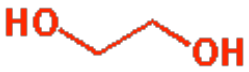
CHEM 263 MIDTERM - Section B1
Wednesday, February 11, 1998
Dr. John C. Vederas

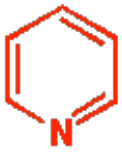
I. Structure and Nomenclature - 40 Points

A. Draw structures for which names are given, or name the given structures by any correct (systematic or common) nomenclature. Be sure to give cis or trans (or if appropriate Z or E) or R or S assignment to the isomer where indicated by asterisks (***). **(2 points each - 16 points total)**

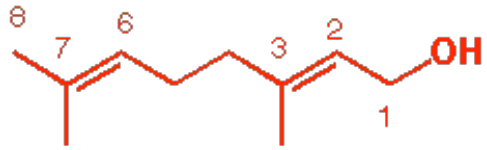
1. ethylene glycol (antifreeze constituent)



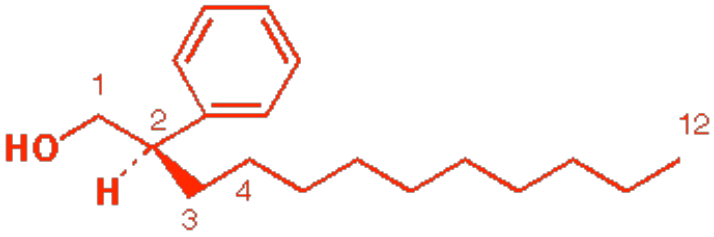
2. pyridine (common solvent



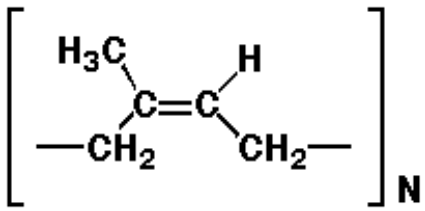
3. trans-3,7-dimethyl-2,6-octadien-1-ol (constituent of citrus oil used in perfumes



4. (R) -2-phenyl-1-dodecanol (use part structure below in your drawing to assist grading)



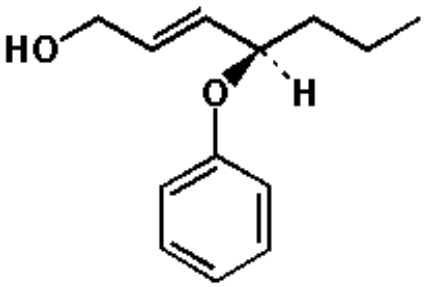
5. common substance - easiest to give its trivial name)



Rubber

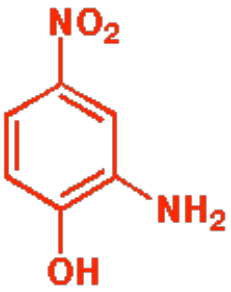
or cis-Polyisoprene

6. (hint name the compound as a substituted alcohol)

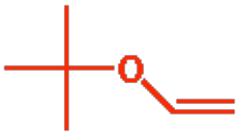


(R)-4-phenoxy-2-hepten-1-ol

7. 2-amino-4-nitrophenol

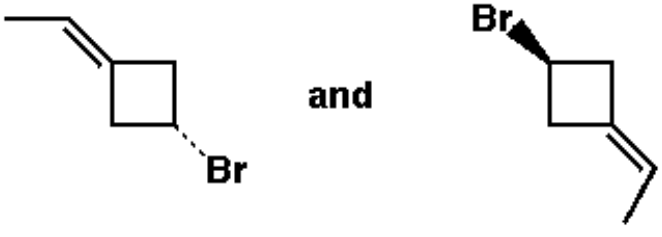


8. *tert*-butyl vinyl ether



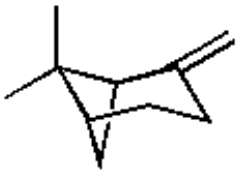
B. Determine whether the following pairs of structures are identical (i.e. different pictures of the same molecule), structural isomers, diastereomers, or enantiomers. **(2 points each - 8 pts total)**.

1.

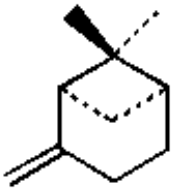


identical

2.

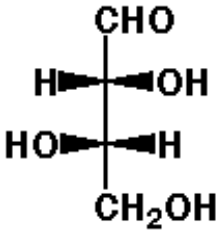


and

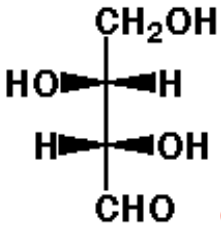


enantiomers

3.

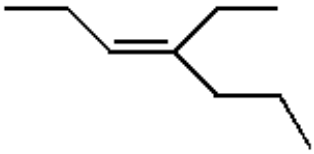


and

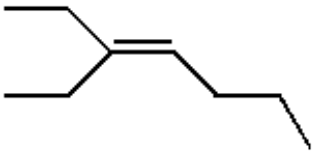


enantiomers

4.

