# Aryl halide and vinyl halide

# Aryl Halides


Aryl halides are halides in which the halogen is attached directly to an aromatic ring.

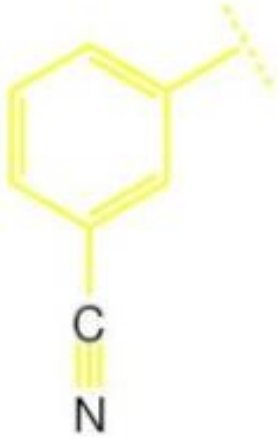
Carbon-halogen bonds in aryl halides are shorter and stronger than carbon-halogen bonds in alkyl halides.

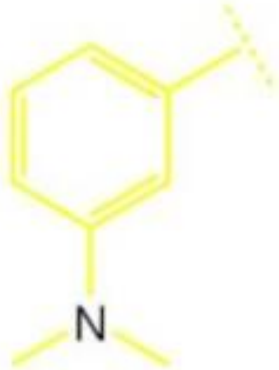
# What's the Difference Between Ar- and Ph-?

Phen I refers specifically to this:



Aryl is a general term for all aromatic ring systems:



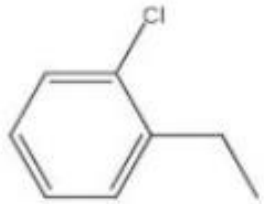

# Nomenclature

Aryl halides are named by prefixing the name of the halogen to benzene. For example:

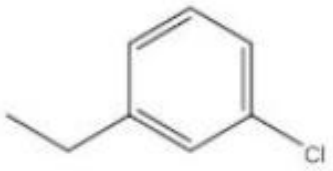
Numbering of the ring begins at the halogen-substituted carbon and proceeds in the direction of the next substituted carbon that possesses the lower number.

## *Ortho, meta or para ?*

Mono-substituted aryl halides are characterised using the prefix ortho (*o*-), meta (*m*-) or para (*p*-) depending on the placement of the substituent from the halogen or the halogen from a higher priority functional group: 1,2-, 1,3- or 1,4- respectively.

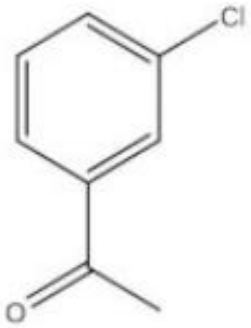



1-chloro-2-ethylbenzene
or
*o*-ethylchlorobenzene

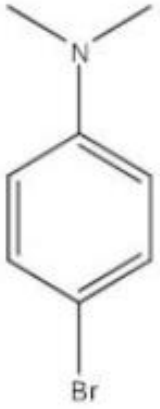



1-chloro-3-ethylbenzene
or
*m*-ethylchlorobenzene

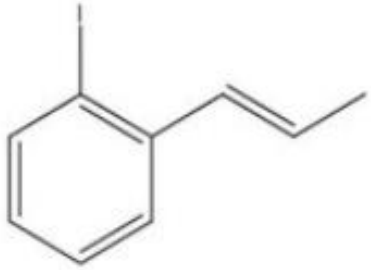

1-chloro-4-ethylbenzene
or
*p*-ethylchlorobenzene



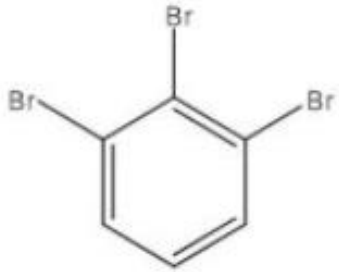

1-(3-chlorophenyl)ethanone



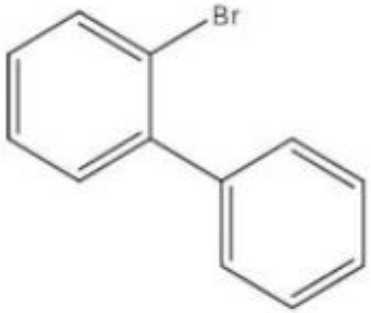

4-bromo-*N*,*N*-dimethylaniline



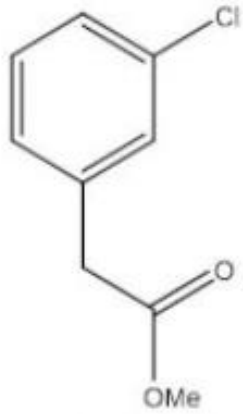

(*E*)-1-iodo-2-(prop-1-enyl)benzene




1,2,3-tribromobenzene




2-bromobiphenyl




methyl 2-(3-chlorophenyl)acetate

# Physical properties

- The physical properties of unsubstituted aryl halides are much like those of the corresponding alkyl halides.

