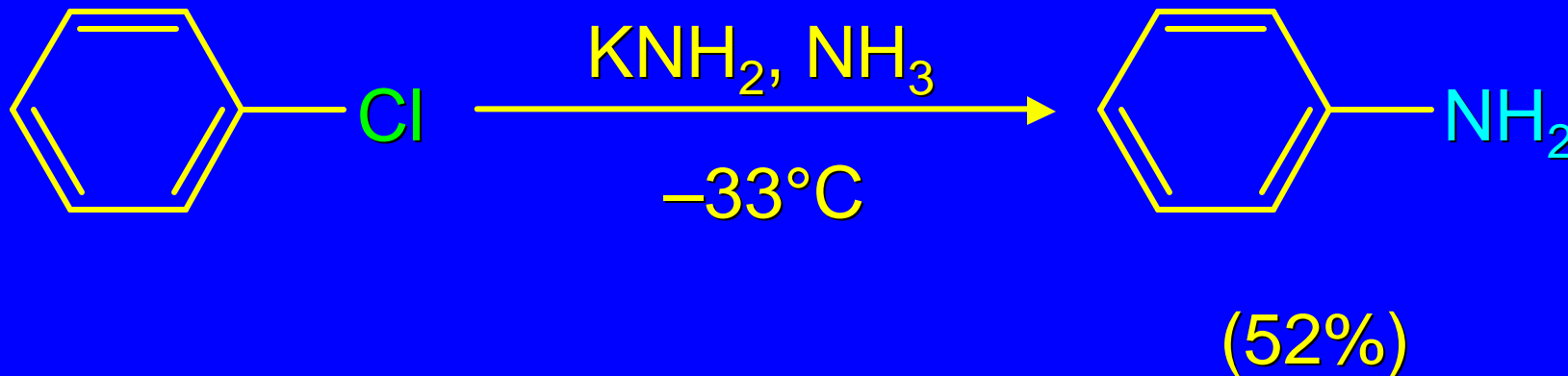


23.8

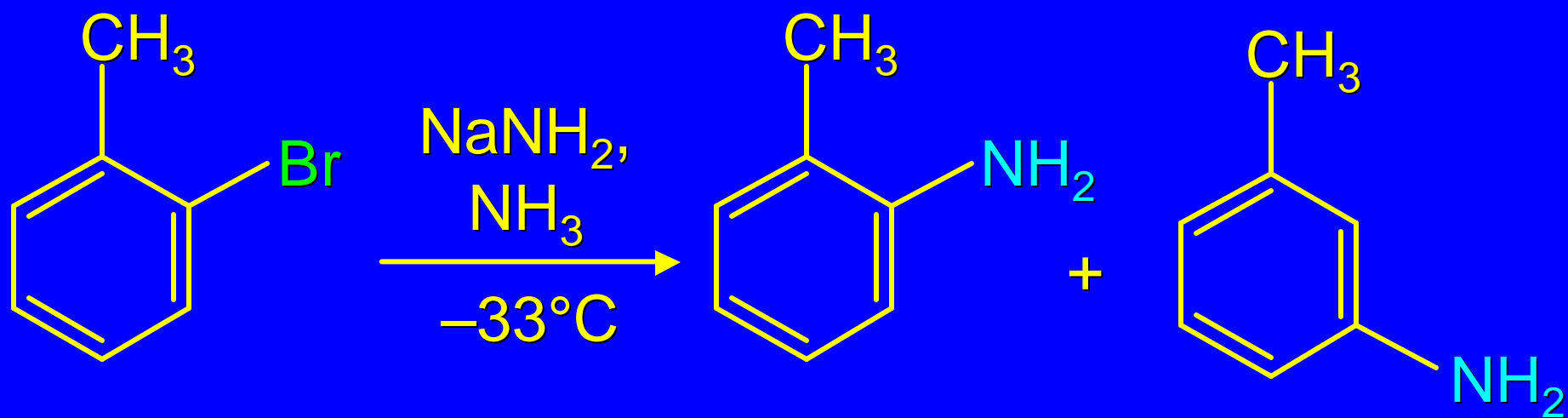
The Elimination-Addition Mechanism
of Nucleophilic Aromatic Substitution:
Benzyne

