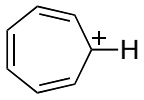
Organic Chemistry
CHM 224

Exam II Questions

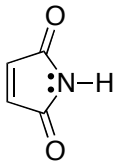
This set of questions is a compilation of old exams, and does not represent the typical length of an exam - there are more examples, therefore this is longer than a standard 1 hour exam.

Draw *p*-bromoaniline

Fill in the blanks below (assume all molecules are relatively flat):

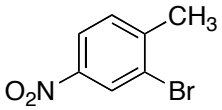


pi electrons in ring _____ p orbital on every atom in ring (yes/no) _____ aromatic (yes/no) _____

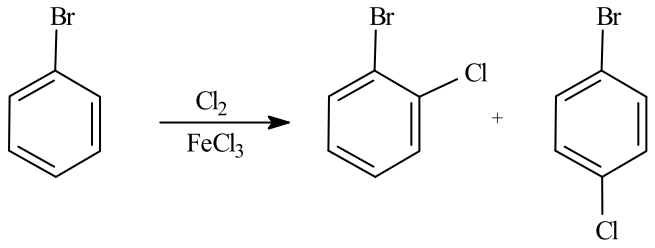


pi electrons in ring _____ p orbital on every atom in ring (yes/no) _____ aromatic (yes/no) _____

(textbook problem #16.69a) What is the BEST method synthesizing the following compound from benzene? Make sure you list the reagents in the correct order.



Consider the reaction below to answer the next two questions.

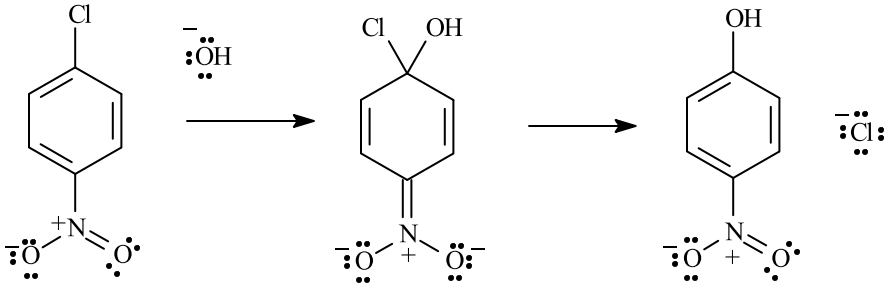


Write the complete stepwise mechanism for the formation of the *ortho* product. Show all intermediate structures and show all electron flow with arrows.

Draw one or more resonance structures for the intermediate aromatic carbocation that explain the directing effect of the bromine atom.

At what position, and on what ring, is the major product of bromination of phenyl benzoate expected to occur? Indicate this position clearly by pointing to it (use an arrow) - explain why you chose the ring you did, and why that particular position on the ring.

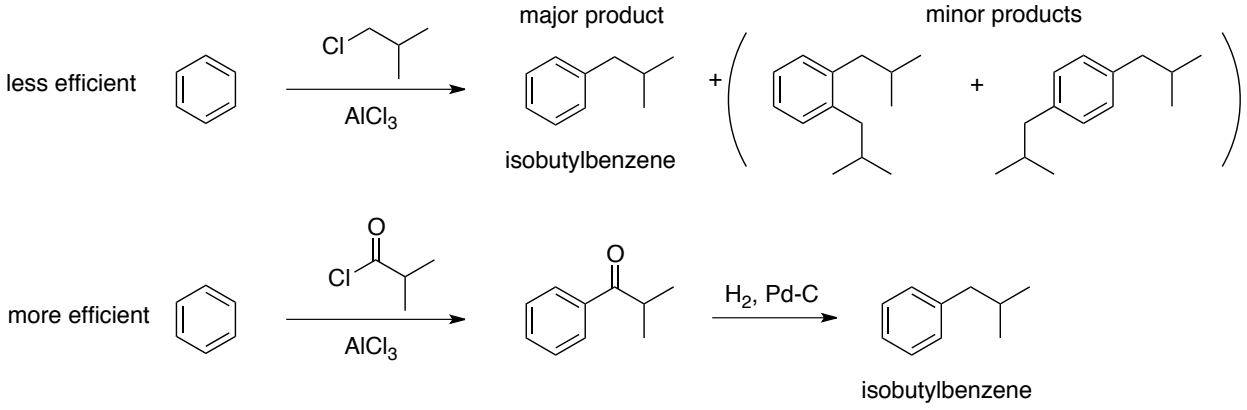
On the structural intermediates below, show all electron flow with arrows for the nucleophilic aromatic subsitution reaction of *p*-nitrochlorobenzene with KOH.



