By- SHAILENDRA SHUKLA SIR

Nucleophilic Aromatic Substitution

(Elimination-Addition Mechanism)

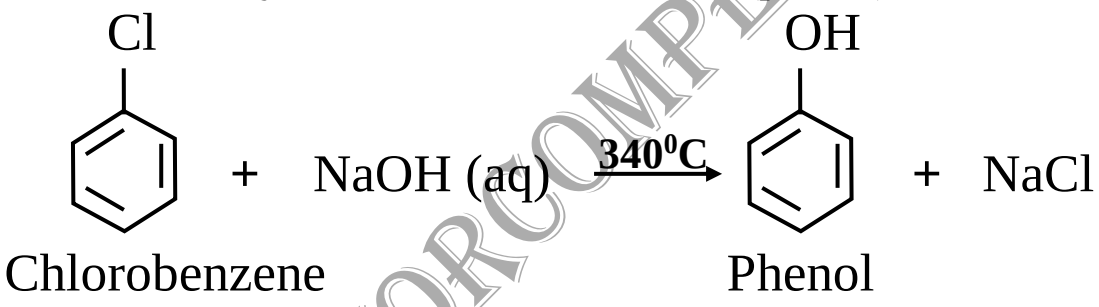
The elimination-addition mechanism involves the elimination of atoms or groups from a substrate molecule to from a highly reactive intermediate, which undergoes addition reaction further to give final product.

The elimination-addition mechanism of nucleophilic aromatic substitution involves benzyne or arynes as reaction intermediate.

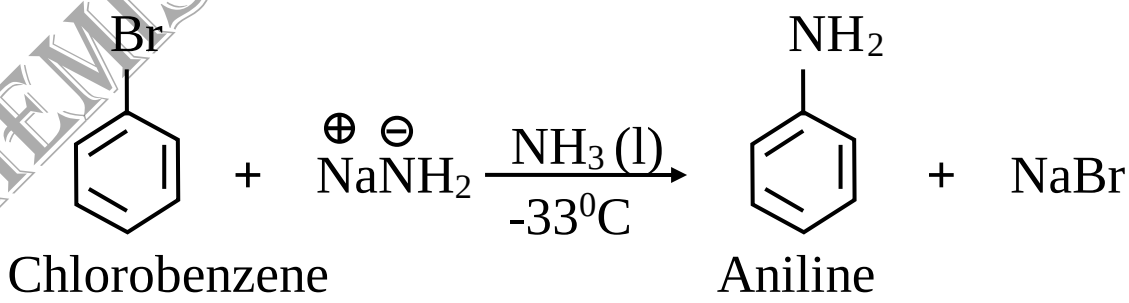
Some examples of elimination-addition mechanism of nucleophilic aromatic substitution involving benzyne or arynes as reaction intermediate are as under-

(1)Hydrolysis of Haloarenes

The reactivity of aryl halides is very low toward nucleophilic substitution. Here, substitution occurs only under forcing conditions such as at high temperatures or by using very strong bases. For example, when chlorobenzene is reacted with sodium hydroxide at 340^0C benzenol (phenol) is obtained.



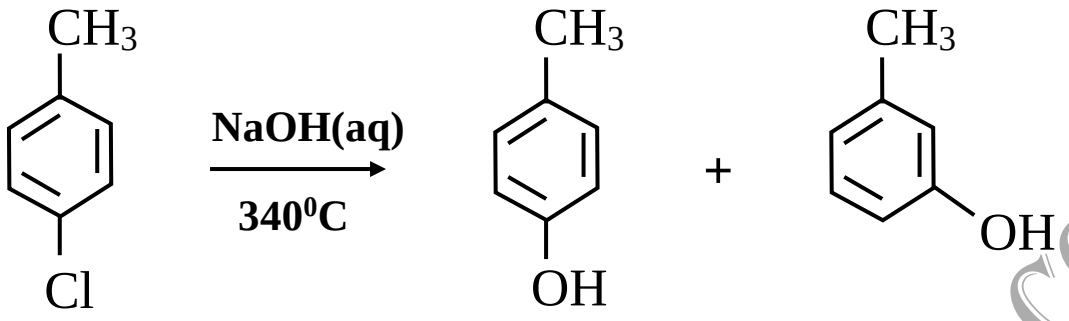
(2)Amination of Haloarenes- When aryl halides are treated with conjugate bases of amines (amide ions), aryl amines are obtained. For example, bromobenzene reacts vigorously with potassium amide in presence of liquid ammonia even at very low temperatures (-33^0C) to form aniline.



