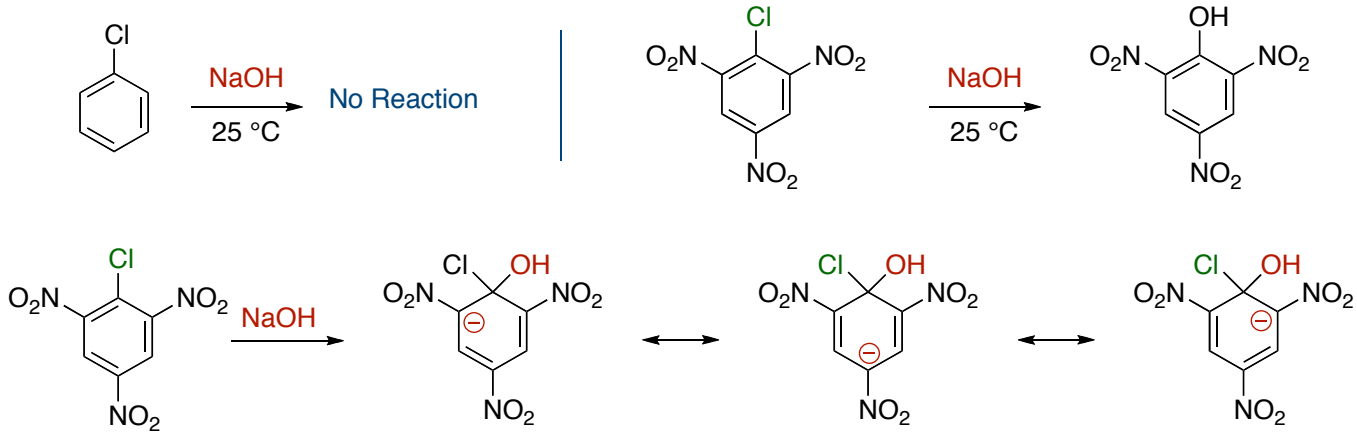
Chem 342 • Organic Chemistry II

Lecture Summary 12 - 11 Feb 2009

Chapter 16 - Chemistry of Benzene: Electrophilic Aromatic Substitution

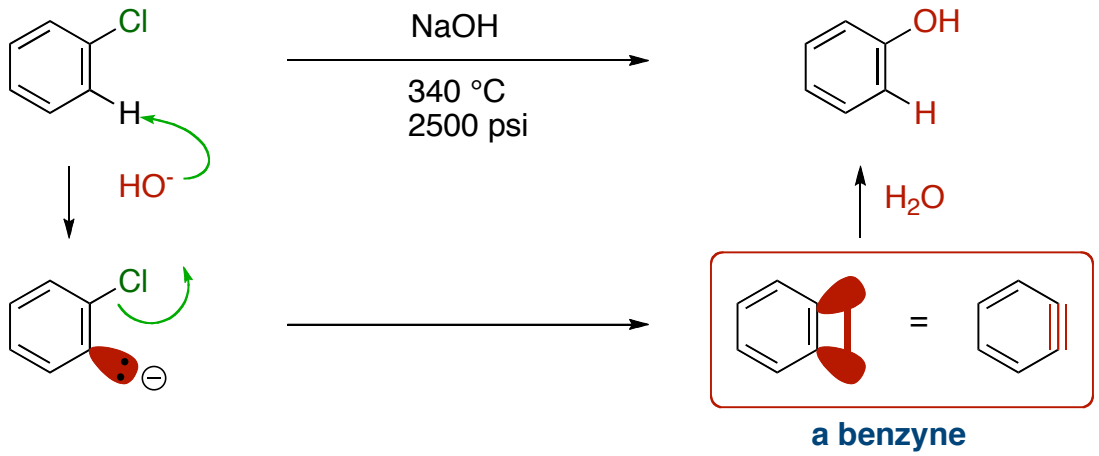
Nucleophilic Aromatic Substitution

Under normal conditions, nucleophiles don't react with aromatic rings. However, if there are good electron withdrawing groups on the ring, nucleophilic substitution can take place. This does not occur by an S_N1 or S_N2 reaction. The mechanism is an addition of the nucleophile followed by loss of the leaving group. The electron withdrawing groups need to be ortho or para to the leaving group. This is where the negative charge appears in the intermediate. Thus, the more you can stabilize the negative charge, the better the reaction will be. Note, that m-nitrochlorobenzene will not undergo nucleophilic substitution, while o- or p-nitrochlorobenzene will.

