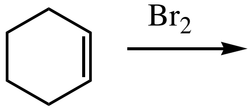
Learning Guide for Chapter 18 - Aromatic Compounds II

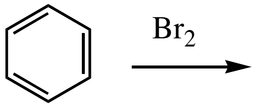
I. Electrophilic aromatic substitution
  - Introduction
  - Mechanism
  - Reagents and Products
  - Electrophiles
  - Effects of Substituents
  - Friedel-Crafts alkylation and acylation

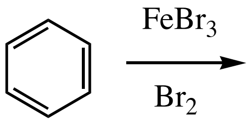
I. Electrophilic Aromatic Substitution

Introduction

Which of the following reactions will give product?





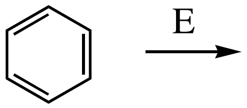


What can you conclude?

Mechanism

In addition reactions of alkenes, how does the C=C react?

When an aromatic ring reacts, it is a very weak nucleophile. What will be formed?



How would the activation energy of the first steps compare?

How would the two electrophiles compare?

Why does the C+ react as an acid rather than an electrophile at the end?

What would you predict about the strength the acid and the base in the second step?

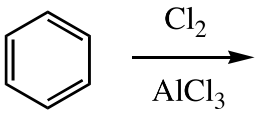
Why is the reaction call "electrophilic aromatic substitution"?

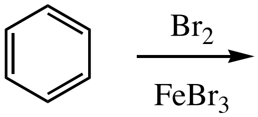
What are the two steps involved?

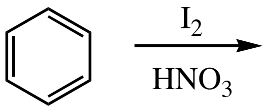
How does this reaction compare to the reactions we studied in the last section?

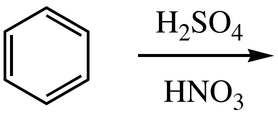
Reagents and Products

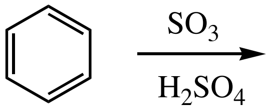
What are the names and products in the following reactions?

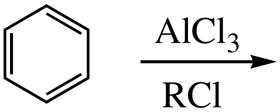


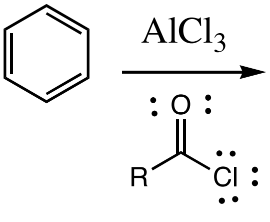












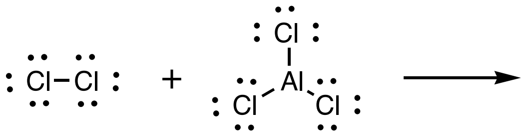
We will focus on the first 5, then come back to the last 2.

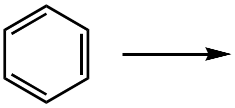
You will need to memorize these reagents and the products that they form; however, you should also be able to use some reasoning based on their mechanisms to help you.

Electrophiles

Most of the reagents require a preliminary reaction in order to form a highly reactive nucleophile. The base required for the second step will be different for each reaction.

chlorination: reactive complex forms between Cl_2 and $AlCl_3$



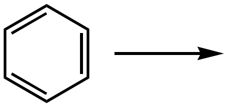


bromination: reactive complex forms between Br_2 and $FeBr_3$.

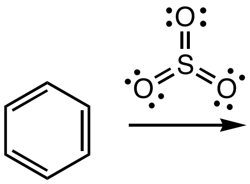
$:\ddot{\underset{..}{Br}}-\ddot{\underset{..}{Br}}: \ + \ FeBr_3 \longrightarrow$

iodination: redox reaction between iodine, nitric acid, and some additional acid

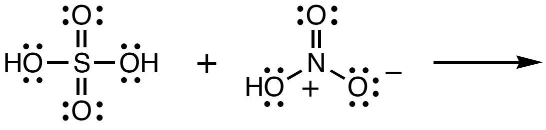
$1/2\ I_2 \ + \ HNO_3 \ + \ H^+ \longrightarrow$

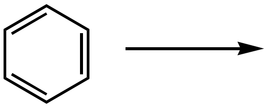


sulfonation: SO_3 is the electrophile; sulfuric acid is the solvent



nitration: sulfuric and nitric acid react to form nitronium ion



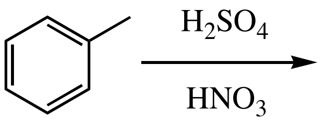


What are the reactive electrophiles and bases in each reaction?

Effects of Substituents

In order for electrophilic aromatic substitution reactions to be useful, they must work on a variety of aromatic compounds. However, when we do the reaction on a ring which already contains some other substituent, some complications come up.

First of all, more than one isomer is possible.



When you isolate these products, you will find that they are present in different amounts. Secondly, the reaction is about 25 times faster with toluene than with benzene.