- Thus, boiling points, melting points, and solubilities of aryl halides are very similar to those of alkyl halides containing the same number of carbon atoms.

## Boiling points

Chlorobenzene, bromobenzene and iodobenzene are all oily liquids. The boiling points increase as the halogen atom gets bigger.

| Compounds | boiling point (°C) |
|---|---|
| $C_6H_5Cl$ | 132 |
| $C_6H_5Br$ | 156 |
| $C_6H_5I$ | 189 |

- The main attractions between the molecules will be van der Waals dispersion forces.

These increase as the number of electrons in the molecule increases. This is the reason that the boiling points increase as the halogen atom gets bigger.

There will also be permanent dipole-dipole attractions involved in the chlorobenzene and bromobenzene, but very little in the iodobenzene. Iodine has much the same electronegativity as carbon.

# Solubility in water

The aryl halides are insoluble in water. They are denser than water and form a separate lower layer.

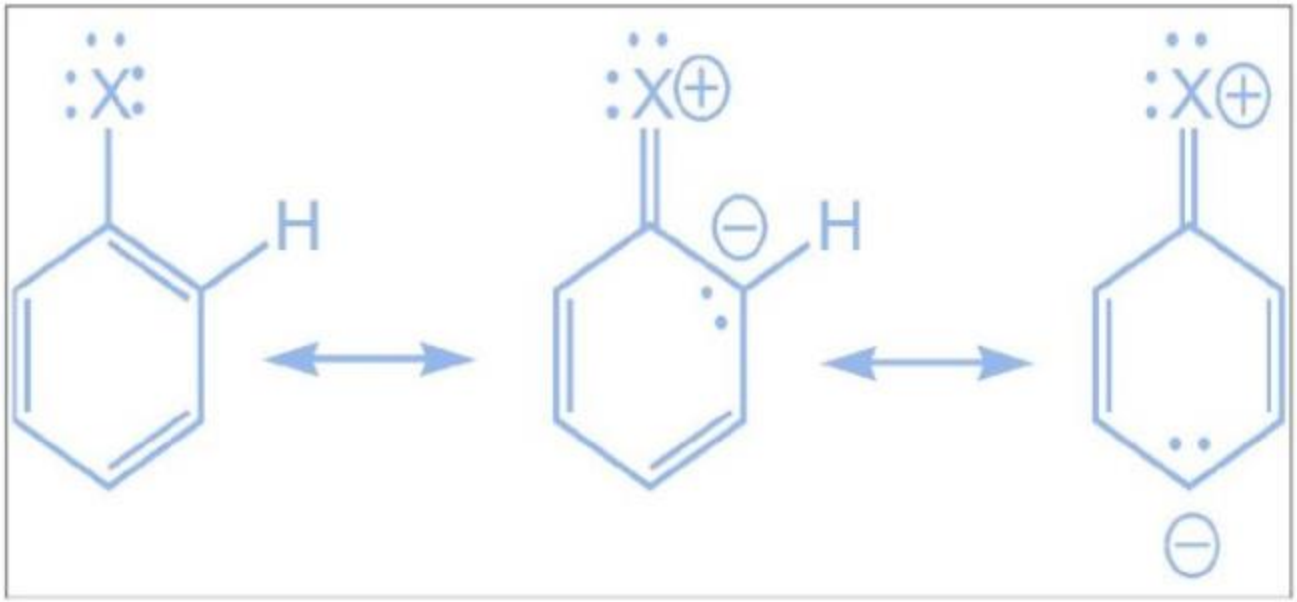
The molecules are quite large compared with a water molecule. In order for chlorobenzene to dissolve it would have to break lots of existing hydrogen bonds between water molecules and also have to break the quite strong van der Waals dispersion forces between chlorobenzene molecules. Both of these cost energy.

The only new forces between the chlorobenzene and the water would be van der Waals dispersion forces.

These aren't as strong as hydrogen bonds (or the original dispersion forces in the chlorobenzene), and so wouldn't get much energy released when they form.

It simply isn't energetically profitable for chlorobenzene (and the others) to dissolve in water.