Aryl Halides Undergo Substitution When Treated With Very Strong Bases



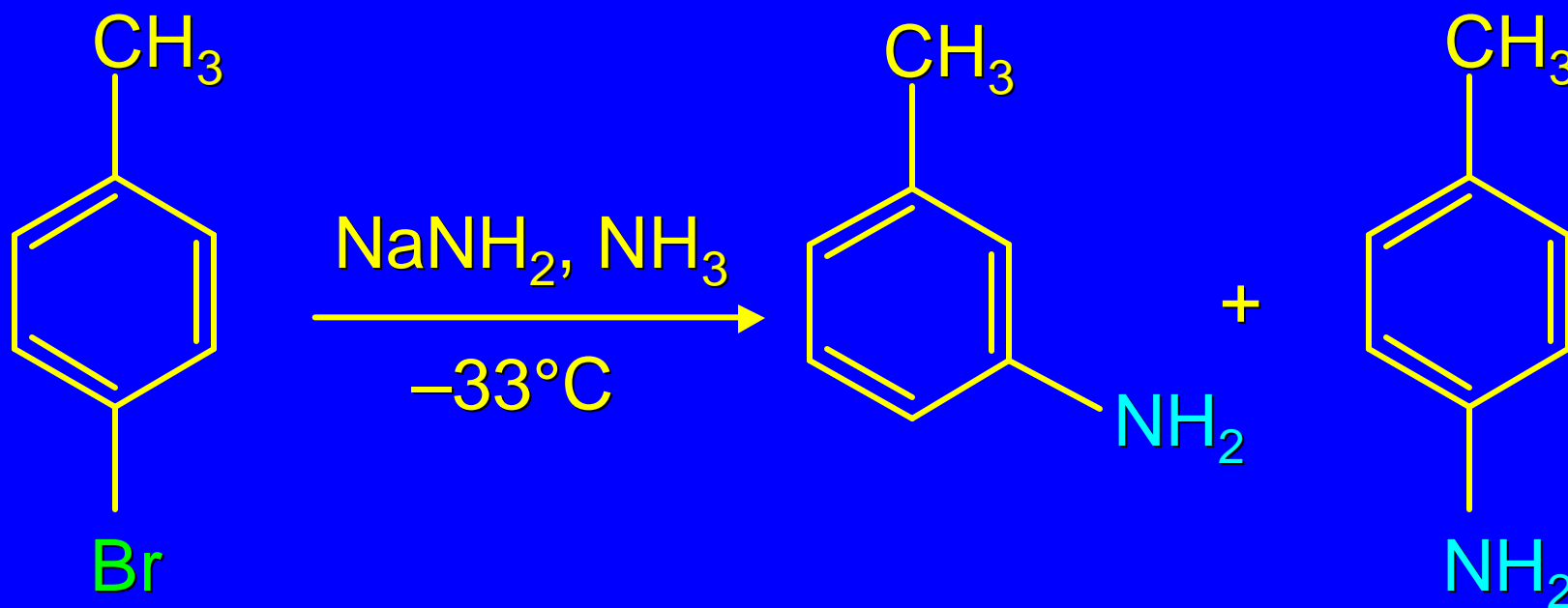
Regiochemistry

new substituent becomes attached to either the carbon that bore the leaving group or the carbon adjacent to it

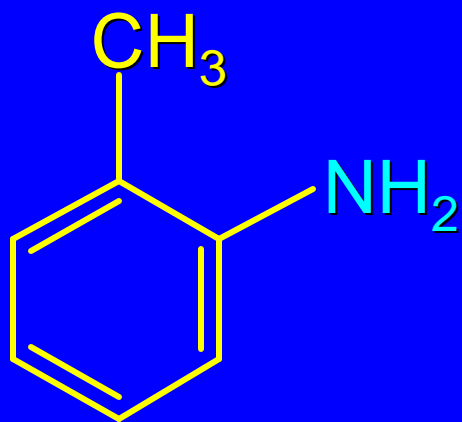
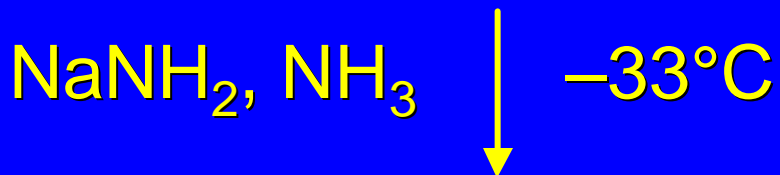
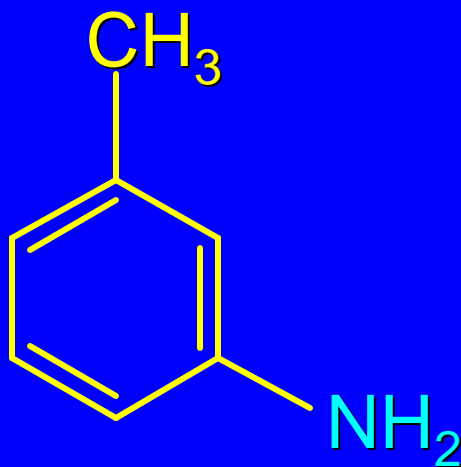


