Midterm Exam 1

Chem 3B, Spring 2016
Monday, February 29, 2016
7:00 – 9:00 pm

Name _____

Student ID _____

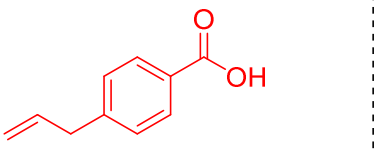
You have 120 minutes to complete this exam.

Please provide all answers in the space provided. Work drawn in the margins may not be picked up by the scanner and therefore will not be graded.

Including this title page, there should be **10** pages (printed on both sides of 5 sheets of paper). The tenth page is blank and may be used as scratch paper if you need it, but please remember to copy your answers into appropriate exam question location.

Point values are listed within each question. The exam is worth 250 points total.

1. A. Draw a structure to match each prompt. (3x8 = 24 pt)



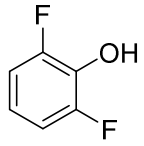
4-allylbenzoic acid

the s-cis conformation of 1,3-butadiene

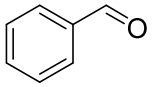
(many other answers possible)

one example of a diene that is NOT conjugated

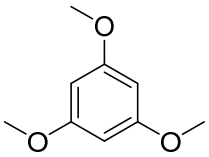
B. Provide systematic name for each of the following structures. (3x8 = 24 pt)



2,6-difluorophenol

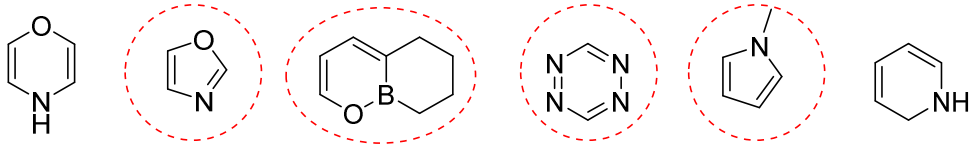


benzaldehyde



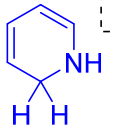
1,3,5-trimethoxybenzene

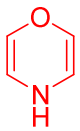
2. A. Circle the aromatic structure(s). (12 pt)



B. Choose one of the structures from part A that you did NOT circle. Draw it below and explain why it is not aromatic. (5 pt)

or



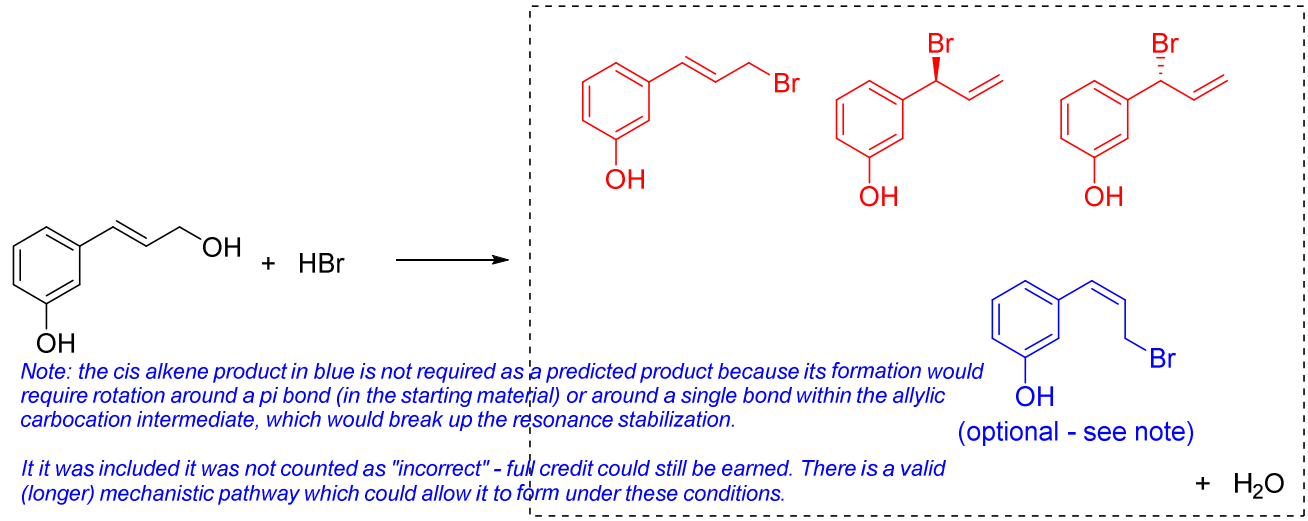


structure

explanation:
If both N and O are sp2 hybridized, then the pi system contains 8 electrons (antiaromatic) (2 pair from pi bonds and one pair from each heteroatom)
If either N or O is sp3 hybridized, then the pi system is not continuous so it cannot be aromatic.

