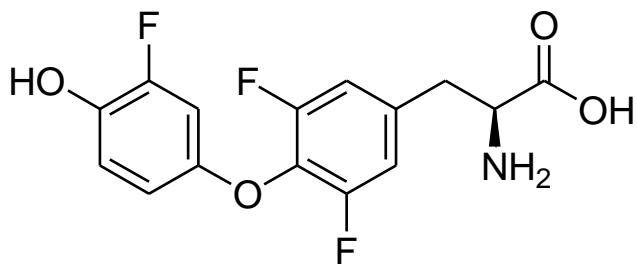


2007 Mechanisms Midterm 100 points NAME: \_\_\_\_\_

1) (12pts): For the below molecule, calculate the number of...

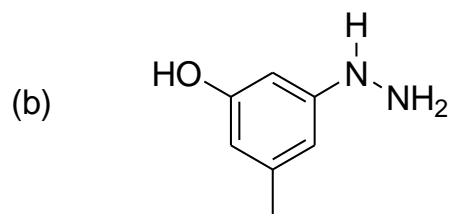
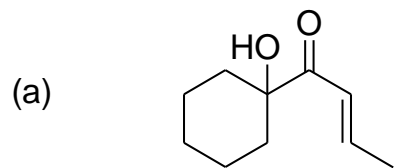


- carbon atoms
  - hydrogen atoms
  - oxygen atoms
  - sp<sup>2</sup> hybridized atoms
  - sp<sup>3</sup> hybridized atoms
  - lone pairs (non bonding pairs) of electrons
- 2) (8pts) What are *resonance structures* ? Provide an example.

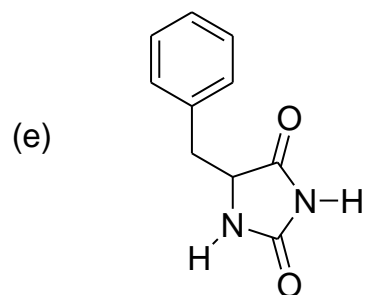
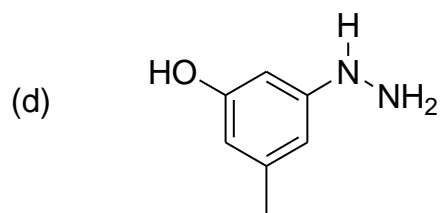
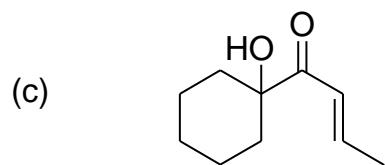
What are *tautomers* ? Provide an example

What is *Occam's Razor* ?

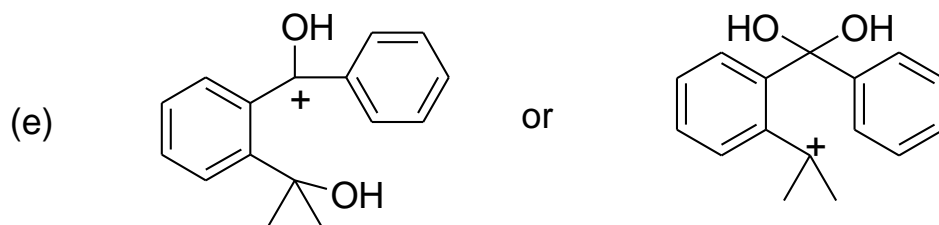
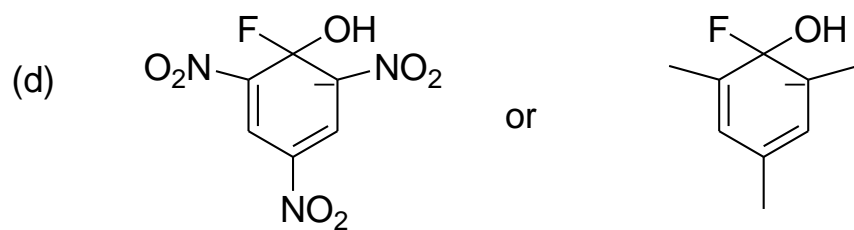
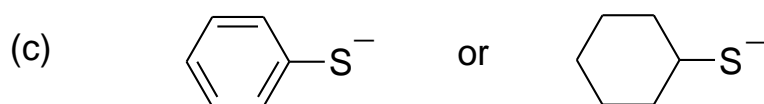
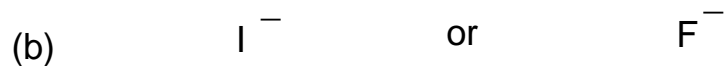
3) (10pts) (i) Circle the most **basic** atom in these molecules.



