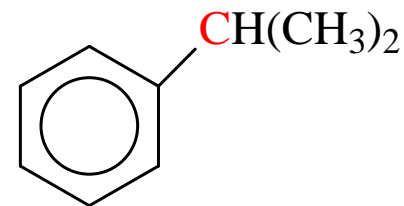
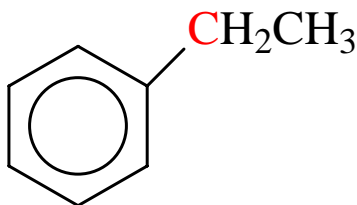
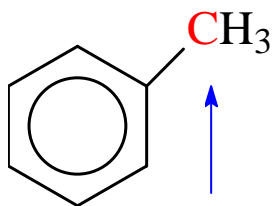


CHAPTER 12

Substituted Benzene

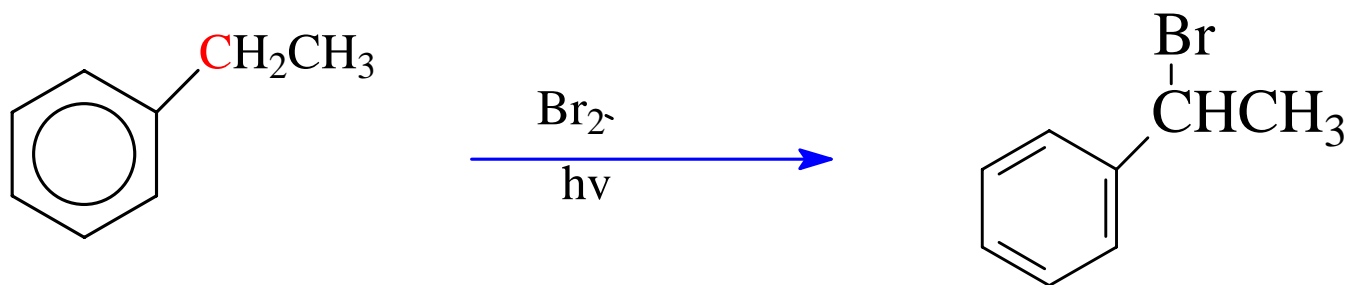
12.1 Alkylbenzenes (Ar-R)

Benzylic carbons:

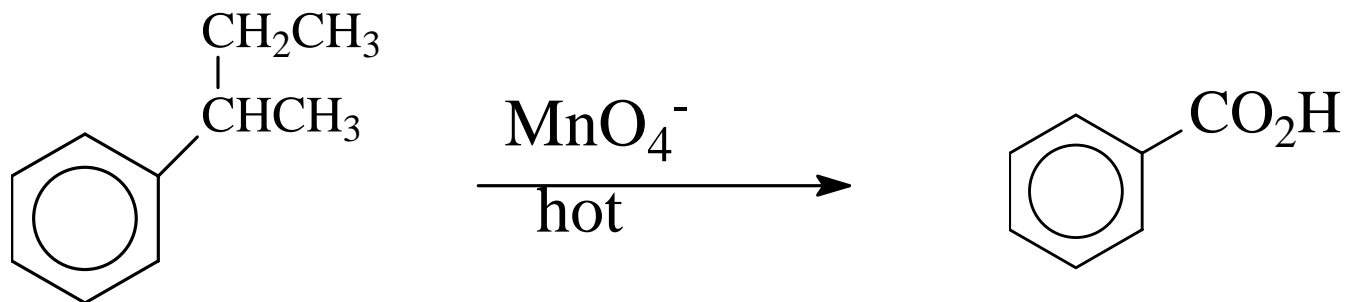
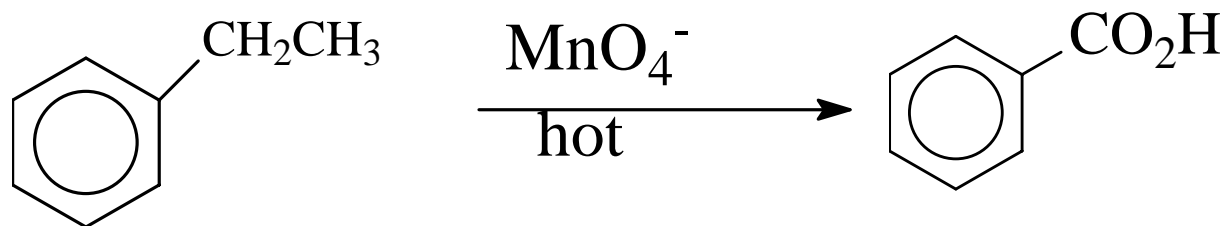
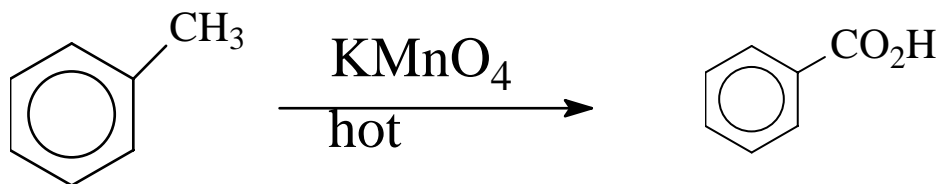
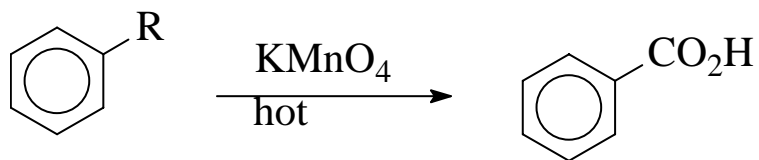


Reactions of Alkylbenzenes

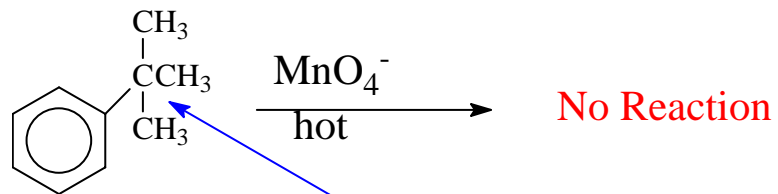
1. Free Radical Halogenation



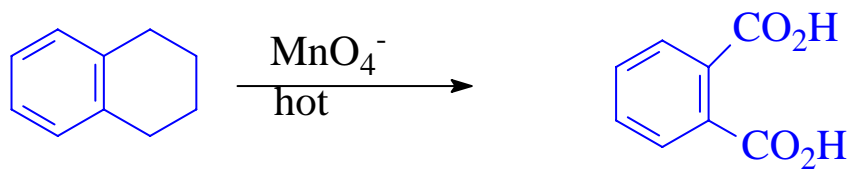
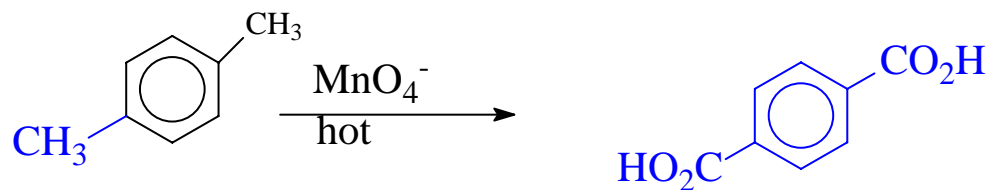
2- Oxidation



Notice:



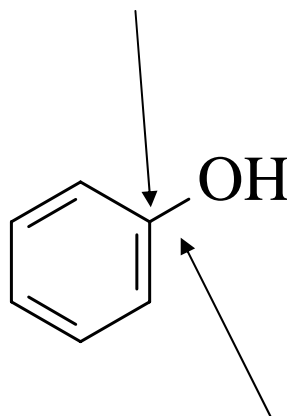
Benzylic carbon has no hydrogen



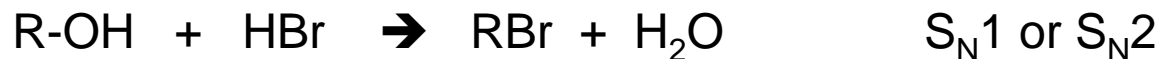
Phenols (ArOH)