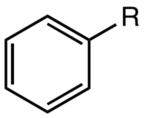
To understand why these ratios of products are formed, and why the reaction is faster, we need to get some more data. What other reactions could we try?

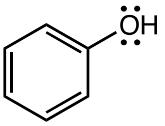
After doing hundreds of these reactions, you can sumarize the results as follows:

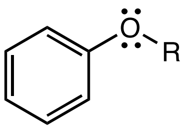
1 - All of the reagents give the same results for a given starting material.

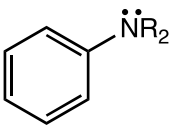
2 - Substituents on the aromatic ring can be divided into three groups:

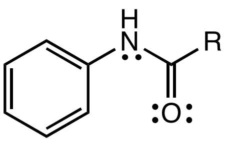
Group 1



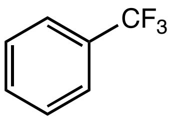


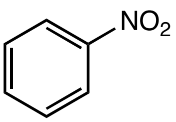


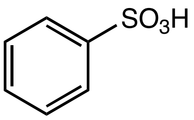


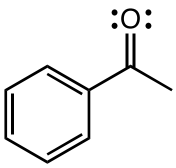


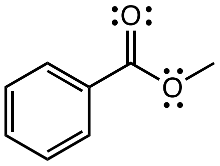
Group 2

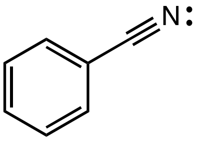




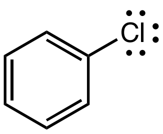


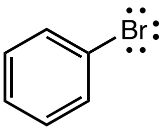






Group 3

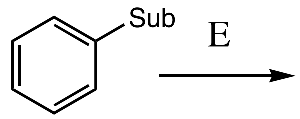




To answer the question why, we must look at how the presence of a substituent affects the rate-limiting step.

Which step will be rate limiting?

Ortho:



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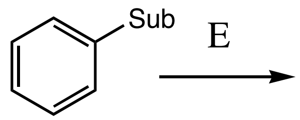

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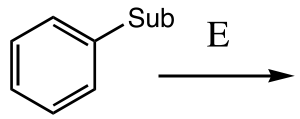
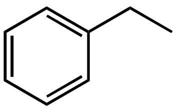


If the substituent can stabilize the positive charge, what will happen to the energy of the intermediate?

If the substituent destabilizes the negative charge, what will happen to the energy of the intermediate?

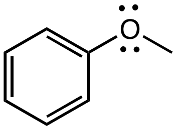
Group 1 - alkyl substituents and substituents with electron pairs on the atom next to the ring

alkyl



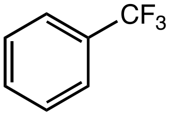
energy diagram

electron-donating



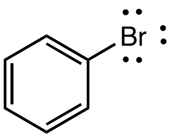
energy diagram

Group 2: substituents with fully or partially positively charged atoms on the benzene ring



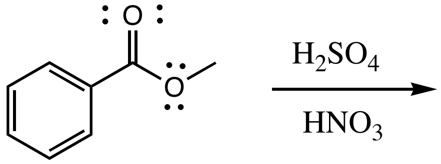
energy diagram

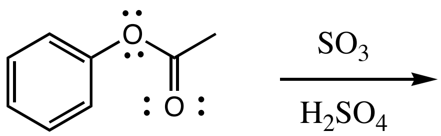
Group 3: halogen substituents

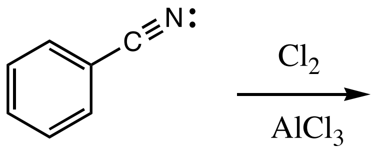


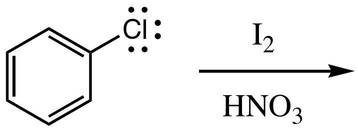
energy diagram

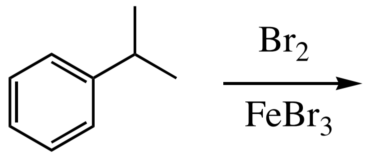
What products will predominate in each of the following cases, and why? Will they be slower or faster than the same reaction on a benzene ring?





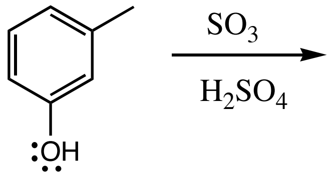


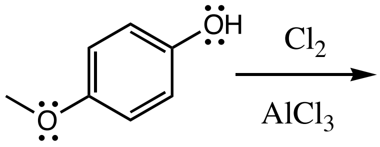




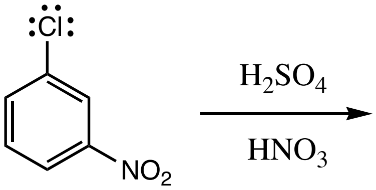
When combining reactions to form syntheses, the directing effect of substituents must be taken into account.

