, for a ring to be aromatic it should have the following properties:

1. Planarity
2. Complete delocalization of the π electrons in the ring
3. Presence of $(4n + 2)$ π electrons in the ring where n is an integer ($n = 0, 1, 2, . . .$)

Properties of Aromatic Compounds

Arenes are mostly nonpolar and non-miscible in water. These compounds usually are unreactive and are used as solvents for various other nonpolar compounds. Their carbon to hydrogen ratio is high therefore, they are characterized by sooty yellow flame.

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Classification of Aromatic Compounds

The classification of arenes is based on the position of the functional group. They are classified into two and we have discussed below:

1.Nuclear Substituted Compounds

In any aromatic compound whenever any substituent or functional group, is directly linked to the benzene ring, it is known as a nuclear-substituted compound.

2. Sidechain Substituted Compounds

In any aromatic compound if the functional group is available in the side chain of the ring then it is known as a sidechain substituted compound. These compounds are named as the phenyl derivatives of the relative aliphatic compounds.

Non-Aromatic Compounds

A cyclic compound which doesn’t necessitate a continuous form of overlapping ring of p orbitals need not be considered as aromatic or even anti aromatic and hence these are termed as nonaromatic or aliphatic.

Difference between Aromatic & Nonaromatic Compounds

- An aromatic compound is characterized by its cyclic and planar structure and along with that conjugated system of the p orbitals which are found to be perpendicular to the molecule’s plane. This conjugation makes the molecule very stable.
- In comparison, a nonaromatic is found to be either non-cyclic or not in a planar form. While an aromatic compound will always follow the Huckel rule with a ***4n+2 electrons conjugation*** and we get to see fully filled orbits as compared to antiaromatic compound with just 4n electrons. This makes the compound very reactive.
- Apart from this, aromatic compound is differentiated from similar nonaromatic compounds by the level of susceptibility. The London diamagnetism leads to larger susceptibility for aromatic compounds. This means aromatic compounds will show diamagnetic susceptibility exaltation and this becomes a criterion for the aromatic character.

Examples of Nonaromatic compounds

1-hexyne 1-heptyne

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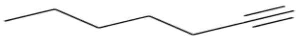
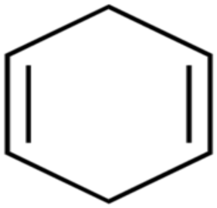
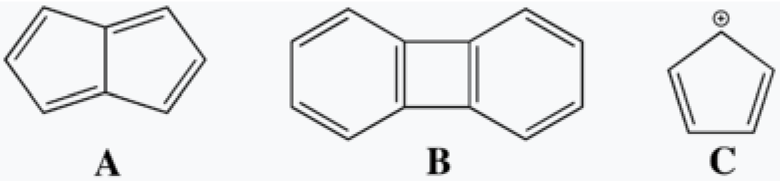


1, 4-cyclohexadiene



ANTI AROMATIC COMPOUNDS

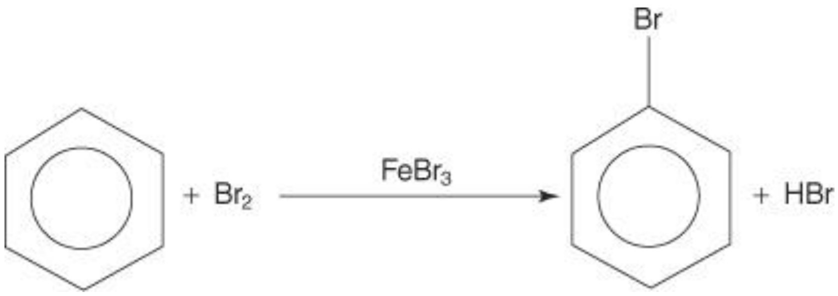
Antiaromaticity is a characteristic of a cyclic molecule with a π electron system that has higher energy due to the presence of 4n delocalised (π or lone pair) electrons in it.
Unlike aromatic compounds, which follow Hückel's rule ([4*n*+2] π electrons)[1] and are highly stable, antiaromatic compounds are highly unstable and highly reactive. To avoid the instability of antiaromaticity, molecules may change shape, becoming non-planar and therefore breaking some of the π interactions. In contrast to the diamagnetic ring current present in aromatic compounds, antiaromatic compounds have a paramagnetic ring current, which can be observed by NMR spectroscopy.



Examples of antiaromatic compounds. A: pentalene; B: biphenylene; C: cyclopentadienyl cation

Electrophilic Aromatic Substitution Reactions

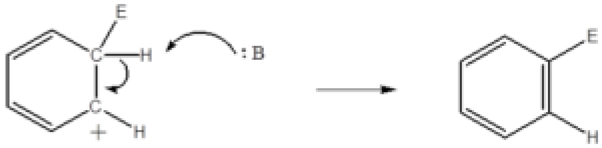
Although aromatic compounds have multiple double bonds, these compounds do not undergo addition reactions. Their lack of reactivity toward addition reactions is due to the great stability of the ring systems that result from complete π electron delocalization (resonance). Aromatic compounds react by electrophilic aromatic substitution reactions, in which the aromaticity of the ring system is preserved. For example, benzene reacts with bromine to form bromobenzene.



Many functional groups can be added to aromatic compounds via electrophilic aromatic substitution reactions. A **functional group** is a substituent that brings with it certain chemical reactions that the aromatic compound itself doesn't display.

The General Mechanism

Step 1 (Slow)



The e- in the pi bond attacks the electrophile

One carbon gets a positive charge the other forms a C-E bond

This forms the arenium ion.
The arenium ion is conjugated but not aromatic.

Step 2 (Fast)

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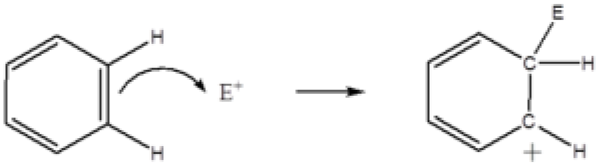


Arenium Ion

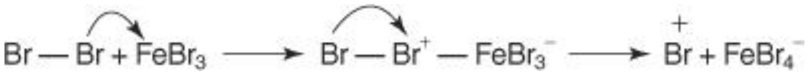
The Loan pair of electron on a base attacks the hydrogen.

This causes the e- in the C-H bond to form a C-C double bond and aromaticity is reformed

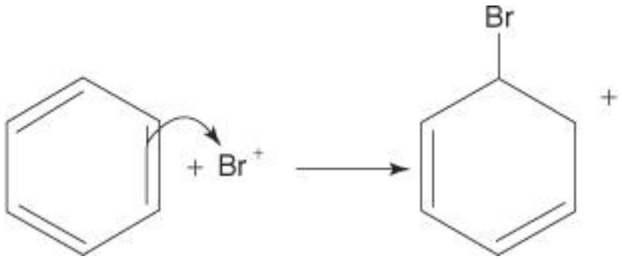
The Bromination of benzene

All electrophilic aromatic substitution reactions share a common mechanism. This mechanism consists of a series of steps.

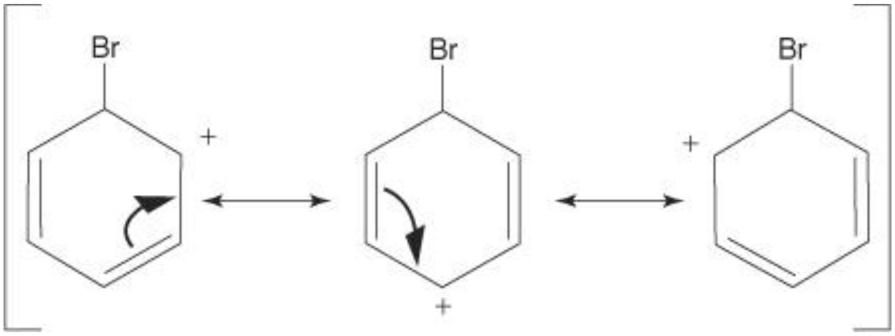
1. An **electrophile** — an electron-seeking reagent — is generated. For the bromination of benzene reaction, the electrophile is the Br+ ion generated by the reaction of the bromine molecule with ferric bromide, a Lewis acid.



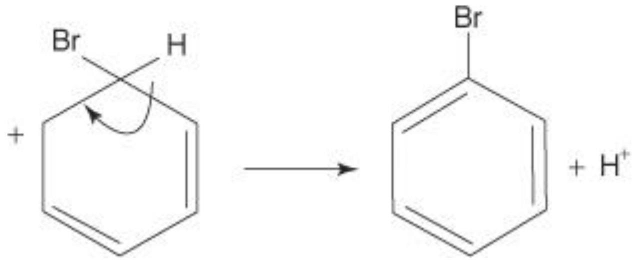
2. The electrophile attacks the π electron system of the benzene ring to form a nonaromatic carbocation.



3. The positive charge on the carbocation that is formed is delocalized throughout the molecule.



4. The aromaticity is restored by the loss of a proton from the atom to which the bromine atom (the electrophile) has bonded.

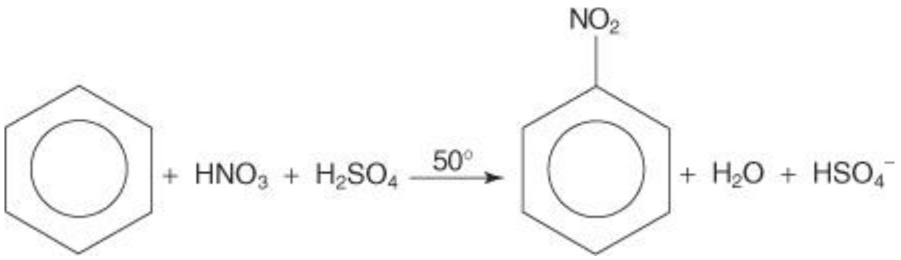


5. Finally, the proton reacts with the FeBr $_4$ $^-$ to regenerate the FeBr $_3$ catalyst and form the product HBr.

$$H^+ + FeBr_4^- \longrightarrow FeBr_3 + HBr$$

The nitration of benzene

In another example of an electrophilic aromatic substitution reaction, benzene reacts with a mixture of concentrated nitric and sulfuric acids to create nitrobenzene.

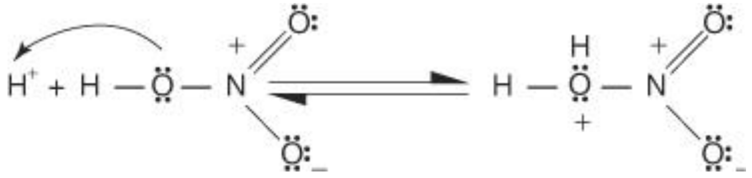


The mechanism for the nitrobenzene reaction occurs in six steps.