A phenol has a hydroxyl group directly attached to the benzene ring

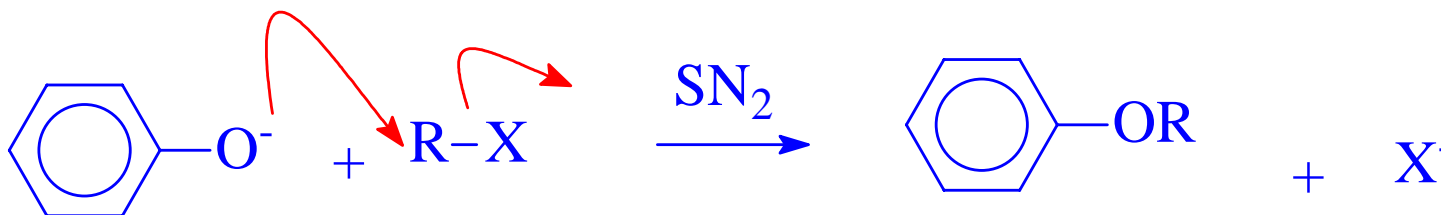
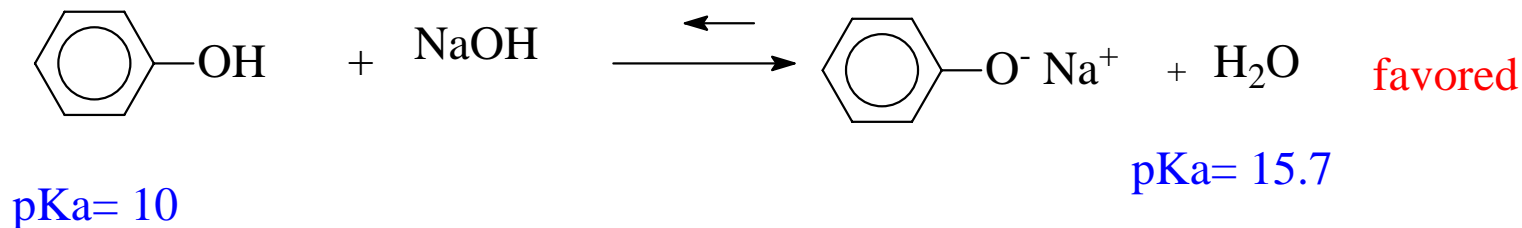
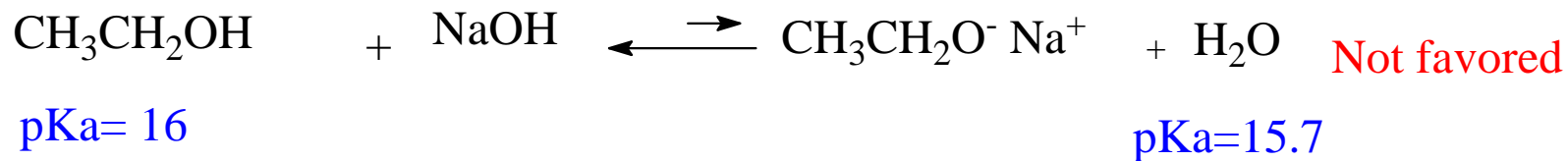
SP²- hybridized carbon



