Learning Guide for Chapter 17 - Aromatic Compounds I

I. Aromaticity
II. Introduction to Compounds containing Benzene Rings
Nomenclature, Properties, Spectroscopy
III. Reactions of Benzylic Carbons
IV. Nucleophilic Aromatic Substitution

I. Aromaticity

The problem of benzene

When was benzene first isolated?

When was its molecular formula discovered?

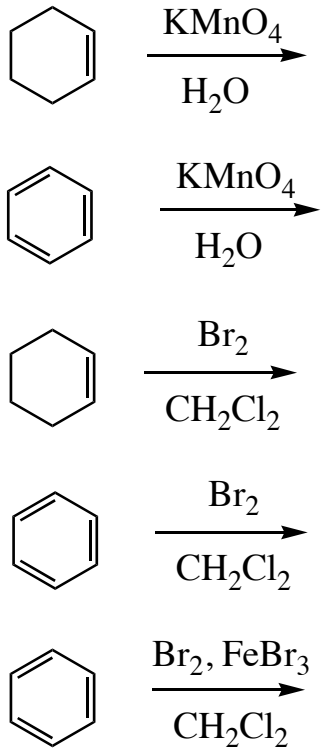
When was the cyclic structure first proposed?

What were the stages in which benzene was discovered?

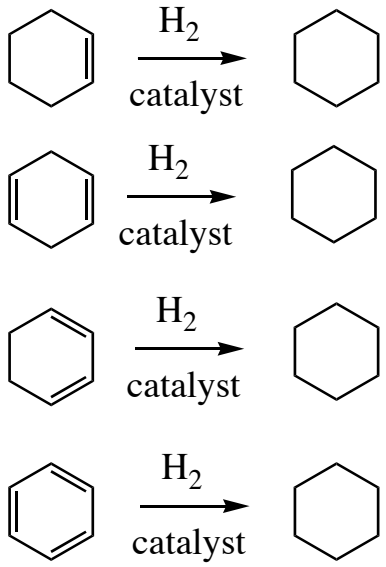
What problem did this proposal have?

What evidence led to the development of a resonance structure model?

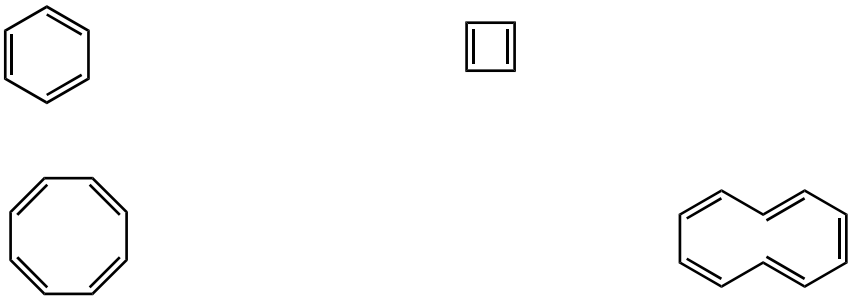
How are benzene reactions different from alkenes and dienes?



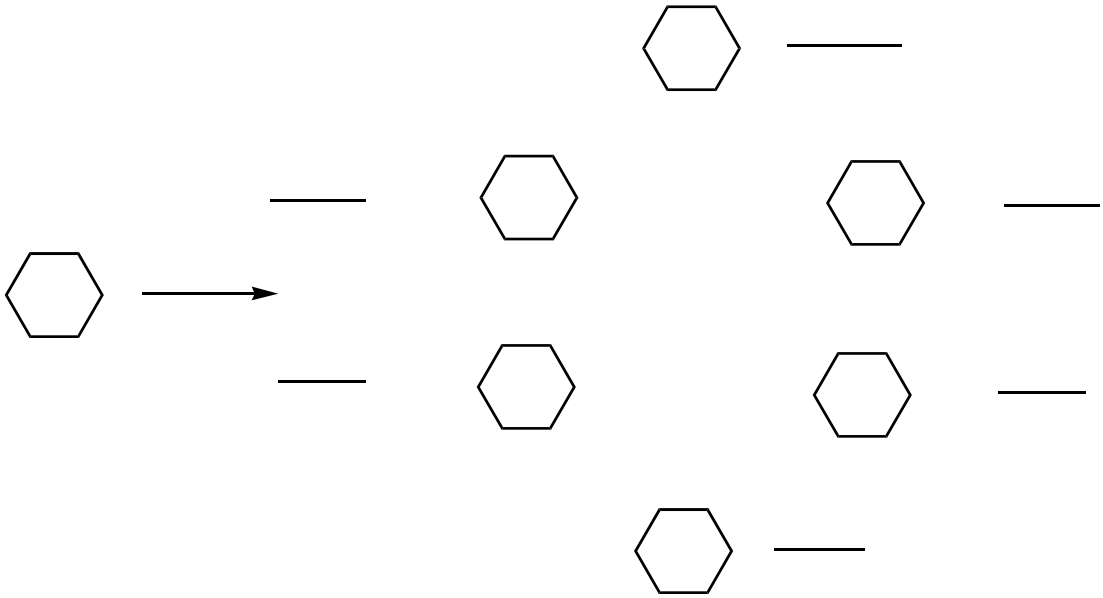
How can heats of hydrogenation show the stability of benzene?



