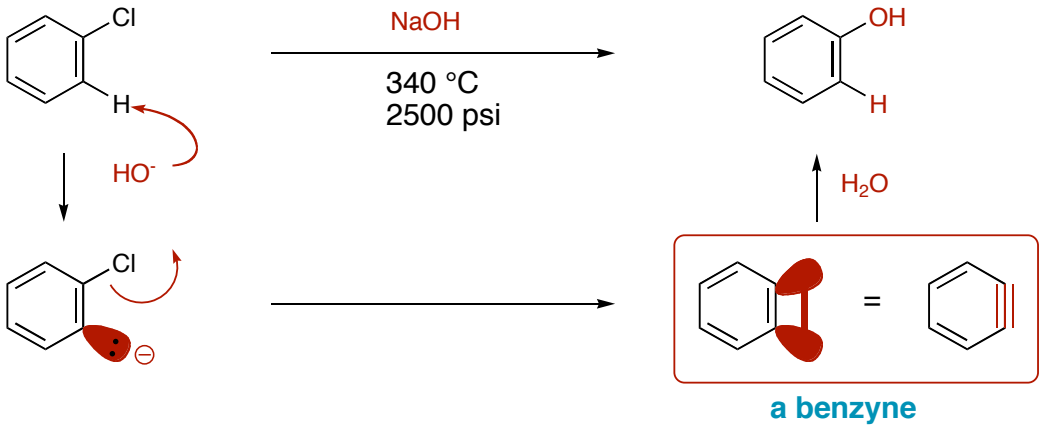
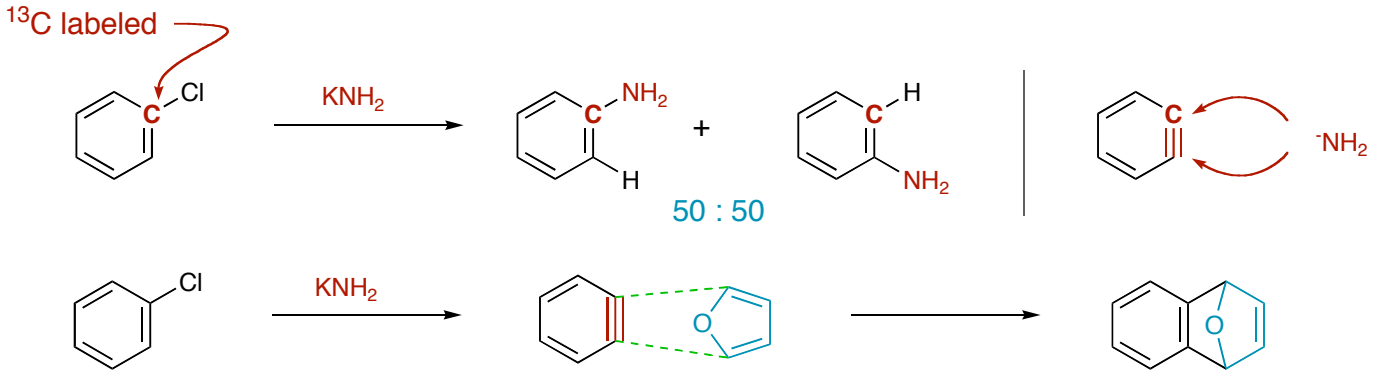
Chapter 16 - Chemistry of Benzene: Electrophilic Aromatic Substitution

Nucleophilic Aromatic Substitution - Benzynes

Under extreme conditions, nucleophilic substitution can occur on aromatic rings without electron withdrawing groups. The mechanism involves an elimination to form a reactive intermediate (benzyne) to which the nucleophile adds.

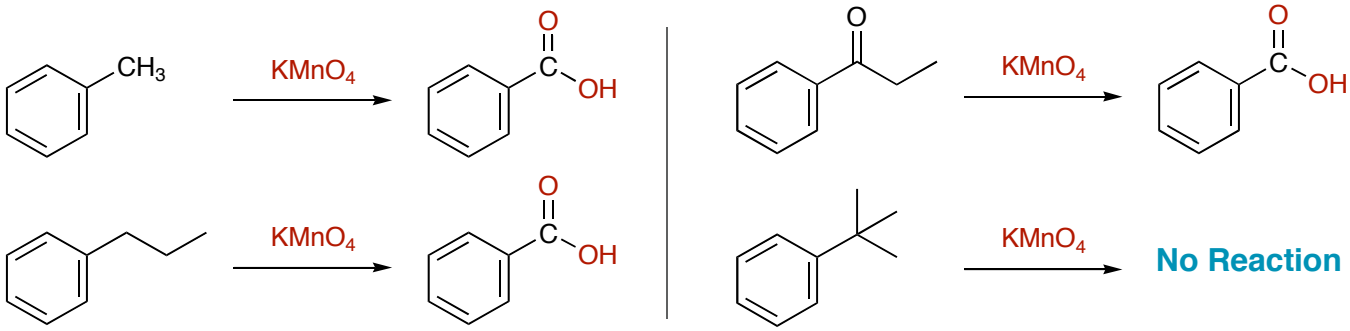


The evidence for the presence of benzynes comes from the formation of two product in equal amount when the starting material is labeled. This suggests a symmetrical intermediate. Also, products of a Diels-Alder reaction indicate that there is a pi-bond in the intermediate.

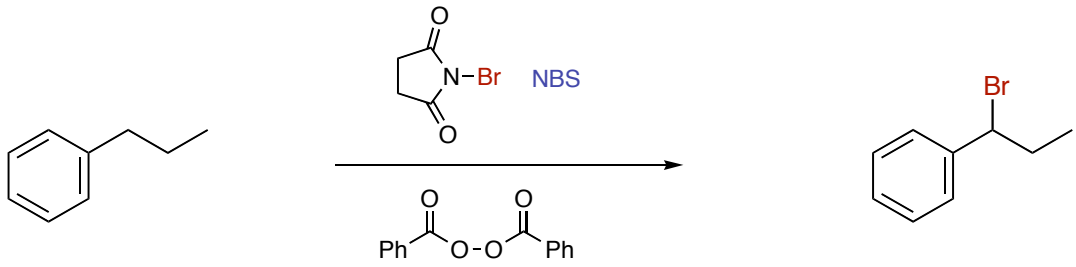


Oxidation of Substituents

Benzene rings are inert to oxidation, but alkyl groups attached to the benzene ring can be readily oxidized to benzoic acids upon treatment with potassium permanganate. This only occurs if there are benzylic hydrogens (or oxygen, e.g. ketone).



Benzylic bromination occurs just like allylic bromination of alkenes. Bromination under these radical conditions occurs in the benzylic position because this is the most stable radical.



Reduction of Substituents

Under normal hydrogenation conditions, benzene rings are not reduced. This requires more forcing conditions and more reactive catalysts. Functional groups attached can be reduced (e.g. alkenes, nitro groups, ketones). This allows you to make products that cannot be obtained by Friedel-Crafts alkylations.