This type of displacement reactions differ from displacement reactions of activated aryl halides. Here, *the entering group does not occupy always the same position of the ring that is vacated by the halogen substituent*. For example, the

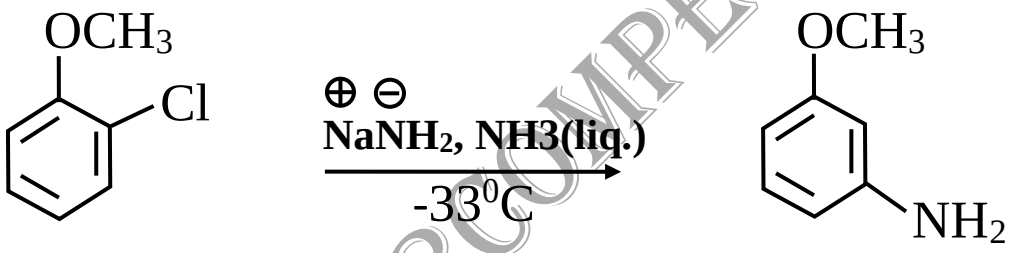
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hydrolysis of 4-chloromethylbenzene at 340°C gives an equimolar mixture of 3- and 4-methylphenols.



4-chloromethylbenzene 4-methylphenol (50%) 3-methylphenol (50%)

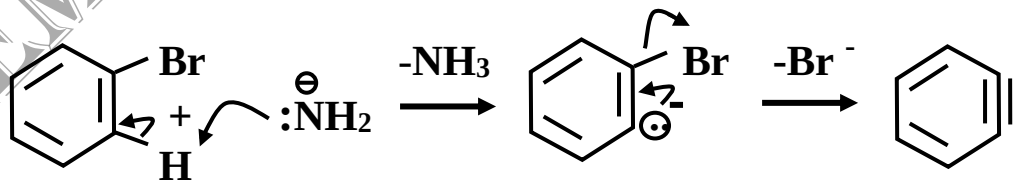
However, the amination of 2-chloromethoxybenzene gives 3-methoxybenzenamine (methoxyaniline) as exclusive product. This result is a violation of the principle of least structural change.



4-chloromethylbenzene 3-methoxylbenzenamine

Mechanism-

The mechanism of this type of reactions has been studied extensively, and many evidences have been found in support of a stepwise process. Here, first aryl halide undergoes a base-catalyzed *elimination* of hydrogen halide (HX) molecule to form benzyne intermediate.

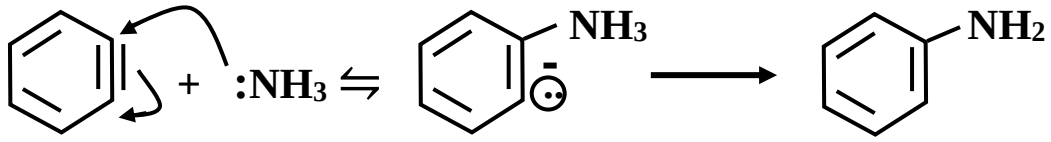


Bromobenzene **Benzyne**

Benzyne or dehydrobenzene is a highly reactive reaction intermediate, which differs from benzene in having two hydrogen atoms lesser but it has an