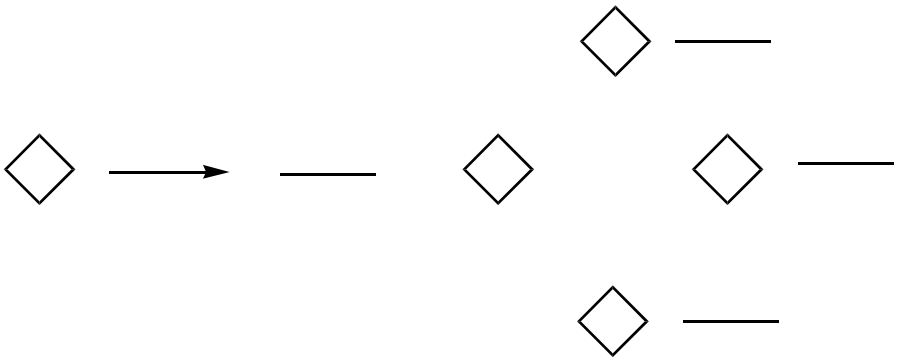
Do other cyclic compounds with alternating double bonds show this unusual stability?



What do the molecular orbitals of benzene look like? What is their energy? Which are occupied?



What about cyclobutadiene?

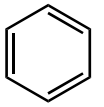
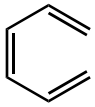


Why is this NOT a stable compound?

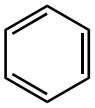
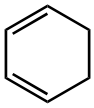
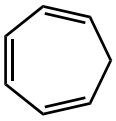
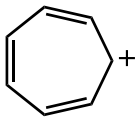
Rules for aromaticity

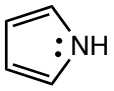
How can aromatic compounds be identified?

1. The compound must be cyclic.

2. Each atom in the ring must have an unhybridized p orbital (sp^2 or sp).

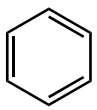
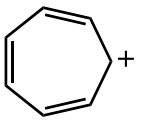



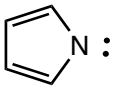
3. The number of electrons in the pi orbitals must equal a number that fits the formula 4n + 2 (Huckels' rule).

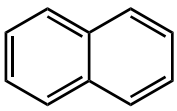
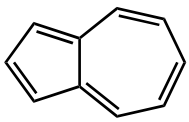
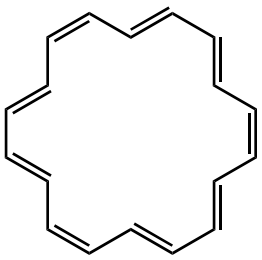
n = 0

n = 1

n = 2



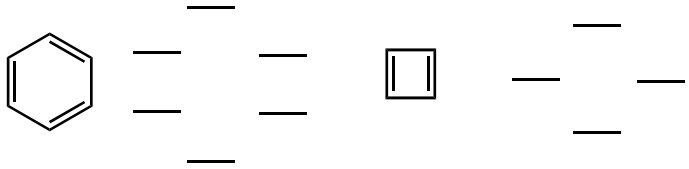




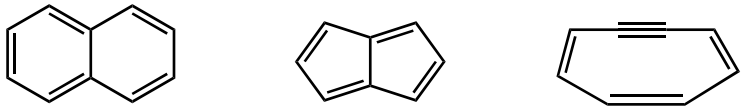
3a. If the molecule fits all of the other conditions for aromaticity, but has a number of pi electrons that fits the formula 4n, it is antiaromatic.