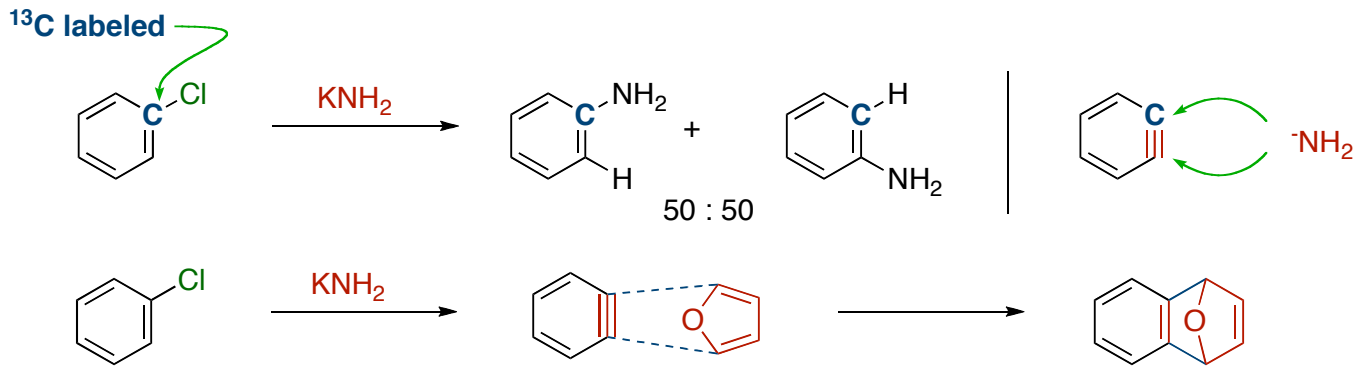


Nucleophilic Aromatic Substitution - Benzynes

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.

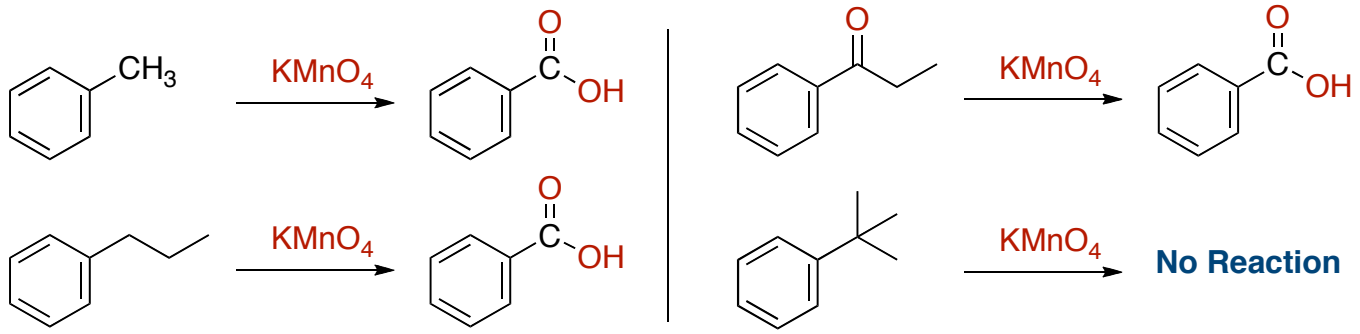


The evidence for the presence of benzynes comes from the formation of two product in equal amount when the starting material is labeled. This suggests a symmetric intermediate. Also, products of a Diels-Alder reaction indicate that there is a pi-bond in the intermediate.