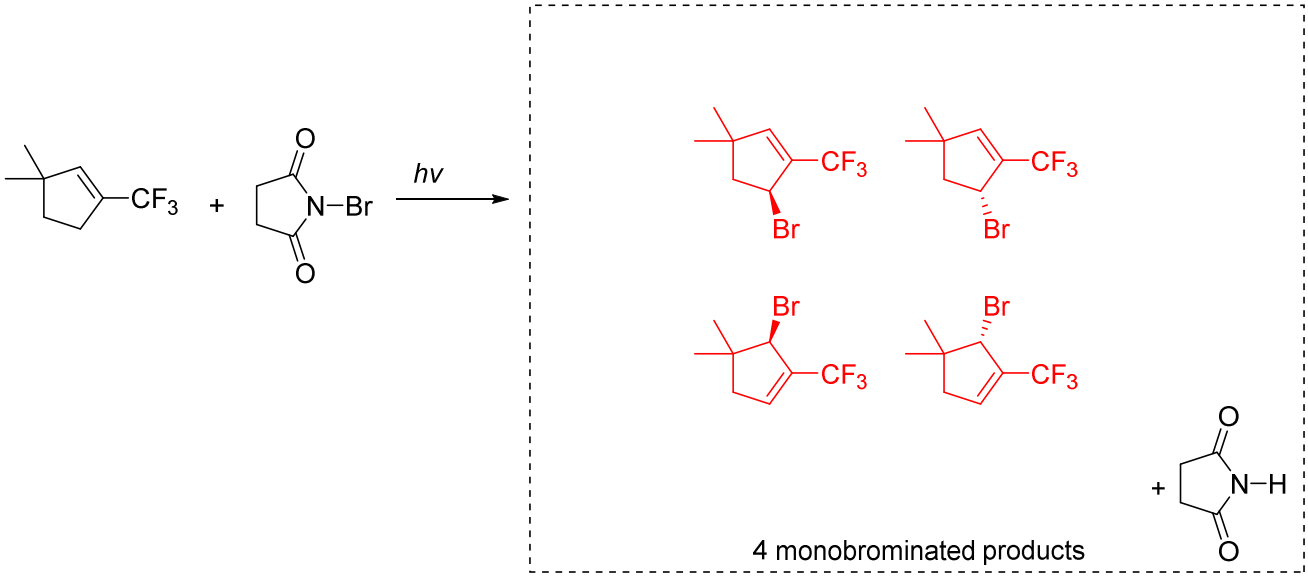
pi system is not cyclic due to the sp3 hybridized carbon at the bottom of the ring (there is no p orbital on that carbon)

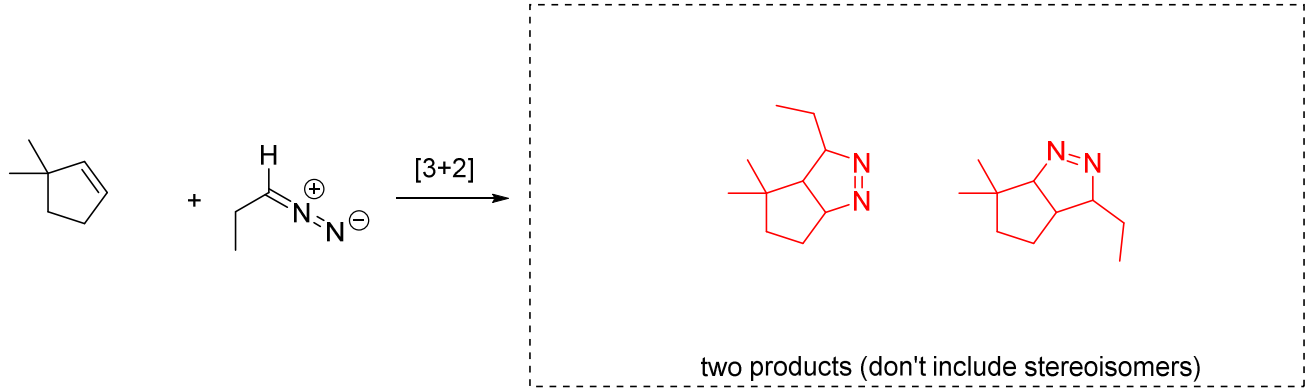
3. Predict all of the possible organic product(s) from the following reactions. Where relevant, show all stereoisomers. Pay particular attention to any information given in the product boxes. Each redundant or wrong answer within a box cancels out a correct answer. (3x10 = 30 pt)



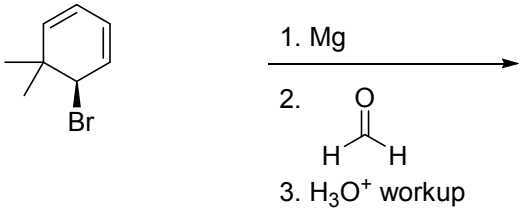
Note: the cis alkene product in blue is not required as a predicted product because its formation would require rotation around a pi bond (in the starting material) or around a single bond within the allylic carbocation intermediate, which would break up the resonance stabilization.