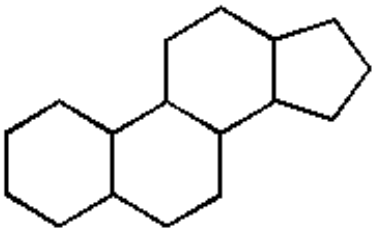


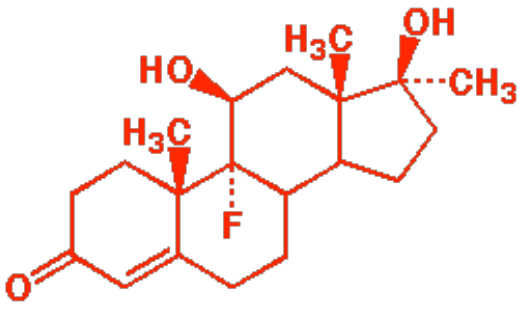
and



structural isomers

C. Fluoxymestrone is a controlled substance and an unnatural anabolic steroid that can enhance performance of athletes. Its complete chemical name is 11-beta,17beta-dihydroxy-9-alpha-fluoro-17alpha-methyl-4-androsten-3-one. Complete its structure using the partial drawing given below. Be sure to provide correct stereochemistry (do not forget the beta-methyl group(s) which are part of the basic skeleton). **(8 points total)**





2. Answer the following questions by giving the correct numbers **(1 point each): (3 pts total)**

a. The number of carbons in the fluoxymestrone molecule is**:** **20**

b. The number of stereogenic (i.e. chiral) centres in dexamethasone is: **7**

(carbons 8,9,10,11,13,14,17)

c. The number of hydrogens in the dexamethasone is**:** **29**

3. Indicate whether the following statements are true (**T**) or false (**F**). No penalty for guessing. **(1 pt each - 6 pts total)**

a. Changing all of the stereocenters in fluoxymestrone to the opposite stereochemistry will generate a diastereomer **False**

b.Changing the 17alpha hydroxy group in fluoxymestrone to b (beta) will generate a structural isomer. **False**

c. Fluoxymestrone has one less carbon than the pregnancy hormone, progesterone. **True**

d. A human produces about 1 *milligram* of male or female sex hormone per day. **True**

e. The pKa of the 17-beta hydroxy group of fluoxymestrone is bout 10. **False**

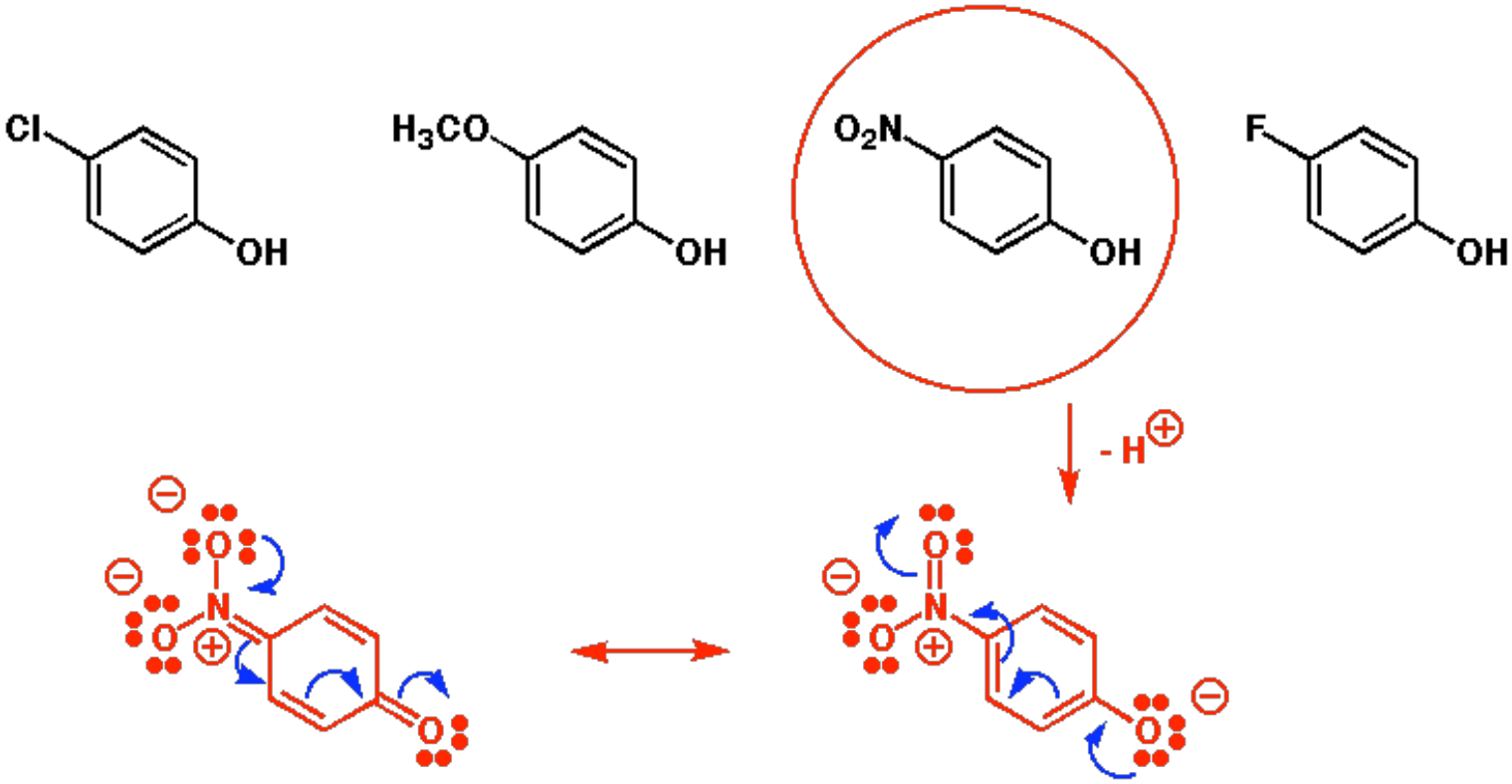
II. Physical Properties and Reactivity - 20 Points