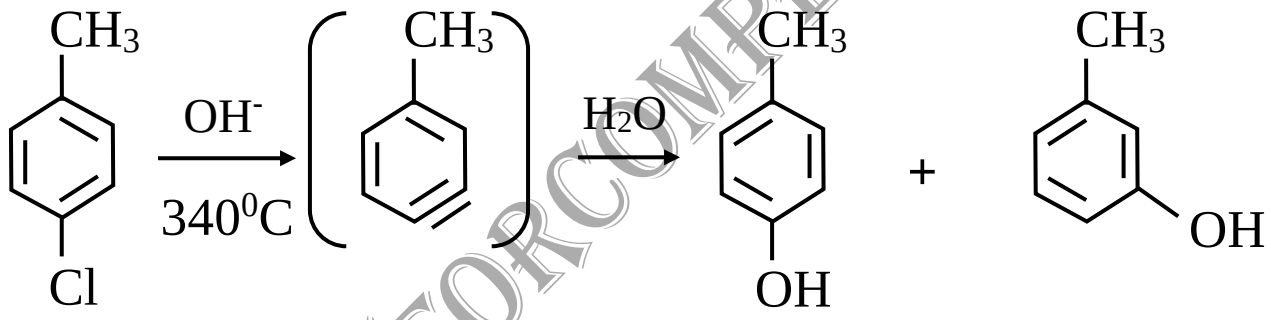
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extra bond between two ortho carbons. Benzyne reacts rapidly with any available nucleophile such as ammonia to give an addition product.



Benzyne Aniline

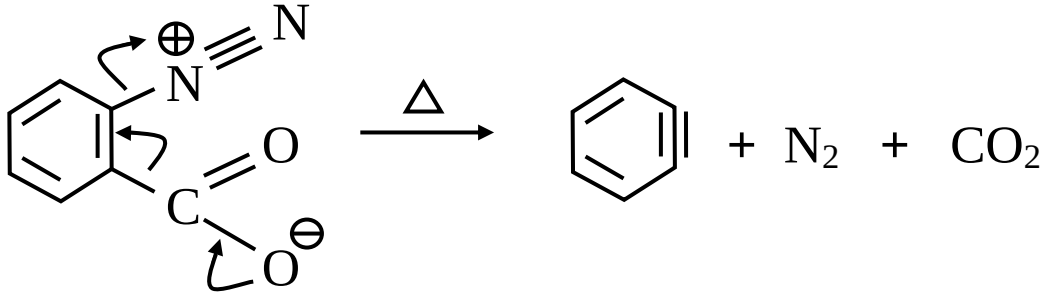
The rearrangements in these reactions result from the attack of the nucleophile at one or the other of the carbons having the extra bond in the intermediate. With benzyne the symmetry is such that no rearrangement is possible, but with the substituted benzynes isomeric products may be formed. For example, the hydrolysis of 4-chloromethylbenzene with aqueous alkalies at 340°C gives an equimolar mixture of 3- and 4-methylbenzenols (3- and 4-methylphenols).



4-chloromethylbenzene 4-methylphenol (50%) 3-methylphenol (50%)

Here, the base that produces benzyne in elimination step is derived from the nucleophile that adds to the benzyne in addition step.

Benzyne can also be generated by thermal decomposition of a 1,2-disubstituted arenes where, both the substituents are leaving groups - one leaving with an electron pair, while the other leaving without the same.