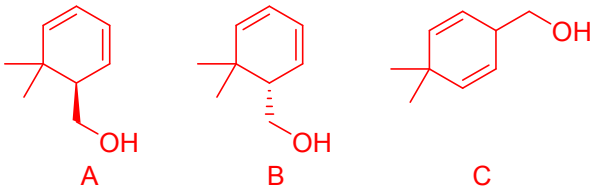
It it was included it was not counted as "incorrect" - full credit could still be earned. There is a valid (longer) mechanistic pathway which could allow it to form under these conditions.



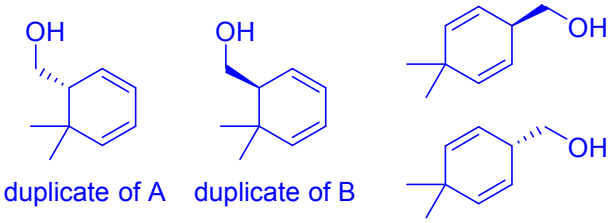


4. Predict all of the possible organic product(s) from the following reactions. Where relevant, show all stereoisomers. Pay particular attention to any information given in the product boxes. Each redundant or wrong answer within a box cancels out a correct answer. (3x10 = 30 pt)

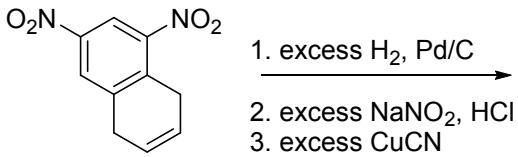


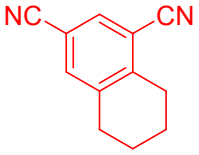


Note: due to symmetry, the following structures are "duplicates" of ones above and should not be included as additional answers:

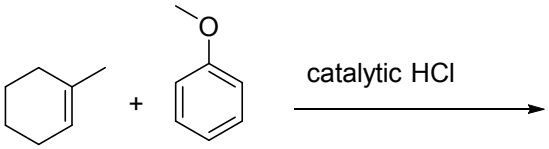


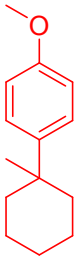
duplicate of A duplicate of B duplicates of C