A. Circle the most acidic of the two alcohols shown below**.** Use two words or less to name the effect that explains why it is much more acidic (more stable anion) than the other (by a factor of ca 1000) **(4 pts)**

Effect: **Inductive**

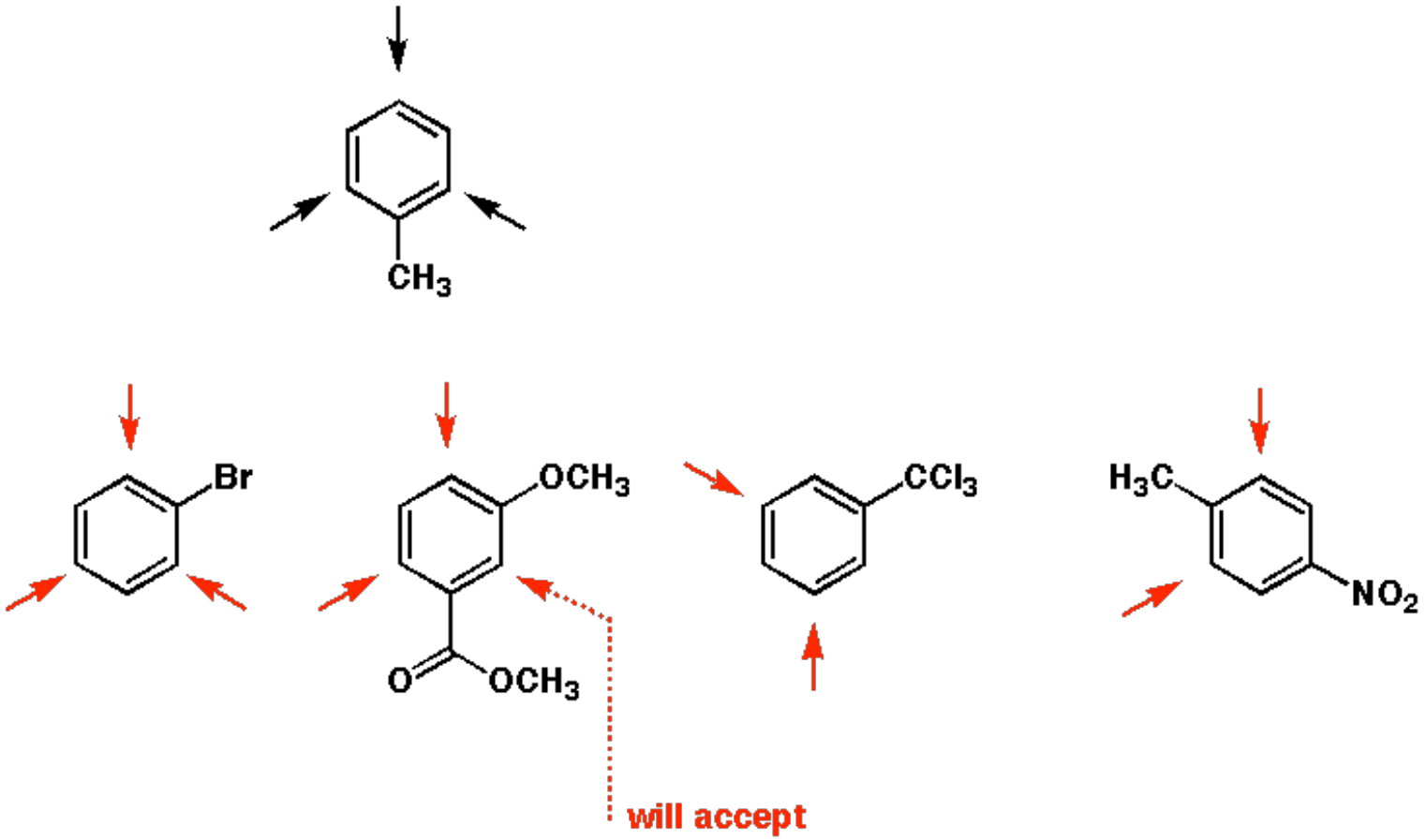
Since alkyl groups donate electrons, the primary alkoxide anion is better able to bear negative charge