# Resonance Picture



# Synthesis of Aryl Halides

The two most common methods of preparing aryl halides are by direct **halogenation of benzene and via diazonium salt reactions.**

Preparing chlorobenzene and bromobenzene by reacting chlorine or bromine with benzene, and preparing iodobenzene from benzenediazonium chloride.

## Preparation of Chlorobenzene

- Benzene reacts with chlorine in the presence of a catalyst, replacing one of the hydrogen atoms on the ring by a chlorine atom.

- The reaction happens at room temperature. The catalyst is either aluminium chloride or iron.

- Strictly speaking iron isn't a catalyst, because it gets permanently changed during the reaction. It reacts with some of the chlorine to form iron(III) chloride, $FeCl_3$.
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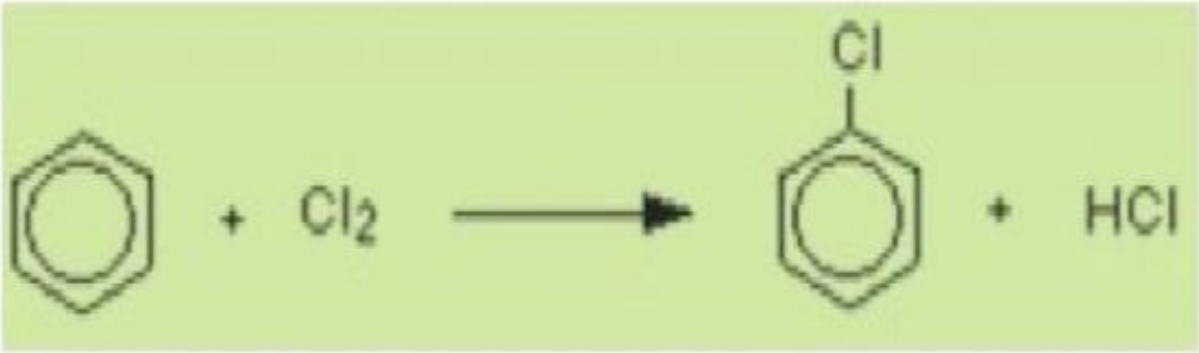
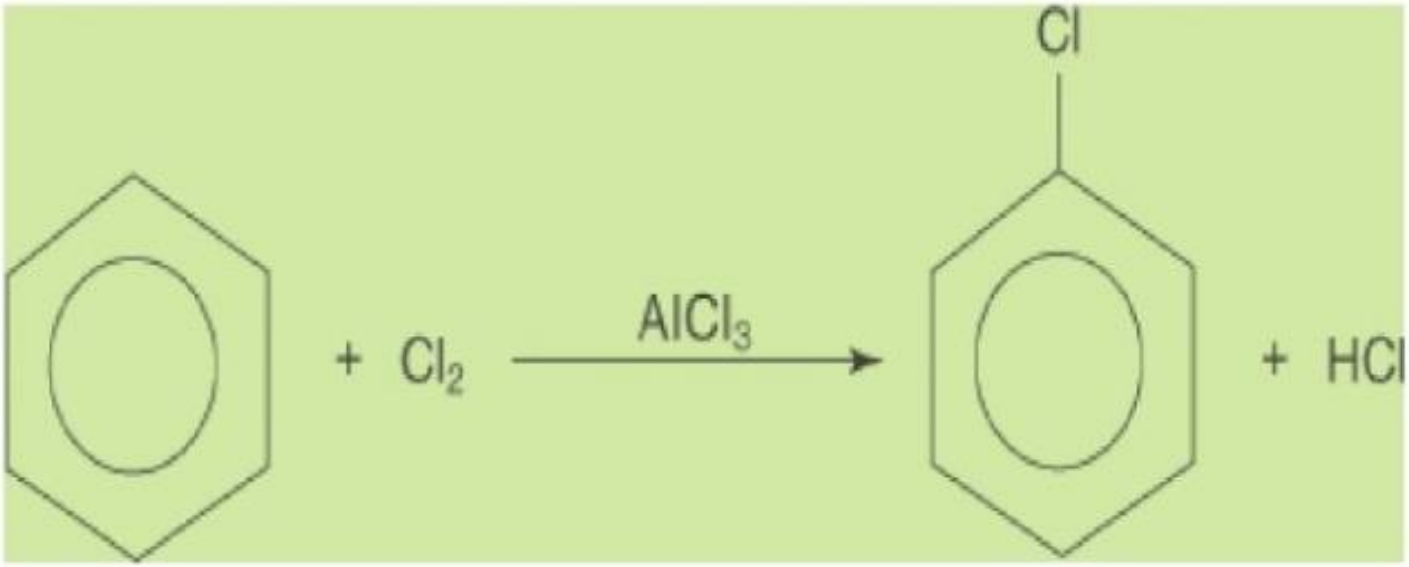