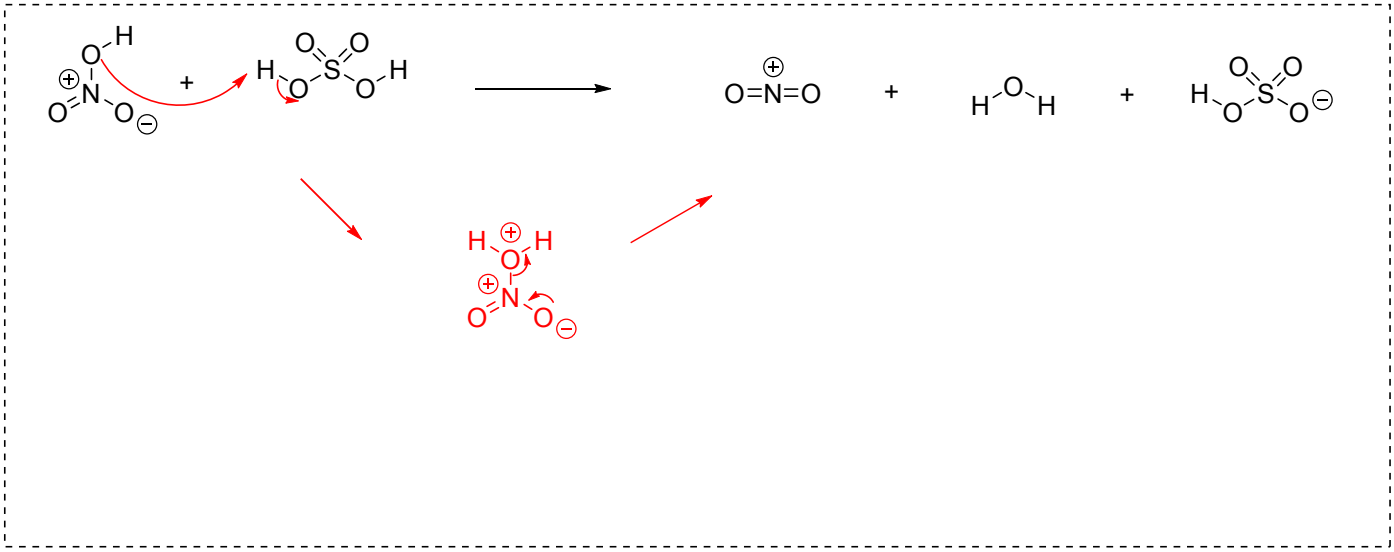
one major product

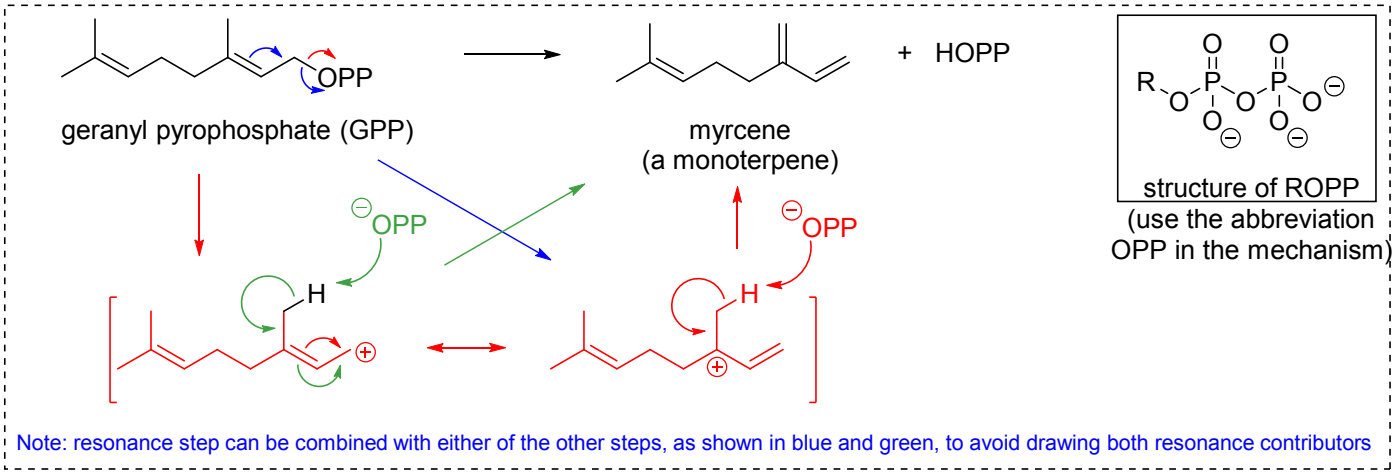




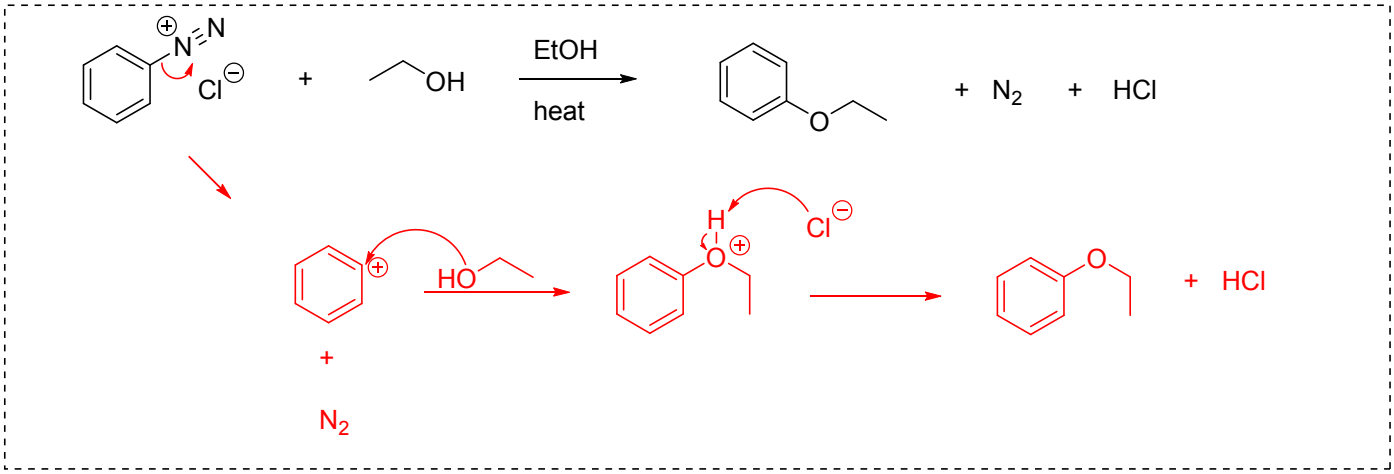
one major product

5. Draw a curved arrow mechanism for each of the reactions shown below. Your mechanism must account for all product(s) shown. (Note: For some of these reactions, there may be other possible products that are not shown. You only need to explain the product(s) pictured in the scheme) (3x10 = 30 pt)