Draw the structure that corresponds to the name given.

m-fluoronitrobenzene

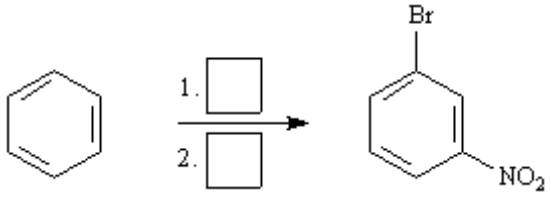
To synthesize isobutylbenzene from benzene, one might consider a simple one-step Friedel-Crafts alkylation reaction. Although isobutylbenzene is made, there are minor disubstitution impurities, and ultimately the chemical yield of isobutylbenzene is low. Despite being a two-step procedure, using a Friedel-Crafts acylation followed by reduction of the intermediate ketone provides isobutylbenzene in higher yields. Explain.



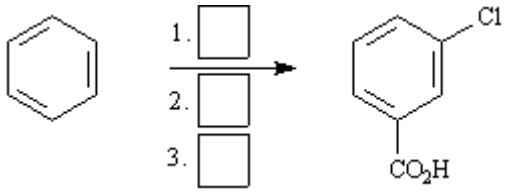
Choose the *best* reagent(s) from the list provided below for carrying out the syntheses in questions 6 and 7. Place the letter of the reagent in the box beside the reaction number over the arrow. There is only one answer for each reaction.

a. $KMnO_4$, H_3O^+
b. Br_2, $FeBr_3$
c. Cl_2, $FeCl_3$
d. CH_3Cl, $AlCl_3$
e. HNO_3, H_2SO_4
f. $ClCO(CH_2)_2CH_3$, $AlCl_3$
g. $CH_3CH_2CH_2CH_2Cl$, $AlCl_3$
h. H_2/Pd
i. NBS, peroxides
j. $(CH_3)_3CCH_2Cl$

1.



2.



Which of the following is an *ortho*- and *para*- director?

a. —NO_2
b. —NH_2
c. —CN
d. —CO_2CH_3

Which of the following is a *meta*- director?

a. —OH
b. —Br
c. —$CH_2CH_2CH_3$
d. —$COCH_3$

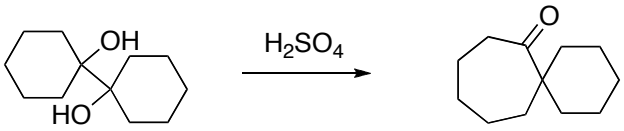
Which of the following is the strongest deactivating group?

a. —CO_2CH_3
b. —I
c. —$COCH_3$
d. —Cl

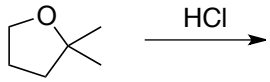
Which of the following is an *ortho*- and *para*- director and a deactivator?

a. —NO_2
b. —F
c. —CN
d. —CH_2CH_3
e. none of these

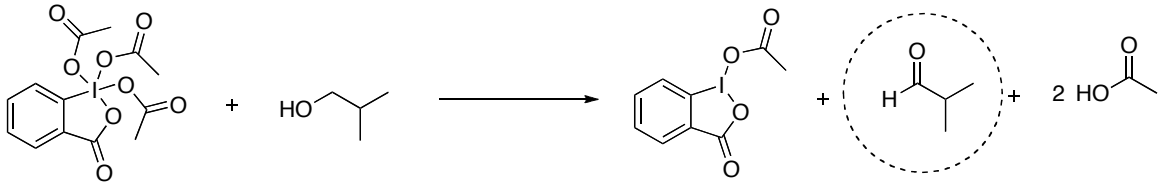
The major organic product of the following Pinacol rearrangement is shown below. Provide a stepwise arrow-pushing mechanism for this transformation.