B. In the group below, circle the most acidic compound. Use two resonance structures of the corresponding anion to show what makes your choice especially acidic. **(4 pts: 1 pt for correct circle)**

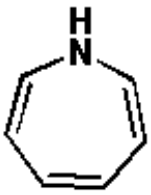


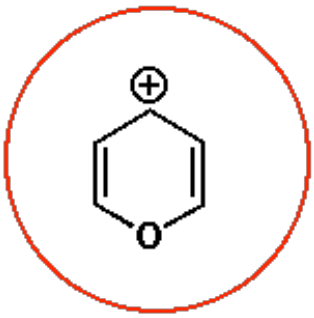
C. In the group below use an arrow to indicate the position(s) on the aromatic ring which would be most likely to be attacked by chlorine in the presence of FeCl3 **(4 pts - 1 pt each)**

Example:



D. One of the two species below is aromatic and the other is not. Circle the aromatic one. Then give the number of pi electrons that both of them have and list the key criteria that make a molecule or ion aromatic. **(8 pts this question: 1 pt for correct circle, 3 pts correct number electrons, 4 pts for requirements for aromaticity below)**





8 π electrons **6 π electrons**

Key Requirements for Aromaticity are (4 pts):

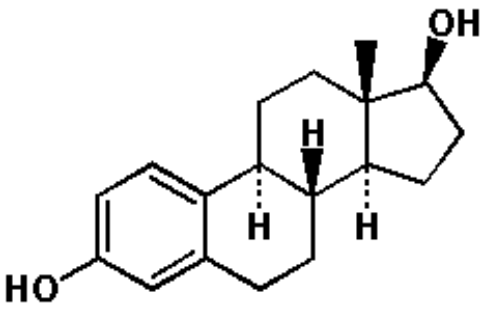
Cyclic , Planar , Conjugated Throughout (around ring)

4n + 2 π electrons n = 0, 1, 2, ...

III. Definitions and Applications - 6 Points

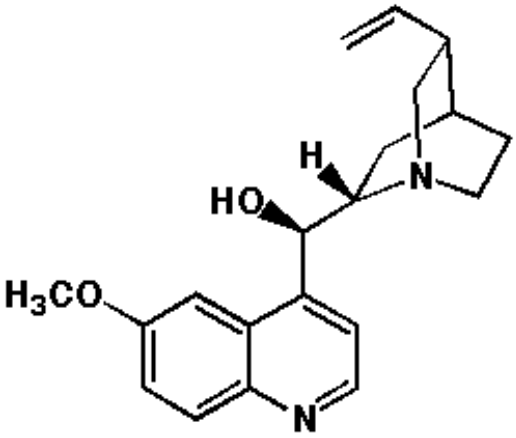
A. The three compounds shown below were discussed in class. Identify them by common name and briefly (10 words or less) describe their importance or use. **(6 pts total - 2 pt each)**

1.



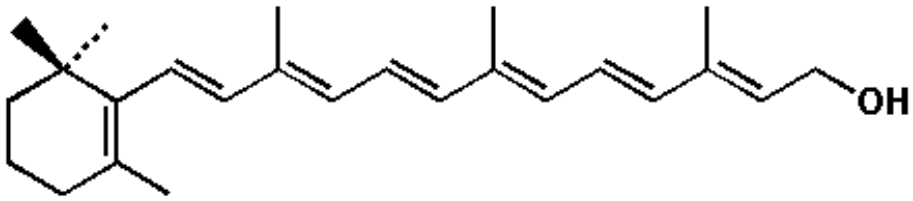
Estradiol - Female Sex Hormone - Isolated by Doisy and Butenandt in 1929

2.



Quinine - Antimalarial Drug

3.