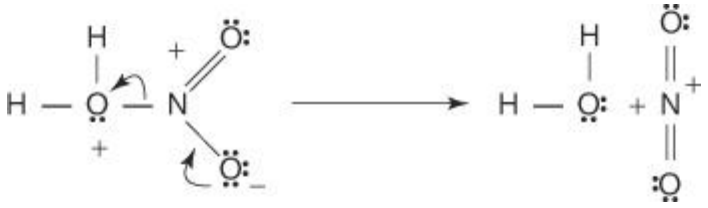
1. Sulfuric acid ionizes to produce a proton.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

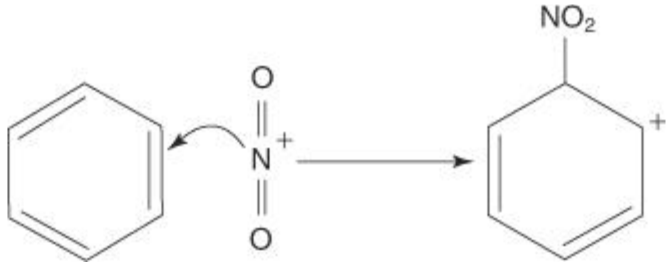
2. Nitric acid accepts the proton in an acid-base reaction.



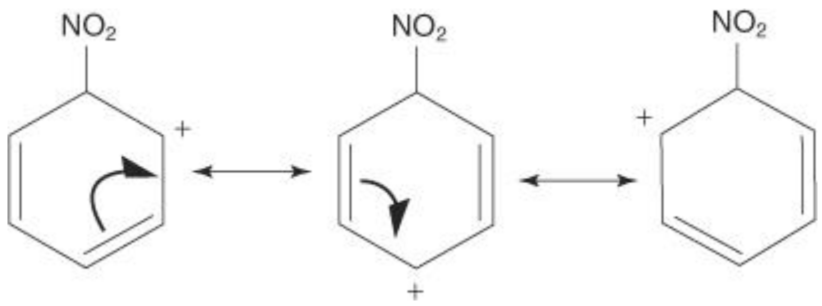
3. The protonated nitric acid dissociates to form a nitronium ion ($^+NO_2$).



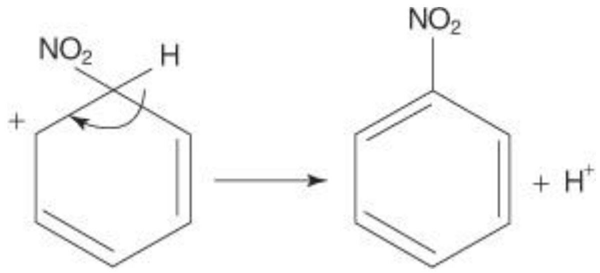
4. The nitronium ion acts as an electrophile and is attracted to the π electron system of the benzene ring.



5. The nonaromatic carbocation that forms has its charge delocalized around the ring.



6. The aromaticity of the ring is reestablished by the loss of a proton from the carbon to which the nitro group is attached.



SULFONATION OF BENZENE

- Overall transformation : **Ar-H** to **Ar-SO_3H**, a sulfonic acid.
- Reagent : for benzene, H_2SO_4 / heat or SO_3 / H_2SO_4 / heat (= fuming sulfuric acid)
- Electrophilic species : SO_3 which can be formed by the loss of water from the sulfuric acid
- Unlike the other electrophilic aromatic substitution reactions, sulfonation is reversible.
- Removal of water from the system favours the formation of the sulfonation product.
- Heating a sulfonic acid with aqueous sulfuric acid can result be the reverse reaction, desulfonation.

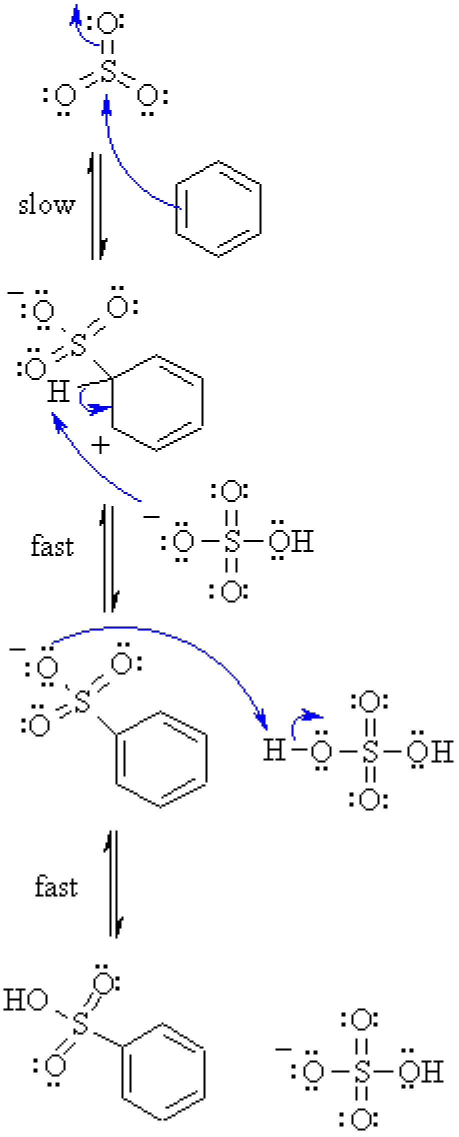
- Sulfonation with fuming sulfuric acid strongly favours formation of the product the sulfonic acid.

MECHANISM FOR SULFONATION OF BENZENE

Step 1:
The p electrons of the aromatic **C=C** act as a nucleophile, attacking the electrophilic S, pushing charge out onto an electronegative O atom. This destroys the aromaticity giving the cyclohexadienyl cation intermediate.

Step 2:
Loss of the proton from the sp^3 C bearing the sulfonyl- group reforms the **C=C** and the aromatic system.

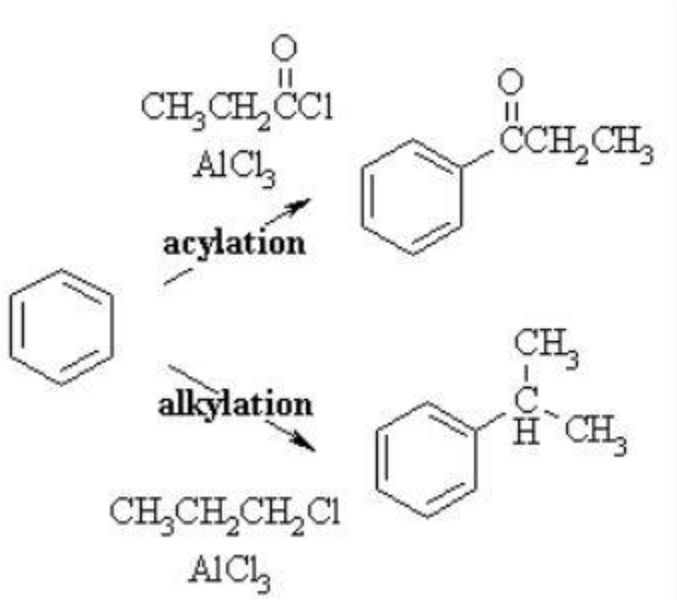
Step 3:
Protonation of the conjugate base of the sulfonic acid by sulfuric acid produces the sulfonic acid.



Friedel-Crafts Reaction

A Friedel-Crafts reaction is an organic coupling reaction involving an electrophilic aromatic substitution that is used for the attachment of substituents to aromatic rings. The two primary types of Friedel-Crafts reactions are the alkylation and acylation reactions. These reactions were developed in the year 1877 by the French chemist Charles Friedel and the American chemist James Crafts.

An illustration describing both the Friedel-Crafts reactions undergone by benzene is provided below.

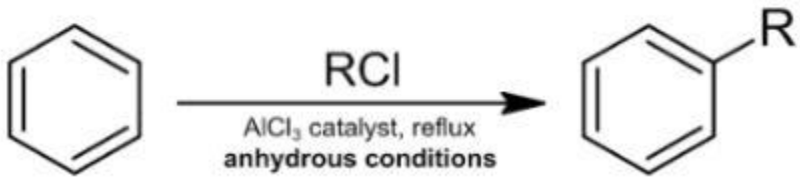


It can be noted that both these reactions involve the replacement of a hydrogen atom (initially attached to the aromatic ring) with an electrophile. Aluminium trichloride ($AlCl_3$) is often used as a catalyst in Friedel-Crafts reactions since it acts as a Lewis acid and coordinates with the halogens, generating an electrophile in the process.

Friedel-Crafts Alkylation

Friedel-Crafts Alkylation refers to the replacement of an aromatic proton with an alkyl group. This is done through an electrophilic attack on the aromatic ring with the help of a carbocation. The Friedel-Crafts alkylation reaction is a method of generating alkylbenzenes by using alkyl halides as reactants.

The Friedel-Crafts alkylation reaction of benzene is illustrated below.



A Lewis acid catalyst such as $FeCl_3$ or $AlCl_3$ is employed in this reaction in order to form a carbocation by facilitating the removal of the halide. The resulting carbocation undergoes a rearrangement before proceeding with the alkylation reaction.

Mechanism

The Friedel-Crafts alkylation reaction proceeds via a three-step mechanism.

Step 1

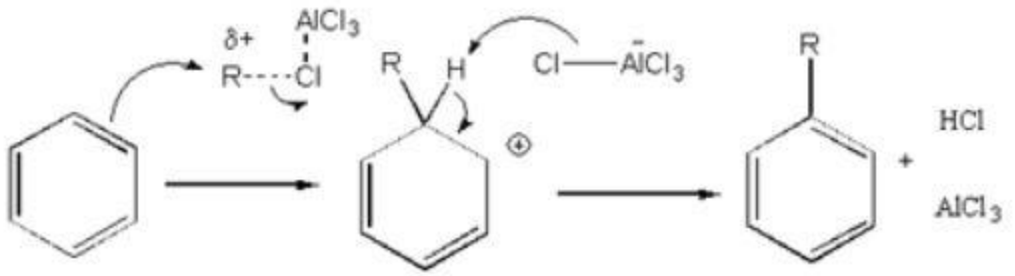
The Lewis acid catalyst ($AlCl_3$) undergoes reaction with the alkyl halide, resulting in the formation of an electrophilic carbocation.

Step 2

The carbocation proceeds to attack the aromatic ring, forming a cyclohexadienyl cation as an intermediate. The aromaticity of the arene is temporarily lost due to the breakage of the carbon-carbon double bond.

Step 3

The deprotonation of the intermediate leads to the reformation of the carbon-carbon double bond, restoring aromaticity to the compound. This proton goes on to form hydrochloric acid, regenerating the $AlCl_3$ catalyst.



An illustration describing the mechanism of the Friedel-Crafts alkylation reaction is provided above.