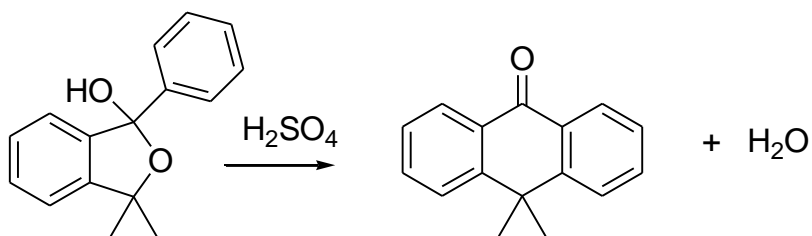
(ii) Circle the most **acidic** atom in these molecules.



4) (10pts) Circle the **more stable species** in each pair.



5) (20pts) For the following transformation:



i) label the carbon atoms in the starting material and product.

ii) how many lone pairs of electrons are in the starting organic molecule?

iii) is this reaction performed under *acidic*, *basic*, or *neutral* reaction conditions ?

iv) Protonation of one of the oxygens, followed by ring opening can produce the two different cations shown in Question 4 part e. Write mechanisms showing the formation of both of these cations.

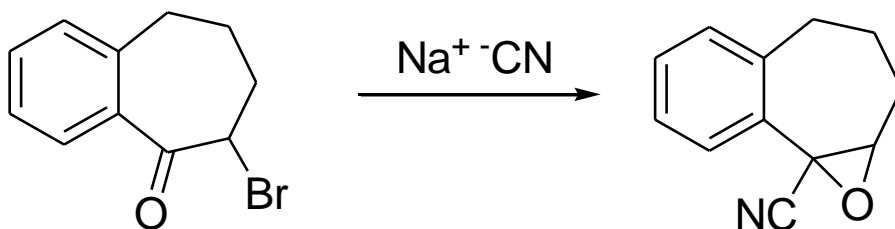
v) Starting at the more stable cation that you chose, write the rest of the mechanism for this transformation.

6) (10pts) The cyanide ion ( $^-\text{CN}$ ) is a strong nucleophile but a weak base.

i) draw a correct Lewis structure for the cyanide ion.

ii) the organic starting material has two electrophilic centers – indicate where these two sites are.

iii) Write the mechanism for this transformation.



7) (15pts) The following cyclization reaction occurs in dilute Sodium Hydroxide.



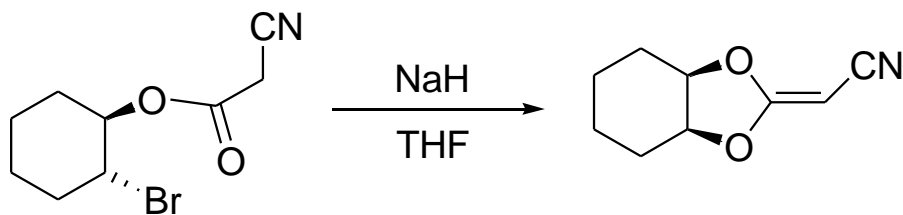
i) The organic starting material can potentially generate two different enolate anions.

- Draw both of these different anions.
- Write the mechanisms for their formation.
- Indicate which anion is the more stable.

ii) This reaction actually *does not* proceed through the more stable anion, but the *other* enolate, which then attacks one of the ketone functionalities. This is followed by a dehydration which yields the  $\alpha, \beta$  *unsaturated carbonyl* product. Write the mechanism for this reaction (paying attention to the reaction conditions).



8) (15 pts) The following transformation is achieved via sodium hydride in THF solvent.



i) Write a correct Lewis structure for ionic sodium hydride – paying special attention to the number of electrons associated with the Hydrogen.

ii) Is sodium hydride considered *acidic* or *basic* ?

iii) why is this reaction performed in an aprotic solvent (like THF) ?

iv) The sodium hydride reacts with the organic starting material to generate an anion which exists in 3 different resonance structures.

-Draw these 3 resonance structures.

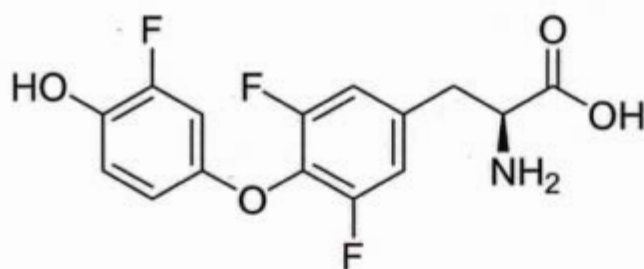
- Show using curly arrows how they interconvert

-Indicate which is the highest energy (least stable) resonance form.

v) What scientific term (which contains zero vowels!) describes the stereochemical relationship between the two Oxygen atoms in the product ?

vi) Write the mechanism for this reaction (which involves the intermediate anion performing a nucleophilic substitution).

1) (12pts): For the below molecule, calculate the number of...



