

ARYL HALIDES

CLASS – B.Sc.

Second SEMESTER

SECTION – A

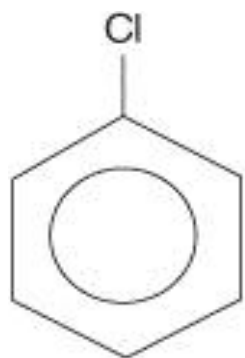
By Prof. Ranjana
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Aryl Halides

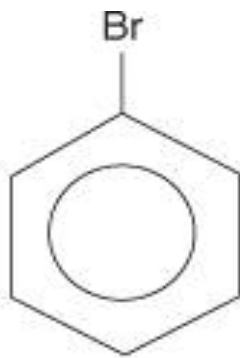
An **aryl halide** is a compound formed by the substitution of a halogen atom for a hydrogen atom on benzene. Another name for an aryl halide is *halo benzene*.

Nomenclature

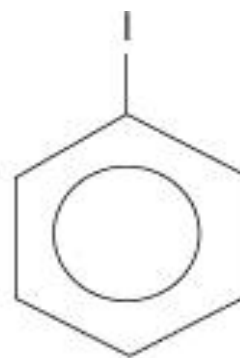
Aryl halides are named by prefixing the name of the halogen to benzene. For example:



chlorobenzene



bromobenzene



iodobenzene

Properties of aryl halides

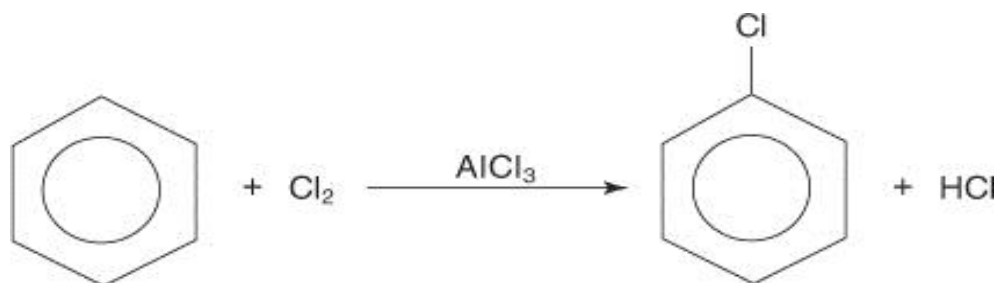
The physical properties of unsubstituted aryl halides are much like those of the corresponding alkyl halides. Thus, boiling points, melting points, and solubilities of aryl halides are very similar to those of alkyl halides containing the same number of carbon atoms.