What are the Limitations of the Friedel-Crafts Alkylation Reaction?

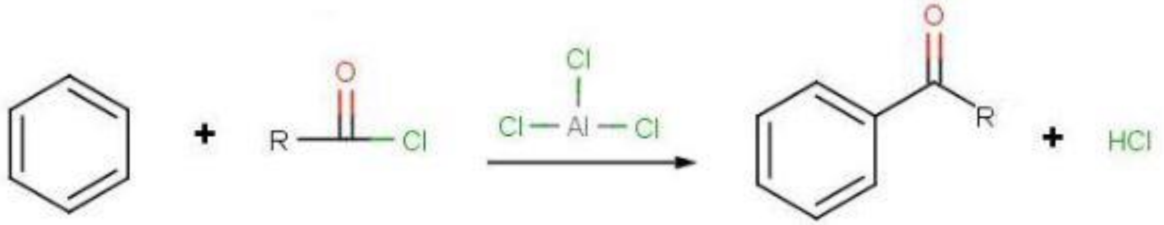
Some important limitations of Friedel-Crafts alkylation are listed below.

- Since the carbocations formed by aryl and vinyl halides are extremely unstable, they cannot be used in this reaction.
- The presence of a deactivating group on the aromatic ring (such as an NH_2 group) can lead to the deactivation of the catalyst due to the formation of complexes.
- An excess of the aromatic compound must be used in these reactions in order to avoid polyalkylation (addition of more than one alkyl group to the aromatic compound).
- Aromatic compounds that are less reactive than mono-halobenzenes do not participate in the Friedel-Crafts alkylation reaction.

It is important to note that this reaction is prone to carbocation rearrangements, as is the case with any reaction involving carbocations.

Friedel-Crafts Acylation

The Friedel-Crafts acylation reaction involves the addition of an acyl group to an aromatic ring. Typically, this is done by employing an acid chloride (R-(C=O)-Cl) and a Lewis acid catalyst such as $AlCl_3$. In a Friedel-Crafts acylation reaction, the aromatic ring is transformed into a ketone. The reaction between benzene and an acyl chloride under these conditions is illustrated below.



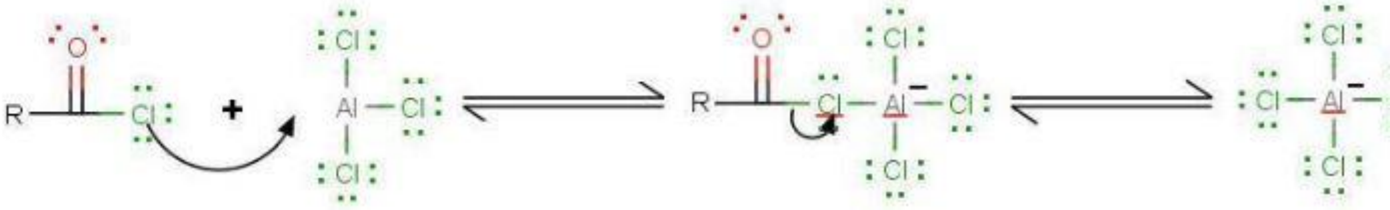
An acid anhydride can be used as an alternative to the acyl halide in Friedel-Crafts acylations. The halogen belonging to the acyl halide forms a complex with the Lewis acid, generating a highly electrophilic acylium ion, which has a general formula of RCO^+ and is stabilized by resonance.

Mechanism

Friedel-Crafts acylations proceed through a four-step mechanism.

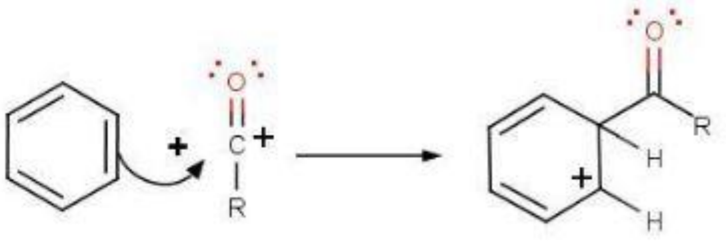
Step 1

A reaction occurs between the Lewis acid catalyst ($AlCl_3$) and the acyl halide. A complex is formed and the acyl halide loses a halide ion, forming an acylium ion which is stabilized by resonance.



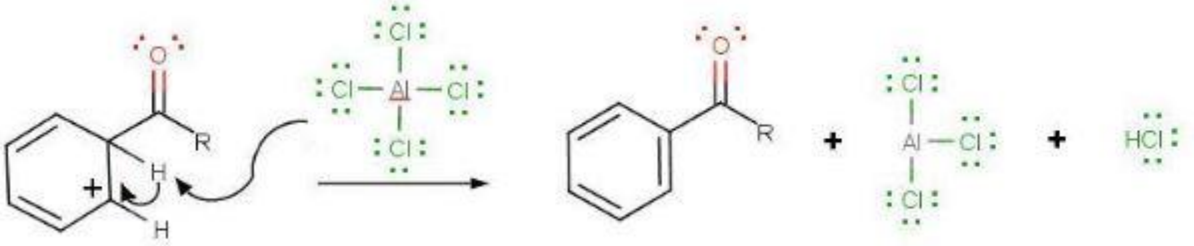
Step 2

The acylium ion (RCO^+) goes on to execute an electrophilic attack on the aromatic ring. The aromaticity of the ring is temporarily lost as a complex is formed.



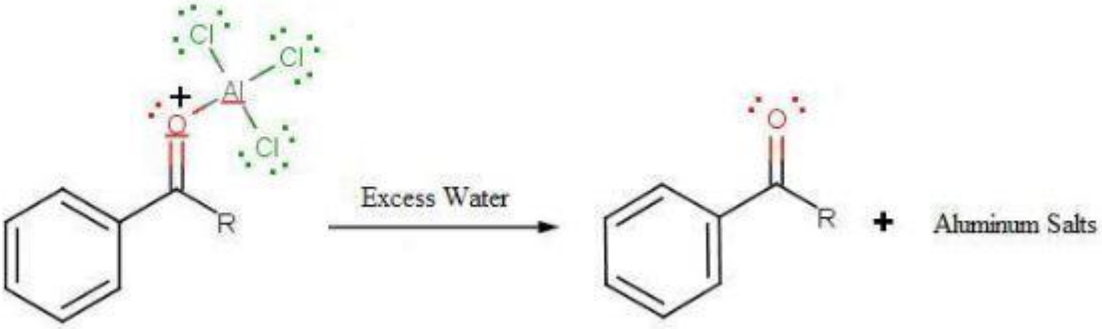
Step 3

The intermediate complex is now deprotonated, restoring the aromaticity to the ring. This proton attaches itself to a chloride ion (from the complexed Lewis acid), forming HCl. The $AlCl_3$ catalyst is now regenerated.



Step 4

The regenerated catalyst can now attack the carbonyl oxygen. Therefore, the ketone product must be liberated by adding water to the products formed in step 3. This step can be illustrated as follows.



Thus, the required acyl benzene product is obtained via the Friedel-Crafts acylation reaction.

Limitations

Despite overcoming some of the limitations of the related alkylation reaction (such as carbocation rearrangement and polyalkylation), the Friedel-Crafts acylation reaction has a few shortcomings.

- The acylation reaction only yields ketones. This is because formyl chloride (H(C=O)Cl) decomposes into CO and HCl when exposed to these conditions.

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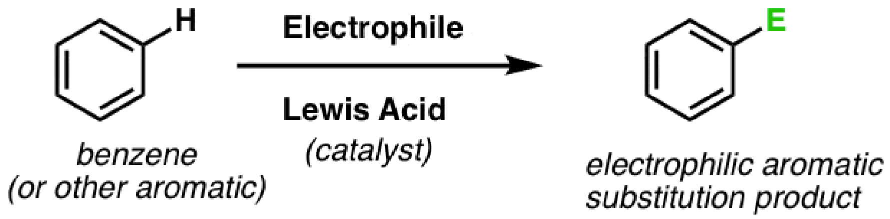
- The aromatic compound cannot participate in this reaction if it is less reactive than a mono-halobenzene.
- Aryl amines cannot be used in this reaction because they form highly un-reactive complexes with the Lewis acid catalyst.

Activating and deactivating substituents

Electrophilic Aromatic Substitution

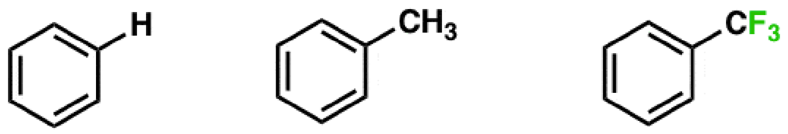


Key Bonds Formed	Key Bonds Broken
C–E	C–H

What happens to the reaction rate if a substituent is added?

- Try replacing one of the hydrogens on benzene with a different substituent
- What happens to the reaction rate?

Example: measured rates for nitration reactions



	Benzene	Methylbenzene	Trifluoromethylbenzene
Relative rate:	**1**	**23**	**2.5×10^{-5}**
	(baseline)	**(faster)**	**(slower)**

An electron-donating group (**CH_3**) results in a **faster** reaction than benzene itself

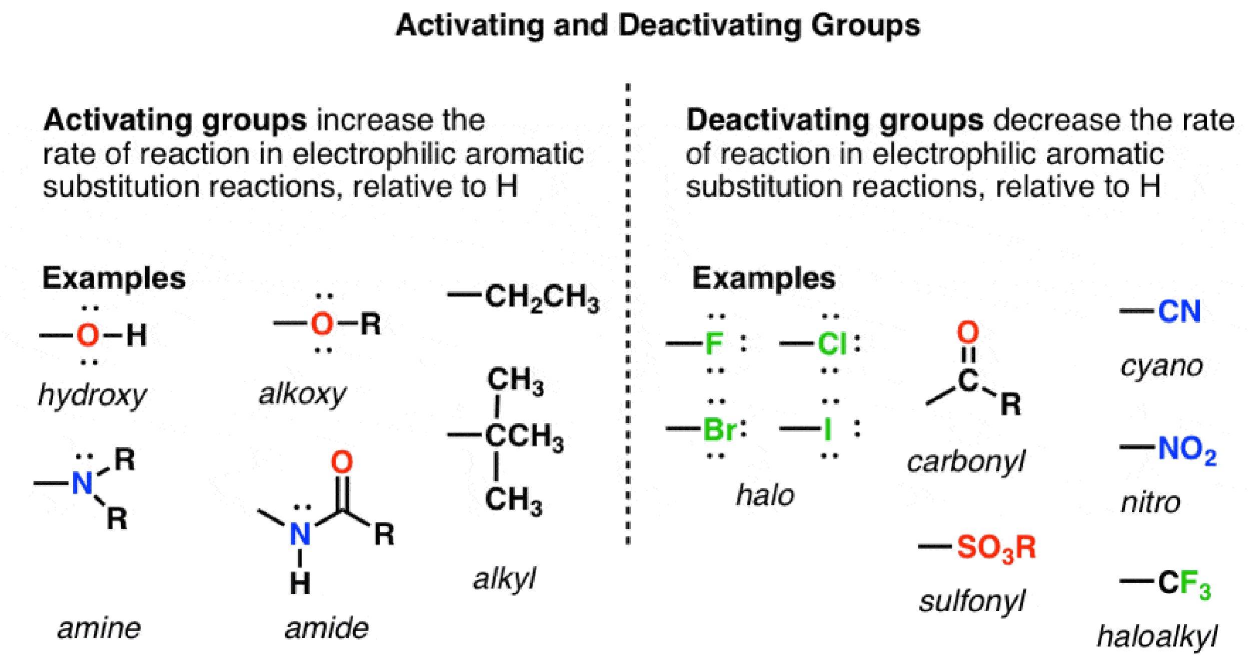
An electron-withdrawing group (**CF_3**) results in a **slower** reaction than benzene

Bottom line: if we swap a hydrogen on benzene for a methyl group, the reaction is faster. If we swap a hydrogen for a trifluoromethyl group, the reaction is slower.