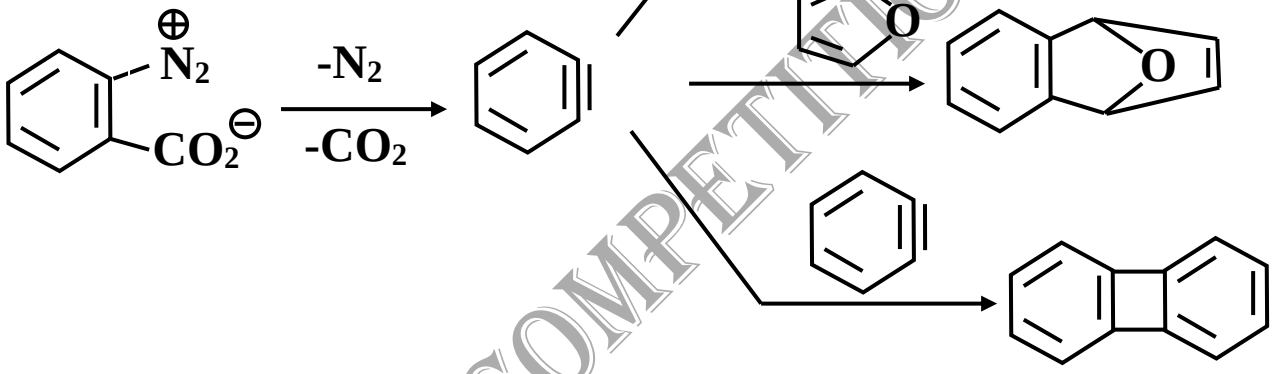


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Here, benzyne produced is trapped by the suitable nucleophile, just as it is formed.

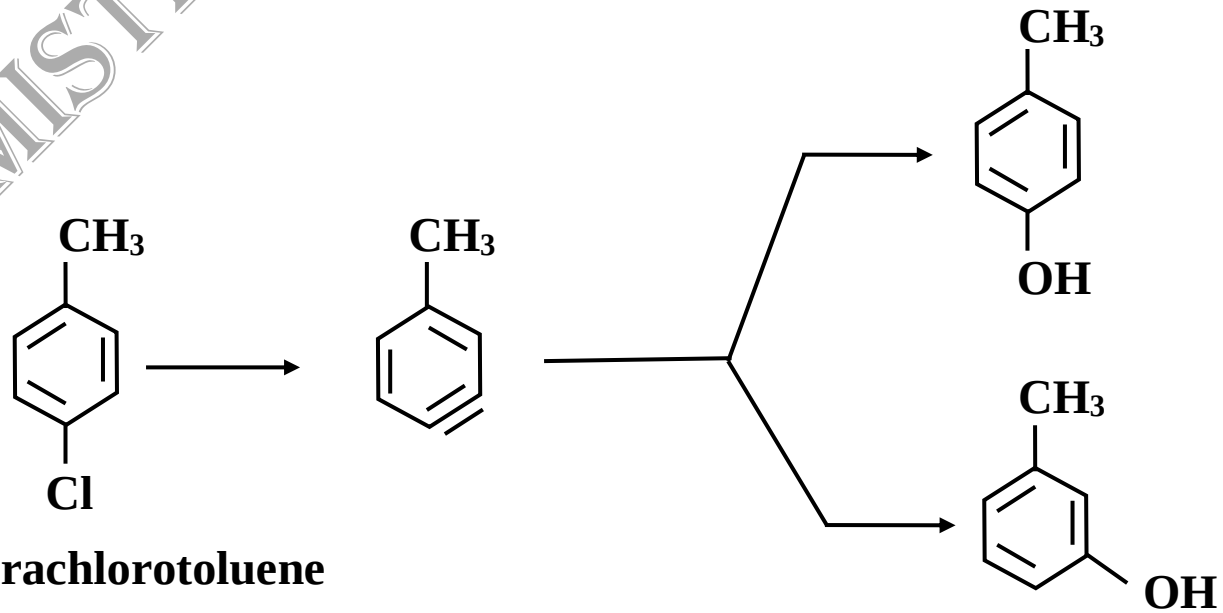
If a conjugated diene is present, it undergoes a [4+2] cycloaddition to form addition compound (adduct).

In absence of a species to which it can react, benzyne itself undergoes [2+2] cycloaddition to form biphenylene.