Synthesis of Aryl Halides

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

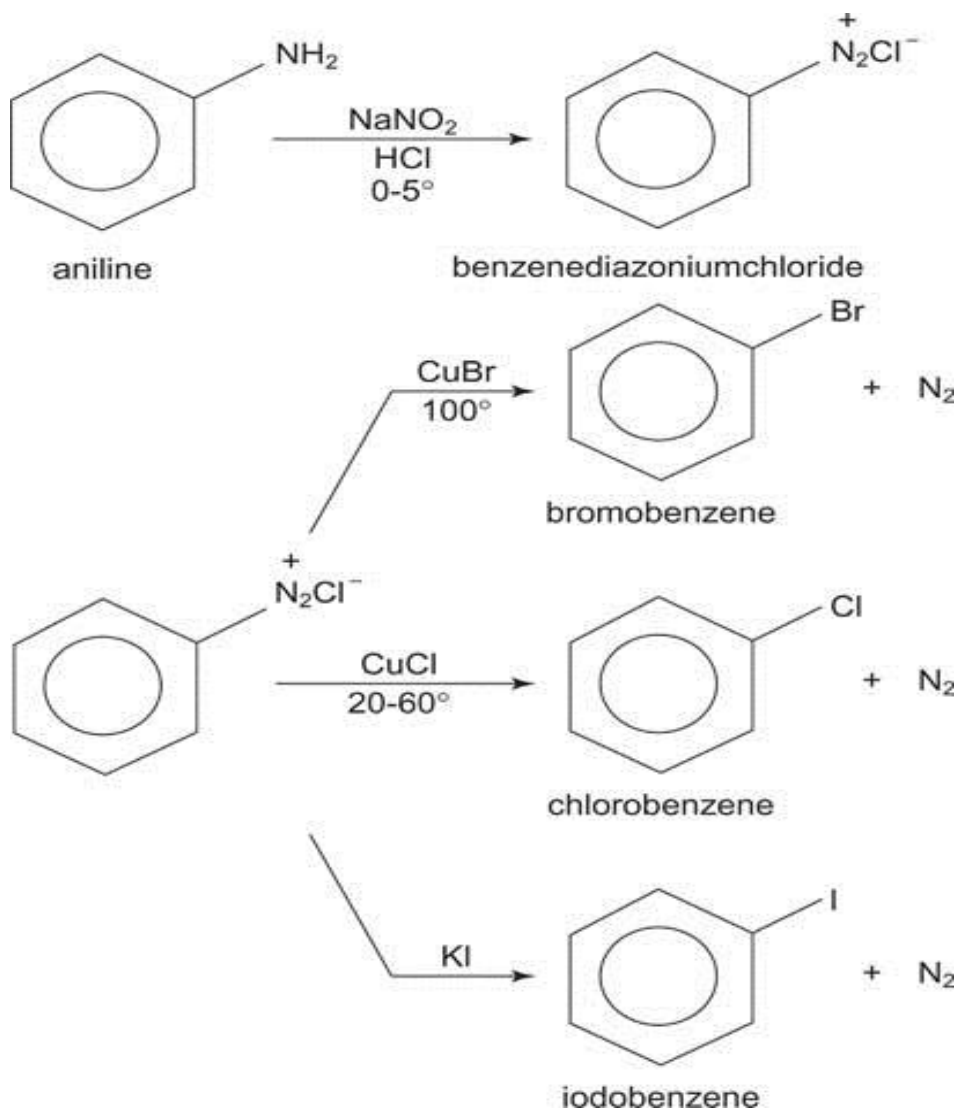
Halogenation of benzene

The halogenation of benzene to synthesize aryl halides is the oldest method known.



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.

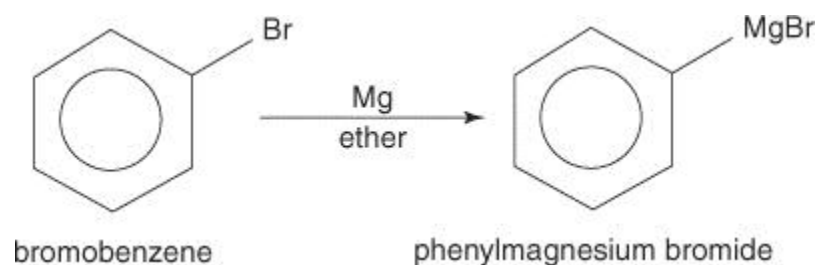


Reactions of Aryl Halides

Following are some typical reactions of aryl halides.

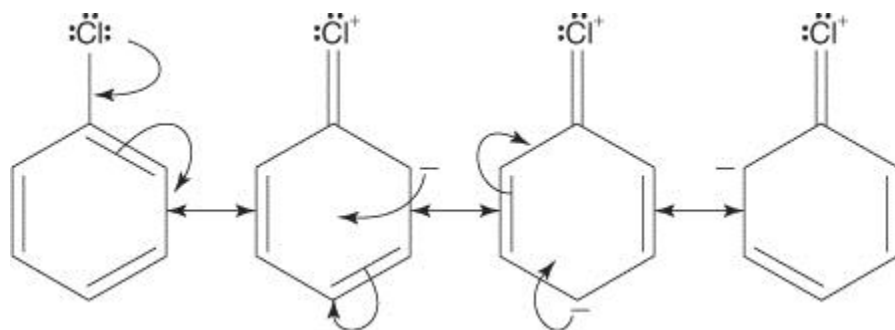
Grignard reaction

Aryl halides form Grignard reagents when reacted with magnesium.