Draw a stepwise arrow-pushing mechanism that leads to the major organic product for the following reaction.



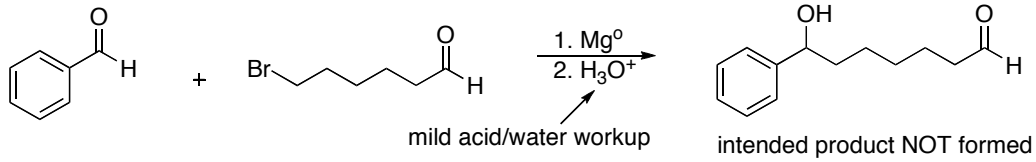
Dess-Martin periodinane cleanly oxidizes primary alcohols to aldehydes (see below). Draw a stepwise arrow-pushing mechanism that accounts for this conversion (the aldehyde product is circled).



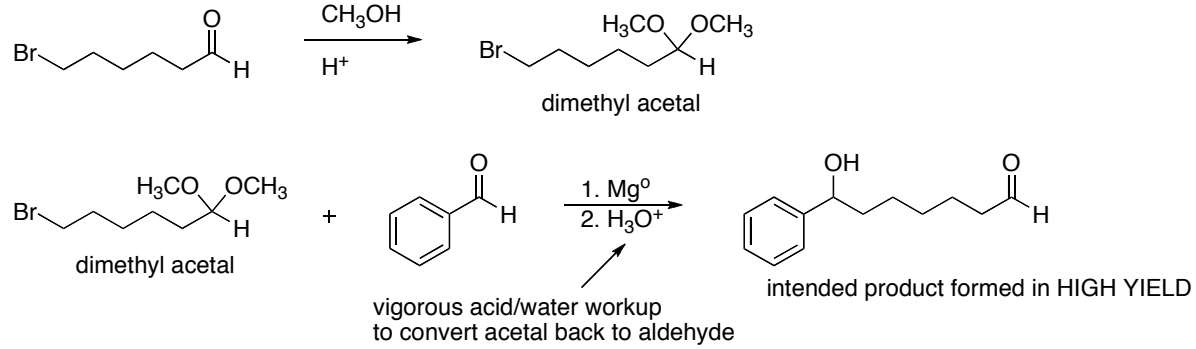
Dess-Martin periodinane

The ability to read a synthesis and ask WHY one would have done it THAT way is important. Consider the following: When Mg^o was added to a mixture of 6-bromohexanal and benzaldehyde (scheme **A**), the intended product (via Grignard reaction) was not formed. However, when 6-bromohexanal was first converted to the dimethyl acetal (scheme **B**) and then reacted in the same manner, the intended product was created in high yield. Provide a detailed rational for WHY scheme **A** did not work, and WHY the two-step scheme **B** does... Hint: It might be helpful to try and determine what WAS formed in scheme A.

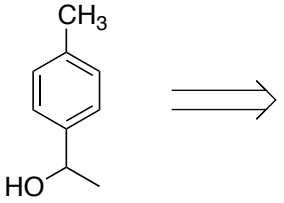
A)



B)



Propose a synthesis of the following alcohol from an alkyl or aryl halide and an aldehyde. Show all starting materials and chemical reagents needed.