C---O bond is not easily broken → **No substitution or elimination reaction**

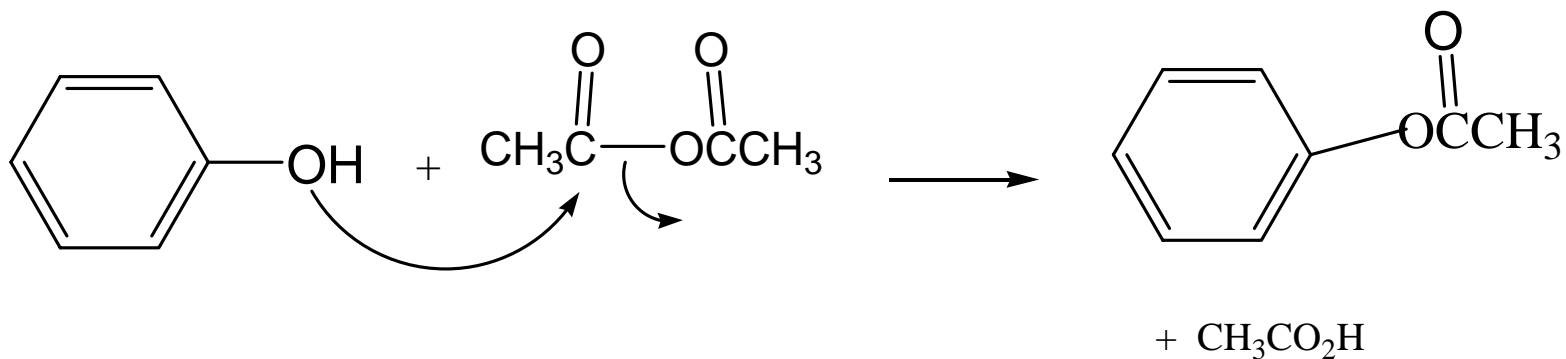


Acidity of Phenols

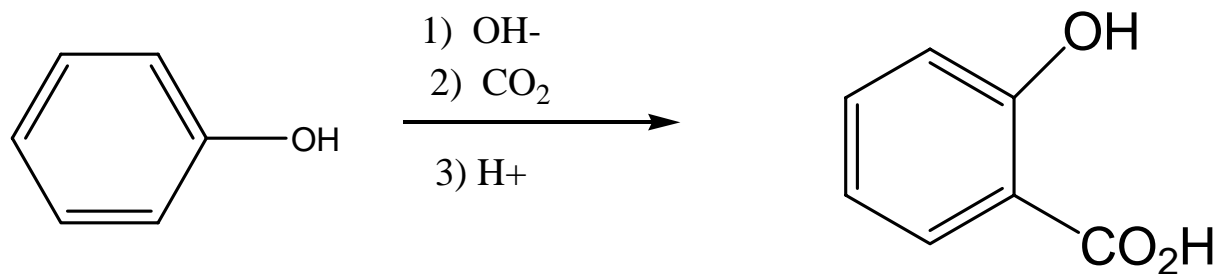


6 a phenoxide ion

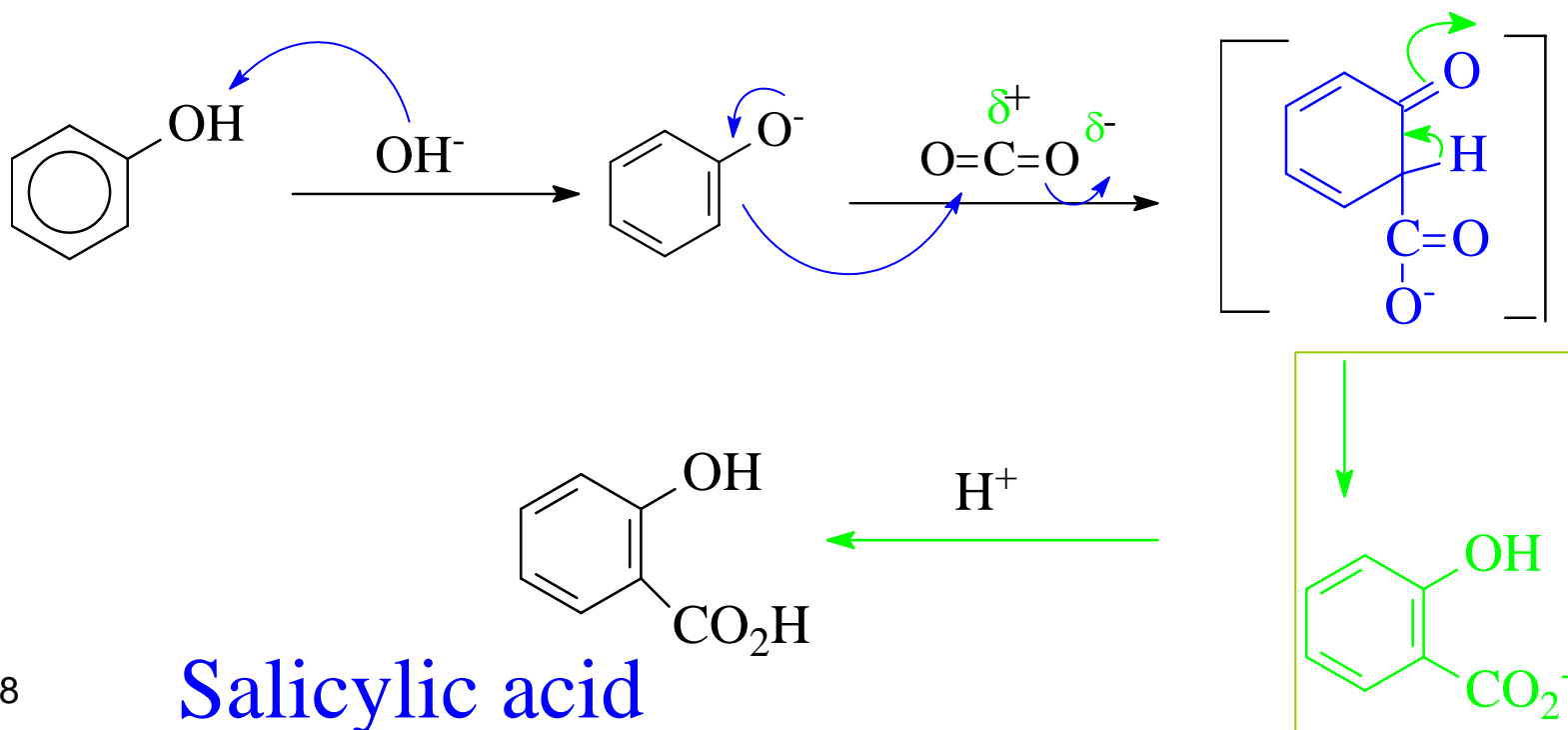
Esterification of phenols



The Kolbe Reaction

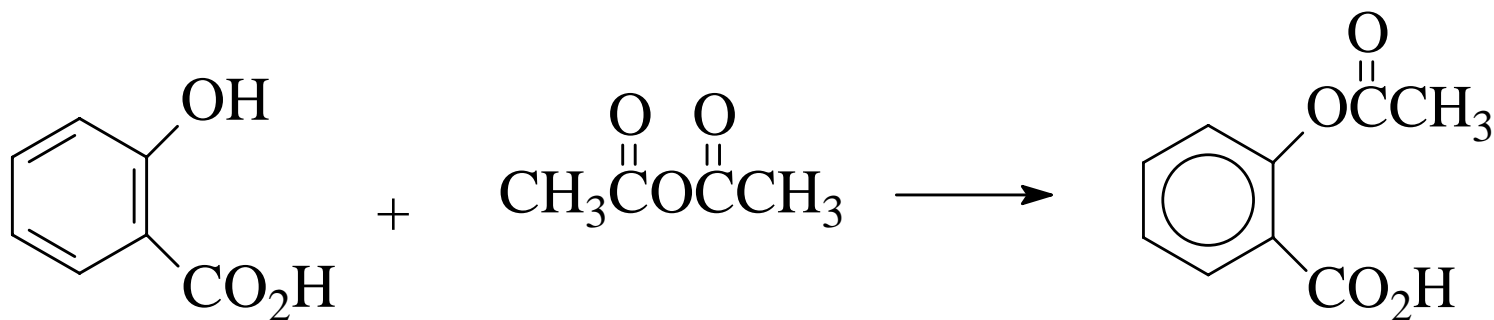


Mechanism



Importance of Kolbe Reaction

To Synthesize aspirin

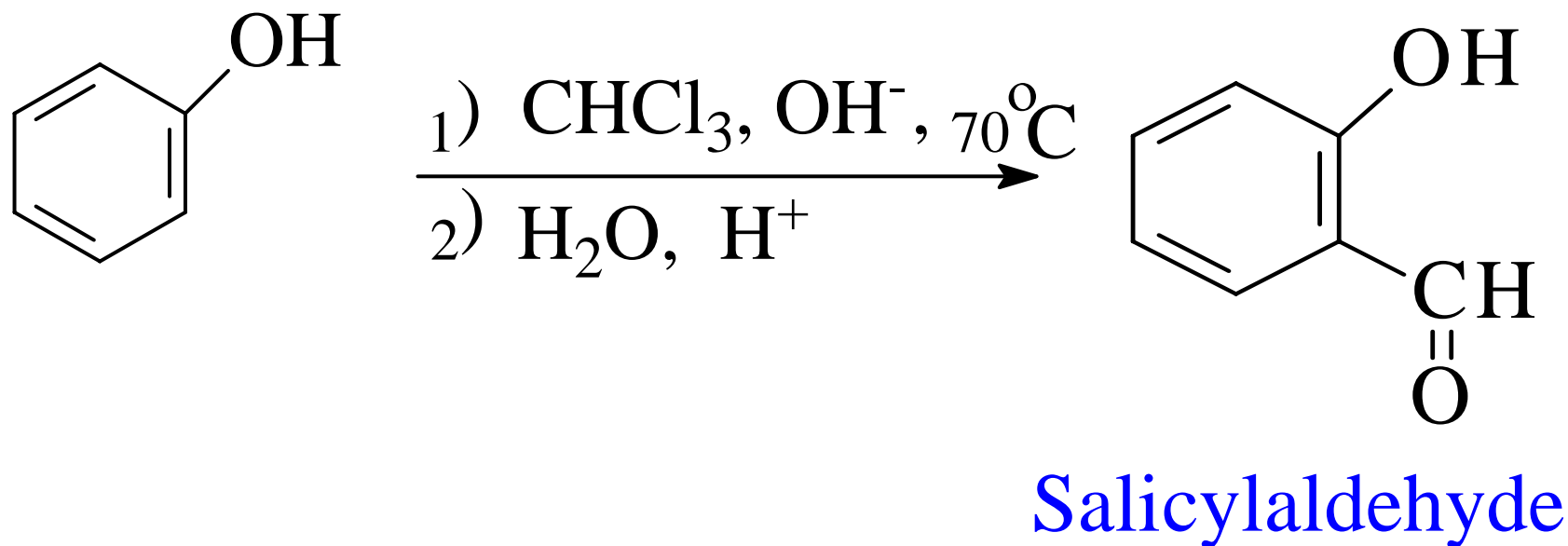


Acetylsalicylic acid

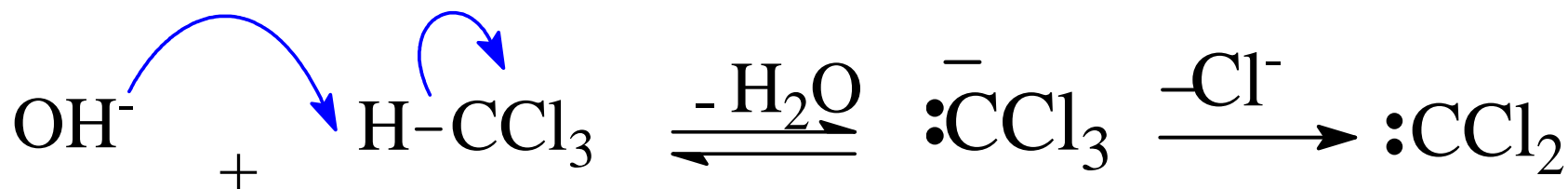
(Aspirin)

The Reimer-Tiemann Reaction

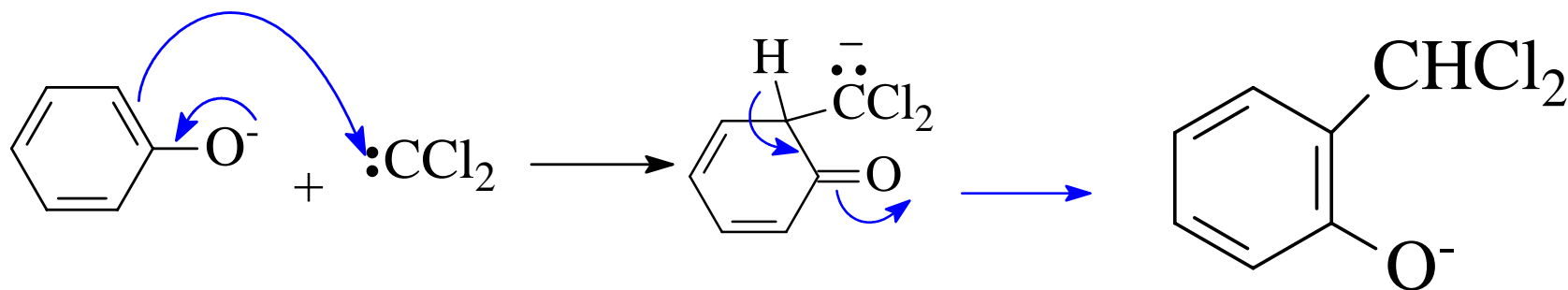
The reaction of phenol with chloroform in the presence of base.



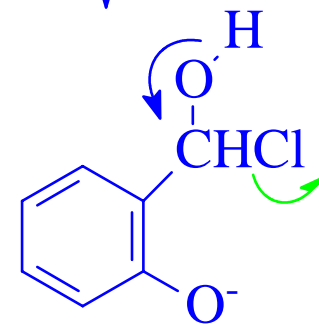
Mechanism:



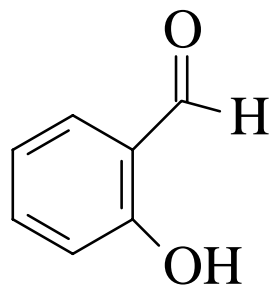
dichlorocarbene



OH^-

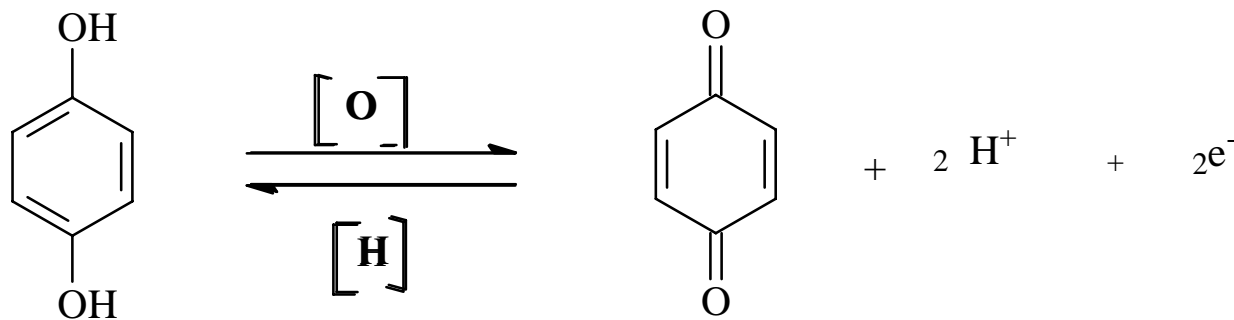


H^+



Oxidation of phenols: phenol resists oxidation

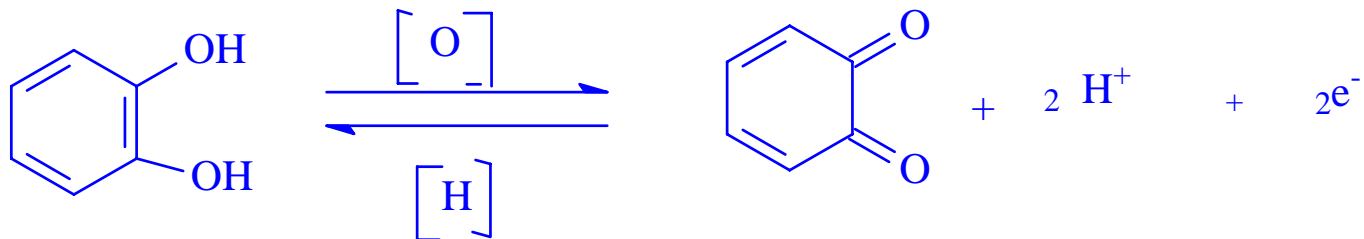
Oxidation of hydroquinones (1,4-dimethoxy benzenes)



