

# CHAPTER 9

## Aromatic Nucleophilic Substitution

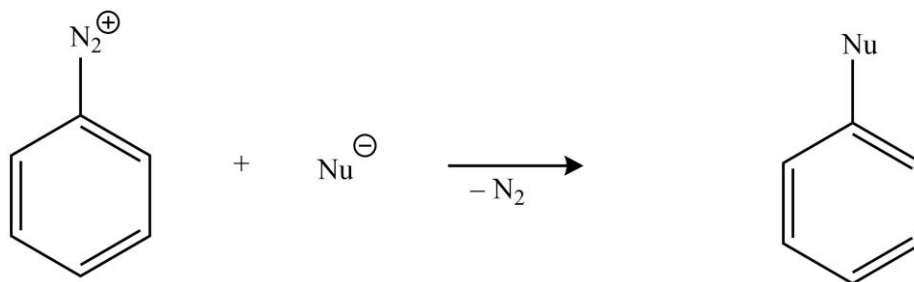
### ❖ The $ArSN_1$ , $ArSN_2$ , Benzyne and $S_{RN}1$ Mechanisms

An aromatic nucleophilic substitution in organic chemistry may simply be defined as a chemical reaction where the nucleophile displaces a good leaving group, such as a halide, on an aromatic ring. The aromatic nucleophilic substitution can primarily occur via three different routes as given below.

#### ➤ $ArSN_1$ or Aryl Cation Mechanism

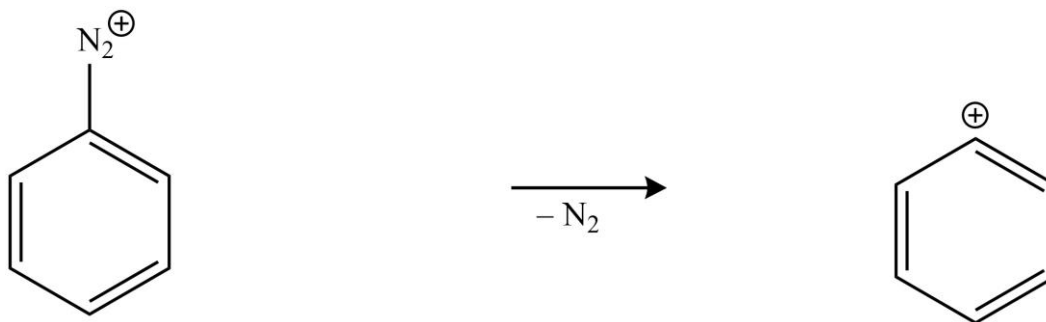
The unimolecular nucleophilic substitution on aromatic rings is mainly given by aromatic diazonium salts. The typical reaction of such type is given below.

**Illustrative reaction:** The typical reaction involving nucleophilic substitution in aromatic compounds is shown below.



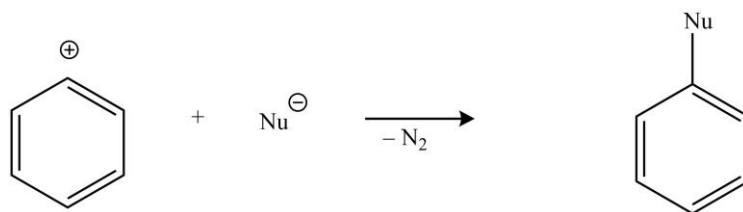
**Mechanism involved:** The proposed mechanism for the reaction given above involves two steps which must be discussed before we give salient features of the same.

i) *Formation of aryl cation:* Now although the aryl carbocation is highly unstable, its formation is still favored due to the high stability of dinitrogen (i.e., good leaving group).



Now although the aryl carbocation is highly unstable, its formation is still favored due to the high stability of dinitrogen (i.e., good leaving group).

ii) *Attack by the Nucleophile:*



Now since the faces of the carbocations formed are homotopic, the  $\text{Nu}^-$  can attack from either side to give the same product.