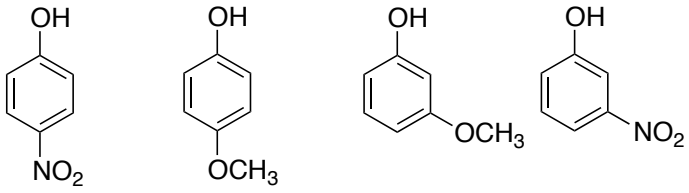


Circle the base that would most likely cause the equilibrium in the following reaction to shift to the right?

$$CH_3OH + base^- \rightleftharpoons CH_3O^- + base\text{-}H$$

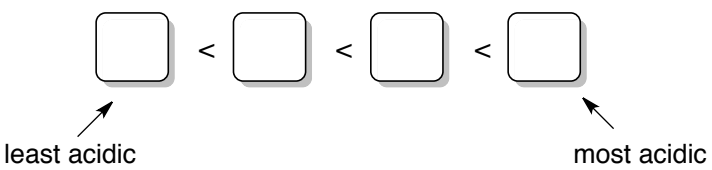
Base choices: $CF_3CH_2O^-$, $CH_3CO_2^-$, $(CH_3)_3O^-$,

Place the following phenols in order of INCREASING acidity:

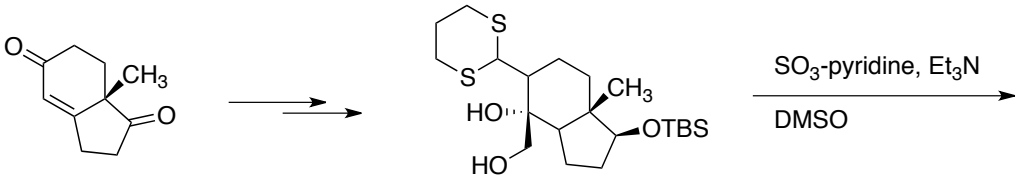


A **B** **C** **D**

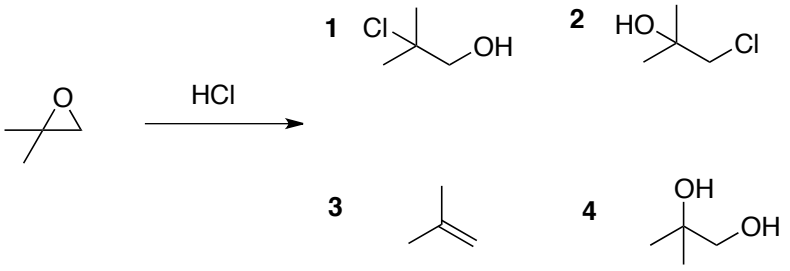
place letters in boxes



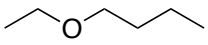
What is the product of the following Swern oxidation?

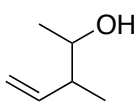


Circle the major organic product obtained from the following reaction?



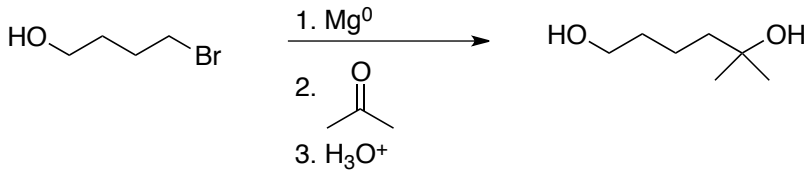
Provide the correct IUPAC name for the molecules drawn in questions 1 through 4.





a. 3-methyl-1-penten-4-ol
b. 3-methyl-4-penten-2-ol
c. 1,2-dimethyl-2-propan-1-ol
d. 2,3-dimethyl-1-propan-3-ol

The proposed Grignard-method shown below to give the diol shown on the right side of the arrow is flawed. Suggest WHY the reaction scheme is flawed, and propose an adjustment (including chemical reagents) to the scheme that would indeed produce the intended diol.



Using the Williamson ether synthesis, propose a synthesis of the following molecule from an alcohol and alkyl halide. Make sure you include all chemical reagents necessary, and show the arrow-pushing mechanism.