This pattern turns out to be general for other electrophilic aromatic substitution reactions as well (chlorination, bromination, Friedel-Crafts, and others).

Let's call a group **activating** that **increases the rate of an electrophilic aromatic substitution reaction, relative to hydrogen**. As we just saw, CH_3 is a perfect example of an activating group; when we substitute a hydrogen on benzene for CH_3, the rate of nitration is increased.

A **deactivating group**, on the other hand, **decreases the rate of an electrophilic aromatic substitution reaction, relative to hydrogen.** The trifluoromethyl group, CF_3, drastically decreases the rate of nitration when substituted for a hydrogen on benzene.



Activating and Deactivating Groups

Activating groups increase the rate of reaction in electrophilic aromatic substitution reactions, relative to H

Deactivating groups decrease the rate of reaction in electrophilic aromatic substitution reactions, relative to H

The direction of the reaction

The activating group directs the reaction to the ortho or para position, which means the electrophile substitute the hydrogen that is on carbon 2 or carbon 4. The deactivating group directs the reaction to the meta position, which means the electrophile substitute the hydrogen that is on carbon 3 with the exception of the halogens that is a deactivating group but directs the ortho or para substitution.

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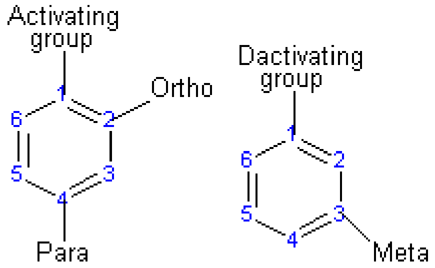
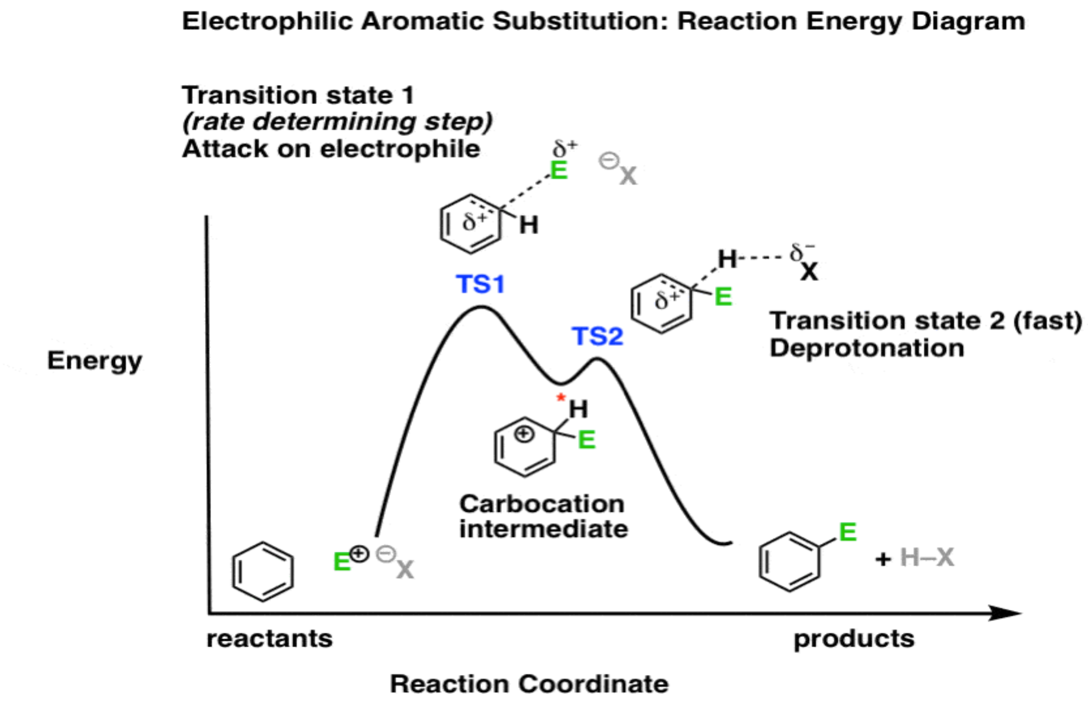


Energy profile diagram



Electrophilic aromatic substitution has two steps (attack of electrophile, and deprotonation) which each have their own transition state. There is also a carbocation intermediate. This means that we should have a “double-humped” reaction energy diagram.Second, the relative heights of the “peaks” should reflect the rate-limiting step.

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We know that electron-donating substitutents increase the rate of reaction (“activating”) and electron-withdrawing substituents decrease the rate of reaction (“deactivating”).

Since electron-donating and electron-withdrawing substitutents affect the nucleophilicity of the pi bond (through pi-donation and pi-acceptance) as well as the stability of the intermediate carbocation, the logical conclusion is that attack on the electrophile (step 1) is the rate-determining step. We therefore should depict it with the higher “hump” in our reaction energy diagram, representing its higher activation energy.

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UNIT – 4 (ALKYL & ARYL HALIDES)

Alkyl Halides

Alkyl halides are organic compounds with the general formula RX, where R denotes the alkyl group and X denotes the halogen.

Nomenclature of Alkyl Halides

Alkyl halides are named in two ways. In the common system, the alkyl group is named first followed by an appropriate word chloride, bromide, etc. The common name of an alkyl halide is always written as two separate words. In the IUPAC system, alkyl halides are named as haloalkanes. The other rules followed in naming compounds is that

- Select the longest chain of carbon atoms containing the halogen atom.
- Number the chain so as to give the minimum number to the carbon carrying halogen atom.
- If multiple bonds (double or triple bond) is present, then it is given the preference in numbering the carbon chain.
- The IUPAC name, of any halogen derivative is always written as one word.

Compound	**Common Name**	**IUPAC Name**
CH_3-Cl	Methyl Chloride	Chloromethane
CH_3-CH_2-Br	Ethyl bromide	Bromoethane
CH_3-C$(CH_3)_2$-Br	tert-Butyl bromide	2-Bromo-2-methylpropane
$CHCl_3$	Chloroform	Trichloromethane
CH_3-CH$(Br)_2$	Ethylidene bromide	1,1-Dibromoethane
CH_2=CH-CH_2-I	Allyl iodide	3-Iodoprop-1-ene

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Alkyl Halide can be classified on the basis of various aspects. They are as follows.

Number of Halogen Atoms

Here, the classification mainly depends on whether they contain one, two, or more halogen atoms in their structure. Under this category we have;

1. Mono Haloalkane

Example: CH_3-CH_2-X [Where X can be Cl, F, Br or I]

2. Dihaloalkane

Example: X-CH_2-CH_2-X [Where X can be Cl, F, Br or I]

3. Trihaloalkane

Example: X-CH_2-CHX-CH_2-X [Where X can be Cl, F, Br or I]

The Position of Halogen atom Along the Chain of Carbon Atom

The classification depends on how the halogen atom is positioned on the chain of carbon atoms.

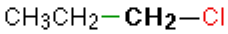
1. Primary alkyl halide
2. Secondary alkyl halide
3. Tertiary alkyl halide

Primary Alkyl Halide

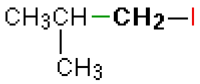
In this type of haloalkanes, the carbon which is bonded to the halogen family will be only attached to one other alkyl group. It doesn't matter how much bulky group is attached to it.

Some examples of primary haloalkanes are,

$CH_3-\mathbf{CH_2}-Br$



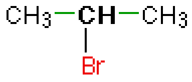
$CH_3CH_2-\mathbf{CH_2}-Cl$



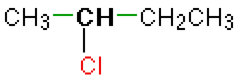
$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H-\mathbf{CH_2}-I$

Secondary Alkyl Halide

In this type of haloalkanes, the carbon atom which is bonded with the halogen atom is joined directly to the other two alkyl groups which can be same or different. Some of the examples are:



$CH_3-\underset{\displaystyle Br}{\underset{|}{\mathbf{CH}}}-CH_3$



$CH_3-\underset{\displaystyle Cl}{\underset{|}{\mathbf{CH}}}-CH_2CH_3$

Tertiary Alkyl Halide

In this type of haloalkanes, the carbon atom which carries the halogen atom is directly bonded to three alkyl group. These alkyl group maybe a combination of the same or different. Some examples are,

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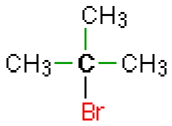
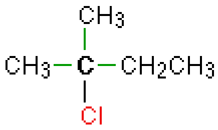
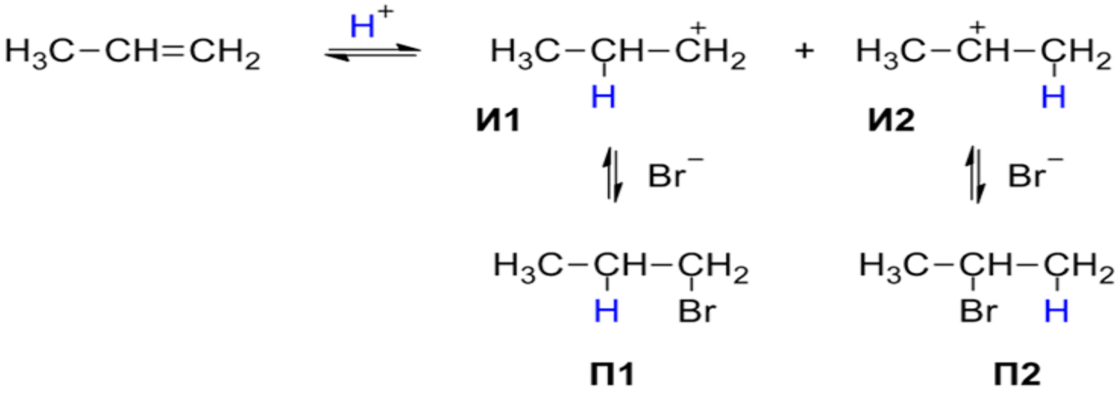



Preparation of Alkyl Halides

1. Preparation of Alkyl Halides from Alkenes



The addition of hydrogen halides to alkenes follows either Markovnikov’s rule or exhibit Kharash effect. All the electrophilic addition reactions of alkenes following Markovnikov rule are known as Markovnikov addition reactions.