Regiochemistry

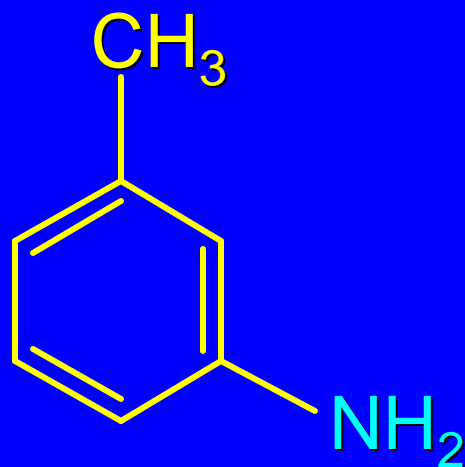
new substituent becomes attached to either the carbon that bore the leaving group or the carbon adjacent to it



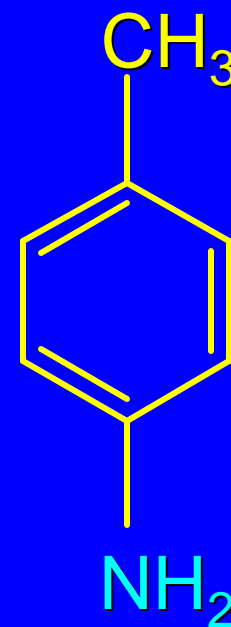
Regiochemistry



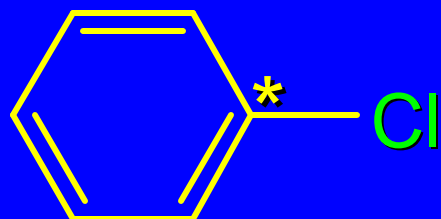
+



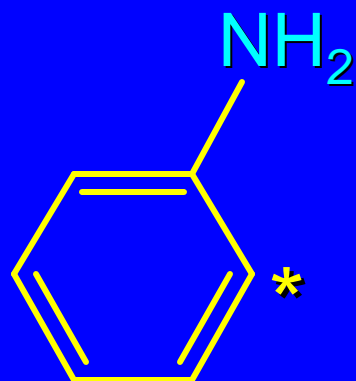
+



Same result using ^{14}C label

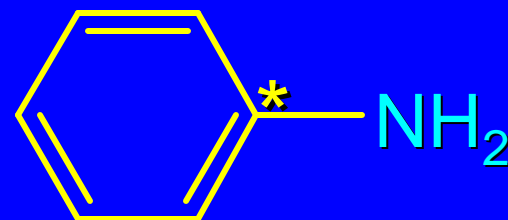


$\text{KNH}_2, \text{NH}_3$ -33°C



(52%)

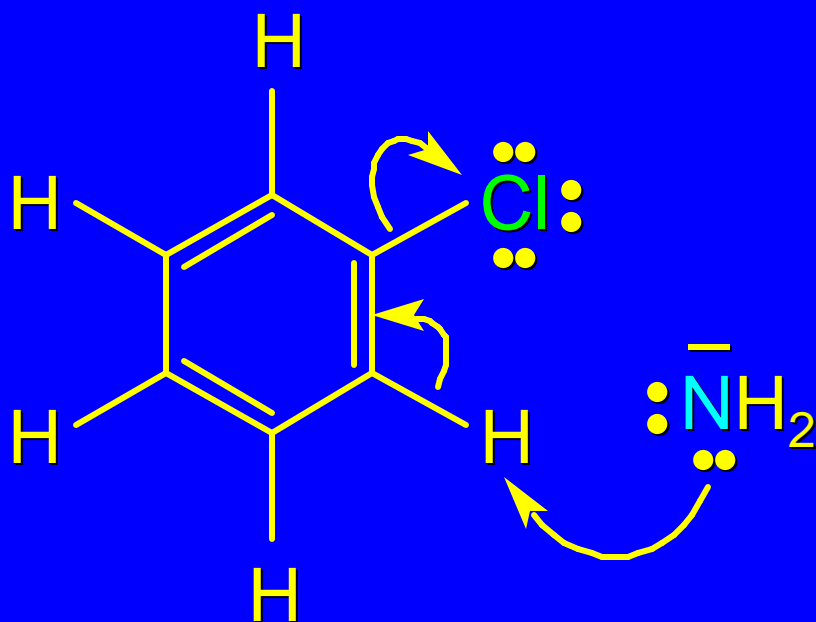
+



(48%)