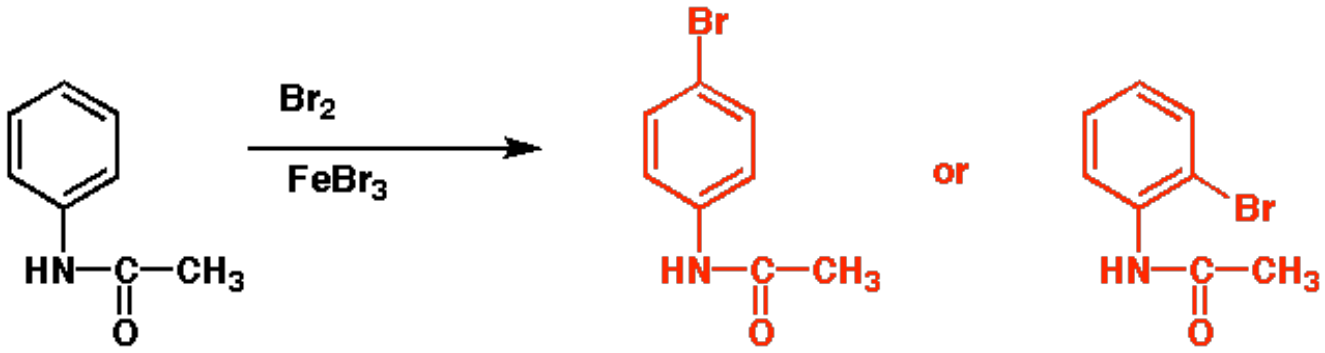


Vitamin A or Retinol - essential dietary nutrient to prevent night blindness

IV. Reactions - 16 Points

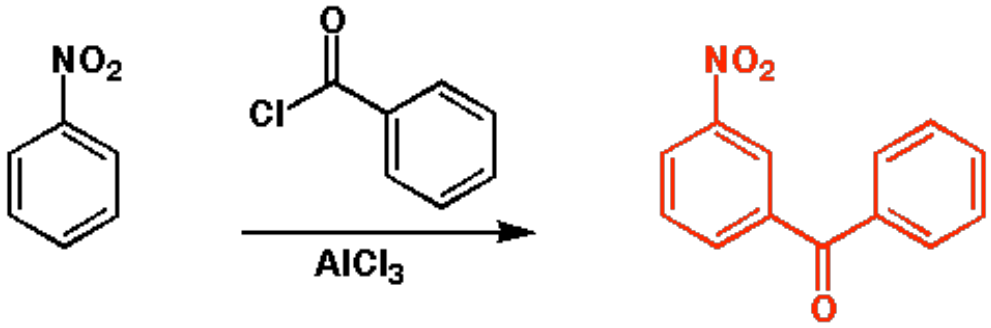
A. Show the structure of the major organic product of each of the following reactions. Show stereochemistry where indicated by asterisks (***). **(2 points each - 8 points total)**

1.

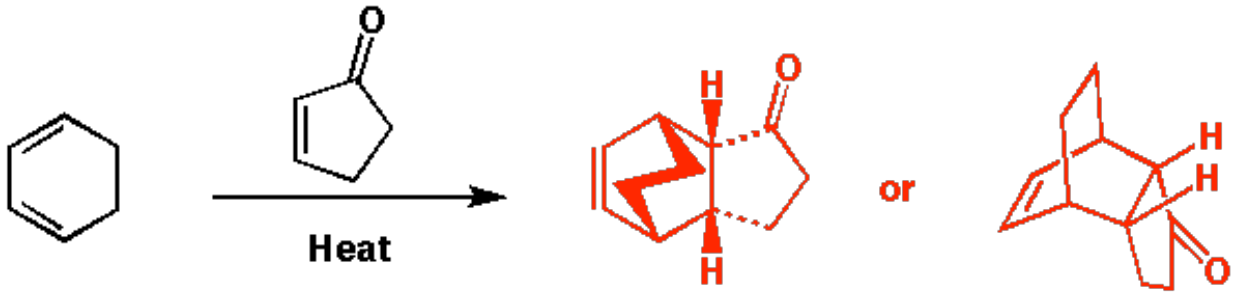


assigned problem 16.24a

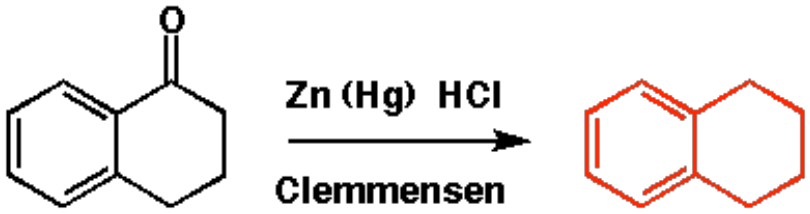
2.



3.

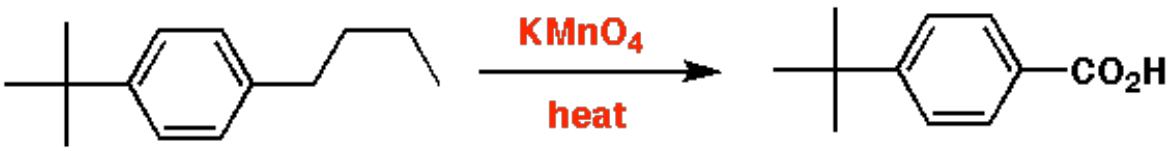


4.