2. Preparation of Alkyl Halides from Alcohols

Alkyl halides can easily be prepared from alcohols upon the addition of halides. In this reaction hydroxyl group of alcohol is replaced with the halogen atom attached to the other compound involved. This reaction requires a catalyst for primary and secondary alcohols whereas it doesn’t require any catalyst for tertiary alcohols.

$$CH_3CH_2OH + SOCl_2 \xrightarrow{\Delta} CH_3CH_2Cl + SO_2 + HCl$$

$$CH_3CH_2OH + PCl_3 \xrightarrow{\Delta} CH_3CH_2Cl + P(OH)_3 + HCl$$

$$CH_3CH_2OH + PCl_5 \xrightarrow{\Delta} CH_3CH_2Cl + POCl_3 + HCl$$

$$CH_3CH_2OH + PBr_3 \xrightarrow{\Delta} CH_3CH_2Br + P(OH)_3 + HBr$$

Preparation of alkyl halides from alcohols

3. Preparation of Alkyl Halides by Free Radical Halogenation

A complex mixture of isomeric mono and polyhaloalkanes obtained upon free radical chlorination or bromination of alkanes.

$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UVlight} CH_3CH_2CHCl\,CH_3 + CH_3CH_2CH_2CH_2Cl$$

Preparation of Alkyl Halides via Free Radical Halogenation

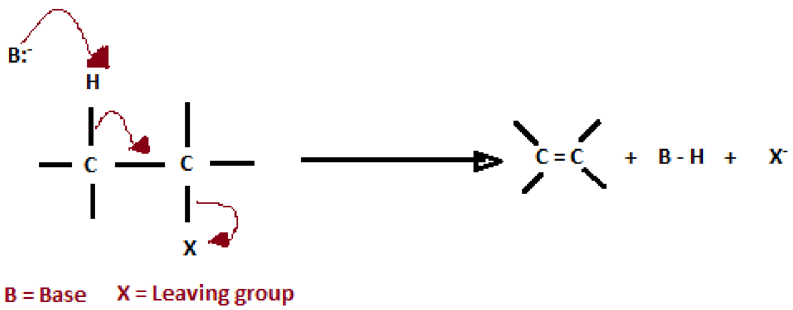
Chemical Reactions

The chemical reaction of haloalkanes can be divided into three categories:

1. Nucleophilic substitution reaction
2. Elimination reaction
3. Reaction with metals

Elimination Reaction

When a haloalkane having – hydrogen atom is heated with alcoholic solution of potassium hydroxide, it will lead to the elimination of hydrogen atom from β – carbon atom and a halogen atom from the α – carbon atom. As a result, an alkene is formed as one of the products. Since β – hydrogen atom is involved in elimination, it is often called β – elimination reaction.



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If there is any possibility of formation of more than one alkene due to the presence of more than one β – hydrogen atoms, usually one alkene is formed as the main product.

. Reaction with metal

Most organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon-metal bonds. Such compounds are known as organo-metallic compounds. An important class of organo-metallic compounds discovered by Victor Grignard in 1900 is alkyl magnesium halide, RMgX, referred as Grignard Reagents. These reagents are obtained by the reaction of haloalkanes with magnesium metal in dry ether.

$CH_3CH_2Br + Mg \xrightarrow{\text{Dry ether}} CH3CH2MgBr$

In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium; the magnesium halogen bond is essentially ionic.

$R^{\partial-}\text{-}Mg^{\partial+}X^{\partial-}$

Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. Even water, alcohols, amines are sufficiently acidic to convert them to corresponding hydrocarbons.

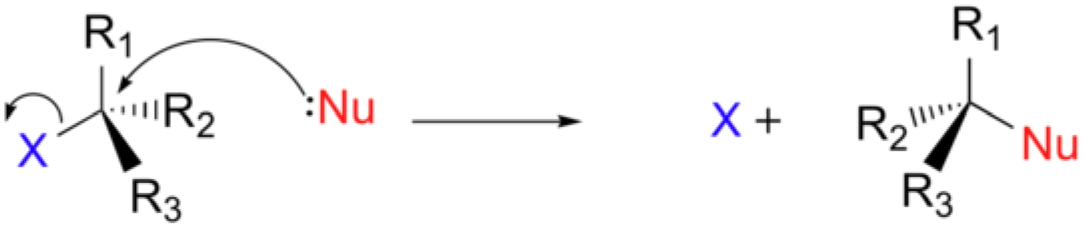
$RMgX + H_2O \rightarrow RH + Mg[OH]X$

It is therefore necessary to avoid even traces of moisture from a Grignard reagent. On the other hand, this could be considered as one of the methods for converting halides to hydrocarbons.

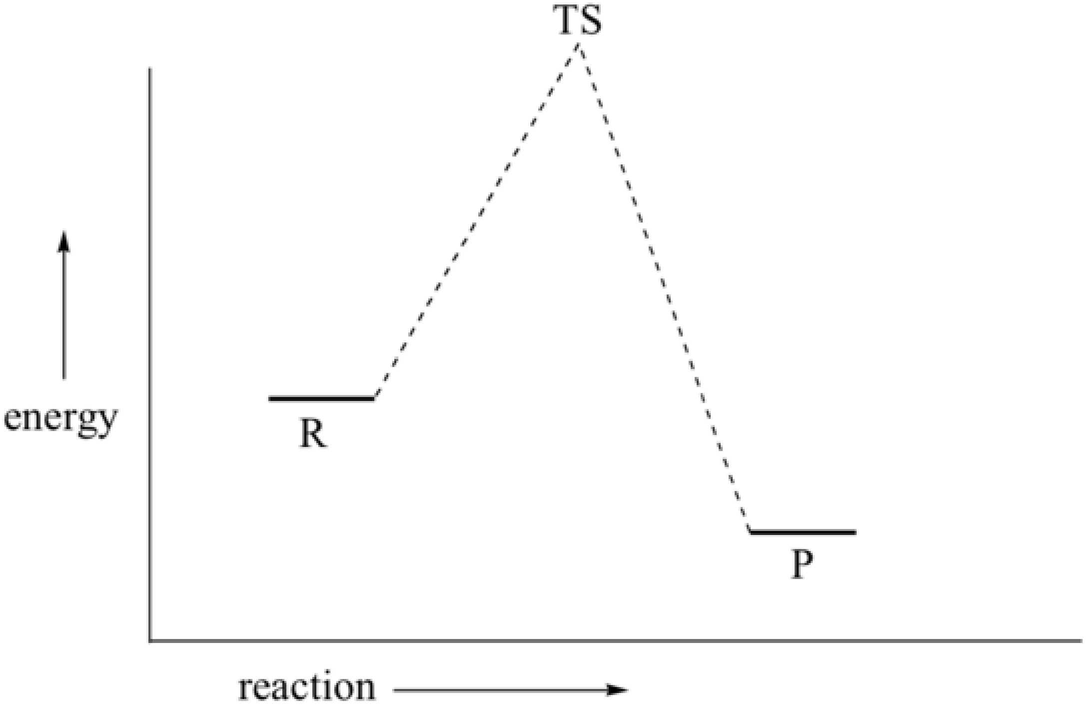
Nucleophilic Substitution Reaction

The S_N2 mechanism

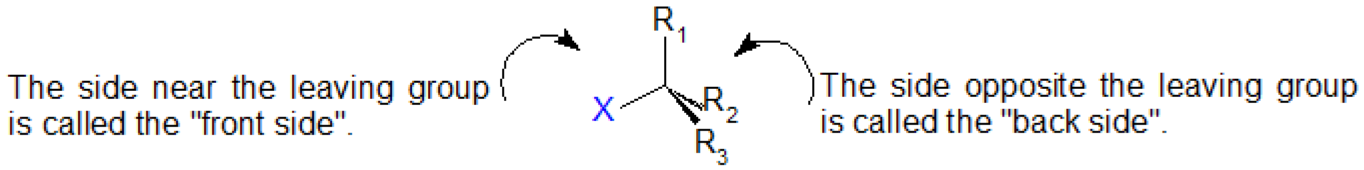
There are two mechanistic models for how an alkyl halide can undergo nucleophilic substitution, S_N2 and S_N1. The S_N2 reaction takes place in a single step with bond-forming and bond-breaking occurring simultaneously. (In all figures in this section, 'X' indicates a halogen substituent).

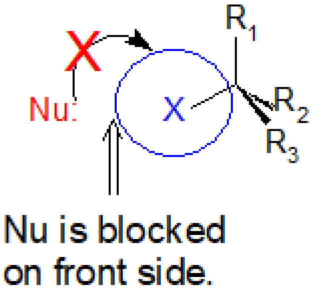


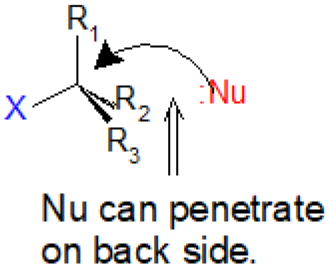
This is called an '**S_N2**' mechanism. In the term S_N2, S stands for 'substitution', the subscript N stands for 'nucleophilic', and the number 2 refers to the fact that it is a **bimolecular reaction**: the overall rate depends on a step in which two separate molecules (the nucleophile and the electrophile) collide. A potential energy diagram for this reaction shows the transition state (TS) as the highest point on the pathway from reactants to products.