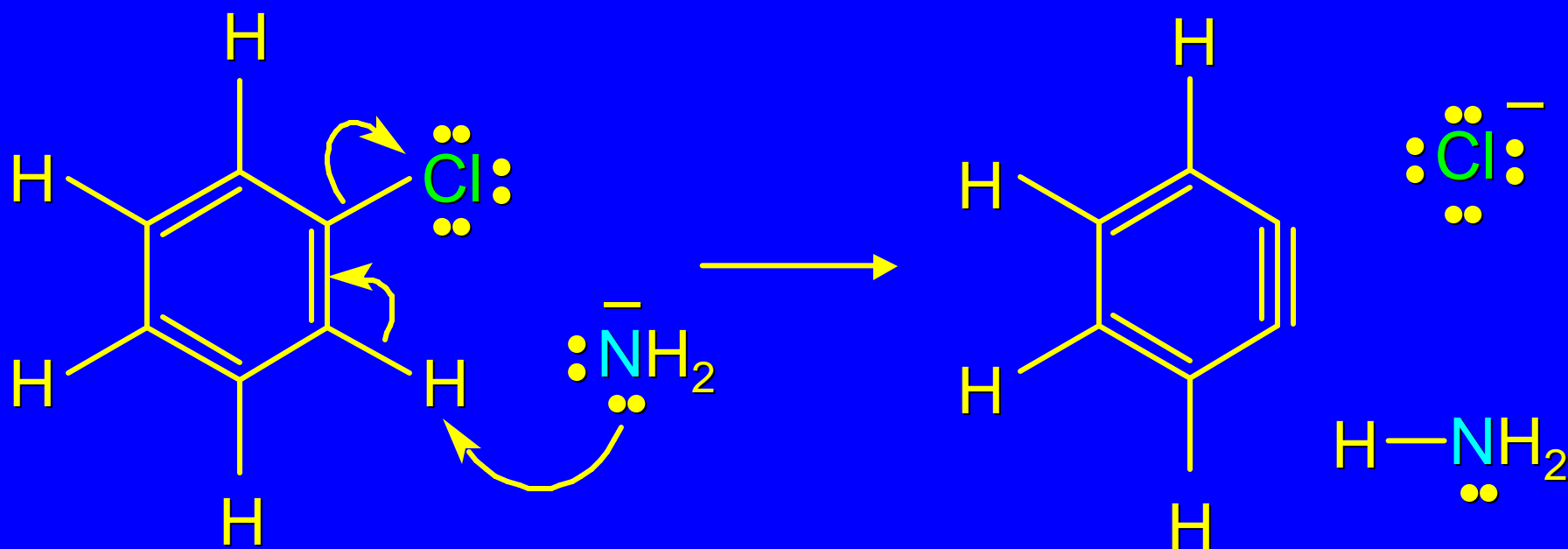
Mechanism

Step 1



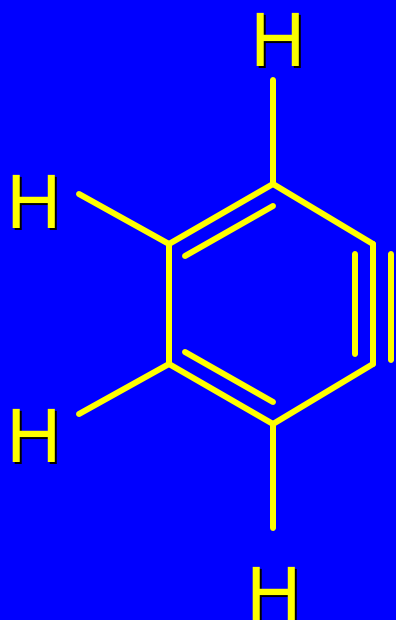
Mechanism

Step 1



compound formed in this step is called *benzyne*

Benzyne

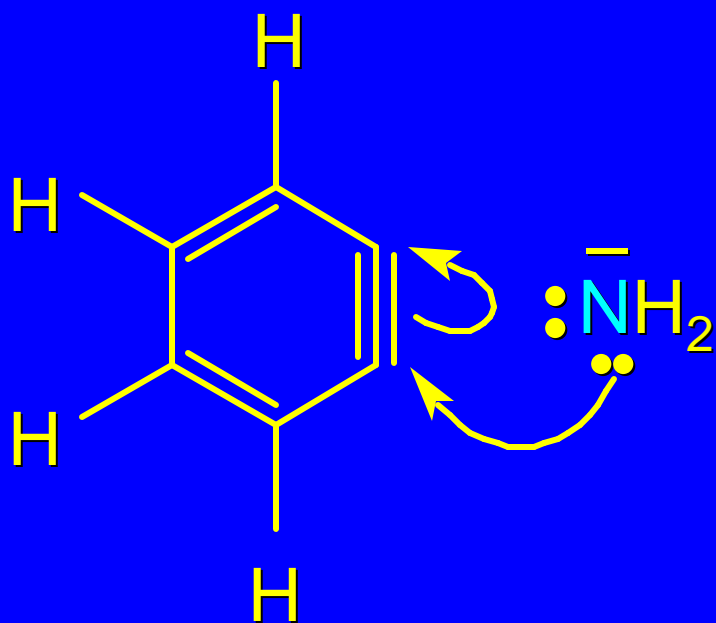


Benzyne has a strained triple bond.

It cannot be isolated in this reaction, but is formed as a reactive intermediate.