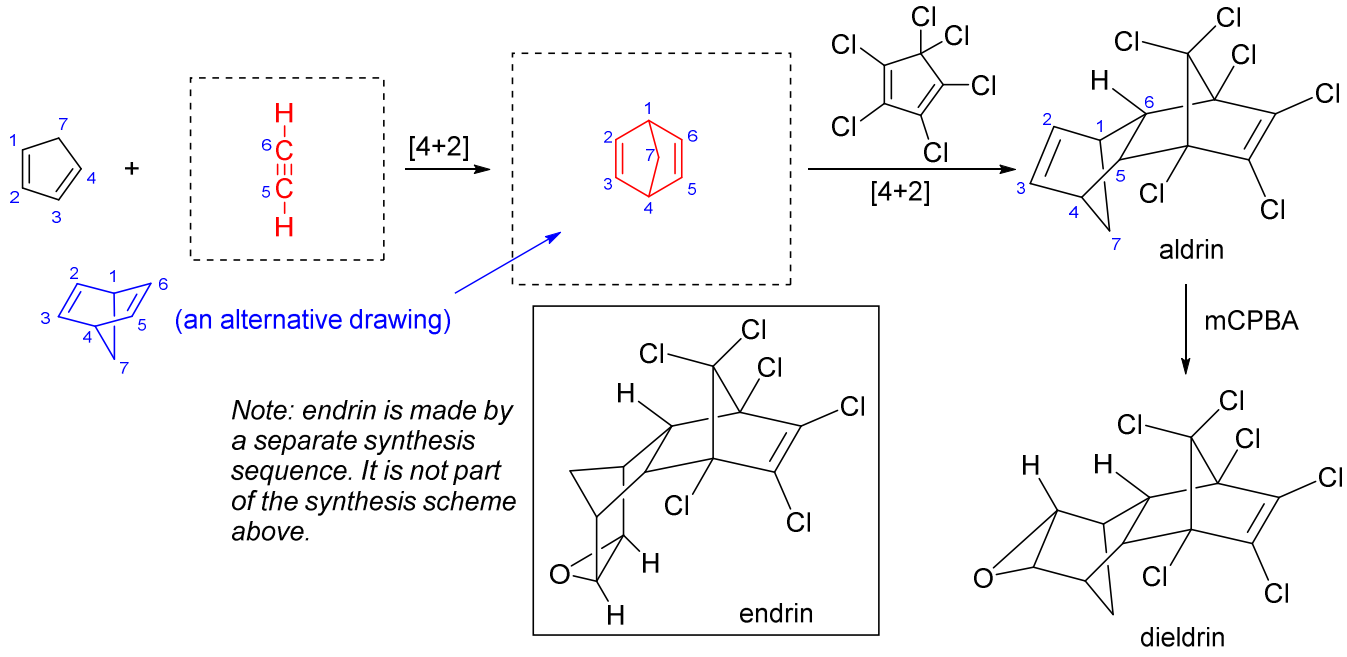


Note: resonance step can be combined with either of the other steps, as shown in blue and green, to avoid drawing both resonance contributors



6. Dieldrin, aldrin, and endrin are pesticides that were banned in most countries starting in the 1970s and 1980s due to their toxicity and their persistence in the environment.

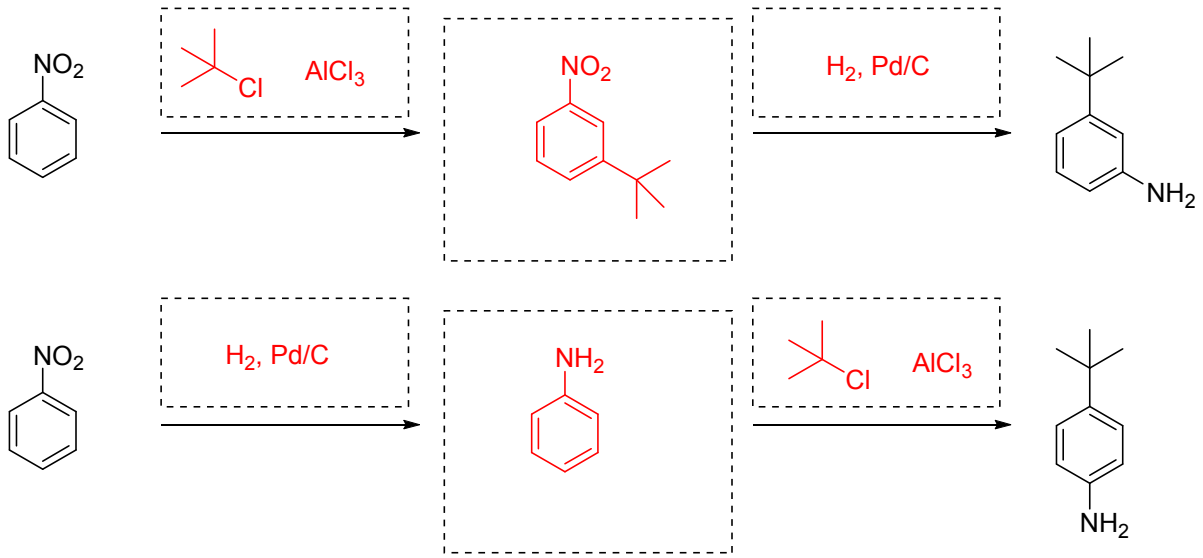
A. Fill in the missing structures in the multistep synthesis scheme leading to dieldrin. (10 pt)



