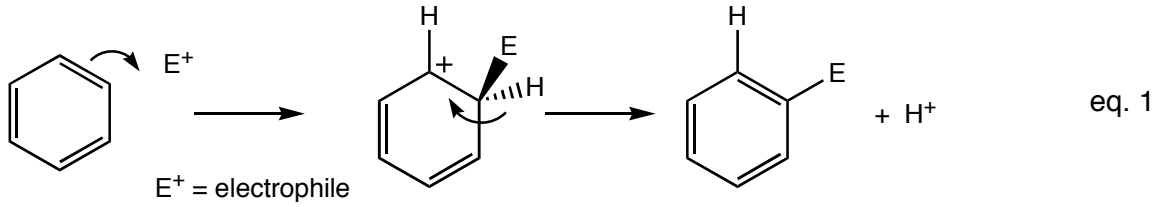
The Reactivity of Substituted Benzenes

Objective

To investigate the reactivity of substituted benzenes and to examine the relationship between electron withdrawing/donating groups and reactivity

Background

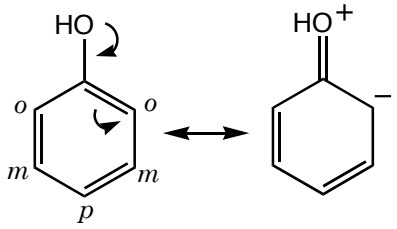
Because aromaticity is a stabilizing influence, benzene rings do not undergo electrophilic additions as typical alkenes or non-aromatic conjugated π systems do. Instead, benzene rings undergo substitution reactions referred to as electrophilic aromatic substitution (eq. 1). Additionally, the low reactivity of benzene rings requires that the electrophile be extremely reactive. For example, Cl_2 will not react with benzene, whereas $FeCl_3 \cdot Cl_2$ will. Due to the Lewis acidity of $FeCl_3$, the Cl_2 bond is strongly polarized producing the super electrophile $[FeCl_4^-][Cl^+]$. This incipient Cl^+ is reactive enough to initiate the reaction.



eq. 1

When discussing carbocation and radical stability we noted the ability of benzene rings to stabilize these structures through delocalization. Essentially, benzene rings stabilize carbocations and radicals by donating electron density from their extended π systems to the electron deficient atom at a benzylic position. Similarly, benzene rings can accept electron density into their π system from electron rich benzylic atoms. Thus, substituents can increase or decrease the electron density on a benzene ring (see Figure 1). Additionally, these changes are not equally distributed across all of the C atoms of the benzene ring. In fact, the changes to the electron density at the ortho (*o*), meta (*m*), and para (*p*) positions can be quite different, this can lead to substantial reactivity differences in substituted benzenes.

Figure 1



Procedure[1]

Selection of Substituted Benzene Ring

Each student will be assigned as starting material. The procedures for synthesizing and isolating the products is the same. The conditions under which the products are

recrystallized are different, and they are described separately.

Bromination of the Substituted Benzene Ring
Add either 0.090 g of acetanilide, 0.060 mL of aniline, or 0.070 mL of anisole to a tared (with cap) 5-mL conical vial. After determining the mass of the aromatic starting material that was added to the vial, add 0.5 mL of glacial acetic acid and a spin vane to the vial. Cap the vial with an air condenser and place the vial into a room temperature (25°C) water bath. While waiting for the aromatic compound to dissolve pack a drying tube with glass wool, and dampen the glass wool, one drop at a time, with approximately 0.5 mL of a 1 M sodium bisulfite solution. The bisulfite will capture any bromine that is released from the reaction.

In a fume hood, obtain 1 mL of the bromine/hydrobromic acid mixture. Cap the vial while transporting it to your work area. Using a Pasteur pipet, transfer the bromine/hydrobromic acid solution through the air condenser to the vial. Attach the previously prepared drying tube to the air condenser and stir the reaction for twenty minutes.

Isolation of the Product
Transfer the reaction mixture to a 25-mL Erlenmeyer flask that contains 5 mL of water and 0.5 mL of a saturated sodium bisulfite solution. Stir the mixture with a glass stirring rod until all of the residual Br_2 is consumed. If the bromine color remains after stirring for 10 minutes, add a few more drops of the saturated sodium bisulfite solution. Place the flask in an ice-water bath. If an oil has formed stir the mixture to induce crystallization. If no precipitate has appeared, scratch the bottom of the flask with a glass stirring rod (the anisole product may require additional time to crystallize). Filter and wash the product with three 1-mL portions of ice-cold water on a Hirsch funnel. Air-dry the product on the Hirsch funnel.

Recrystallization
Brominated aniline: Transfer your product to a 25-mL Erlenmeyer flask, and recrystallize the material from hot 95% ethanol. Filter and dry the product on a Hirsch funnel. Determine the mass and the melting point of your product.

Brominated acetanilide: Transfer your product to a Craig tube and recrystallize the material from hot 95% ethanol. Air-dry your product, and determine the mass and the melting point of your product.

Brominated anisole: Transfer your product to a Craig tube and recrystallize the material from hot hexane. Air-dry your product, and determine the mass and the melting point of your product.

Identification of the Brominated Product
Compare your melting point to the melting point of the compounds listed in the following table.

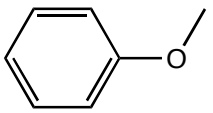
Experimental Report

Identify your product (draw its structure), report the amounts of the aromatic reactant (mass and moles) used, the actual yield in g and mol, and the percent yield (if your yield was too low to be determined reliably, report the theoretical yield). Report your observed melting point and the "literature" value from the table below.

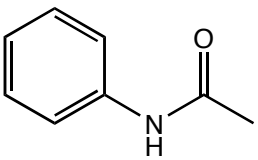
Table 1. Melting Points of Brominated Compounds[2]

Molecule	Melting Point (°C)
o-bromoanisole	3
p-bromoanisole	13
2,4-dibromoanisole	60
2,6-dibromoanisole	12
2,4,6-tribromoanisole	87
o-bromoaniline	32
p-bromoaniline	66
2,4-dibromoaniline	80
2,6-dibromoaniline	87
2,4,6-tribromoaniline	122
o-bromoacetanilide	99
p-bromoacetanilide	168
2,4-dibromoacetanilide	145
2,6-dibromoacetanilide	208
2,4,6-tribromoacetanilide	232

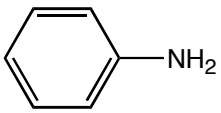
Draw resonance structures for the aniline, anisole, and acetanilide.



anisole



Acetanilide



aniline

Determine whether the substituents are electron donating or electron withdrawing and rank the substituents in order of increasing ability to donate electron density into the benzene ring. Support your reactivity ordering with data from your experiment and data from your peers. You report must be typed. You many neatly hand draw the structures. Do not write a detailed "Experimental Report".

[1]Adapted from Pavia, Lampman, Kriz, and Engel, "Relative Reactivities of Several Aromtic Compounds", *Introduction to Organic Laboratory Techniques: A Microscale Approach.* Saunders College Publishing, 1999.

[2]Ibid