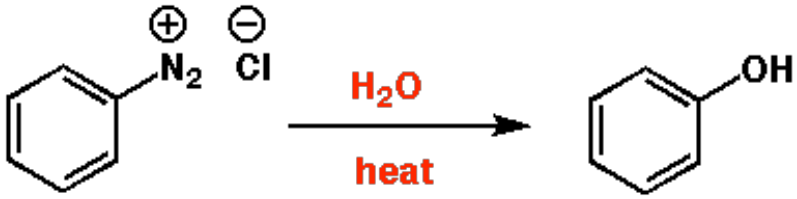
B. Show reagents that will do the required transformations. In some cases two or three steps may be necessary. **(2 pts each - 8 pts total)**

1.

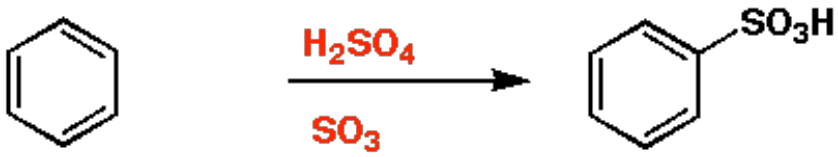


Assigned problem 17.10

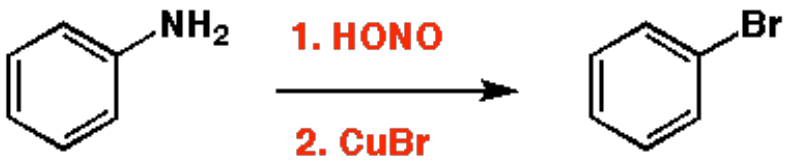
2.



3.



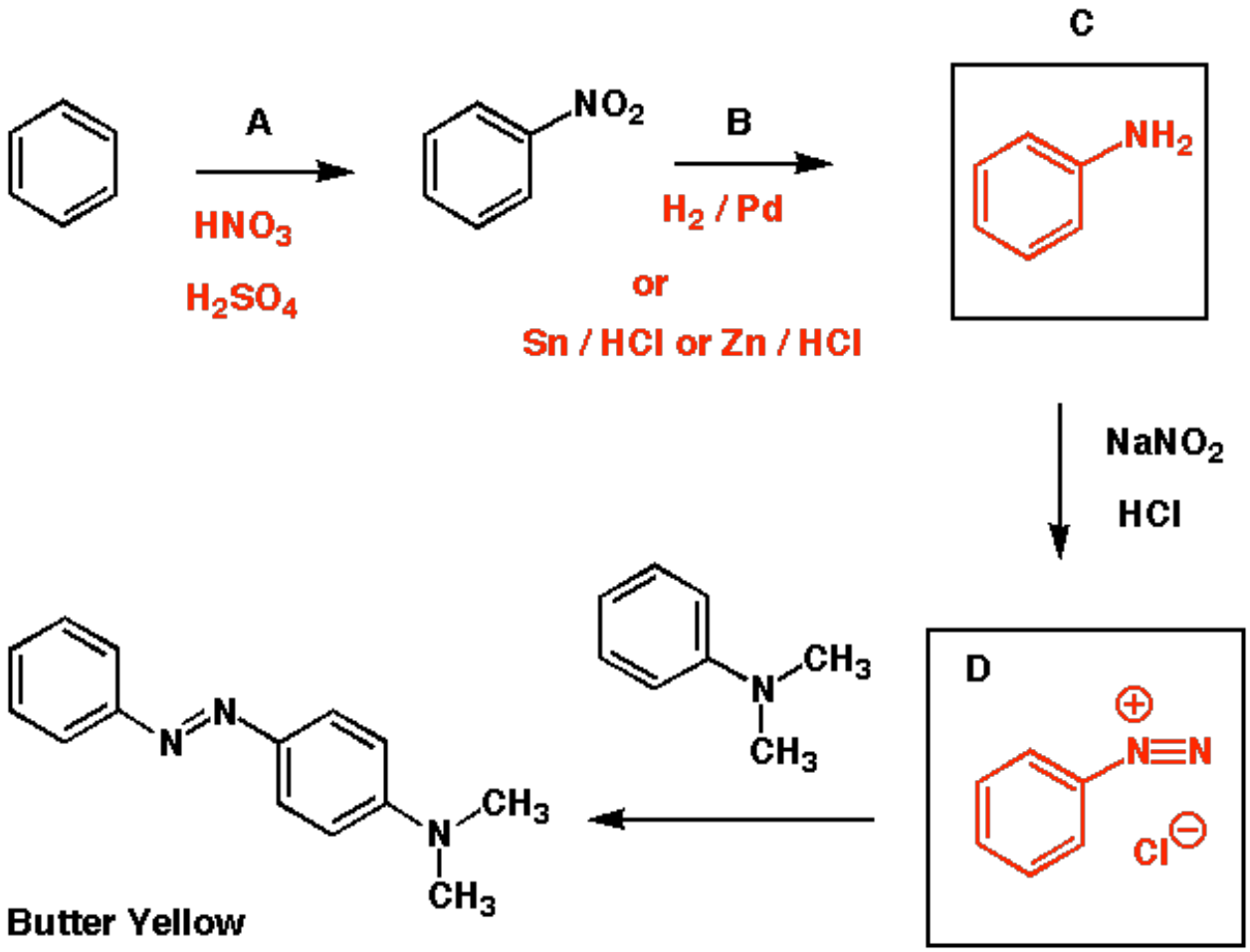
4.



