Organic Chemistry

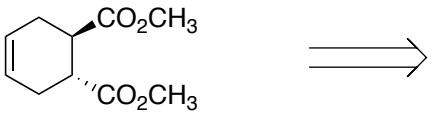
CHM 224

Exam II Questions

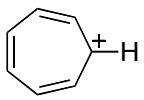
This set of questions is a compilation of old exams, and does not represent the typical length of an exam - there are more examples, therefore this is longer than a standard 1 hour exam.

Draw *p*-bromoaniline

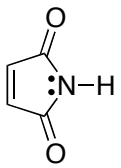
The following molecule was prepared using a Diels Alder reaction. Write the structures of the starting diene and dienophile necessary. Pay special attention to the stereochemistry of the dienophile



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

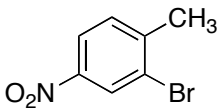


pi electrons in ring _____ p orbital on every atom in ring (yes/no) _____ aromatic (yes/no) _____

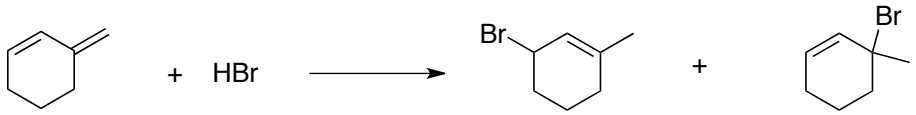


pi electrons in ring _____ p orbital on every atom in ring (yes/no) _____ aromatic (yes/no) _____

(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 questions 1 - 5.



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

1. The nucleophile in the first part of this reaction is (**A** - **D**) _____.

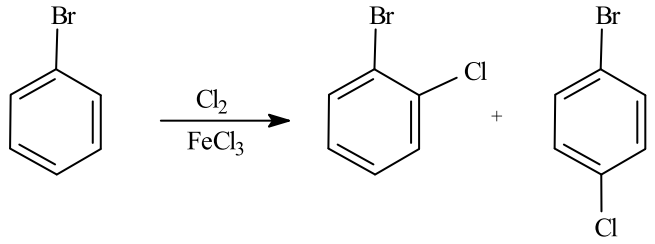
2. The electrophile in the first part of this reaction is (**A** - **D**) _____.

3. The kinetically controlled product in this reaction is (**A** - **D**) _____.

4. The product that results from 1,4-addition is (**A** - **D**) _____.

5. Draw a stepwise arrow-pushing mechanism that accounts for the formation of both products shown (**C** and **D**). Show all intermediate structures.

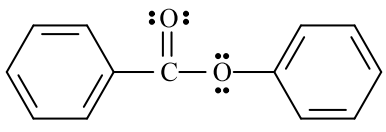
Consider the reaction below to answer the next two questions.



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.

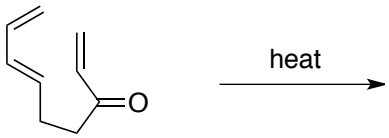


phenyl benzoate

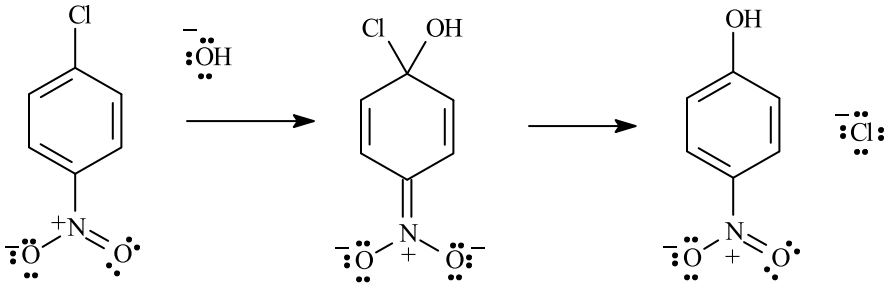
When an organic molecule is irradiated with ultraviolet radiation, the energy absorbed by the molecule corresponds to:

a. the amount necessary to increase molecular motions in functional groups
b. the amount necessary to excite electrons from one molecular orbital to another
c. the amount necessary to "flip" the spin of atomic nuclei
d. the amount necessary to strip a molecule of one electron to generate a radical cation

Draw the product of the following intramolecular Diels Alder reaction.