hydroquinone

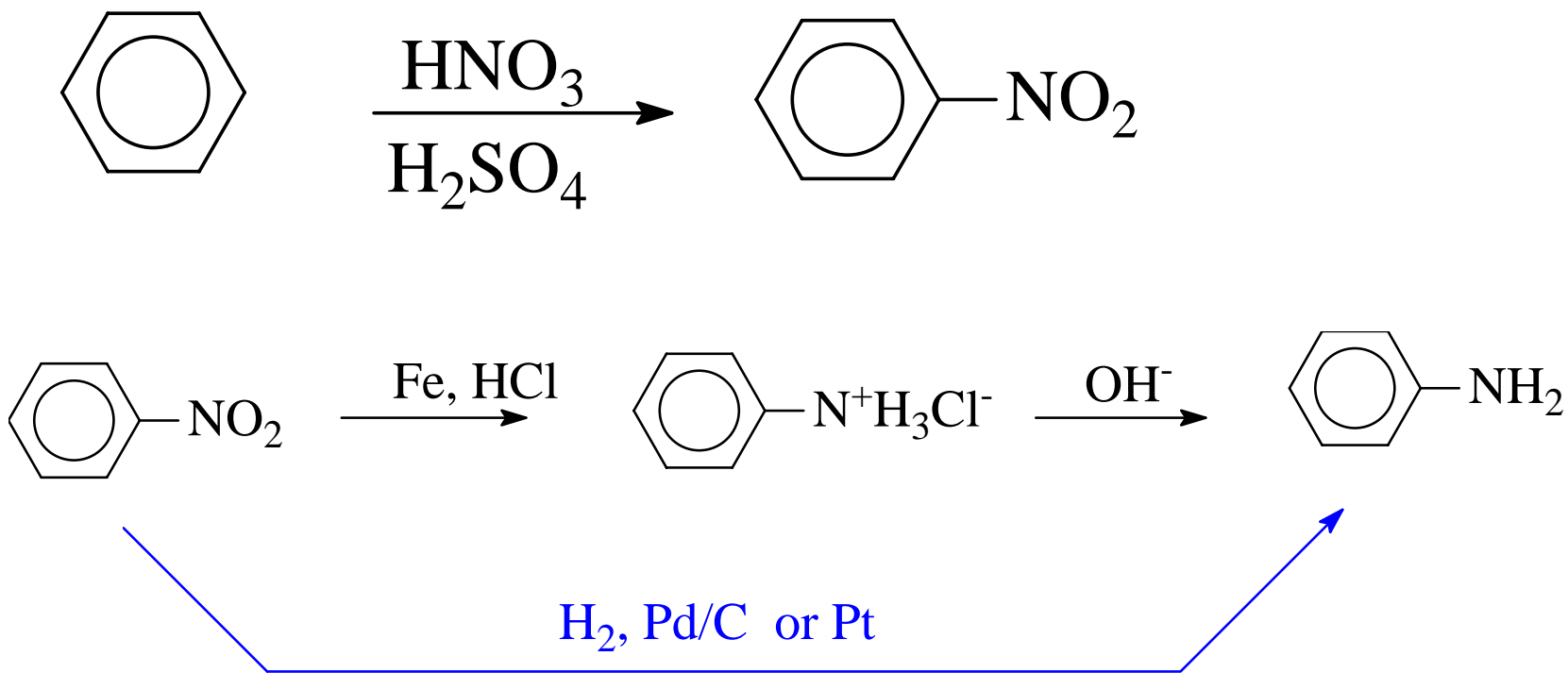
1,4-benzoquinone

(quinone)

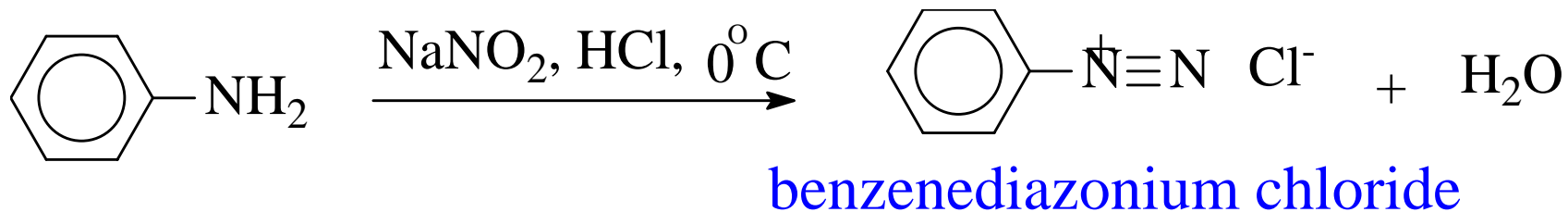


1,2-benzoquinone

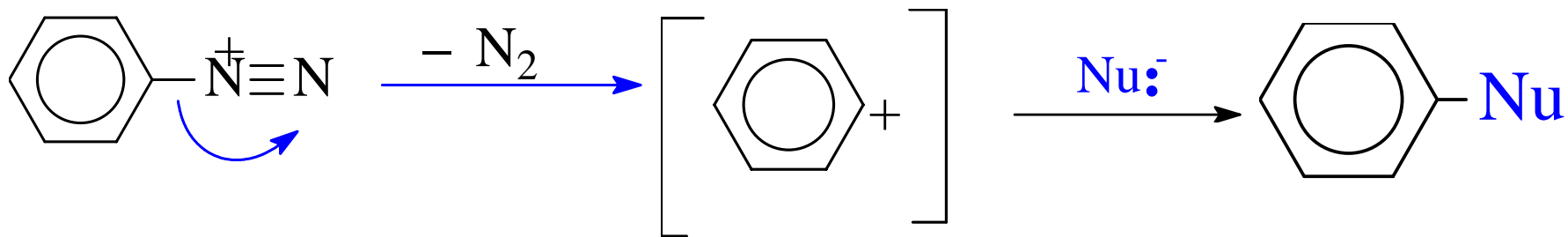
Preparation of Aniline



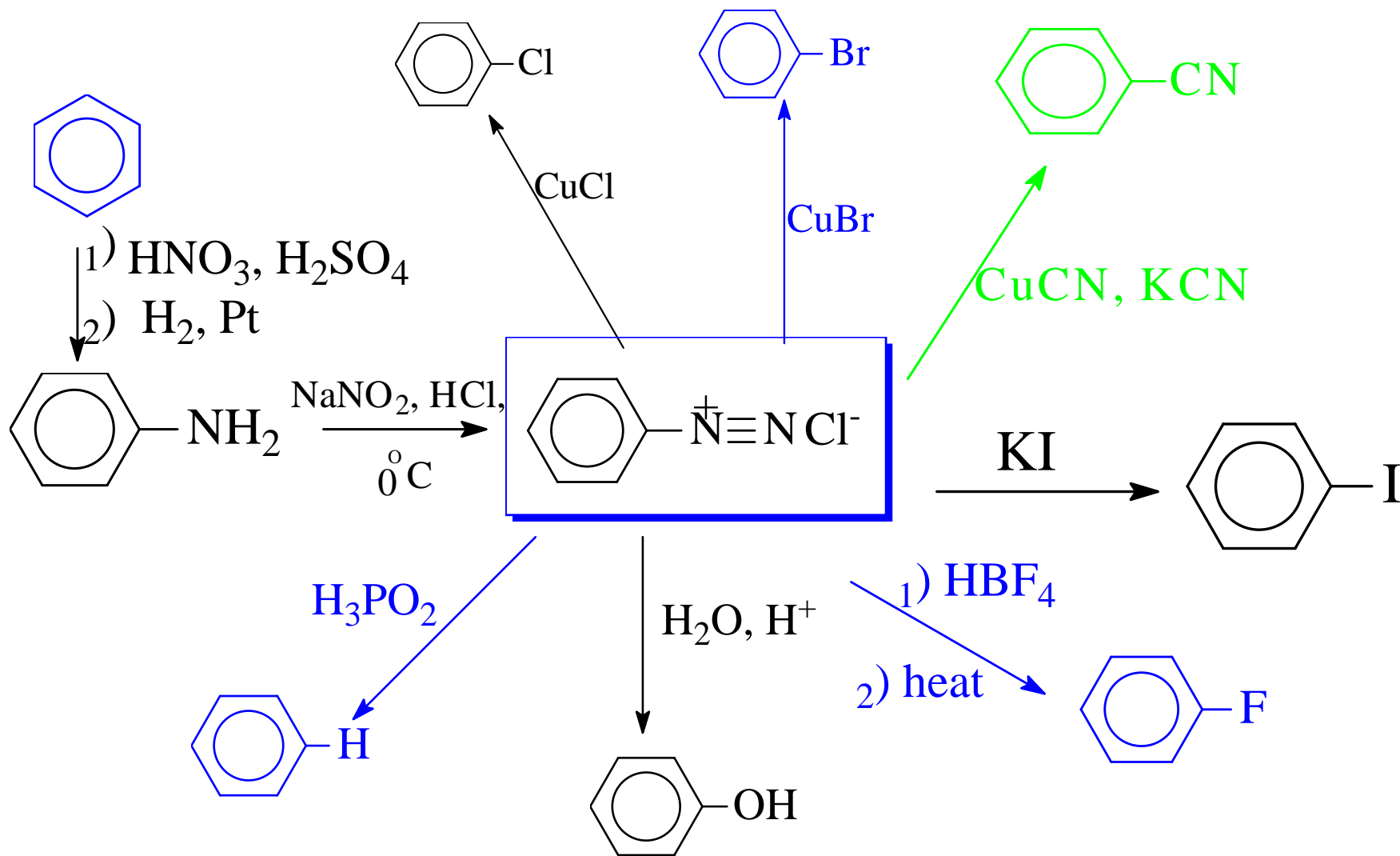
Benzenediazonium Salts



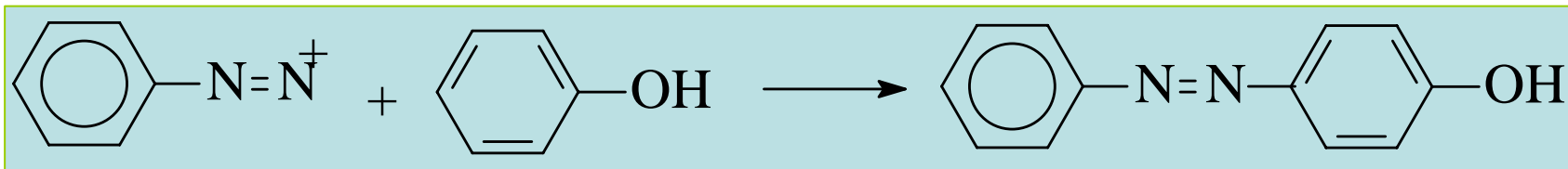
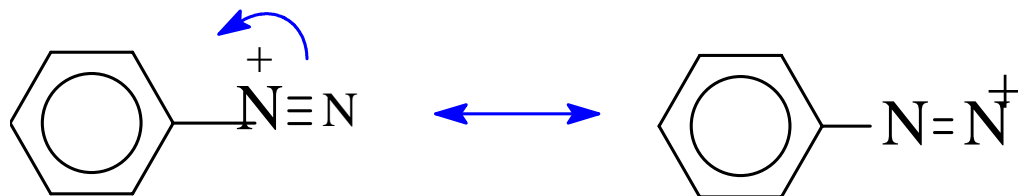
very reactive \implies Excellent leaving ability of N_2 gas