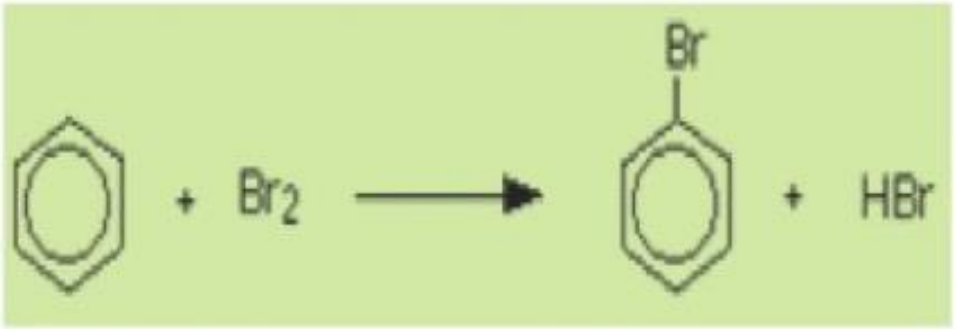
The reaction between benzene and chlorine in the presence of either aluminium chloride or iron gives chlorobenzene.



# Preparation of Bromobenzene

- The reaction between benzene and bromine in the presence of either aluminium bromide (rather than aluminium chloride) or iron gives bromobenzene.

- Iron is usually used because it is cheaper and more readily available. If we use iron, it is first converted into iron(III) bromide by the reaction between the iron and bromine.