Substitution reaction

Aryl halides are relatively unreactive toward nucleophilic substitution reactions. This lack of reactivity is due to several factors. Steric hindrance caused by the benzene ring of the aryl halide prevents S_N2 reactions. Likewise, phenyl cations are unstable, thus making S_N1 reactions impossible. In addition, the carbon-halogen bond is shorter and therefore stronger in aryl halides than in alkyl halides. The carbon-halogen bond is shortened in aryl halides for two reasons. First, the carbon atom in aryl halides is sp^2 hybridized instead of sp^3 hybridized as in alkyl halides. Second, the carbon-halogen bond has partial double bond characteristics because of resonance.

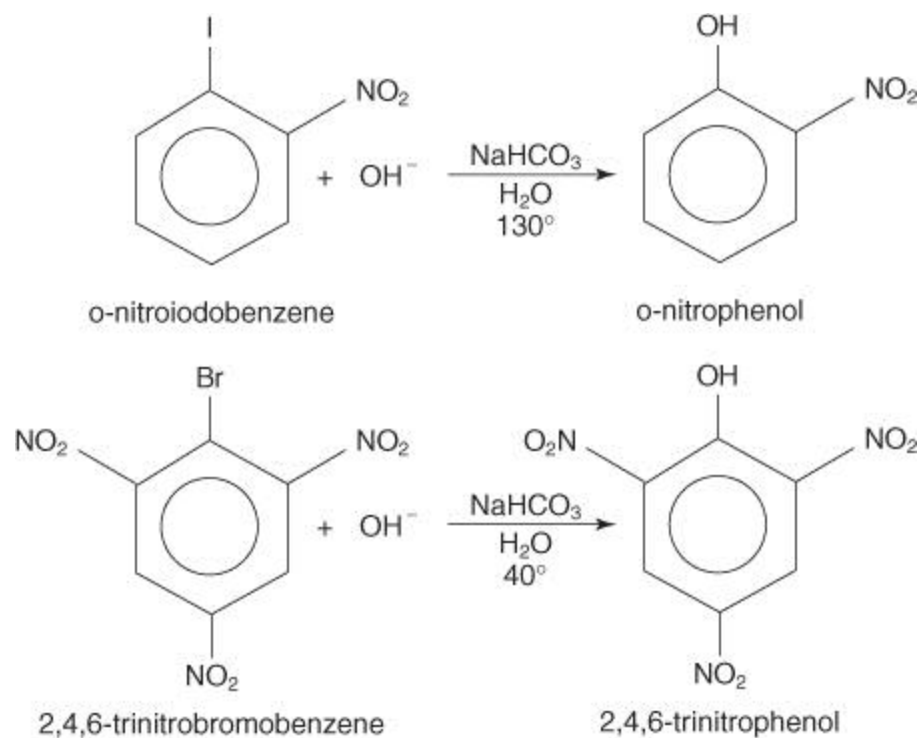


Because three of the four resonance structures show a double bond between the carbon and halogen atoms, the hybrid structure must have double bond character.

S_NAR reactions

Nucleophilic substitution reactions can occur with aryl halides, provided that strong electron-withdrawing groups (deactivators) are located ortho and/or para to the carbon atom that's attached to the halogen. (This arrangement makes the carbon susceptible to nucleophilic attack.)

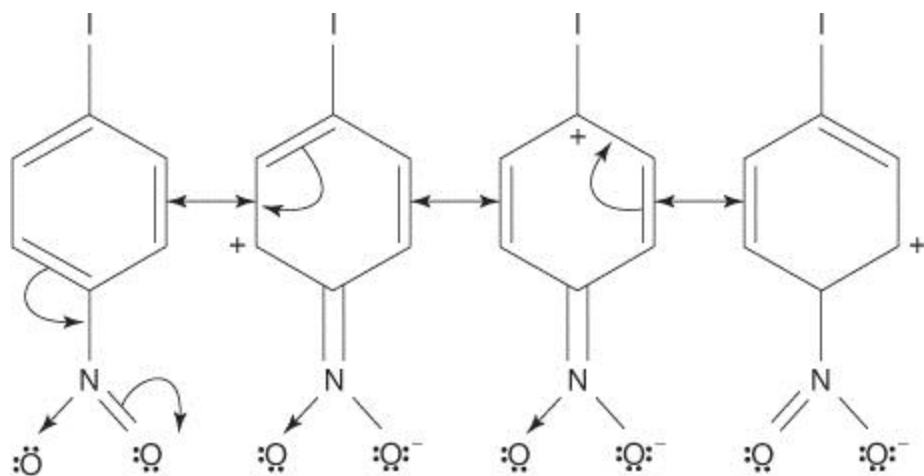
The examples below illustrate S_N substitutions on deactivated aryl halides.