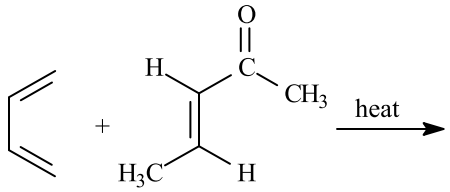
On the structural intermediates below, show all electron flow with arrows for the nucleophilic aromatic subsitution reaction of *p*-nitrochlorobenzene with KOH.



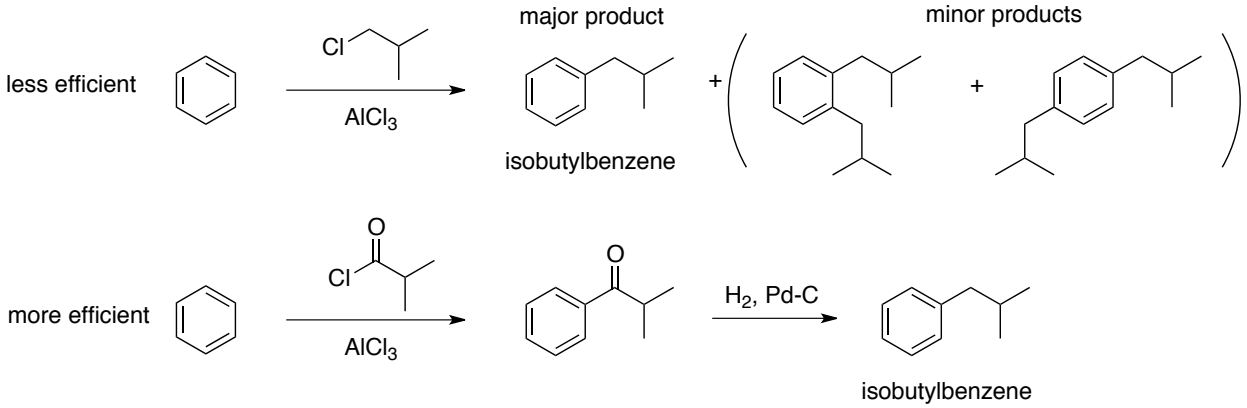
Draw the structure that corresponds to the name given.

m-fluoronitrobenzene

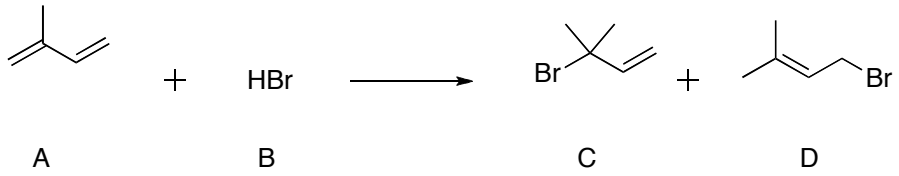
Write the structure(s) of the product(s) for the Diels-Alder reaction below (no mechanism is needed). *Be sure to indicate any relevant stereochemistry*.



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.



The following questions refer to the following chemical reaction:



The acid in the first step of this reaction mechanism is _____

The base in the first step of this reaction mechanism is _____

The kinetically controlled product of this reaction is _____

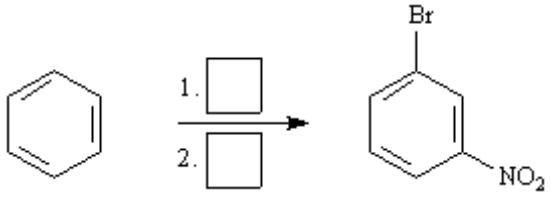
The product that has the lowest overall energy is _____

Starting from **A** and **B**, draw a **STEPWISE** arrow-pushing mechanism that accounts for the formation of **D**.

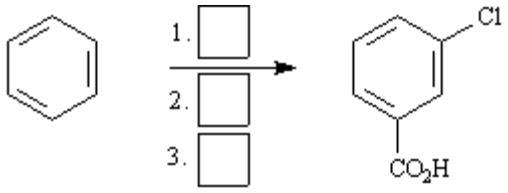
Choose the *best* reagent(s) from the list provided below for carrying out the syntheses in questions 6 and 7. Place the letter of the reagent in the box beside the reaction number over the arrow. There is only one answer for each reaction.

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. $(CH_3)_3CCH_2Cl$

6.



7.



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