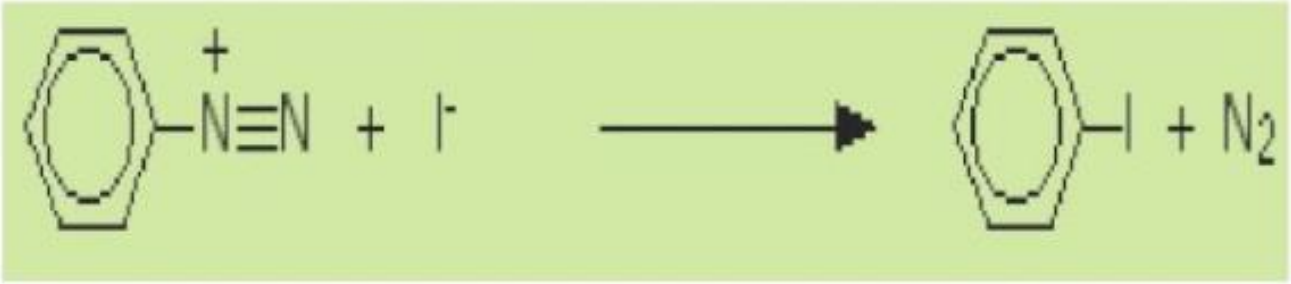


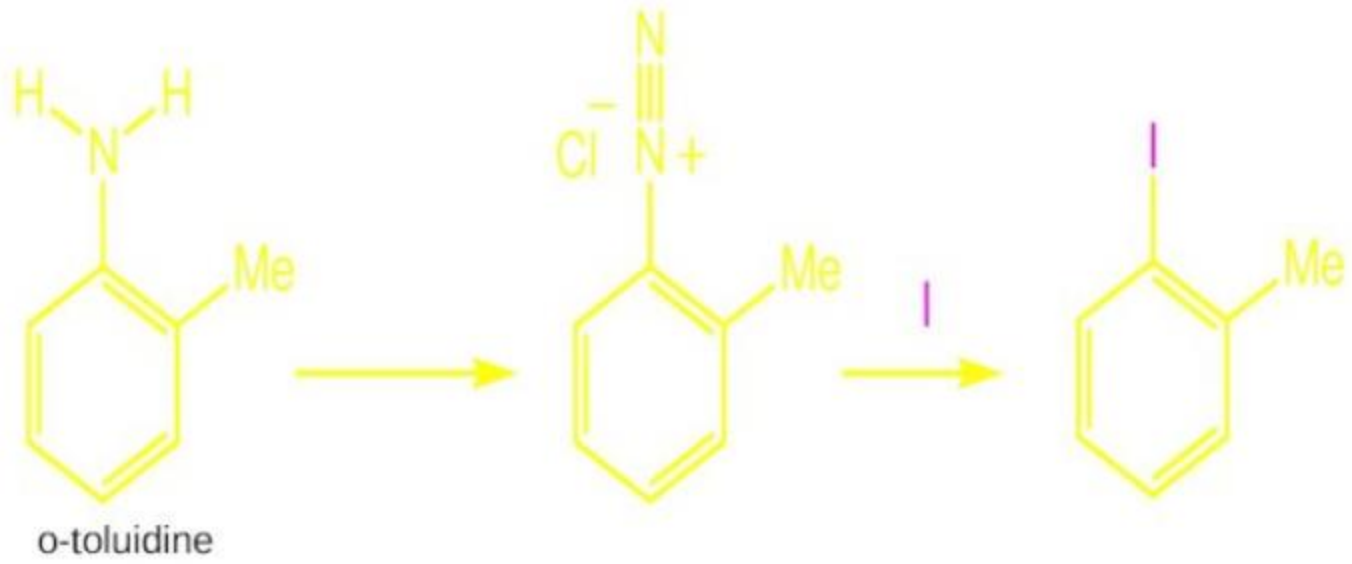
# Preparation of Iodobenzene

- Iodobenzene can be made from the reaction of benzene with iodine if they are heated under reflux in the presence of concentrated nitric acid, but it is normally made from benzenediazonium chloride solution. That's what we will concentrate on here.

- If you add cold potassium iodide solution to ice-cold benzenediazonium chloride solution, nitrogen gas is given off, and you get oily droplets of iodobenzene formed.

- There is a simple reaction between the diazonium ions present in the benzenediazonium chloride solution and the iodide ions from the potassium iodide solution.