S_NAR mechanism

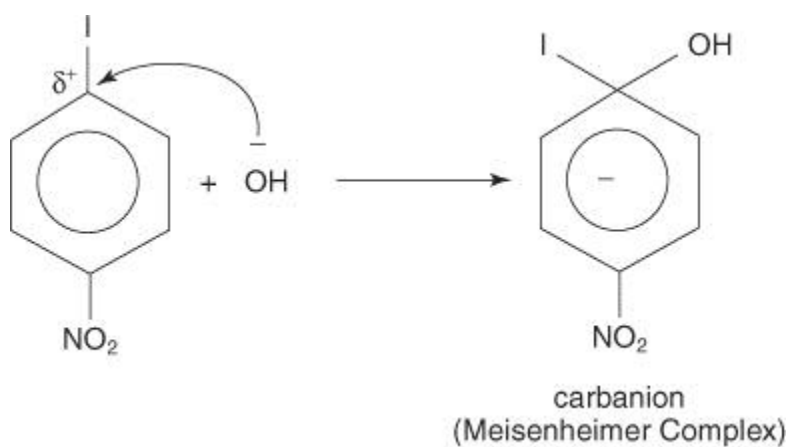
The S_NAR mechanism is an addition-elimination mechanism that proceeds through a carbanion with delocalized electrons (a Meisenheimer complex). The following steps show the mechanism for the formation of p-nitrophenol from p-nitroiodobenzene.

1. The nitro group, a strong deactivating group, produces a partial positive charge on the carbon that bears the halogen atom in the aryl halide.

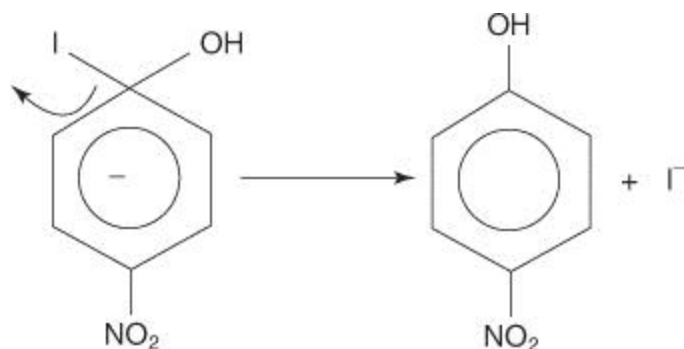


Because one of the resonance structures has a positive charge on the carbon attached to the halogen, this carbon acts as a weak nucleus.

2. The hydroxide ion is attracted to the weak nucleus, forming a carbanion with delocalized electrons.

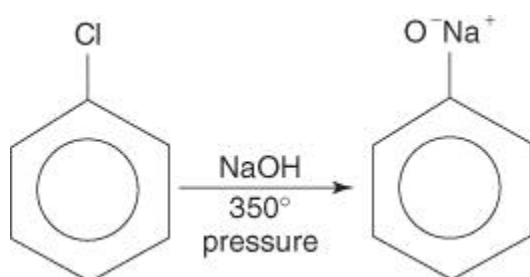


3. The complex eliminates an iodide ion to form a phenol.

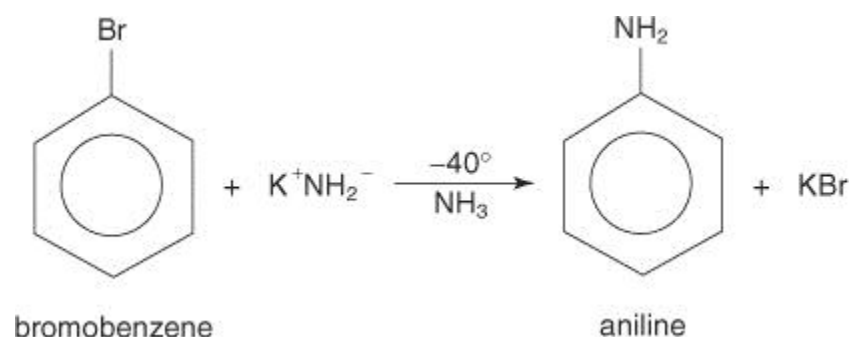


Elimination-addition reactions

Aryl halides generally do not undergo substitution reactions. However, under conditions of high temperature and pressure, these compounds can be forced to undergo substitution reactions. For example, under high temperature and pressure, chlorobenzene can be converted into sodium phenoxide when reacted with sodium hydroxide.