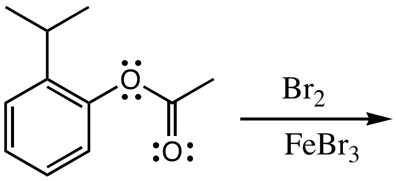
When more than one substituent is present, they may reinforce the directing effect, or they may conflict.

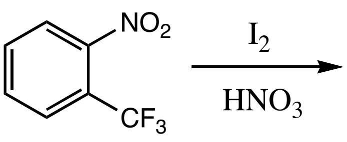




When conflicts occur, what takes priority?

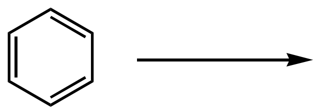


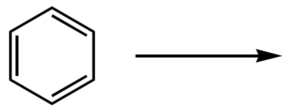




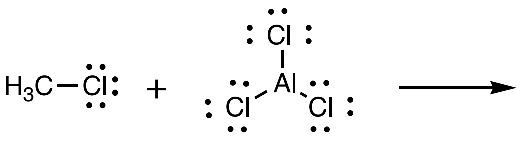
Friedel-Crafts Alkylation and Acylation

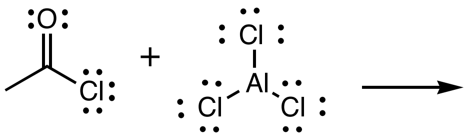
What reagents are needed for Freidel-Crafts alkylation and acylation reactions? What substituent is added?



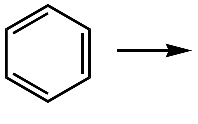


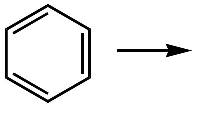
How do the reactive electrophiles form?





How does the aromatic ring react with these electrophiles?





What are the three major limitations of the Freidel-Crafts alkylation reaction?

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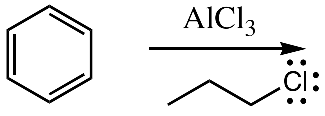
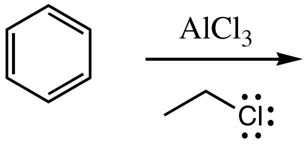
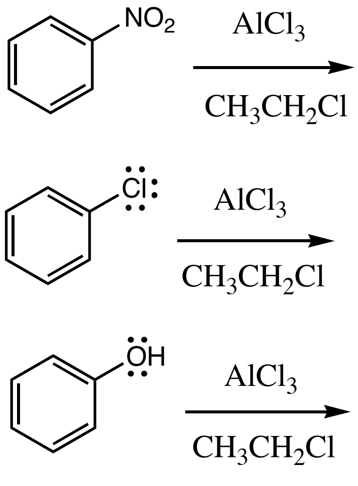


2)

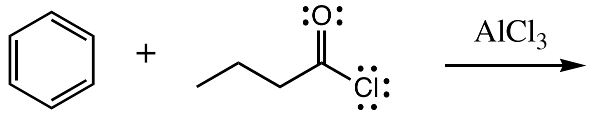


3)



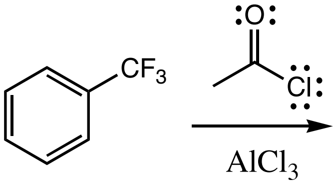
Which of these limitations does acylation overcome?

1)

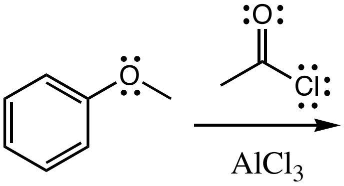


2)

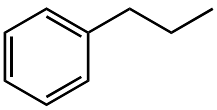
3)

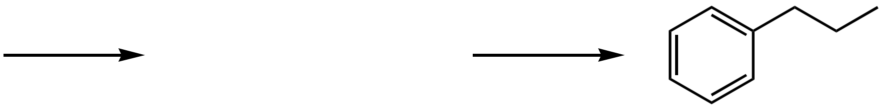


How are acylation product distributions different from other electrophilic aromatic substitutions?



How can the Clemmenson reaction be used with Freidel-Crafts acylation to give products that could not be made with Friedel Crafts alkylation?





How could 1-isobutyl-4-nitrobenzene be synthesized from benzene?

What about 1-isobutyl-3-nitrobenzene?

Synthesize 1-ethoxy-2,4-dinitrobenzene from benzene.