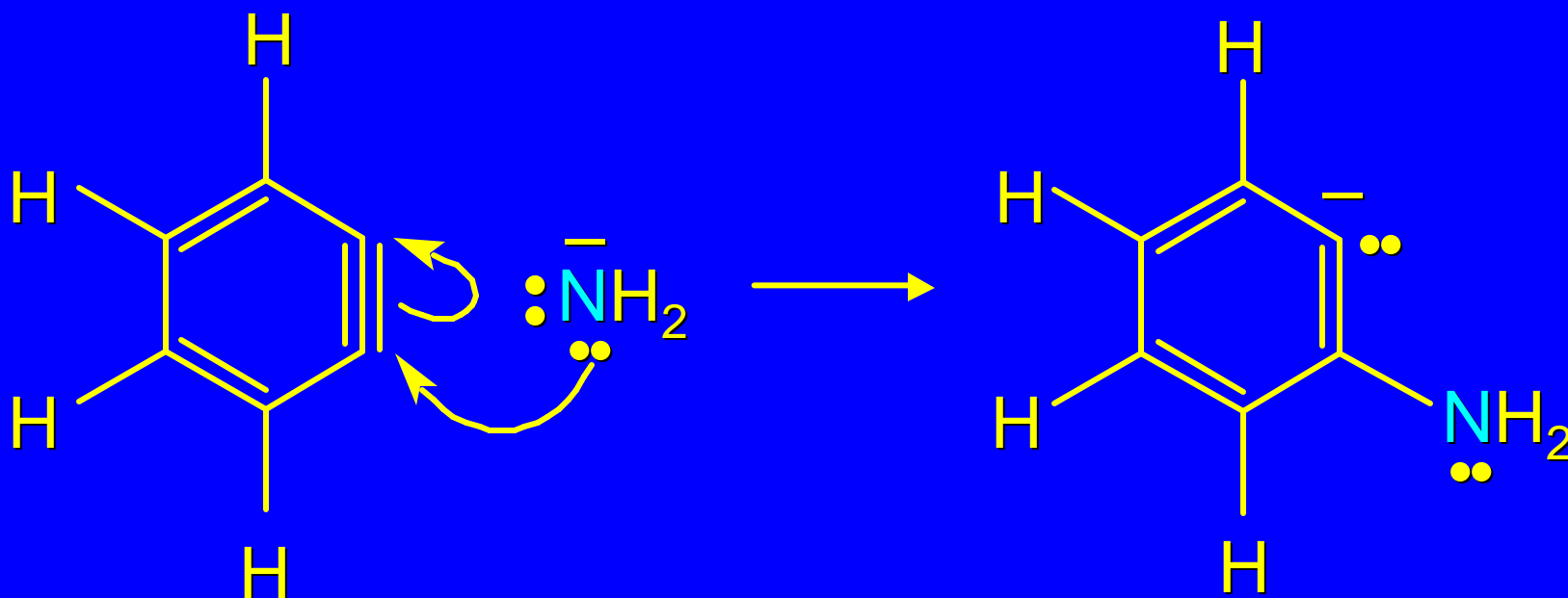
Mechanism

Step 2



Mechanism

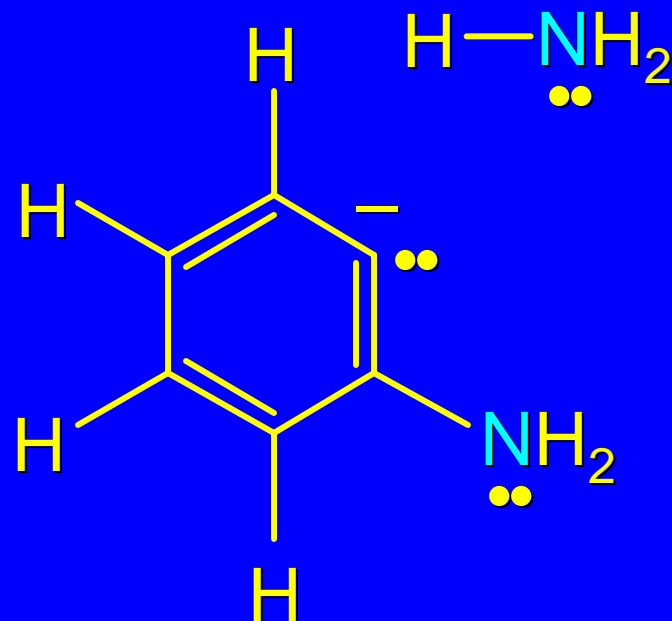
Step 2



Angle strain is relieved. The two sp -hybridized ring carbons in benzyne become sp^2 hybridized in the resulting anion.