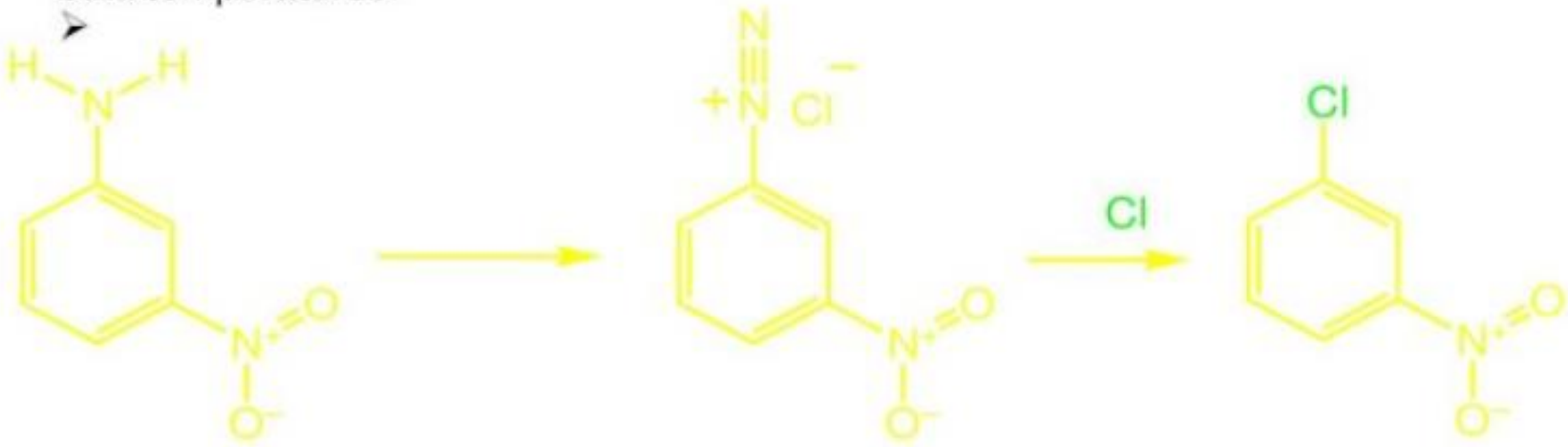

o-toluidine

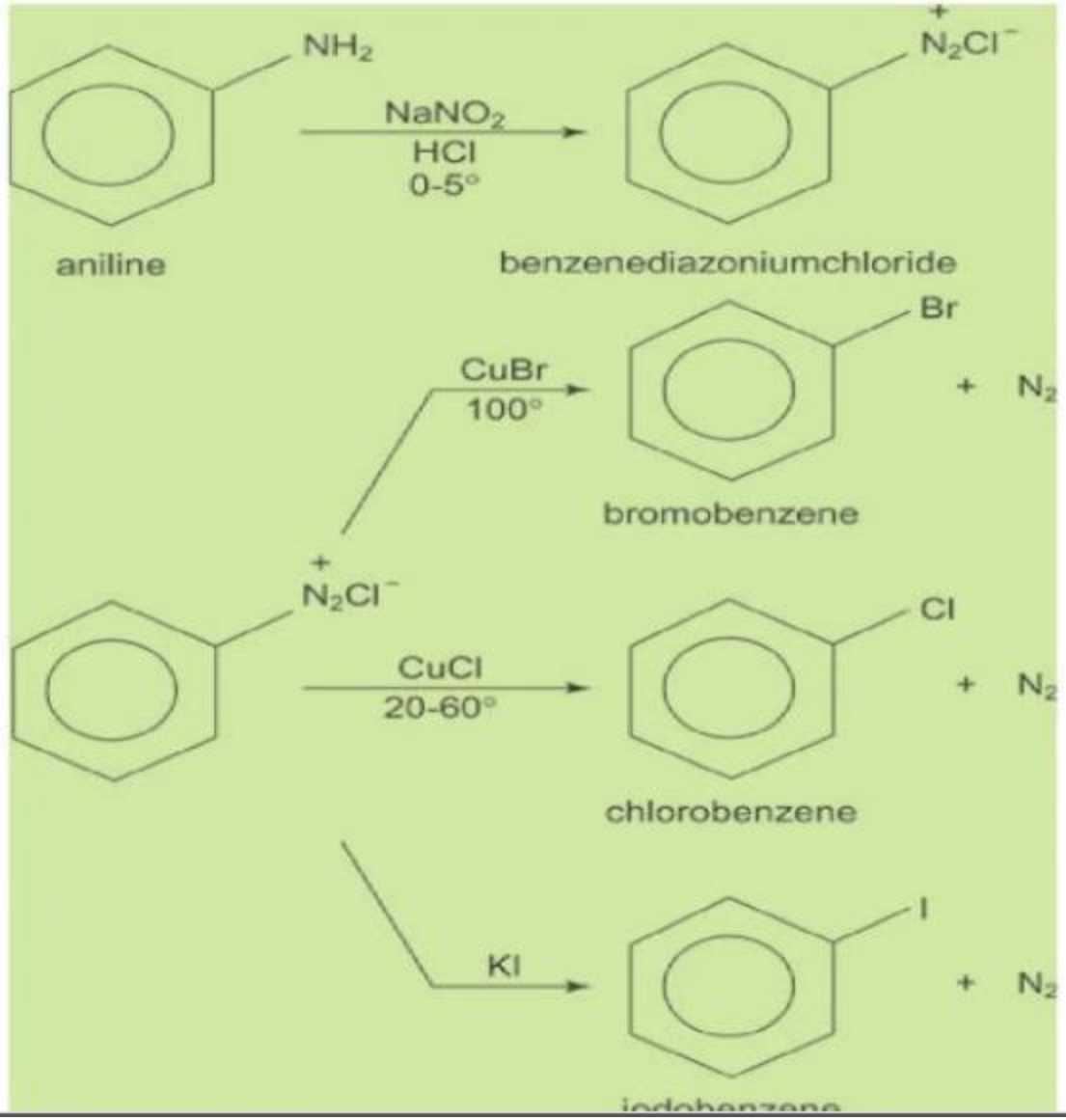
# Sandmeyer reaction

- A second method for preparing aryl halides is the Sandmeyer reaction.