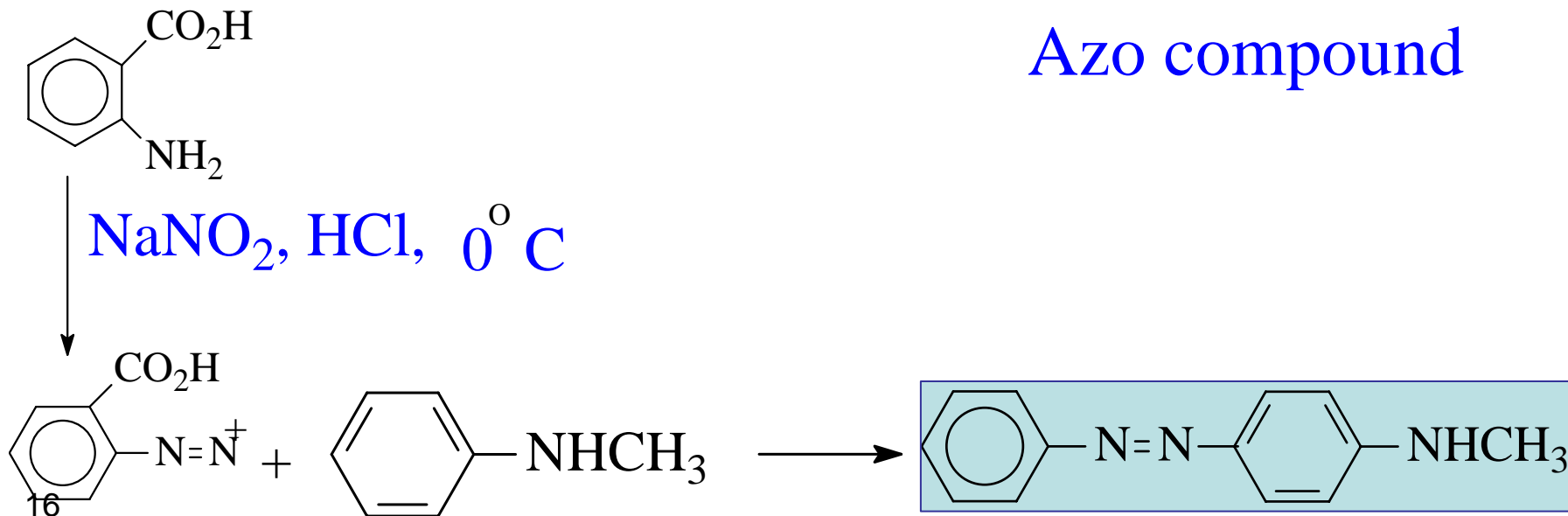
Reactions of benzenediazonium Salts



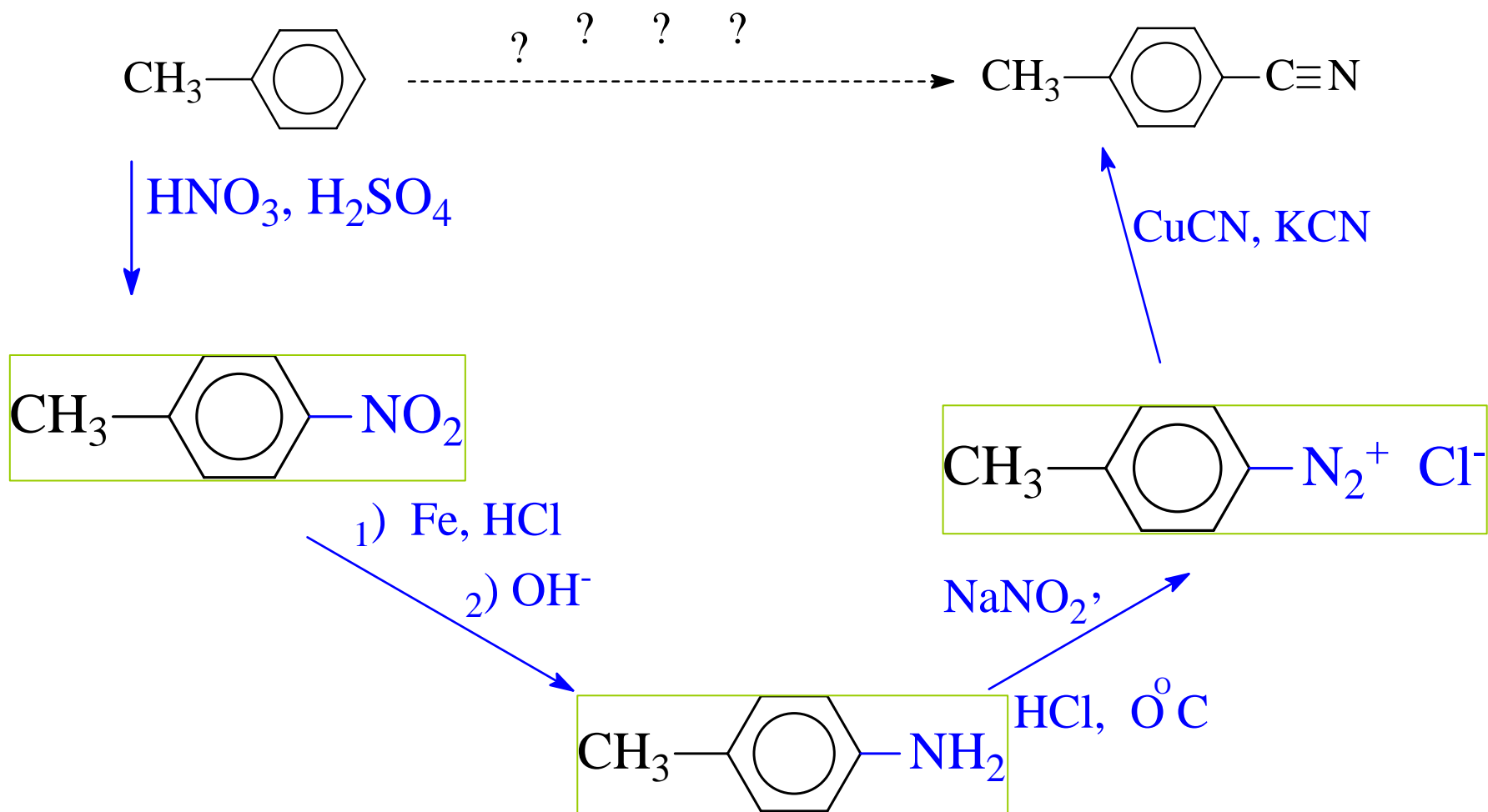
Coupling reactions



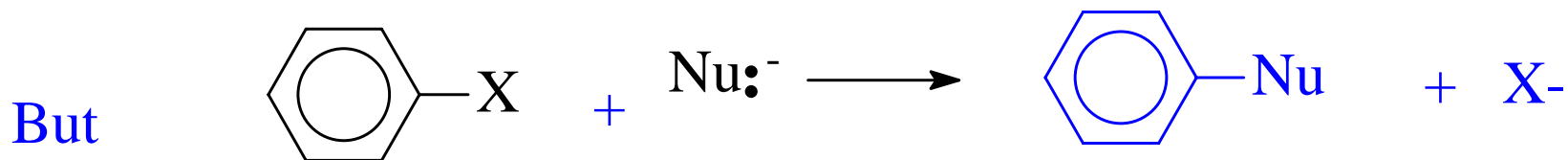
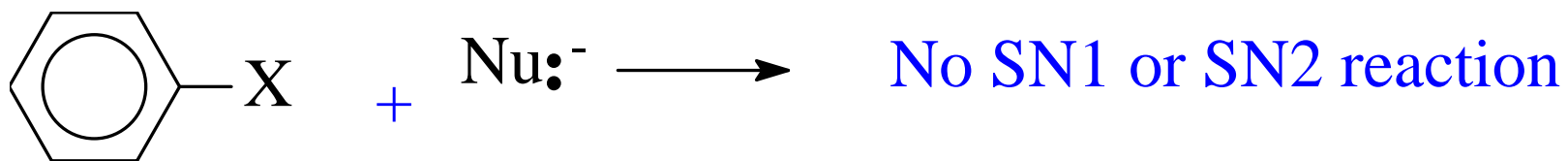
Azo compound