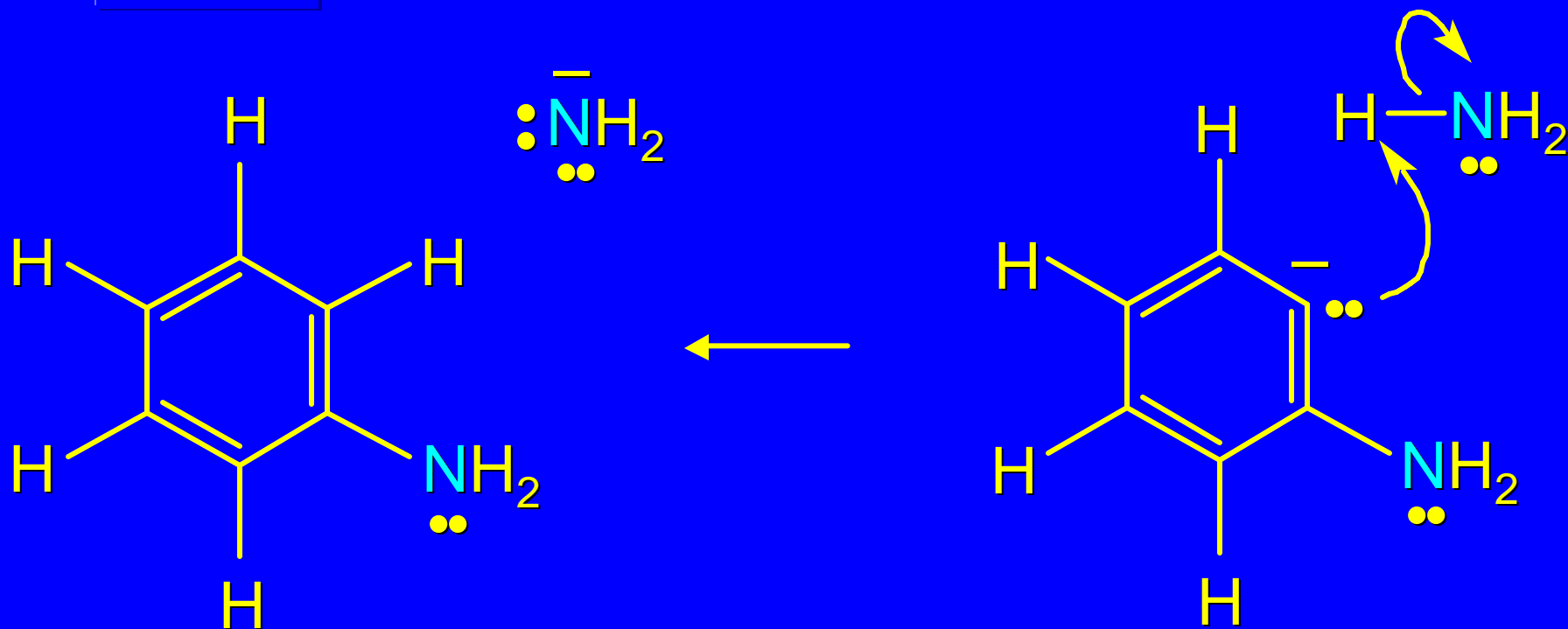
Mechanism

Step 3



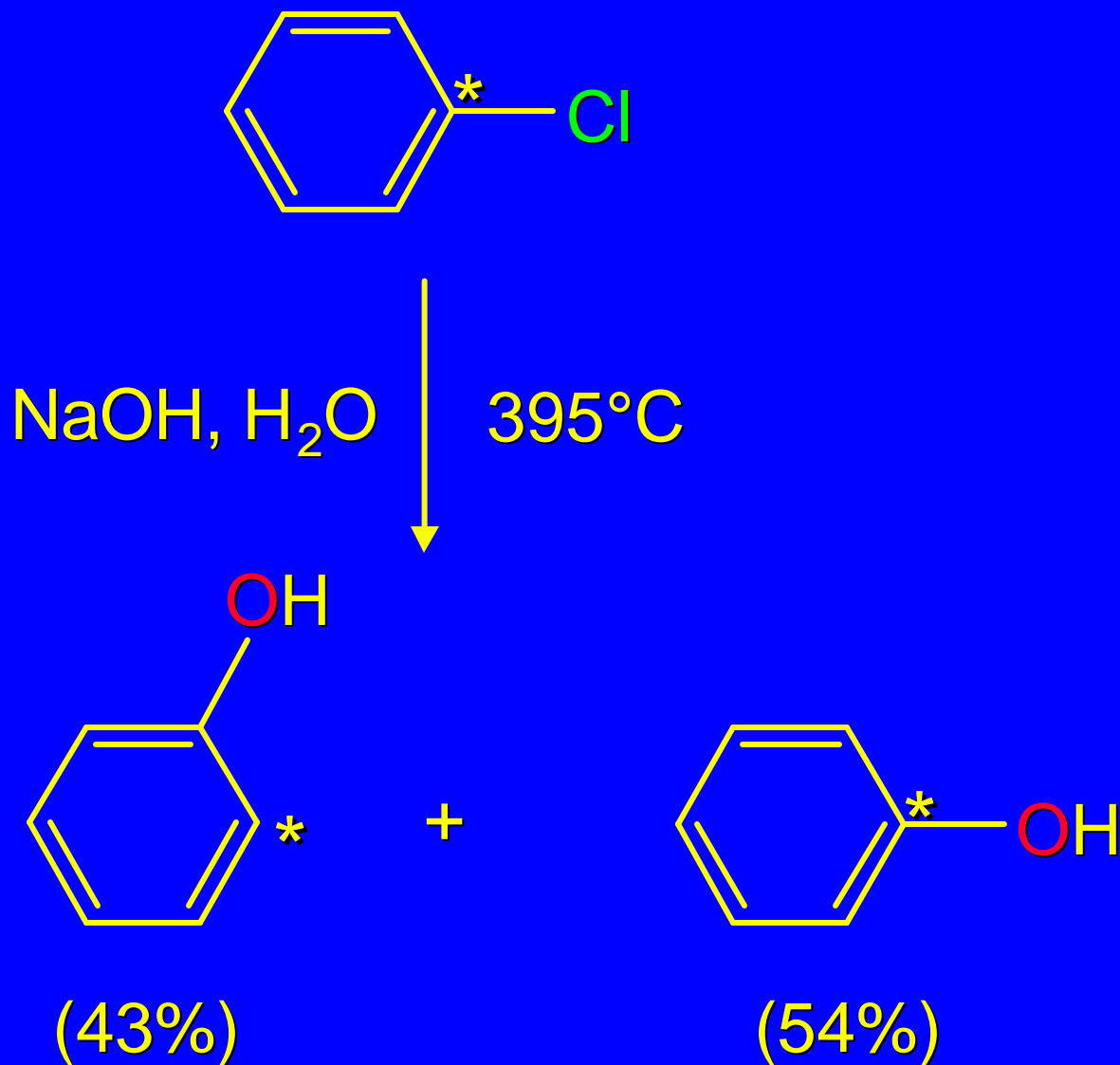
Mechanism

Step 3



Hydrolysis of Chlorobenzene

^{14}C labeling indicates that the high-temperature reaction of chlorobenzene with NaOH goes via benzyne.