**Salient Features:** The main features of the mechanism involved in aromatic nucleophilic substitution unimolecular or  $\text{ArSN}_1$  type reactions are given below.

i)  $\text{ArSN}_1$  reactions follow first-order kinetics with the rate law

$$\text{Rate} = k[\text{RX}]$$

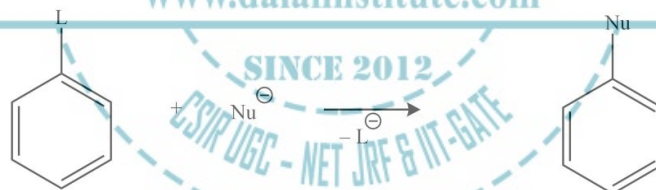
Where  $k$  is the rate constant and  $[\text{RX}]$  represents the molar concentration of the substrate.

ii) The presence of +R groups at *ortho* and *para* positions raises the reactivity of the substrate and vice-versa.

➤ ***ArSN<sub>2</sub> or Addition-Elimination Mechanism***

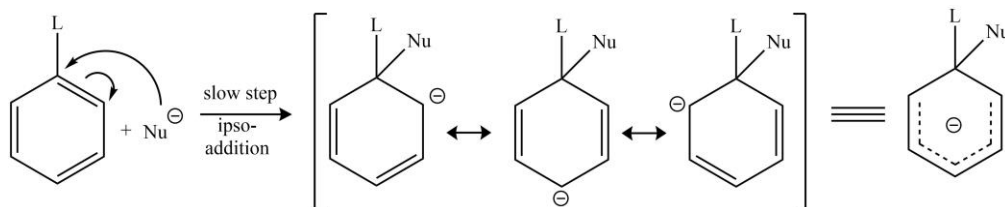
The bimolecular nucleophilic substitution on aromatic rings is most common among the class. The typical reaction of such type is given below.

**Illustrative reaction:** The typical reaction involving this type of mechanism is given below.



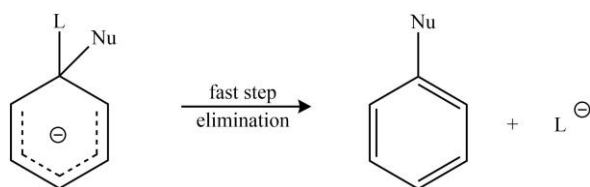
**Mechanism involved:** The proposed mechanism for the reaction given above involves two steps which must be discussed before we give salient features of the same.

i) *ipso-addition of the nucleophile:*



Now although an ion is no longer an aromatic species; however, it is relatively stable due to the delocalization of the negative charge over 3 carbon atoms by the pi system.

ii) *Elimination of the leaving group:*



**Salient Features:** The main features of the mechanism involved in aromatic nucleophilic substitution bimolecular or  $\text{ArSN}_2$  type reactions are given below.

i)  $\text{ArSN}_2$  reactions follow second-order kinetics with the rate law

$$\text{Rate} = k[\text{RX}][\text{Nu}]$$

Where  $k$  is the rate constant. The symbol  $[\text{RX}]$  and  $[\text{Nu}]$  represent the molar concentration of the substrate and attacking nucleophiles, respectively.

ii) The reactivity increases as the leaving group gets better.

iii) The rate of the substitution increases as the  $-I$  or  $-R$  effect of the groups attached  $o$ - and  $p$ -positions increases.

iv) The reactivity is also proportional to the electronegativity of the heteroatom (if any) in the ring.

v) The  $\text{ArSN}_2$  reactions are favored in polar aprotic solvents.

➤ **Aryne (Benzyne) or Elimination-Addition Mechanism**

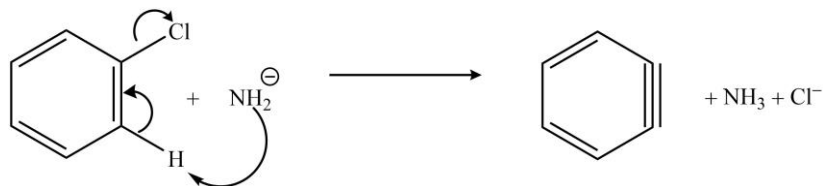
The elimination-addition mechanism involves a highly unstable intermediate called benzyne (dehydrobenzene). A typical reaction of such type is given below.