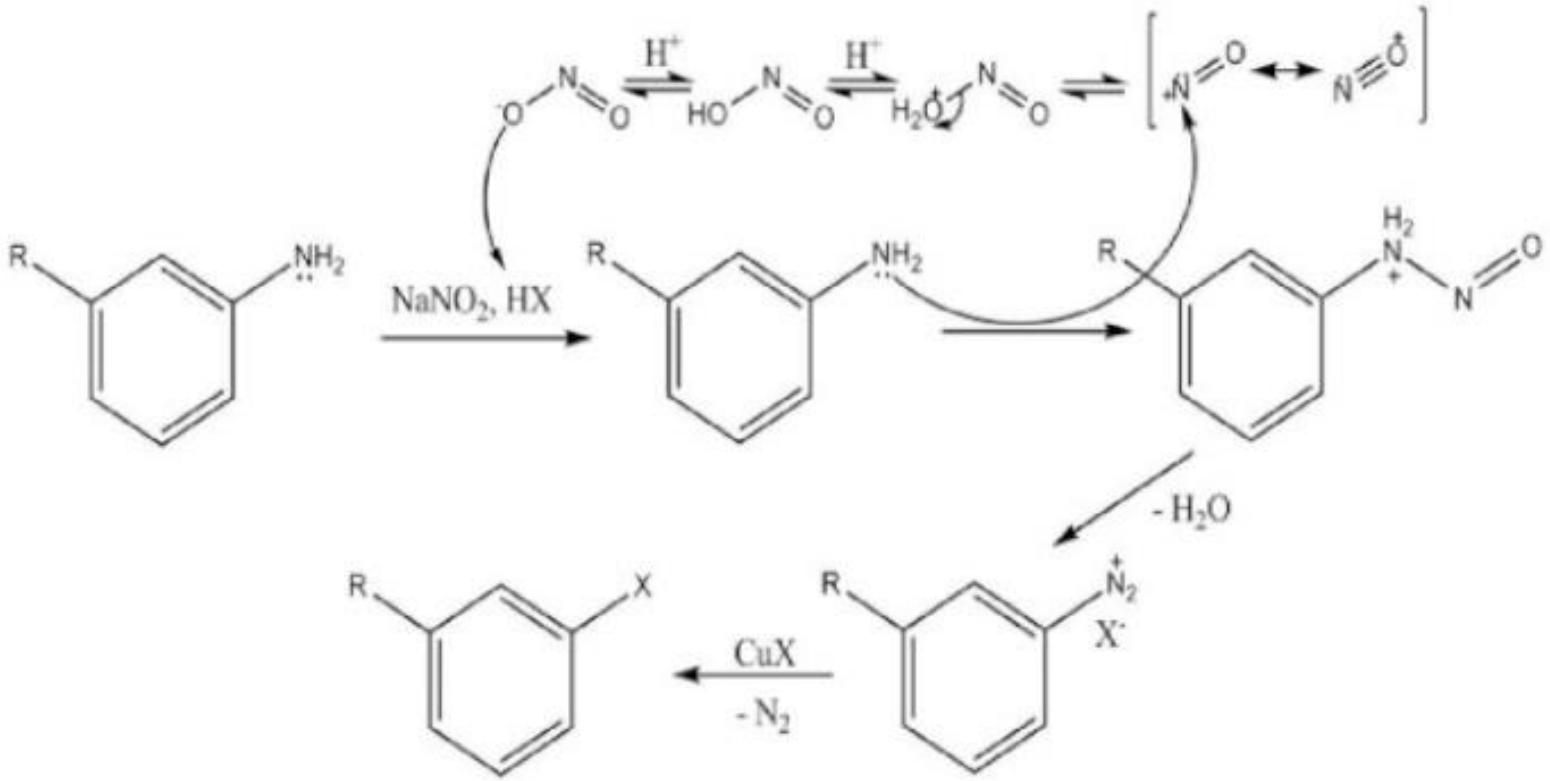
- During a **Sandmeyer reaction,** a diazonium salt reacts with copper (I) bromide, copper (I) chloride, or potassium iodide to form the respective aryl halide.

- The diazonium salt is prepared from aniline by reaction with nitrous acid at cold temperatures.