Synthesis involving diazonium salts

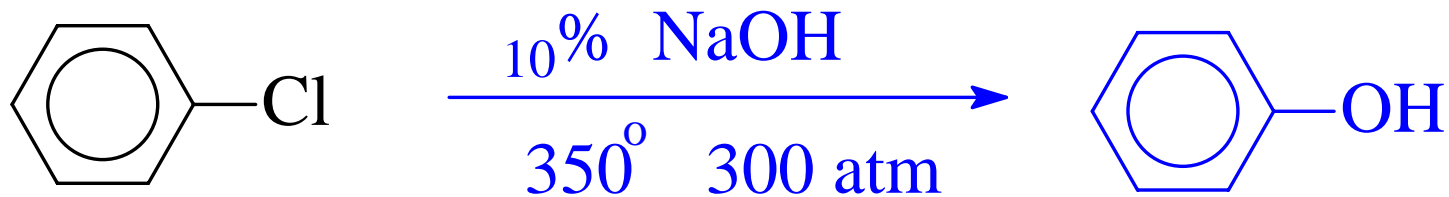


Nucleophilic Aromatic Substitution

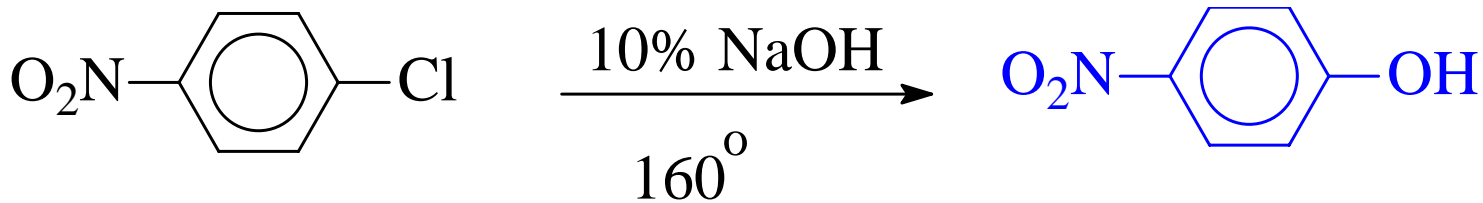


Nucleophilic Aromatic Substitution

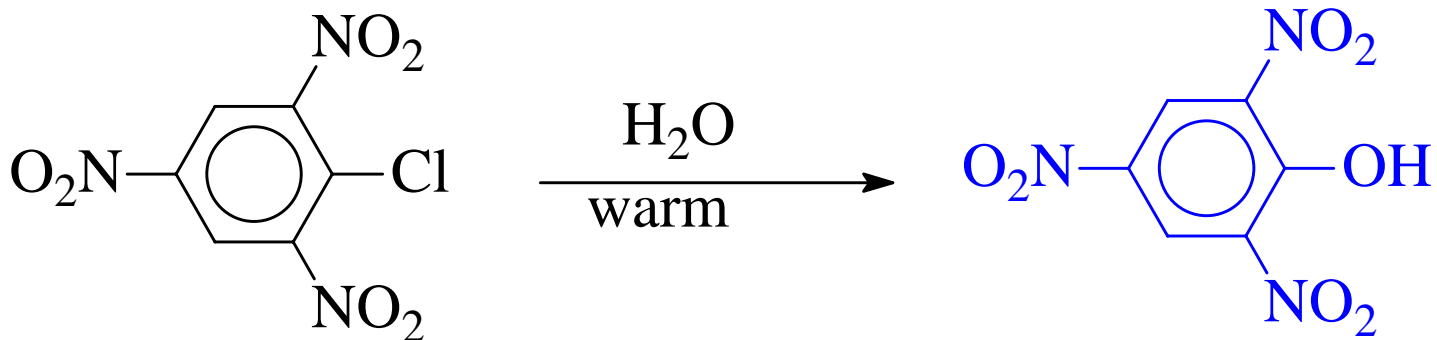
Examples



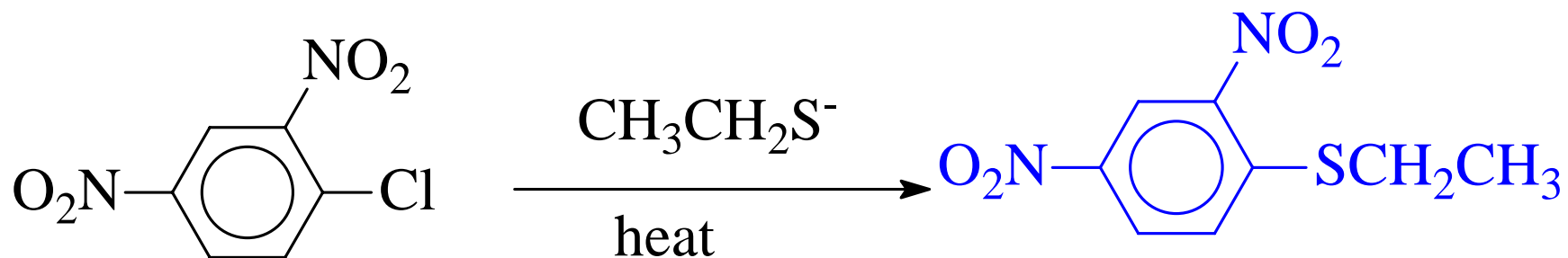
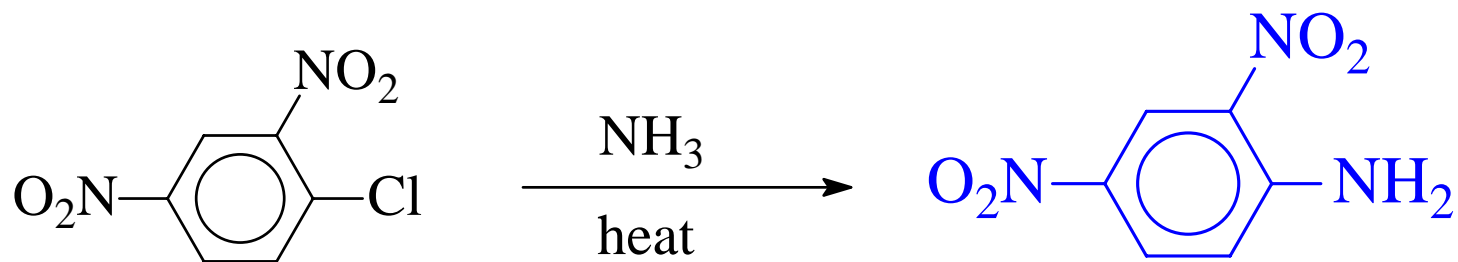
Increasing
Nucleophilicity
towards Nu:-