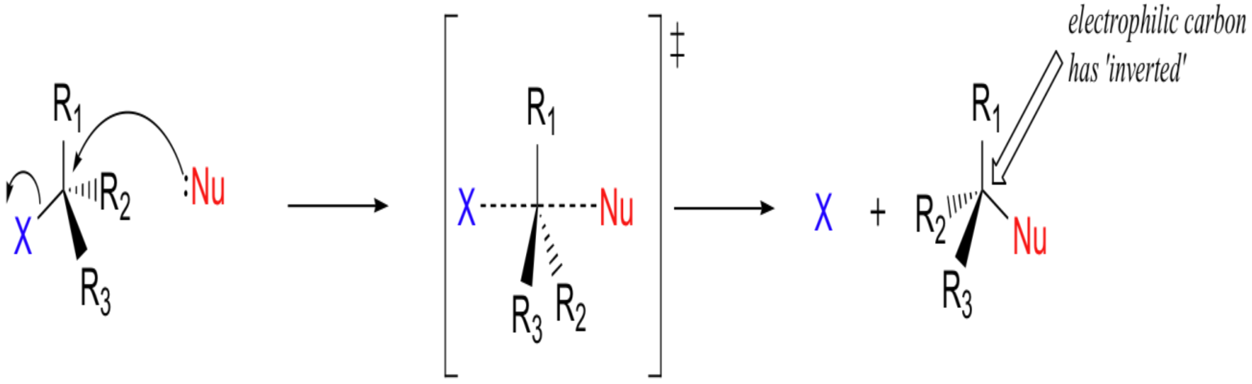
If you look carefully at the progress of the S_N2 reaction, you will realize something very important about the outcome. The nucleophile, being an electron-rich species, must react with the electrophilic carbon from the *back side* relative to the location of the leaving group. Approach from the front side simply doesn't work: the electron rich, leaving group blocks the way with electrostatic repulsion and steric hindrance.







The result of this backside penetration is that the stereochemical configuration at the central carbon *inverts* as the reaction proceeds. In a sense, the molecule is turned inside out. At the transition state, the electrophilic carbon and the three 'R' substituents all lie on the same plane.



transition state

What this means is that S_N2 reactions whether enzyme catalyzed or not, are inherently stereoselective: when the substitution takes place at a stereocenter, we can confidently predict the stereochemical configuration of the product. Below is an animation illustrating the principles we have just learned, showing the S_N2 reaction between hydroxide ion and methyl iodide. Notice how backside attack by the hydroxide nucleophile results in inversion at the tetrahedral carbon electrophile.

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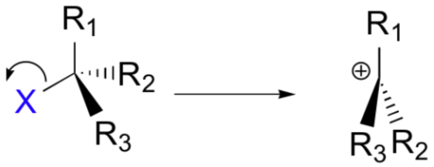
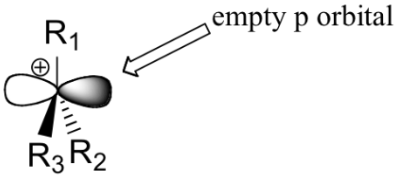
The S_N1 mechanism with Stereochemistry

A second model for a nucleophilic substitution reaction is called the '**dissociative**' or '**S_N1**' mechanism. In many cases, the nucleophile is the solvent, so this mechanism can also be called "solvolysis".

Step1: In the S_N1 mechanism, the carbocation forms when the C-X bond breaks *first*, before the nucleophile approaches



Th carbocation has a central carbon with only three bonds and bears a formal charge of +1. Recall that a carbocation should be pictured as *sp^2* hybridized, with trigonal planar geometry. Perpendicular to the plane formed by the three *sp^2* hybrid orbitals is an empty, unhybridized *p* orbital.



Step 2: The nucleophile reacts with the empty, 'electron hungry' *p* orbital of the carbocation to form a new bond and return the carbon to tetrahedral geometry. Because of this trigonal planar geometry, the nucleophile can approach the carbocation from either lobe of the empty p orbital (aka either side of the carbocation). This means that about half the time the product has the same stereochemical configuration as the starting material (retention of configuration), and about half the time the stereochemistry has been inverted. In other words, *racemization* of the product occurs during SN1 reactions if the electrophilic carbon is chiral. If the intermediate from a chiral alkyl halide survives long enough to encounter a random environment, the products are expected to be racemic (a 50:50 mixture of enantiomers). On the other hand, if the departing halide anion temporarily blocks the front side, or if a nucleophile is oriented selectively at one or the other face, then the substitution might occur with predominant inversion or even retention of configuration.

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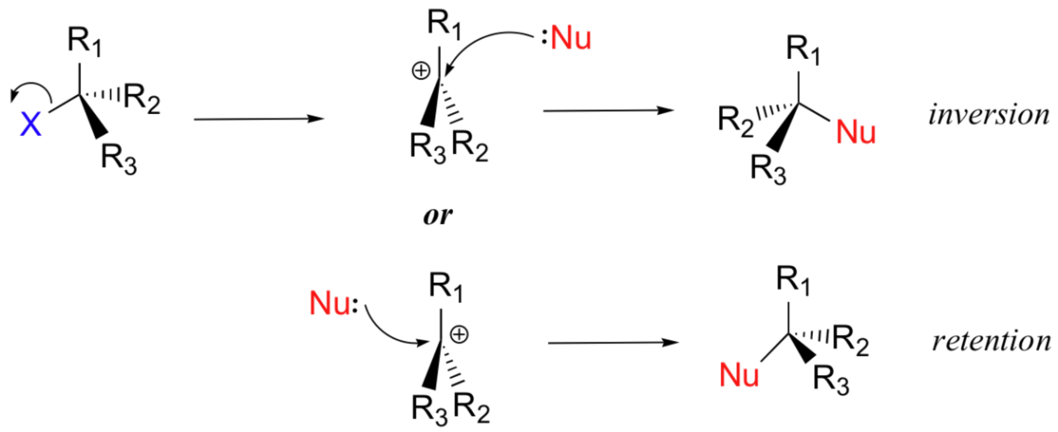
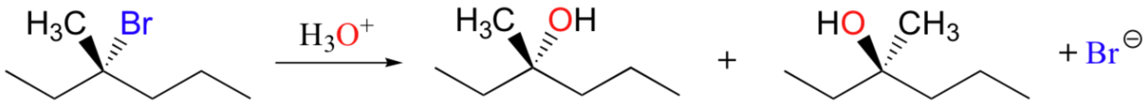
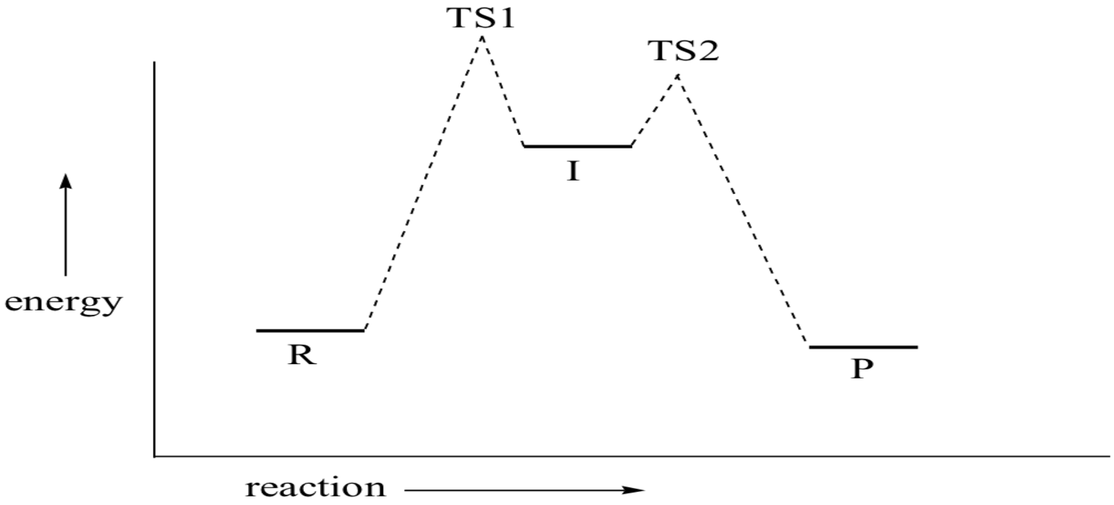
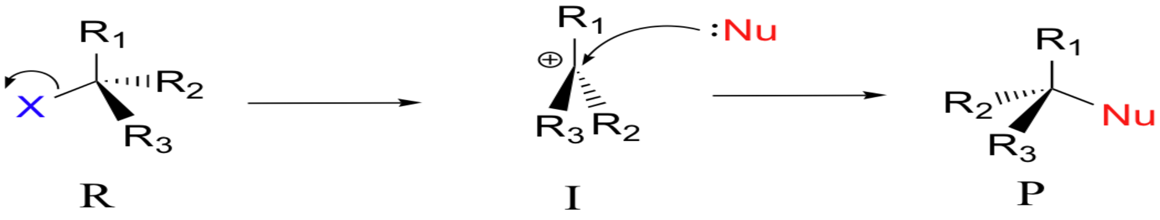


As an example, the tertiary alkyl bromide below, (S)-3-bromo-3-methylhexane, would be expected to form a racemic mix of *R*- and *S*-3-methyl-3-hexanol after an S_N1 reaction with water as the nucleophile.







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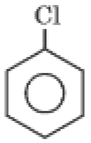
Aryl halide

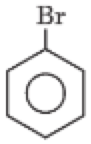
Aryl halide is a chemical compound containing arenes, where one or more hydrogen atoms are bonded to the aromatic ring are replaced with halogens. They are generally denoted by “Ar-X” where ‘X’ denotes the halogen atom attached and ‘Ar’ stands for the aryl group.

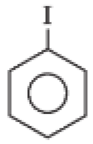
Nomenclature of Haloarenes

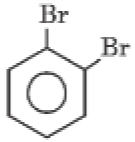
- Aryl halides are named by prefixing “halo” to the name of the parent aromatic hydrocarbon.
- If there is more than one substituent on the ring then the relative positions of the substituents are indicated by mathematical numerals.
- In the common system, the relative position of two groups is shown by prefixes ortho, meta or para.

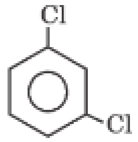
The common and IUPAC names of some representative haloarenes are given below.