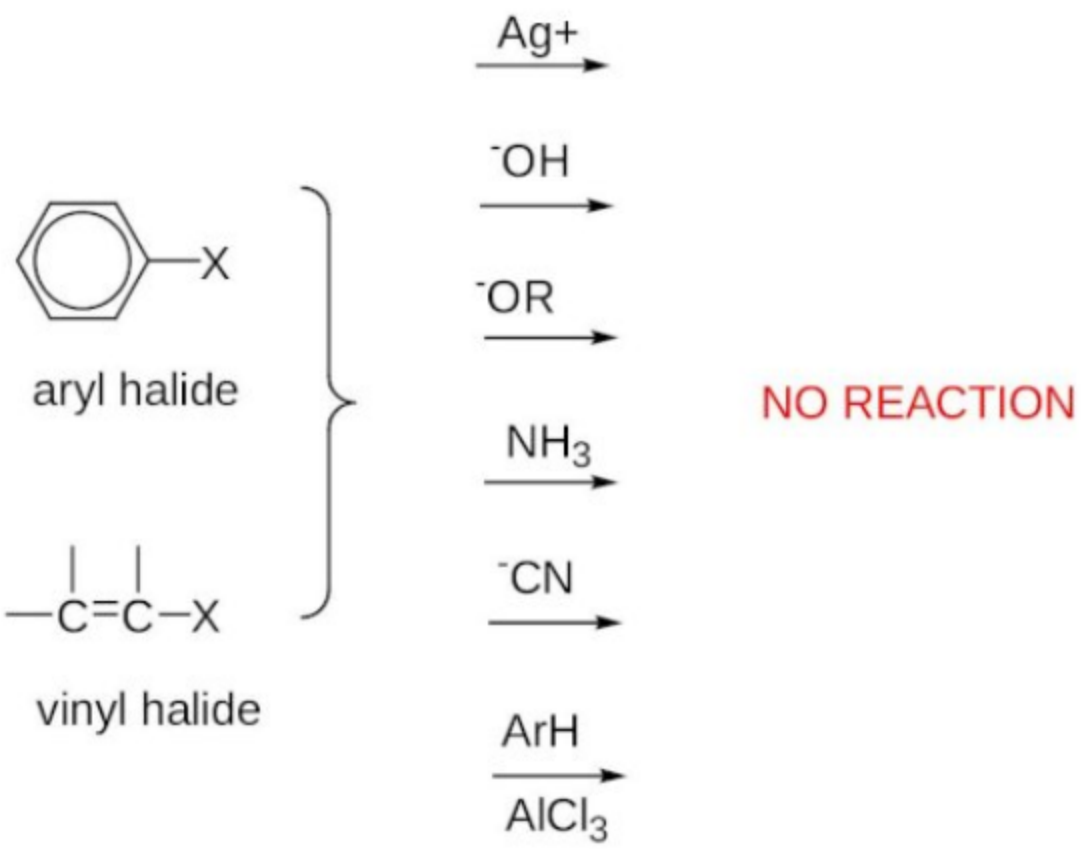

NH2
NaNO2
HCl
0-5°
+
N2Cl−
aniline
benzenediazoniumchloride
CuBr
100°
Br
+ N2
bromobenzene
+
N2Cl−
CuCl
20-60°
Cl
+ N2
chlorobenzene
KI
I
+ N2

An aromatic (or heterocyclic) amine quickly reacts with a nitrite to form an aryl diazonium salt, which decomposes in the presence of copper(1) salts, such as copper (1)b chloride, to form the desired aryl halide.The reaction is a radical nucleophilic aromatic substitution



# Reactions of alkyl halides

| | | |
|---|---|---|
| 1. | $S_N2$ | NR |
| 2. | E2 | NR |
| 3. | organo metallic compounds | similar |
| 4. | reduction | similar |


Ag+
⁻OH
⁻OR
NH3
⁻CN
ArH
AlCl3
X
aryl halide
C=C–X
vinyl halide
NO REACTION

Bond Lengths (Å)

| | C—Cl | C—Br | |
|---|---|---|---|
| $CH_3$—X | 1.77 | 1.91 | |
| $C_2H_5$—X | 1.77 | 1.91 | $sp^3$ |
| $(CH_3)_3C$—X | 1.80 | 1.92 | |
| $CH_2$=CH—X | 1.69 | 1.86 | |
| $C_6H_5$—X | 1.69 | 1.86 | $sp^2$ |

- In aryl halides, the carbon to which the halogen is attached is $sp^2$ hybrizided. The bond is stronger and shorter than the carbon-halogen bond in aliphatic compounds where the carbon is $sp^3$ hybridized.
- Hence it is more difficult to break this bond and aryl halides resist the typical nucleophilic substitution reactions of alkyl halides.
- The same is true of vinyl halides where the carbon is also $sp^2$ hybridized and not prone to nucleophilic substitution.
- In a manner analogous to the phenols & alcohols, we have the same functional group in the two families, aryl halides and alkyl halides, but very different chemistries.