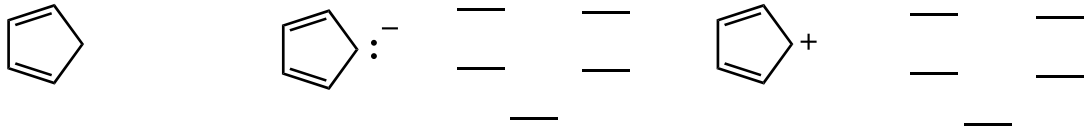
n = 1

n = 2

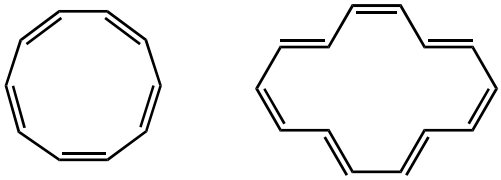
n = 3



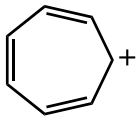
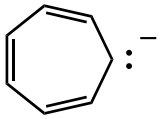
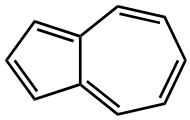
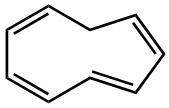
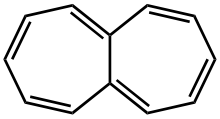
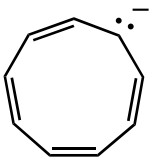
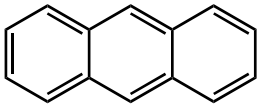




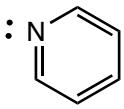
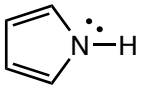
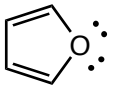
4. The compound must be planar.



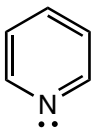
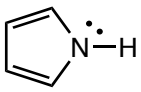
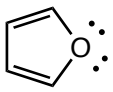
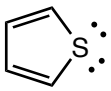
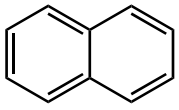
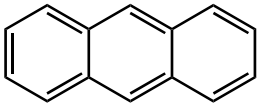
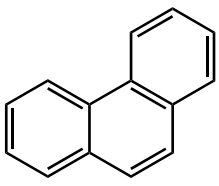
Are the following compounds aromatic, antiaromatic, or nonaromatic?

What orbital is each of the lone pairs in the following compounds in?

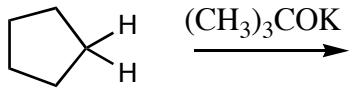




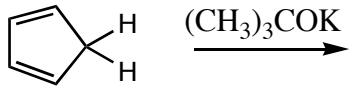
How does the aromatic stabilization of different compounds compare?

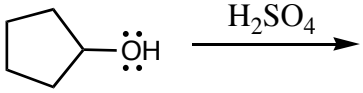
Effects of aromaticity on reactions

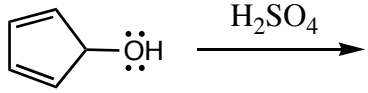
How does aromaticity affect the formation of anions?

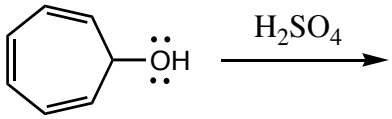




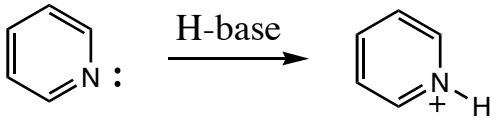
How does aromaticity affect the formation of carbocations?

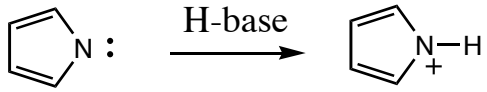






How does aromaticity affect the acidity of rings containing nitrogen?

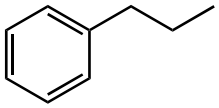




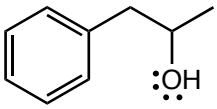
II. Introduction to Compounds containing Benzene Rings

Nomenclature

When a benzene ring is the principle chain, how is a compound named?



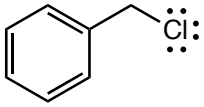
Under what conditions might a benzene ring be present but not the principle chain?

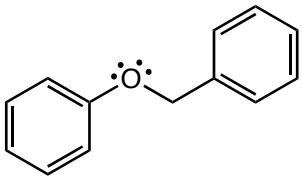


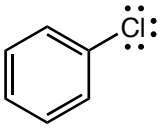
How is a benzene ring named as a substitutent?

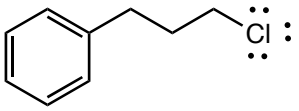
When is "benzyl" used?