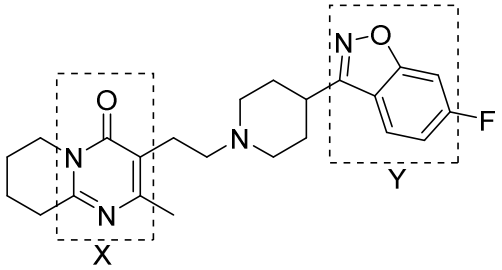
B. What is the relationship between endrin and dieldrin? Circle one: (5 pt)

(Identical) (Enantiomers) (Constitutional Isomers) (Diastereomers) (Regioisomers) (None of these)

7. Fill in the missing reagents and structures in the following synthesis schemes. Assume that only one major product forms in each reaction. Do not combine multiple reaction steps in a single box (no numbered steps within a box). (30 pt)

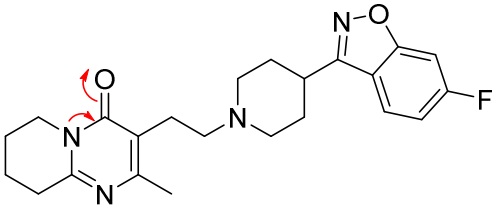


8. Risperidone, an antipsychotic medication used to treat schizophrenia, contains two separate aromatic π systems, labeled X and Y on the structure below.

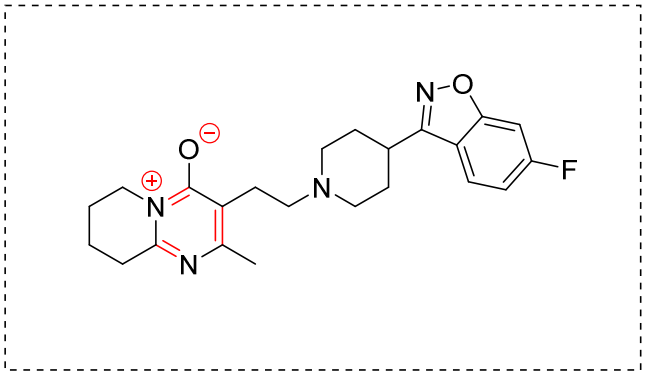


risperidone

A. Draw curved arrows and the resulting resonance contributor of risperidone that clearly shows the aromaticity of the π system labeled X. A template is provided below for your convenience. (6 pt)

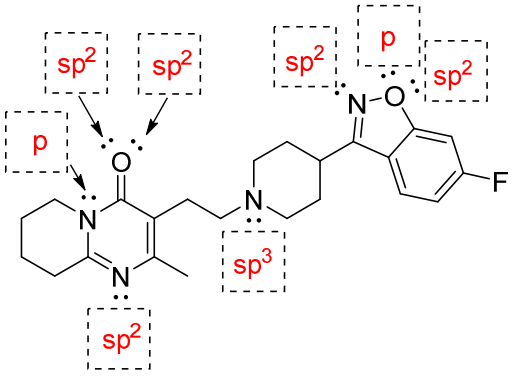


(add curved arrows)



a resonance contributor demonstrating aromaticity of the X π-system

B. On the structure of risperidone below, label for the type of orbital occupied by each pair of electrons (s, p, sp, sp^2, sp3). (8 pt)