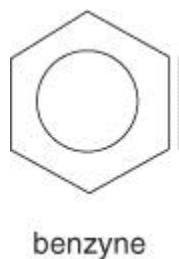


Similarly, at a very low temperature, bromobenzene reacts with potassium amide (KNH_2) dissolved in liquid ammonia to form aniline.



Mechanism for aniline formation

The elimination-addition mechanism for the formation of aniline proceeds via a benzyne intermediate. A **benzyne** is a benzene molecule that contains a theoretical triple bond. Thus, the following structure represents benzyne:



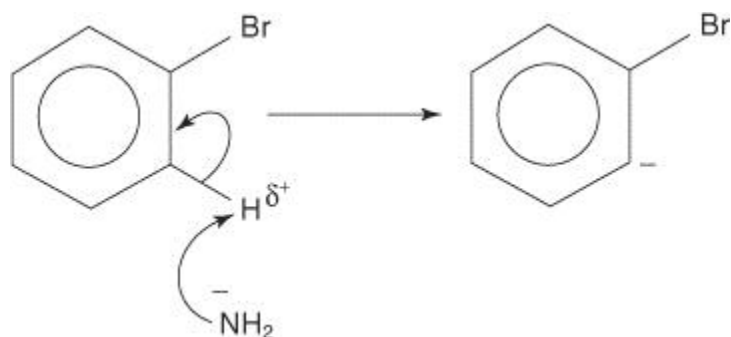
A triple bond doesn't exist in the true benzyne structure. The extra bond results from the overlap of sp^2 orbitals on adjacent carbon atoms of the ring. The axes of these sp^2 orbitals are in the same plane as the ring, and therefore, they don't overlap with the π orbitals of the aromatic system. Consequently, there's little to no interference with the

aromatic system. The additional bond is weak and benzyne is thus highly unstable and highly reactive. Figure shows the true structure of benzyne:

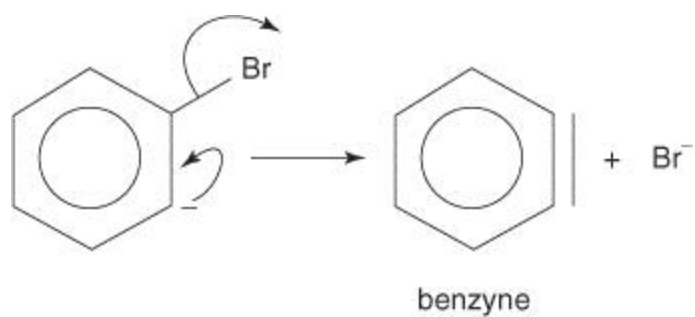
Figure 1

The following four steps outline the mechanism for aniline formation.

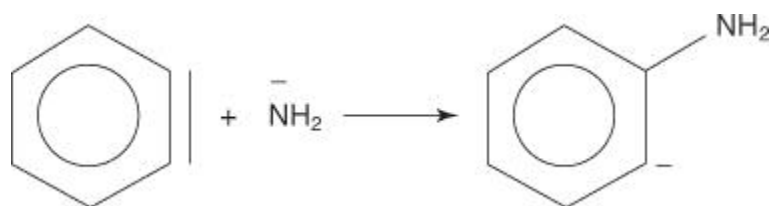
1. An amide ion, a very strong base, removes a weak proton from the carbon that is alpha to the carbon bonded to the bromine.



2. The carbanion electrons are stabilized by being attracted to the electronegative bromine, which results with the loss of a bromide ion.



3. The highly unstable and very reactive benzyne reacts with a second amide ion, creating a new carbanion.



4. The new carbanion abstracts a proton from an ammonia molecule in an acid-base reaction, leading to the formation of aniline.