23.9

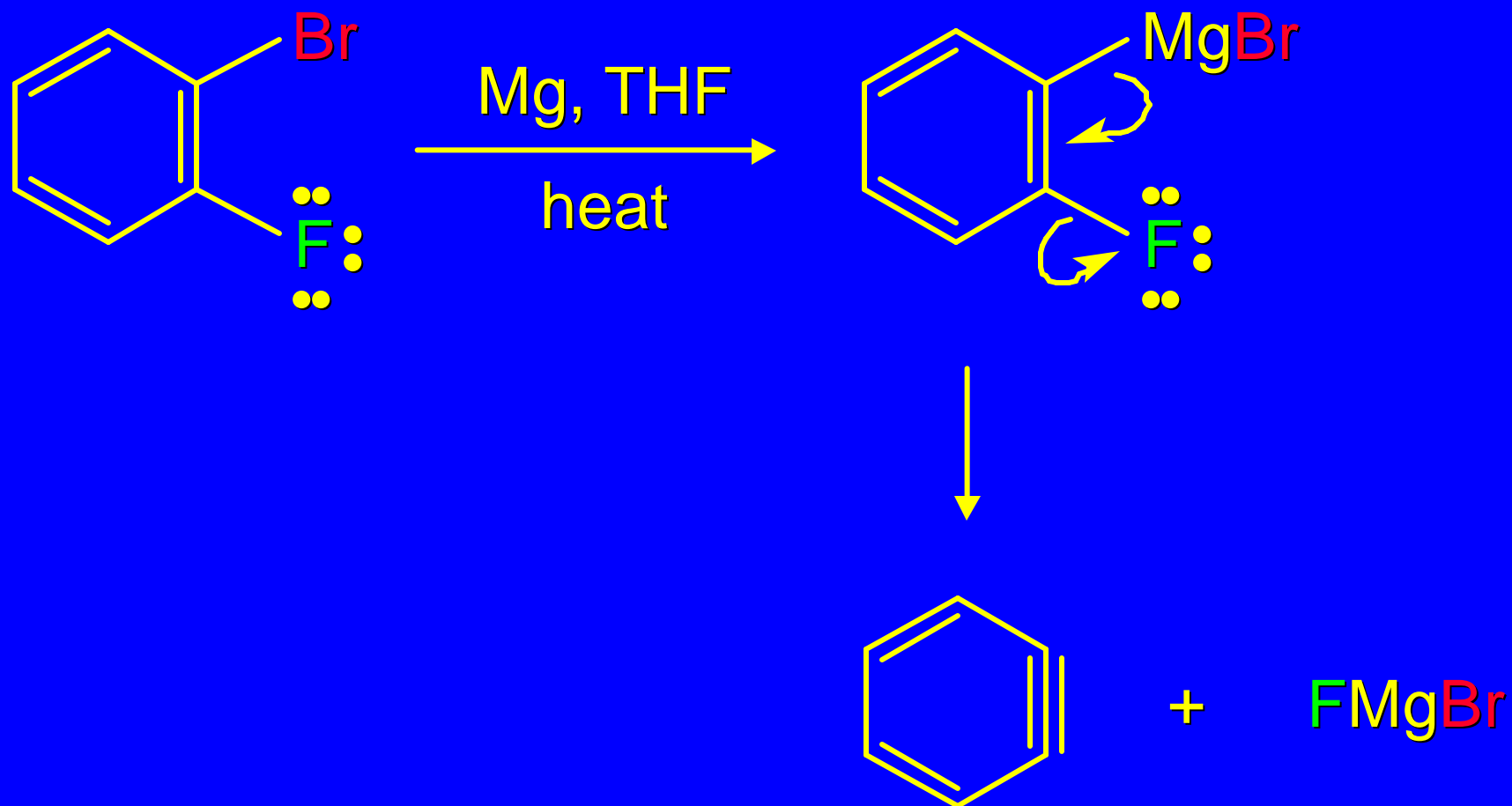
Diels-Alder Reactions of Benzyne

Other Routes to Benzyne

Benzyne can be prepared as a reactive intermediate by methods other than treatment of chlorobenzene with strong bases.

Another method involves loss of fluoride ion from the Grignard reagent of 1-bromo-2-fluorobenzene.

Other Routes to Benzyne



Benzyne as a Dienophile

Benzyne is a fairly reactive dienophile, and gives Diels-Alder adducts when generated in the presence of conjugated dienes.

Benzyne as a Dienophile