P-nitrophenol



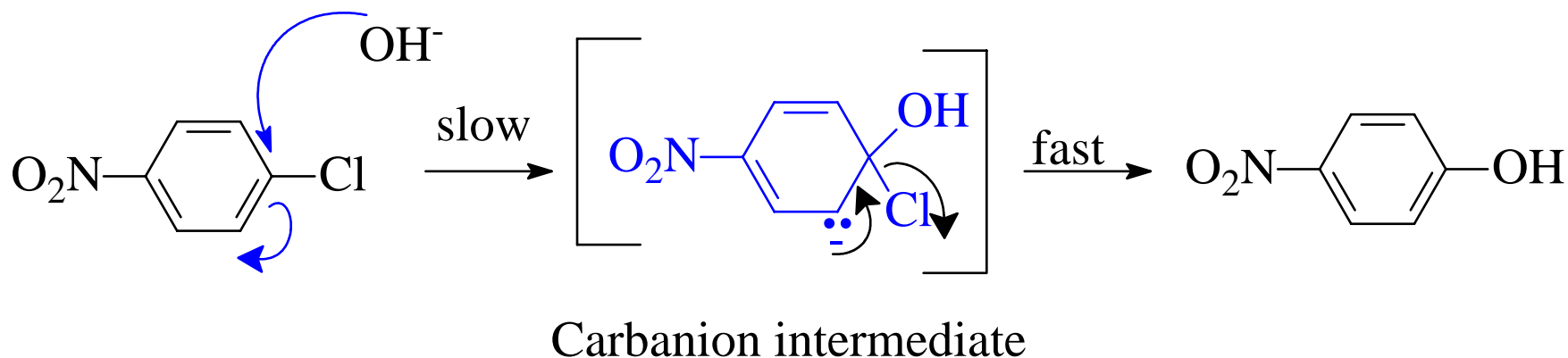
Other nucleophiles



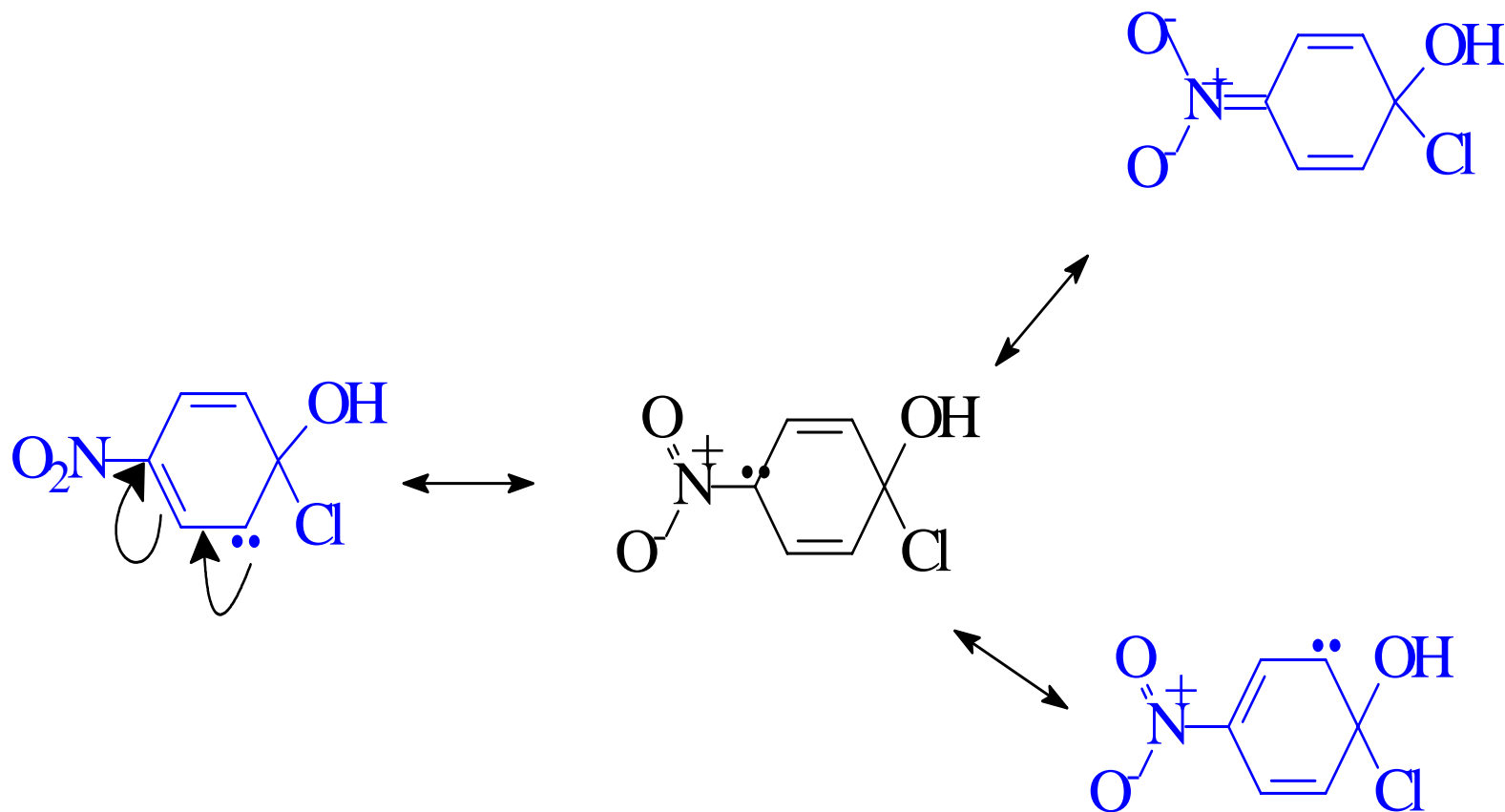
Carbanion Mechanism:

If the ring is activated toward nucleophilic substitution by an electron withdrawing group (i.e. NO_2)

Two steps 1) addition of Nu^- to form carbanion
2) Loss of the halide ion

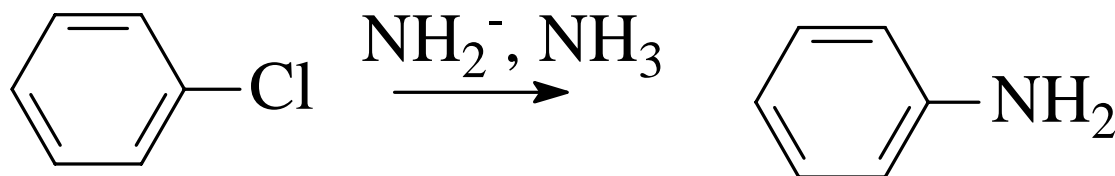


Carbanion intermediate is stabilized by resonance

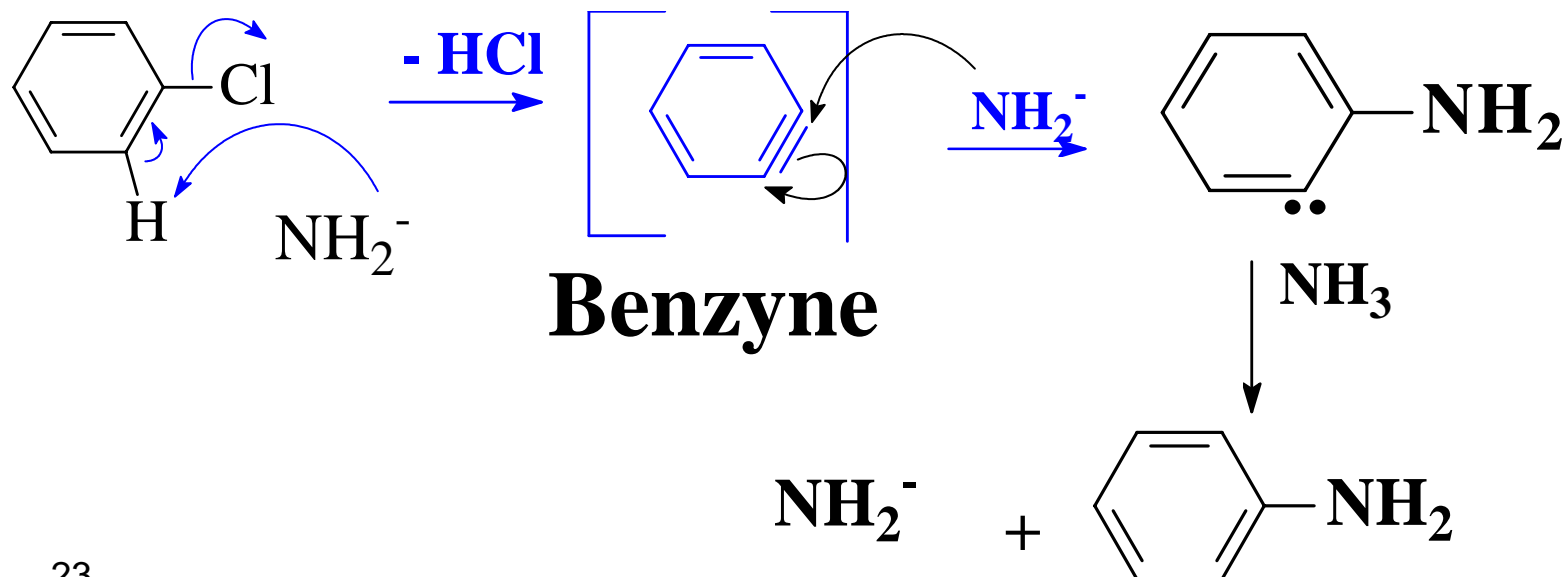


Benzyne Mechanism:

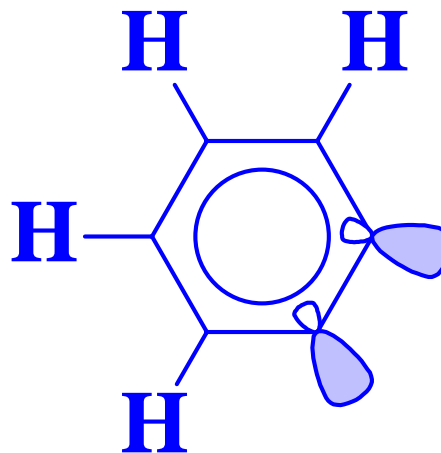
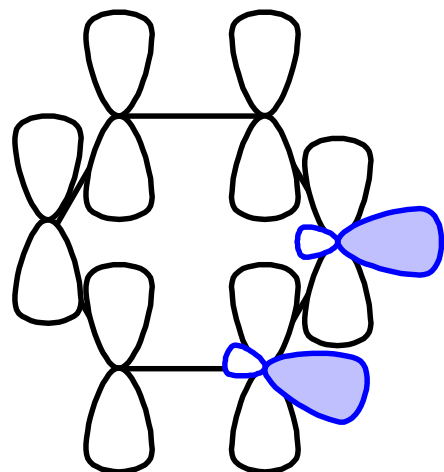
If there is no electron withdrawing substituent on the ring.



Mechanism

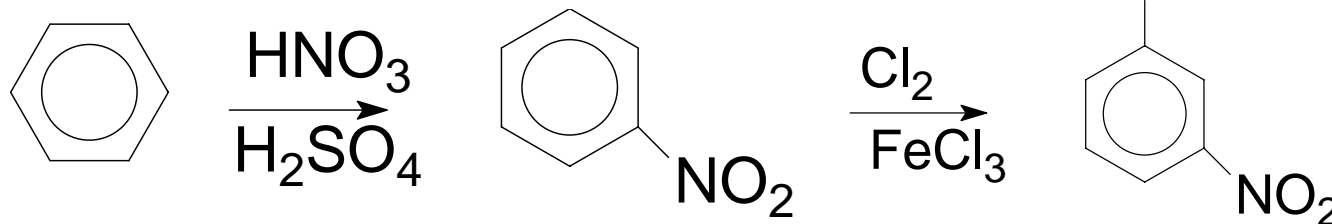
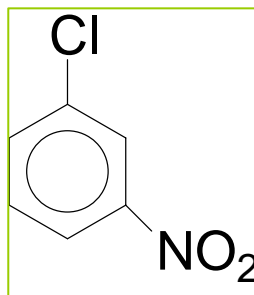