What names would the following compounds have?

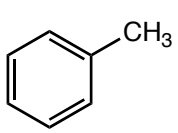


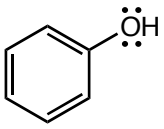


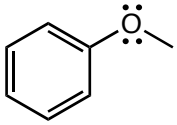


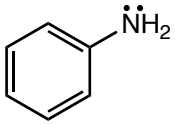


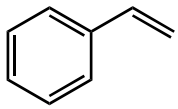
Each of the following has a common name which must be memorized. What are they?

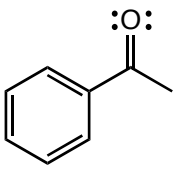


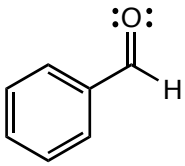


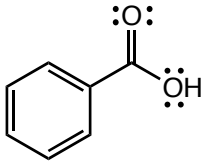




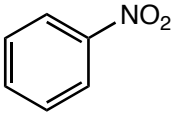




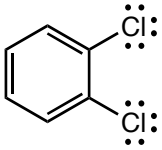


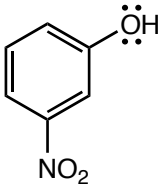


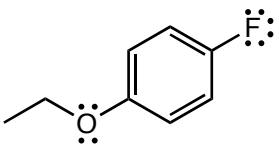
An NO_2 group is commonly found only on benzene rings. What does this stand for, and what is it called?



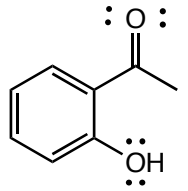
An older system of numbering is used when there are only two substituents on the ring. How could it be used to name the following compounds?



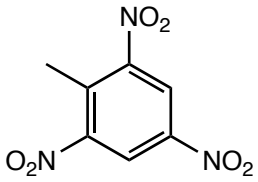


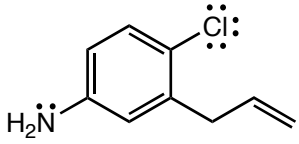


How do OH and C=O groups compare in priority?

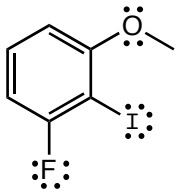


If a common name is used, what priority does its group get?



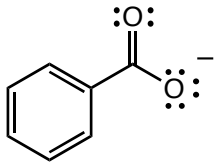


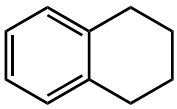
If no groups have priority, how do you decide?

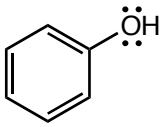


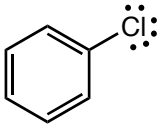
Physical Properties

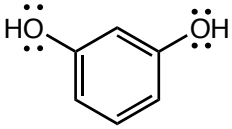
Put the following compounds in order of water solubility.



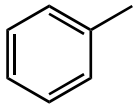


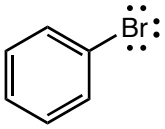


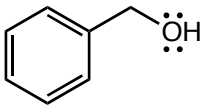




Which of the following is less dense, more dense, and about the same density as water?

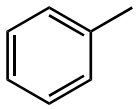


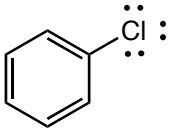


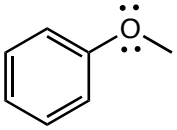


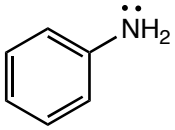
Which benzene compounds are liquids? Which are solids?

liquids:

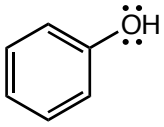


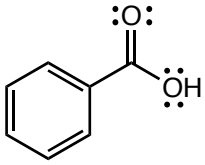


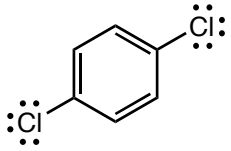


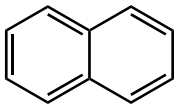


solids:









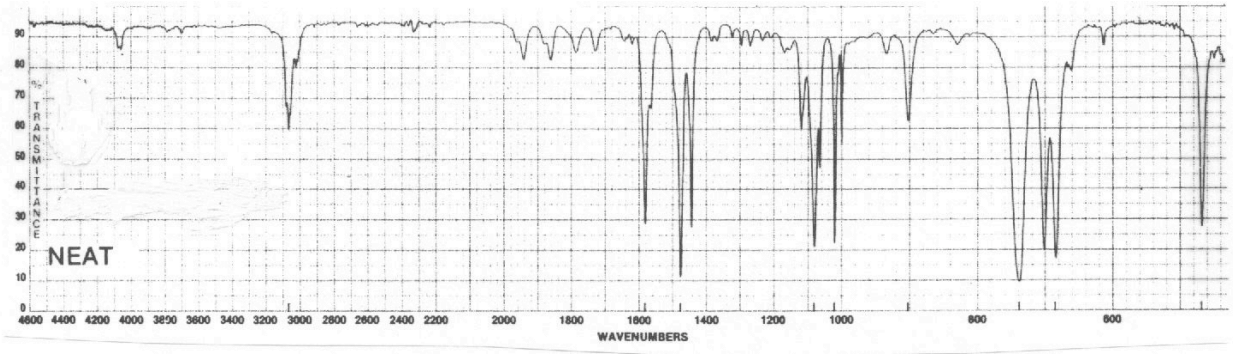
What factors affect boiling points?

What factors affect melting points?

Spectroscopy

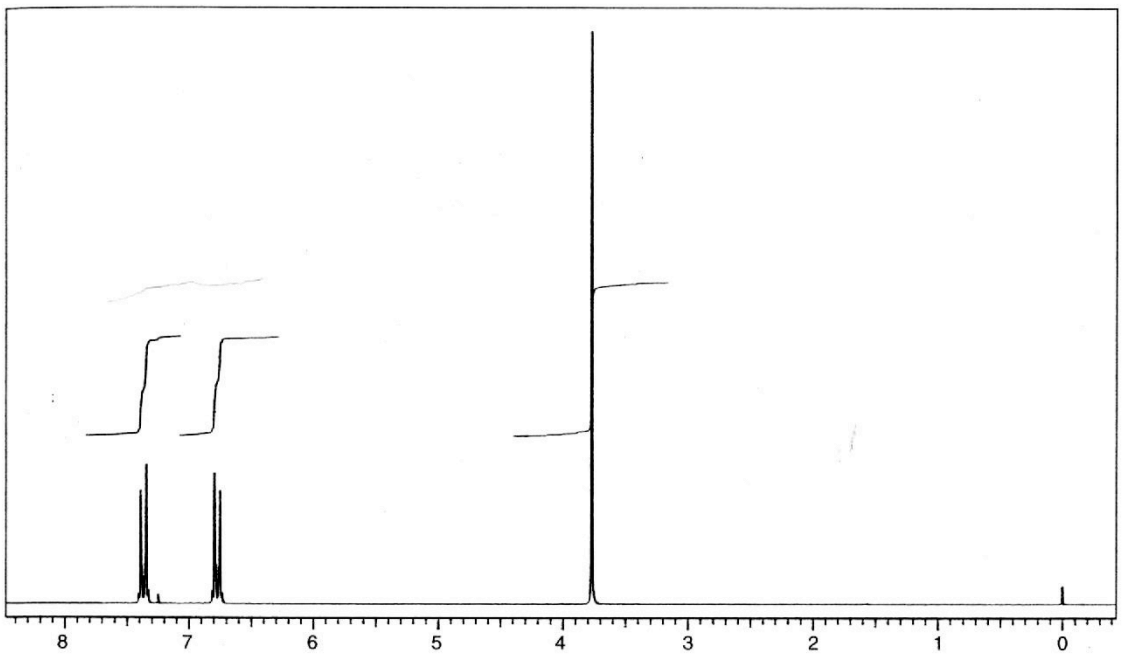
What IR bands do compounds containing benzene rings have?

Locate these bands on the spectrum of toluene:



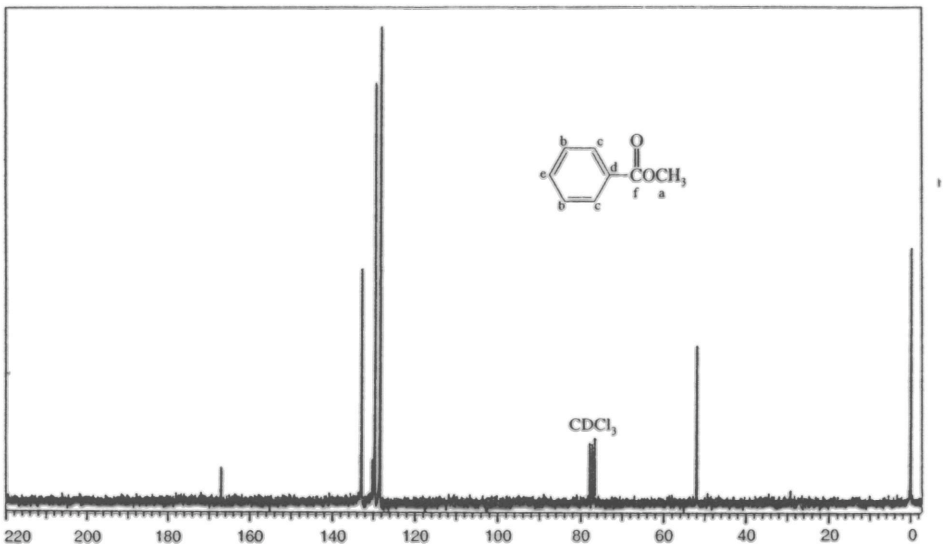
What chemical shift do H's next to benzene rings have?