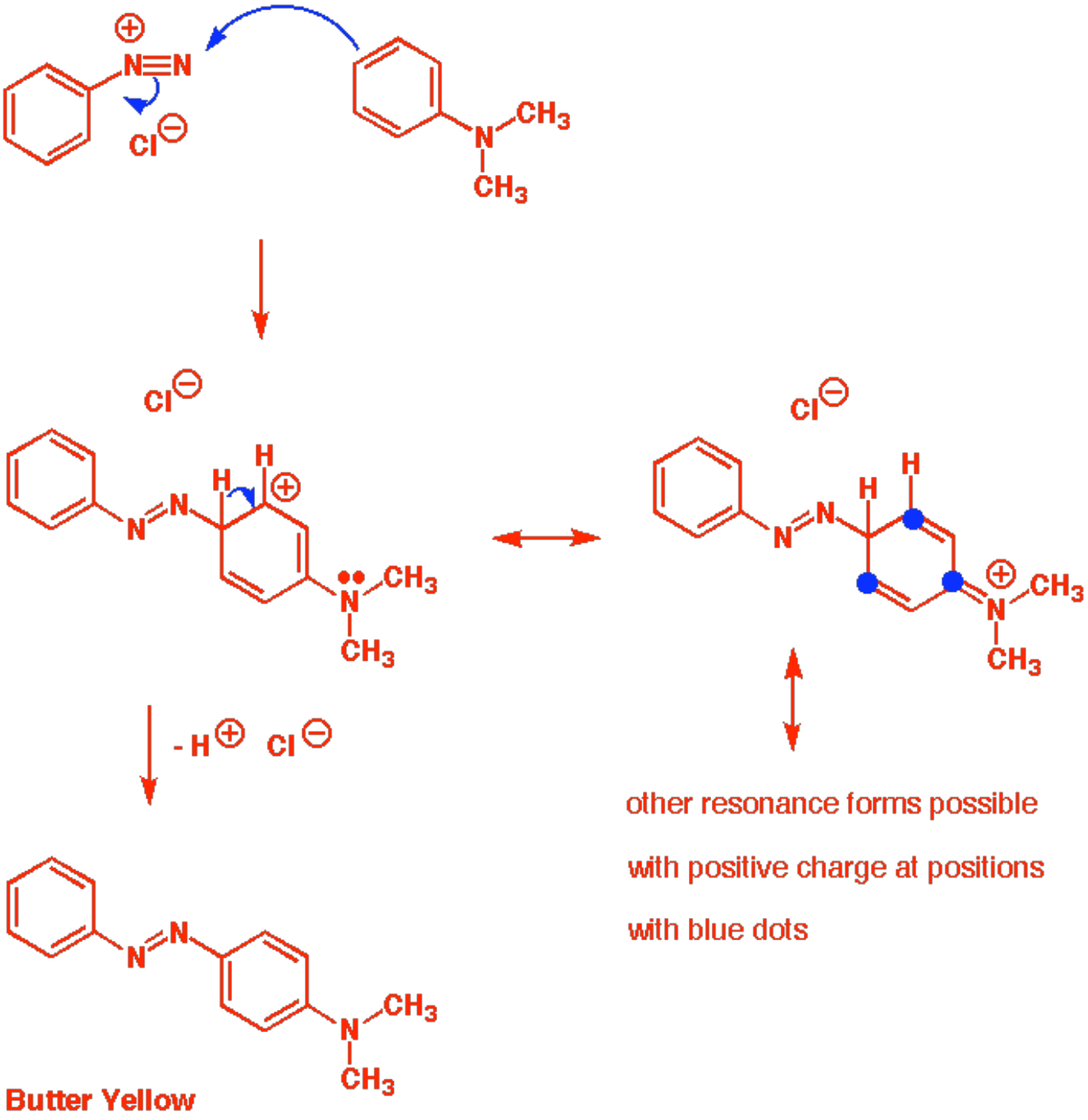
Instead of HONO use $NaNO_2$ and H^+

V. Synthesis and Mechanism - 18 Points

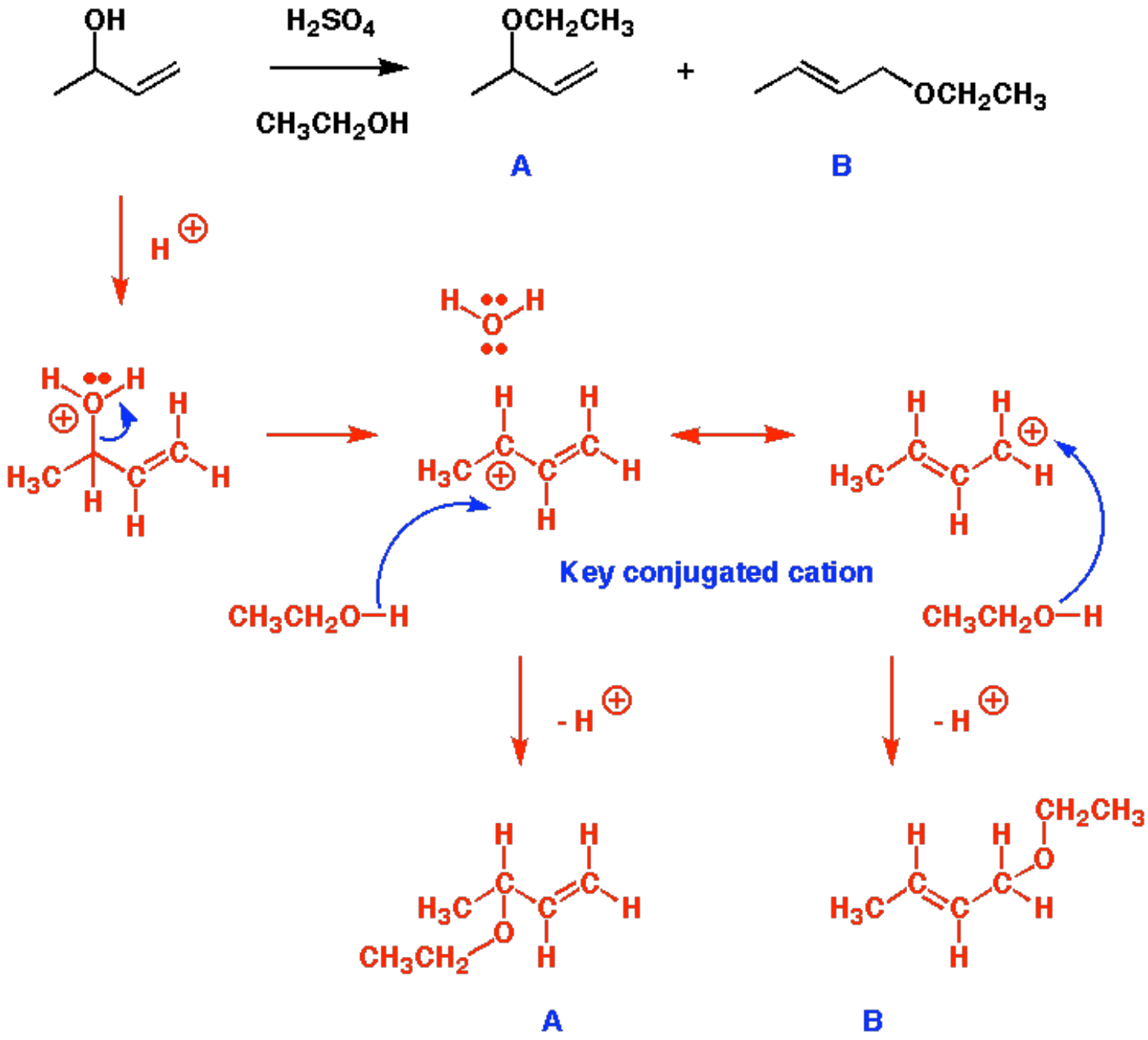
A. The synthetic dye known as Butter Yellow can be synthesized from N,N-dimethylaniline and benzene in several steps. The steps are shown, but are missing the necessary reagents and interemediates. Provide the missing reagents and intermediates to show how to complete the synthesis of Butter Yellow. (Assigned Reading Chapter 23, Section 23.10) **(8 pts total - 2 pts each)**



B. For the last step in the formation of Butter Yellow (reaction with N,N-dimethylaniline) provide a detailed mechanism using curved arrows to show the movement of electrons. Show the key resonance stabilized intermediate that is formed. **(4 points)**



C. Provide a detailed "step by step" mechanism for the reaction shown below. Be sure to show the stuctures of key intermediates and indicate the movement of electrons using the curved arrow convention. Use resonance theory to explain why two products are produced. Assigned problem 17.21 **(6 points)**


OH
H2SO4
CH3CH2OH
OCH2CH3
+
OCH2CH3
A
B
H
Key conjugated cation
CH3CH2O—H
CH3CH2O—H
- H
- H
CH2CH3
A
B