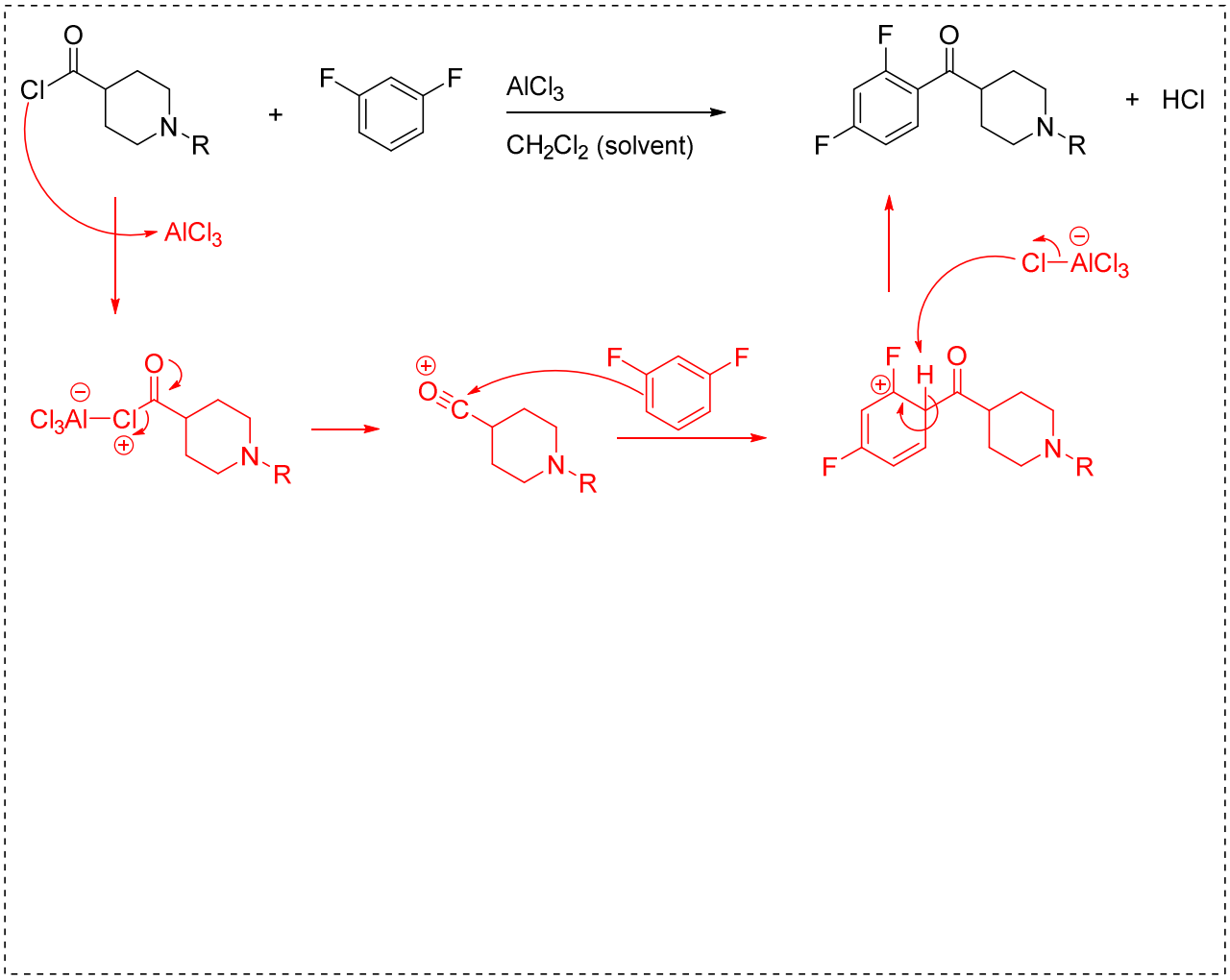
(orbital labels for lone pairs)

C. How many electrons are in each aromatic π system? (6 pt)

X ____6_____ electrons

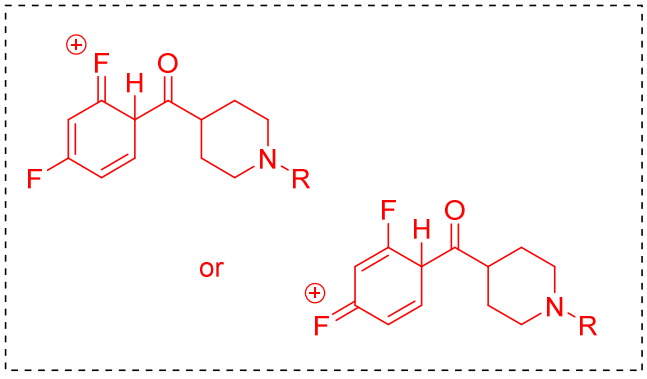
Y____10_____ electrons

D. One of the steps in the synthesis of risperidone is the electrophilic aromatic substitution shown below. Draw a **curved arrow mechanism** for this reaction. (10 pt)