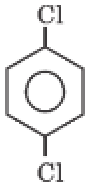

Chlorobenzene

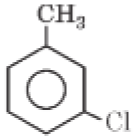

Bromobenzene

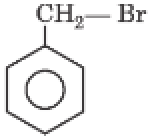

Iodobenzene


1,2-Dibromobenzene
(*ortho*-Dibromobenzene)


1, 3-Dichlorobenzene
(*meta*-Dichlorobenzene)


1,4-Dichlorobenzene
(*para*-Dichlorobenzene)

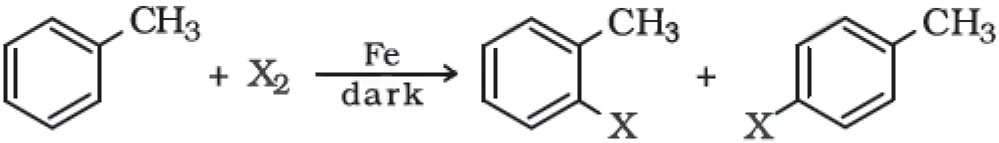

3-Chlorotoluene
(*meta*-Chlorotoluene)


Phenylbromomethane
(Benzyl bromide)

Preparation of Aryl Halides

1. Preparation of Aryl Halides via Electrophilic Substitution Reactions

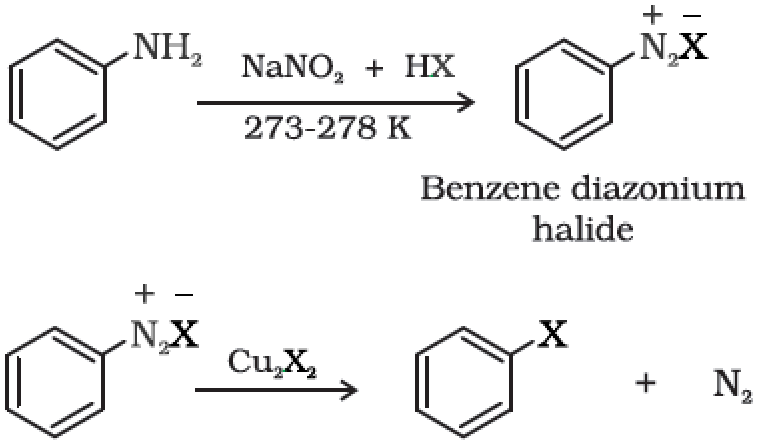
Aryl halides can be prepared by electrophilic aromatic substitution of arenes with halogens in the presence of a Lewis acid.



Preparation of aryl halides via electrophilic substitution reactions

2. Preparation of Aryl Halides through Sandmeyer's Reaction

Aryl halides can also be prepared by mixing the solution of freshly prepared diazonium salt from the primary aromatic amine with cuprous chloride or cuprous bromide.



Preparation of aryl halides through Sandmeyer's reaction

Nucleophilic Substitution

The carbon-halogen bonds of aryl halides are like those of alkenyl halides in being much stronger than those of alkyl halides . *The simple aryl halides generally are resistant to attack by nucleophiles in either ,* S_N1 *or* S_N2 *reactions* . However, this low reactivity can be changed dramatically by changes in the reaction conditions and the structure of the aryl halide. In fact, nucleophilic displacement becomes quite rapid when the aryl halide is activated by substitution with strongly electron-attracting groups such as NO_2, and when very strongly basic nucleophilic reagents are used.

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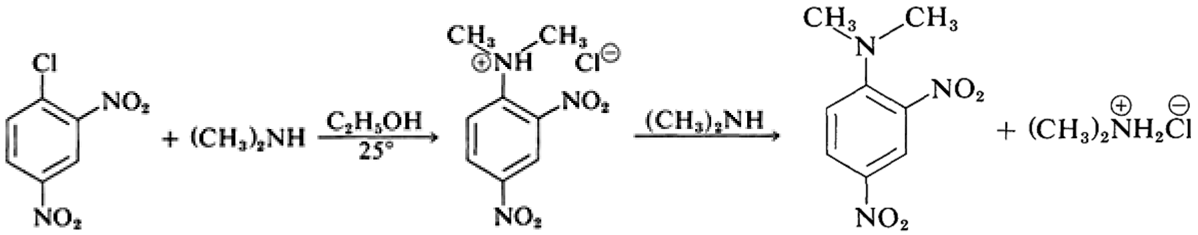
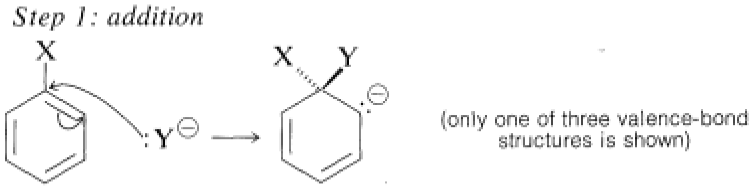
Addition-Elimination Mechanism of Nucleophilic Substitution

Although the simple aryl halides are inert to the usual nucleophilic reagents, *considerable activation is produced by strongly electron-attracting substituents provided these are located in either the* ortho *or* para *positions, or both*. For example, the displacement of chloride ion from 1-chloro-2,4-dinitrobenzene by dimethylamine ethanol solution at room temperature. Under the same occurs readily in conditions chlorobenzene completely fails to react; thus the activating influence of the two nitro groups amounts to a factor of at least 10^8



The generally accepted mechanism of nucleophilic aromatic substitution of aryl halides carrying activating groups involves two steps

The first step involves attack of the nucleophile y^- at the carbon bearing the halogen substituent to form an intermediate carbanion 4



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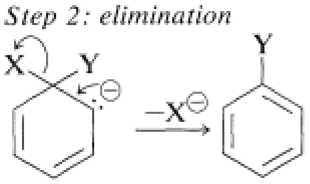
In the second step, loss of an anion, x^- or y^-, regenerates an aromatic system, and, if x^- is lost, the overall reaction is nucleophilic displacement of X by Y



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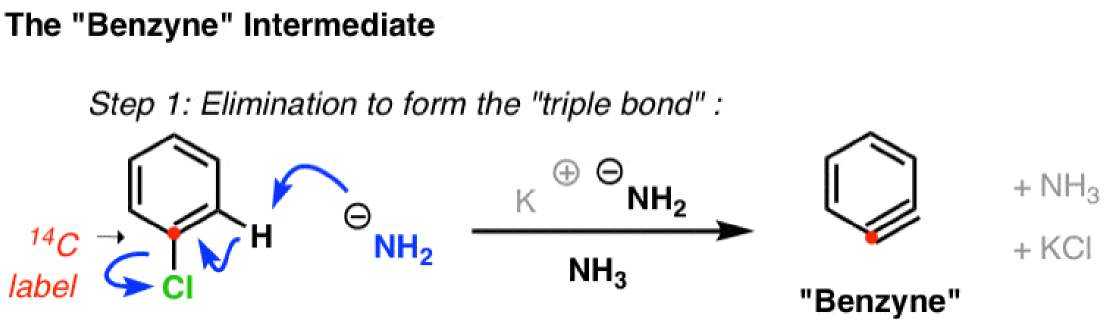
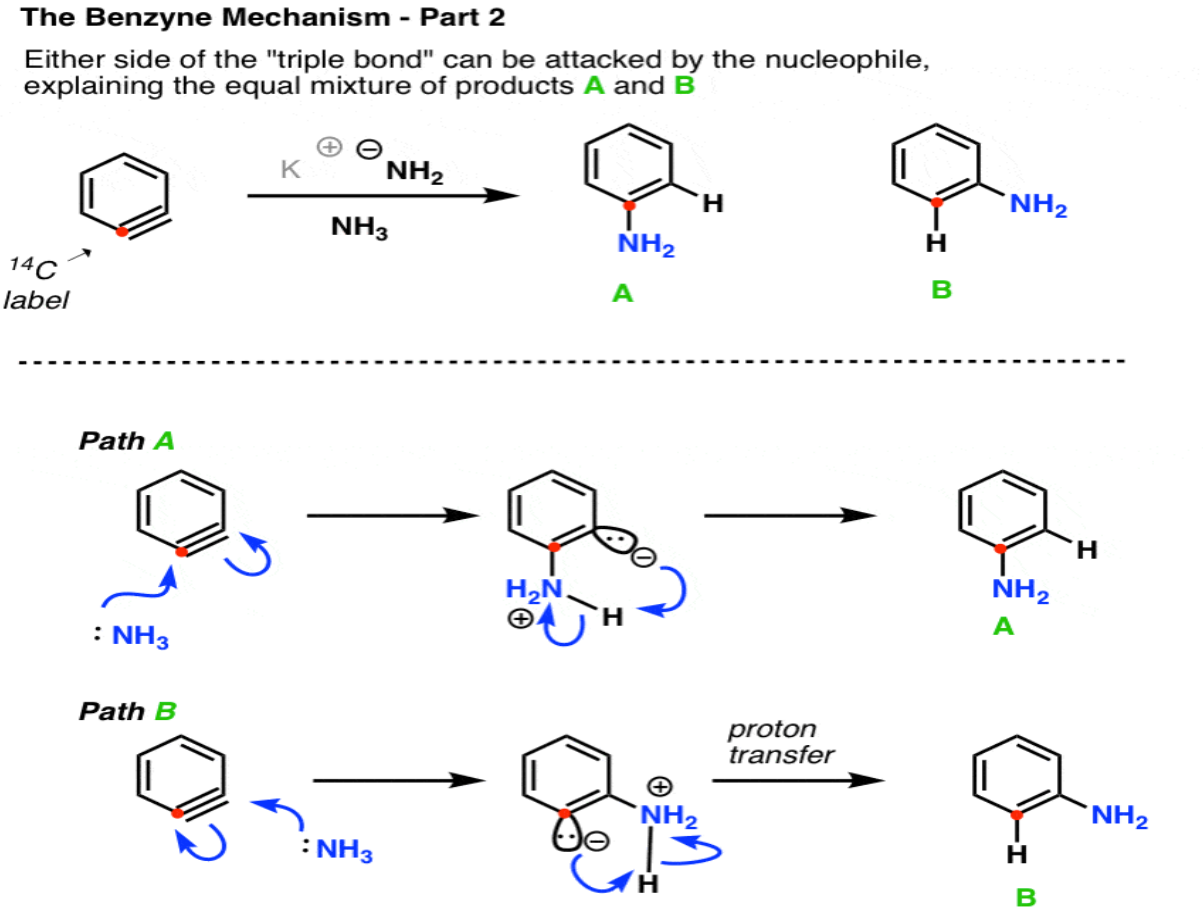
Elimination-Addition Mechanism of Nucleophilic Aromatic Substitution

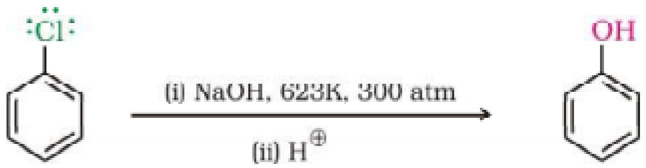


In the second step (addition), attack of the can come at **either** side of the triple bond, resulting in about a 1:1 mixture of the product with NH_2 attached to the labeled carbon (**A**) and NH_2 adjacent to the labeled carbon (**B**).