**Illustrative reaction:**

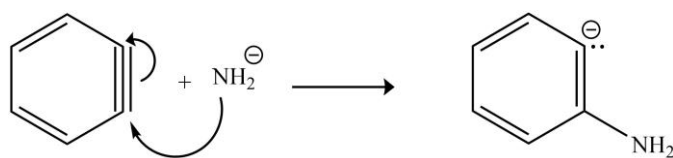


**Steps involved:** The proposed mechanism for the reaction given above involves two steps which must be discussed before we give salient features of the same.

i) *First step is the elimination of proton ortho to the substituent present and formation of benzyne:*



ii) *Attack of amide ion on the benzyne intermediate:*



iii) Abstraction of the proton from ammonia:



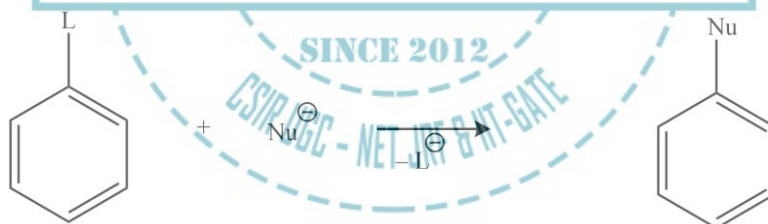
**Salient Features:** The main features of the mechanism involved in aromatic nucleophilic substitution via benzyne are given below.

- i) At least one hydrogen must be present at ortho position in the inactivated aryl halide.
- ii) The incoming group may or may not occupy the position vacated by the leaving group i.e. cine substitution.

➤ **Substitution Radical Nucleophilic Unimolecular ( $S_{RN}1$ )**

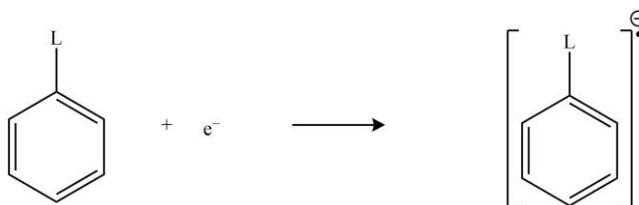
Radical-nucleophilic aromatic substitution or  $S_{RN}1$  in organic chemistry is a type of substitution reaction in which a certain substituent on an aromatic compound is replaced by a nucleophile through an intermediary free radical species.

**Illustrative reaction:**

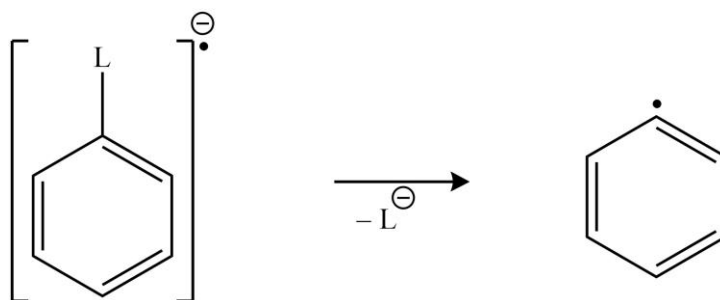


**Mechanism involved:** The proposed mechanism for the reaction given above involves two steps which must be discussed before we give salient features of the same.

- i) *Formation of radical anion:* The aryl halide accepts an electron from a radical initiator to form a radical anion.



- ii) *Transformation of radical anion into aryl radical:*



iii) Attack of the nucleophile on the aryl radical:



iv) Transfer of electron to new aryl halide:



**Salient Features:** The main features of the mechanism involved in  $S_{\text{RN}}1$  (substitution radical nucleophilic unimolecular) type reactions are given below.

i)  $S_{\text{RN}}1$  reactions follow first-order kinetics with the rate law

$$\text{Rate} = k[\text{RX}]$$

Where  $k$  is the rate constant and  $[\text{RX}]$  represents the molar concentration of the substrate.

ii) The phenyl radical can also abstract any loose proton to form arene in a chain termination reaction to yield the final product.

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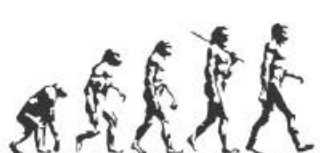
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