Benzyne

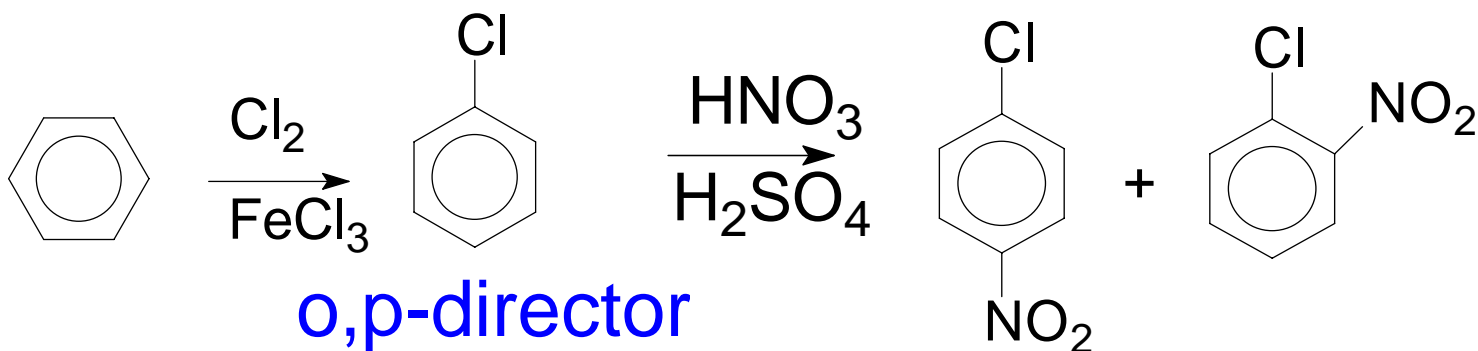


Syntheses of substituted benzene compounds

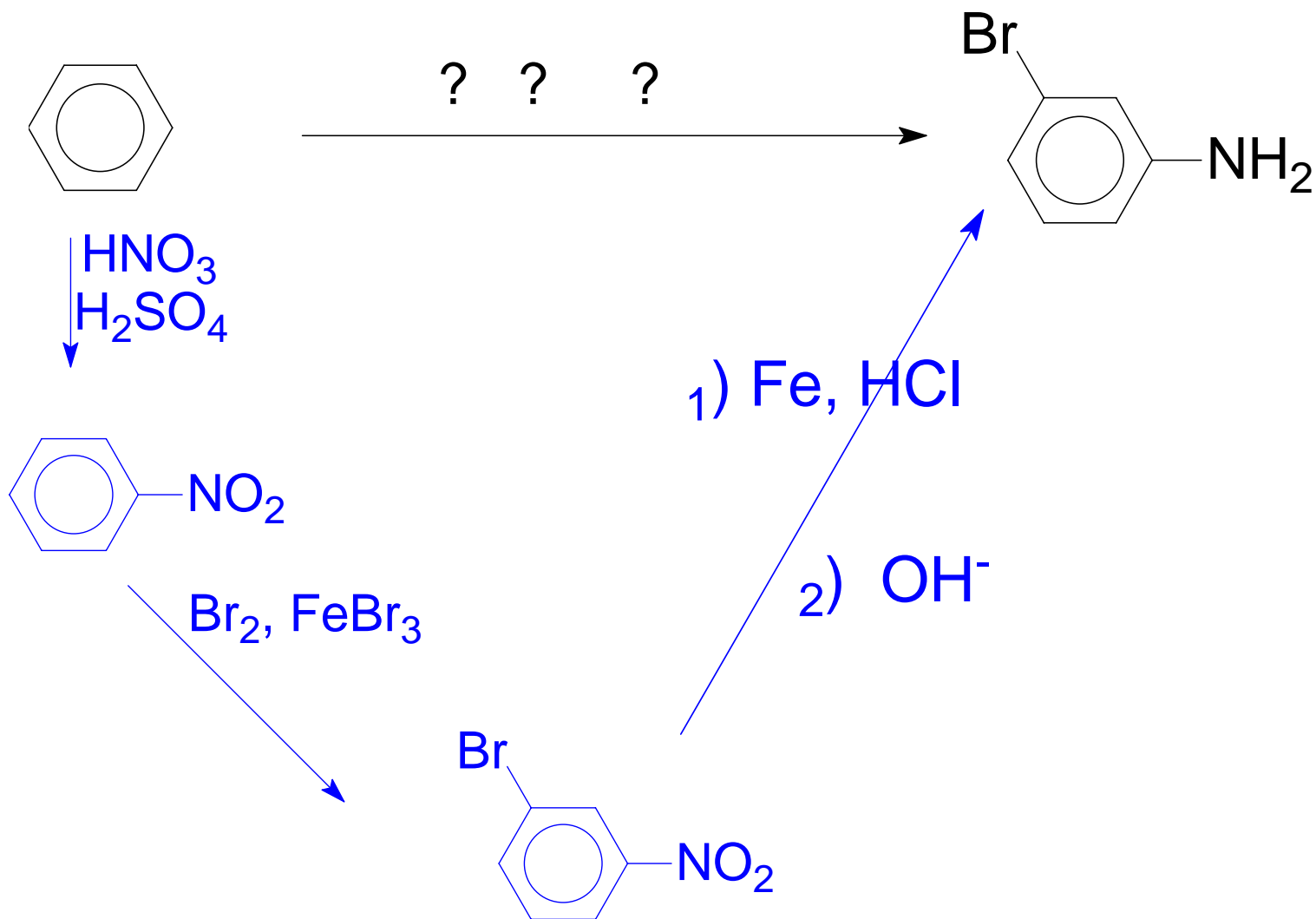
- How would you synthesize



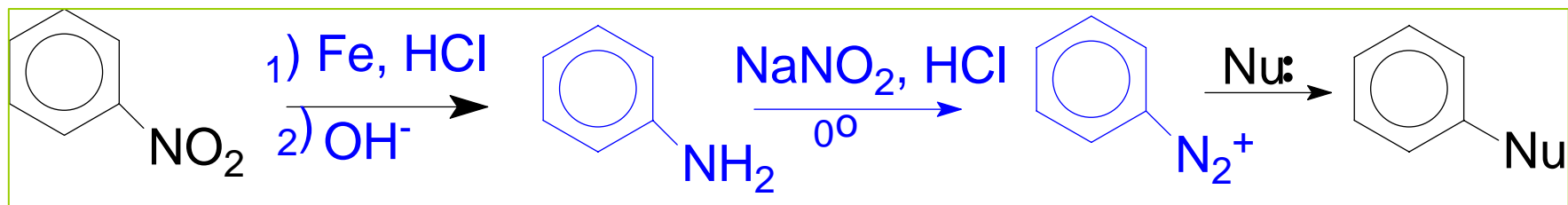
- But IF YOU START WITH CHLORINATION



Syntheses



Note: Nitro group can be converted to arylamines which in turn can also be converted to aryldiazonium salts, => making a diversity of substituted products

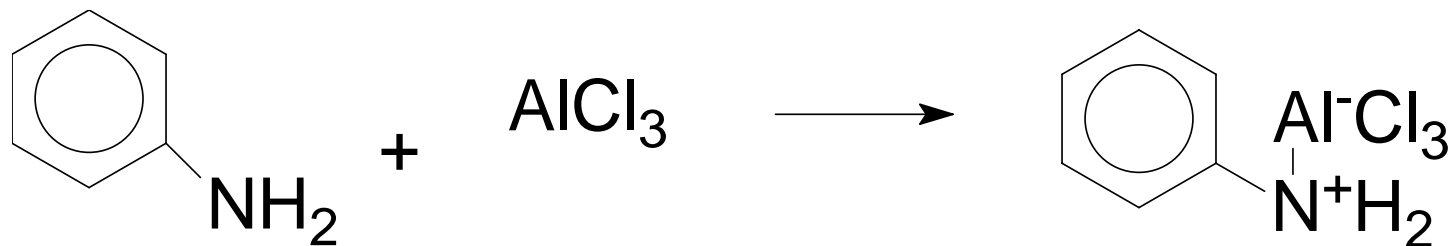


m-director

o,p-director

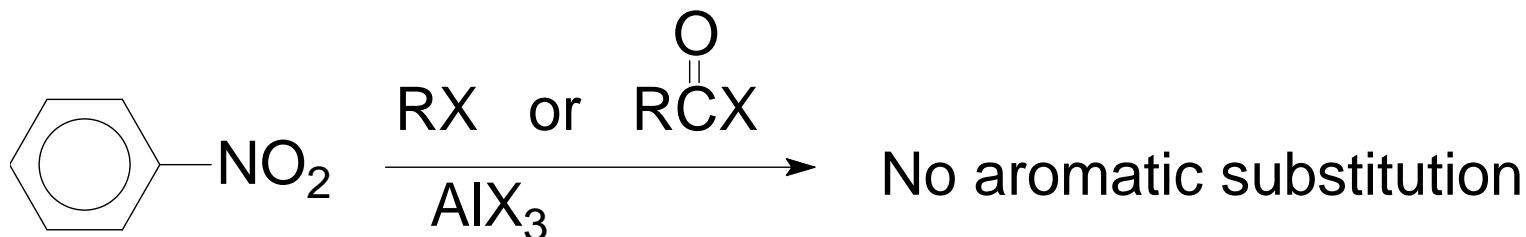
easily displaced

Notice: Amino group does not undergo Friedel-Crafts reaction because an amino group reacts with Lewis acid since it is basic to form strongly deactivating group

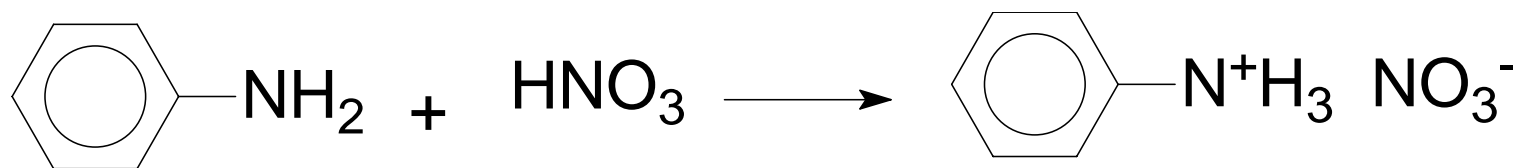


strongly deactivating

Nitrobenzene does not undergo Friedel-Crafts reactions



Notice: An amino group is o,p-director, but an ammonium group ($-\text{NR}_3^+$) is an m-director and deactivating.



o,p-director

m-director

Sulfonic acid group (-SO₃H)

The sulfonic acid group is easily removed and can be displaced by a variety of reagents.