Which substitution pattern is easy to recognize?



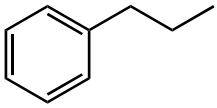
What can you tell from ^{13}C NMR?

Where do carbons in aromatic rings appear?

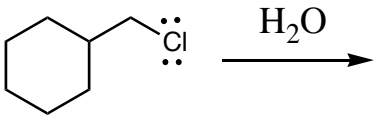


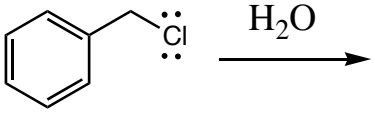
III. Reactions of Benzylic Carbons

Which is the benzylic carbon in the following compound?

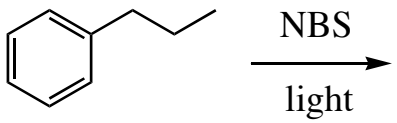


Which of the following will react, and why?

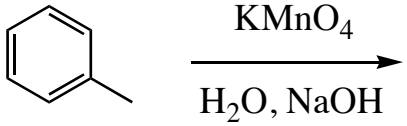




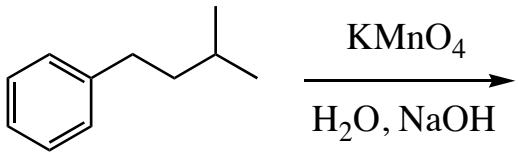
There will be only one major product of the following reaction. What will it be and why?



There is also an oxidation reaction that is unique to benzylic carbons.

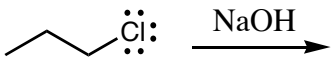


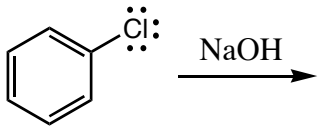
What happens if there are other carbons attached to the benzylic carbon?

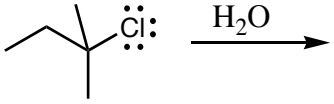


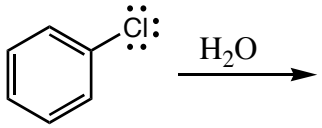
IV. Substitution Reactions of Aryl Halides

Which of the following reactions will give a product?







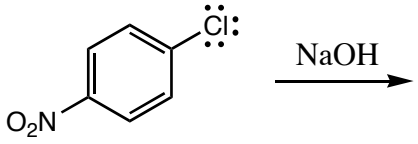


Conclusion:

What are the two ways around this?

Nucleophilic Aromatic Substitution

Why do strong electron-withdrawing groups allow substitution to occur?



Would a nitro group in any other position work?

Would extra nitro groups help?

Would any other groups work?

Which step is rate-limiting?

Which halides will be fastest?

What kinds of nucleophiles will work in this reaction? What kinds of products do they make?

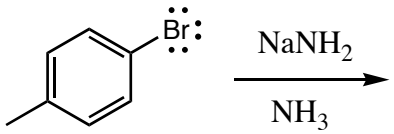
What is the main limitation of this reaction?

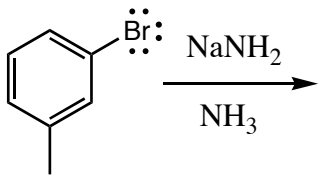
Elimination-Addition

Why does using a really strong base allow substitution to occur?

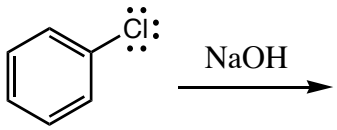
How does this compare to the previous reaction?

What would happen if there was a substituent present?





Is there any way in which NaOH could be used?



What are the limitations of this reaction?