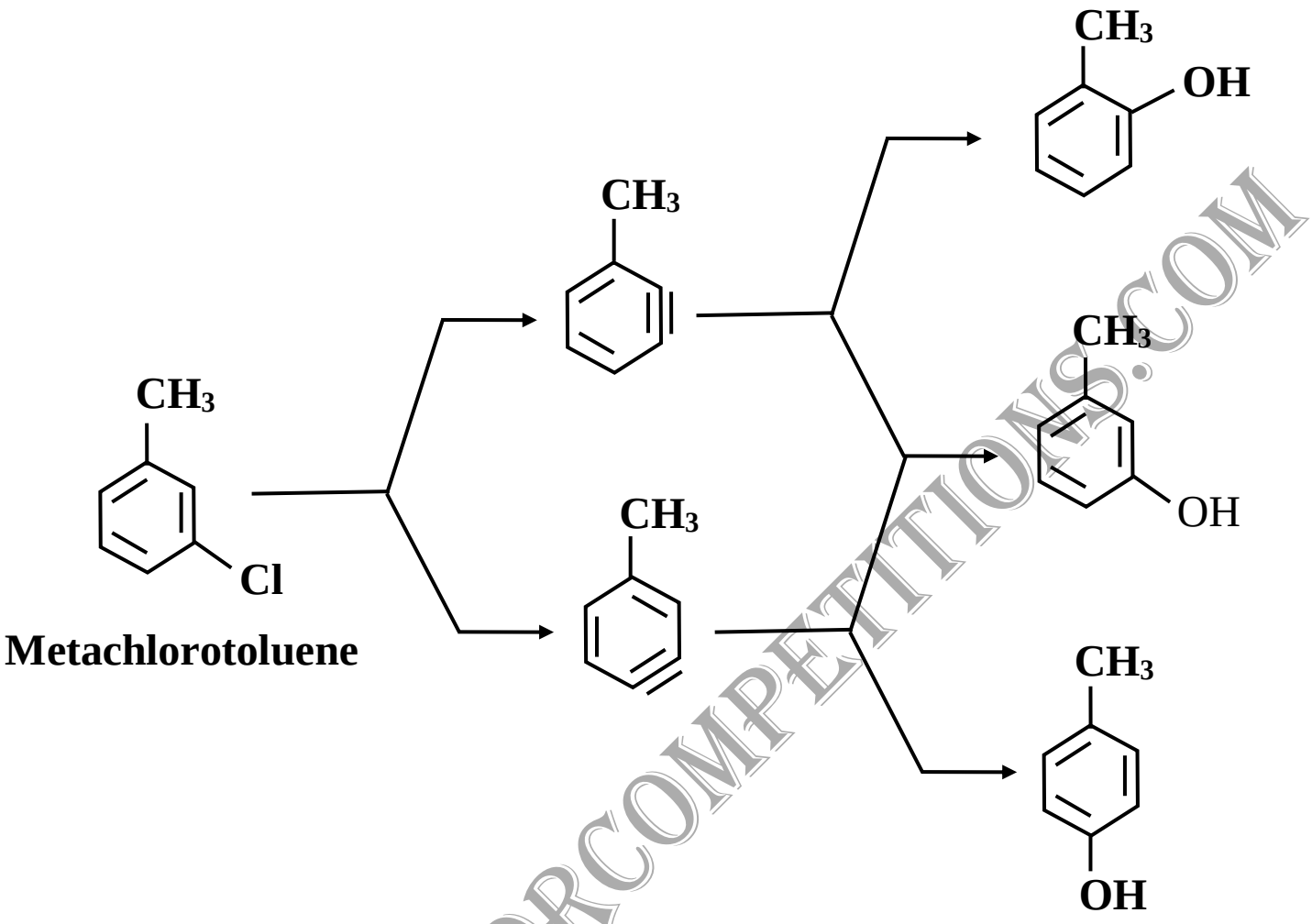
Ques.- When *p*-chlorotoluene is reacted with NaOH, two products are formed. *m*-chlorotoluene in this reaction gives three products. Explain why ?

Ans.- This reaction involves the formation of benzyne as reaction intermediate. Here, p-chlorotoluene produces only one type of benzynes and therefore, allows the formation of only two products, while the *m*-chlorotoluene produces two different types of benzynes which give three different products.



Parachlorotoluene

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Metachlorotoluene

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