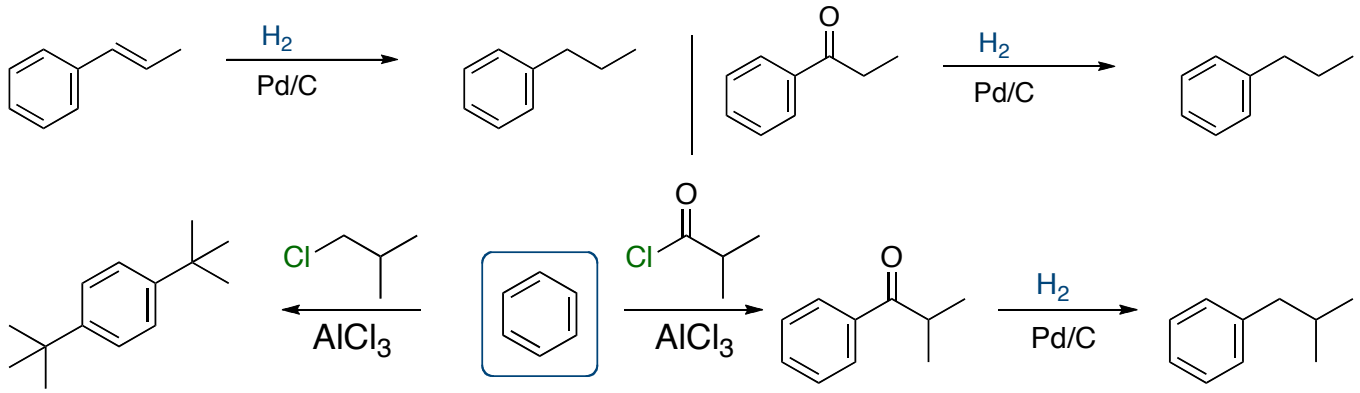
Oxidation of Substituents

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).

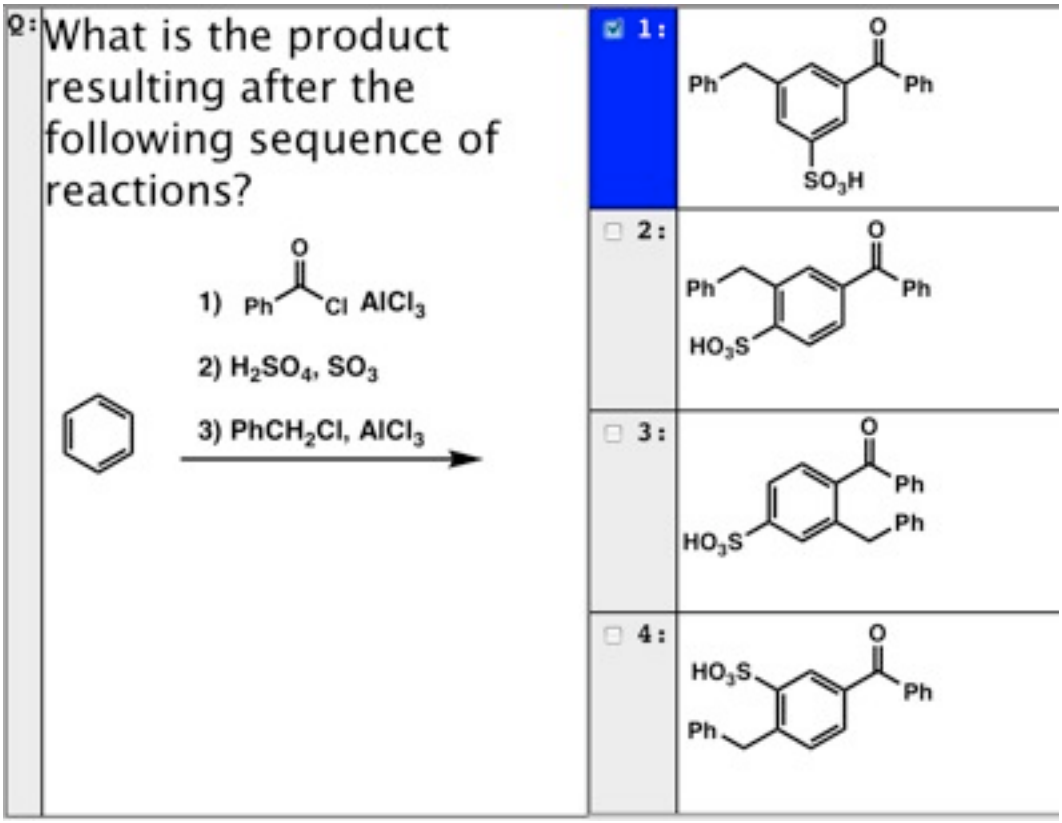


Reduction of Substituents

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.



Daily Quiz


Q: What is the product resulting after the following sequence of reactions?
1) Ph Cl AlCl3
2) H2SO4, SO3
3) PhCH2Cl, AlCl3
1:
2:
3:
4:
Ph
Ph
SO3H
HO3S