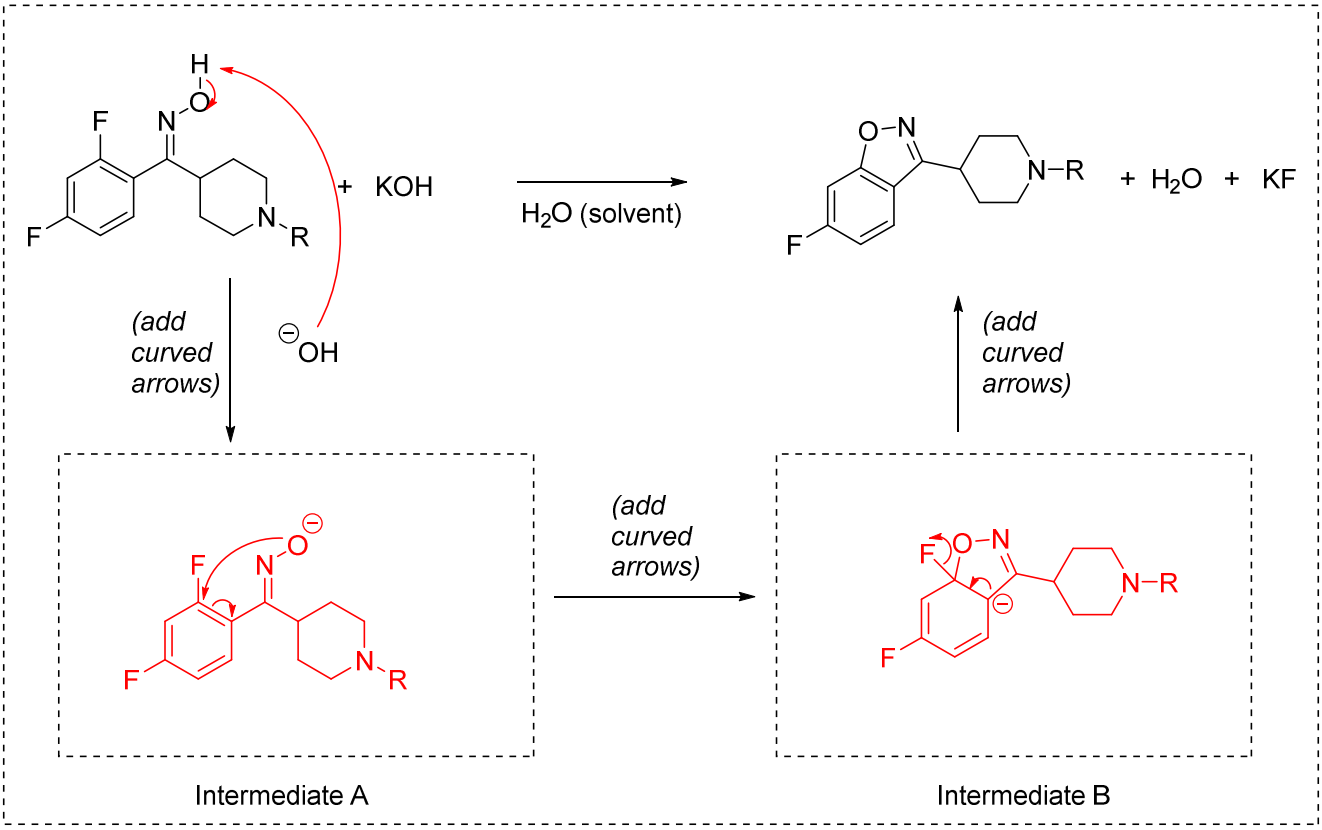


E. Are the fluorine atoms acting as (ortho/para or meta) directing groups in the reaction above? (circle one) (2 pt)

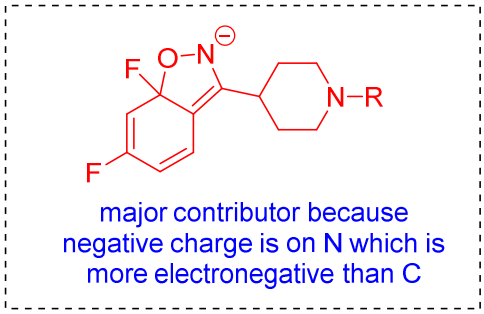
F. Draw the major resonance contributor of the intermediate (from the reaction above) that clearly demonstrates the reason for the directing effect of one of the fluorine atoms. (3 pt)



G. A later step in the synthesis of risperidone is the nucleophilic aromatic substitution shown below. **Add curved arrows and structures** to complete the mechanism for this reaction. (10 pt)



H. Intermediate B is stabilized by resonance. Is the resonance contributor that you drew above the most important contributor? (YES or NO) (circle one). If you circled NO, then draw the most important resonance contributor in the space below. If you circled yes, cross out the box below. (5 pt)



major resonance contributor of Intermediate B

This page is intentionally blank and may be used as scratch paper if you need it, but please remember to copy your answers into appropriate exam question location.