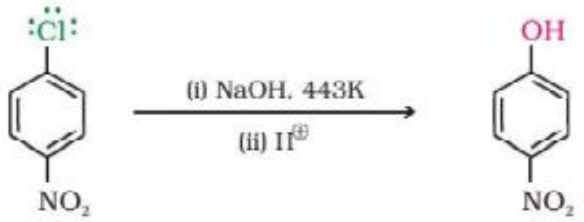


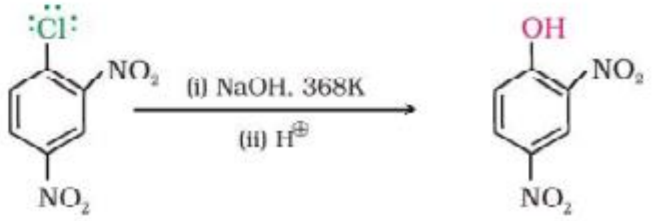
Replacement by hydroxyl group

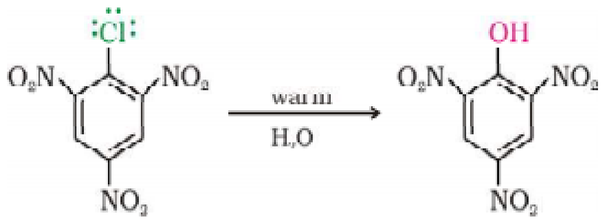
Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution at a temperature of 623K and a pressure of 300 atmospheres.



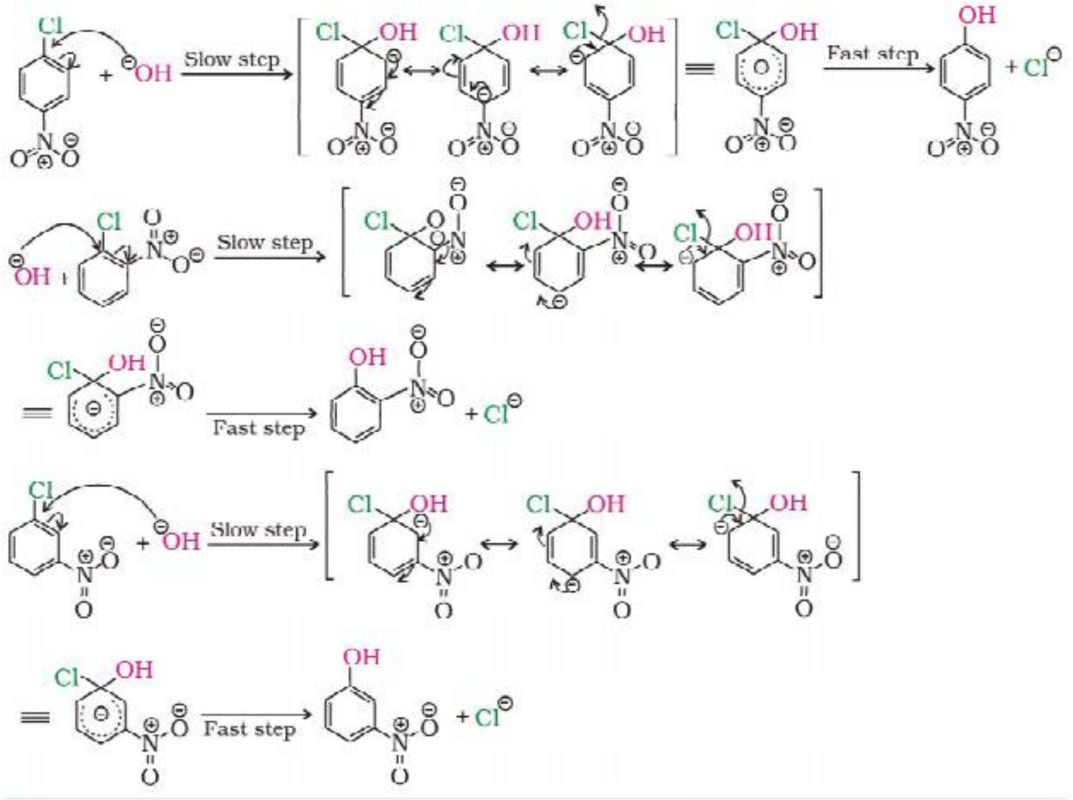
The presence of an electron withdrawing group (-NO2) at ortho- and para-positions increases the reactivity of haloarenes.





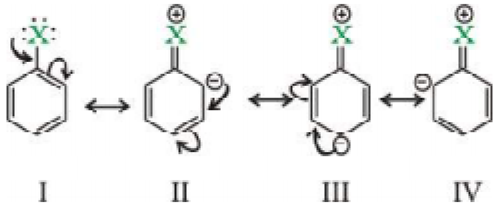


The effect is pronounced when (-NO2) group is introduced at orthoand para- positions. However, no effect on reactivity of haloarenes is observed by the presence of electron withdrawing group at meta-position. Mechanism of the reaction is as depicted:

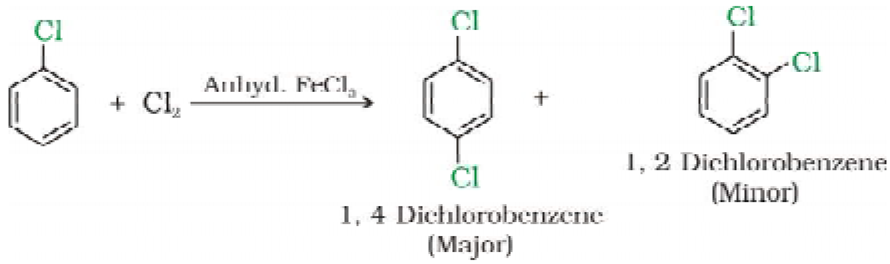


Electrophilic substitution reactions

Haloarenes undergo the usual electrophilic reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel-Crafts reactions. Halogen atom besides being slightly deactivating is o, pdirecting; therefore, further substitution occurs at ortho- and parapositions with respect to the halogen atom. The o, p-directing influence of halogen atom can be easily understood if we consider the resonating structures of halobenzene as shown:



Due to resonance, the electron density increases more at ortho- and para-positions than at meta-positions. Further, the halogen atom because of its the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.
(i) Halogenation



(ii) Nitration

(iii) Sulphonation

(iv) Friedel-Crafts reaction

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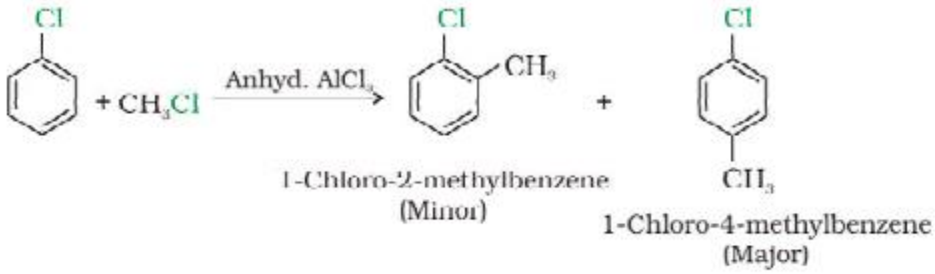
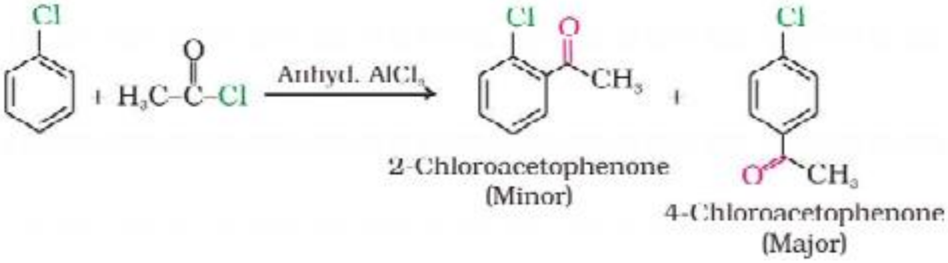




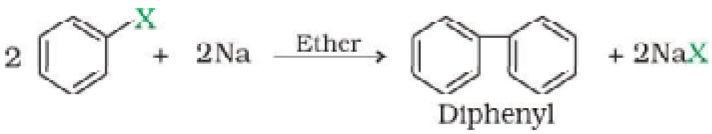
3. Reaction with metals

Wurtz-Fittig reaction

A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether and is called Wurtz-Fittig reaction.

Fittig reaction

Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction.



Relative Reactivity of Alkyl Halide V/S Ally , Vinyl and Aryl

$CH_2{=}CH{-}Cl$ (Vinyl chloride) and $CH_2{=}CH{-}CH_2{-}Cl$ (Allyl chloride)

In allyl chloride, chlorine is attached to *sp*3 carbon atom.
In vinyl chloride, chlorine is attached to *sp*2 carbon atom.

*sp*2 carbon atom is more electronegative than *sp*3 carbon atom.

Hence, the bond pair of electrons of C-Cl bond in allyl chloride are less strongly held than that in vinyl chloride and the removal of chlorine is easier in allyl chloride than in vinyl chloride.
Hence, allyl chloride is more reactive than vinyl chloride.

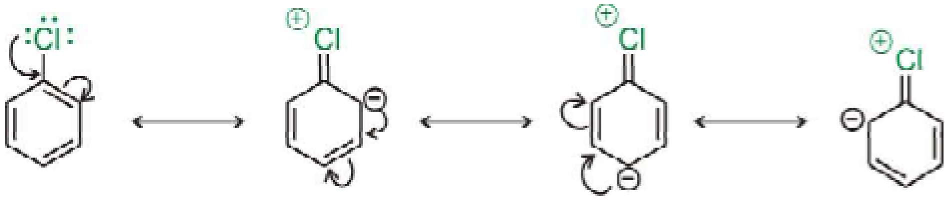
If compared to Alkyl Halides, Viny halides are less reactive towards nucleophilic substitution than Alkyl Halides. In vinyl halide the loan pair on halogen participates in delocalization with its conjugated double bond. This +R effect introduces a double bond character between carbon & halogen, which decreases the positive charge on carbon. Due to reduced electrophilic character of carbon in vinyl halide, the nucleophilic reagent does not attacks it readily

In Allyl halide, the reactivity towards nucleophilic substitution is more than alkyl halide. In allyl halide the removal of x^- results in formation of allyl carbocation , which is stable due to delocalizaton

$H_2C{=}CH{-}CH_2{-}X \rightarrow H_2C{=}CH{-}C^+H_2 \leftrightarrow H_2C^+{-}CH{=}CH_2$

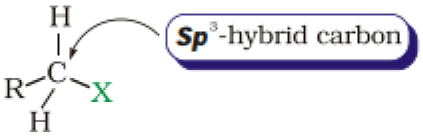
Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

(i) Resonance effect : In haloarenes, the electron pairs on halogen atom are in conjugation with p-electrons of the ring and the following resonating structures are possible.



C Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

Difference in hybridisation of carbon atom in C X bond: In haloalkane, the carbon atom attached to halogen is sp3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp2-hybridised.



The sp2 hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C X bond more tightly than sp3-hybridised carbon in haloalkane with less schararcter. Thus, C Cl bond length in haloalkane is 177pm while in haloarene is 169 pm. Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

(iii) Instability of phenyl cation: In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, SN1 mechanism is ruled out.

(iv) Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.