- a) carbon atoms 15
- b) hydrogen atoms 12
- c) oxygen atoms 4
- d)  $sp^2$  hybridized atoms 14
- e)  $sp^3$  hybridized atoms 9
- f) lone pairs (non bonding pairs) of electrons 18

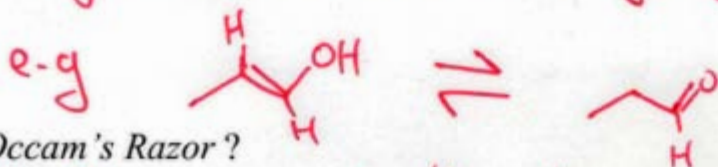
2) (8pts) What are *resonance structures*? Provide an example.

Resonance structures differ only in their location in electron density.



What are *tautomers*? Provide an example

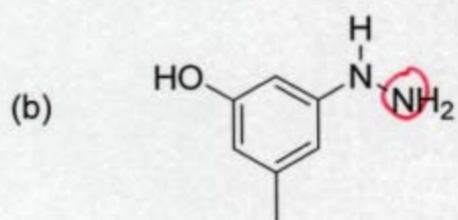
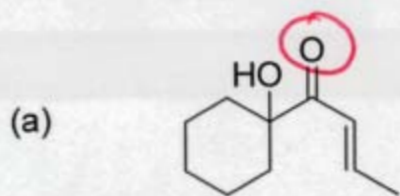
Tautomers are isomers that differ in the location of easily exchangeable atoms (often acidic hydrogens).



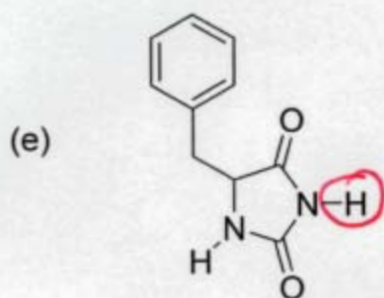
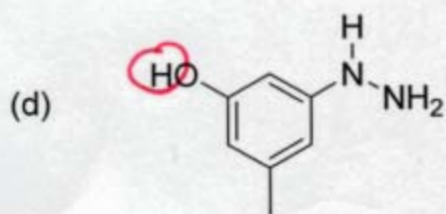
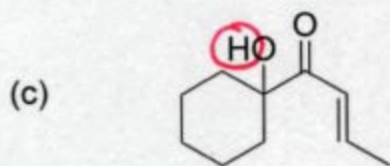
What is *Occam's Razor*?

If all other things are equal, the simplest solution is usually the best solution.

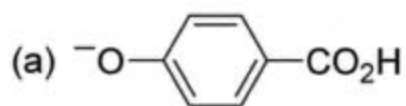
3) (10pts) (i) Circle the most **basic** atom in these molecules.



(ii) Circle the most **acidic** atom in these molecules.



4) (10pts) Circle the **more stable species** in each pair.



or



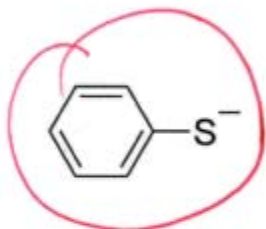
(b)



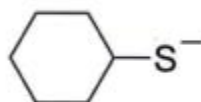
or



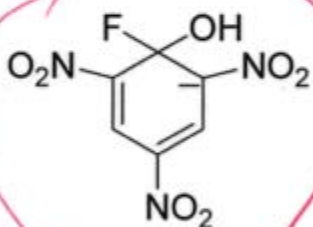
(c)



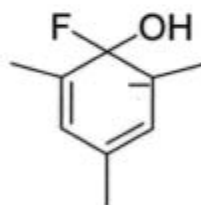
or



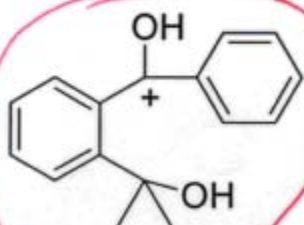
(d)



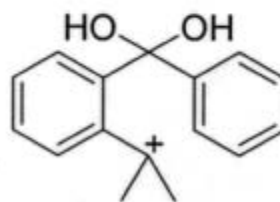
or



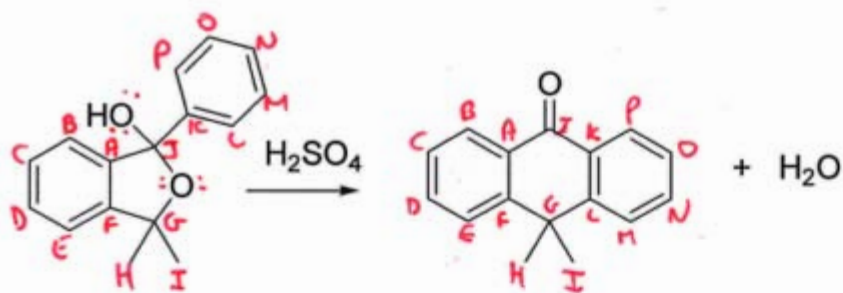
(e)



or



5) (20pts) For the following transformation:



i) label the carbon atoms in the starting material and product.



ii) how many lone pairs of electrons are in the starting organic molecule?

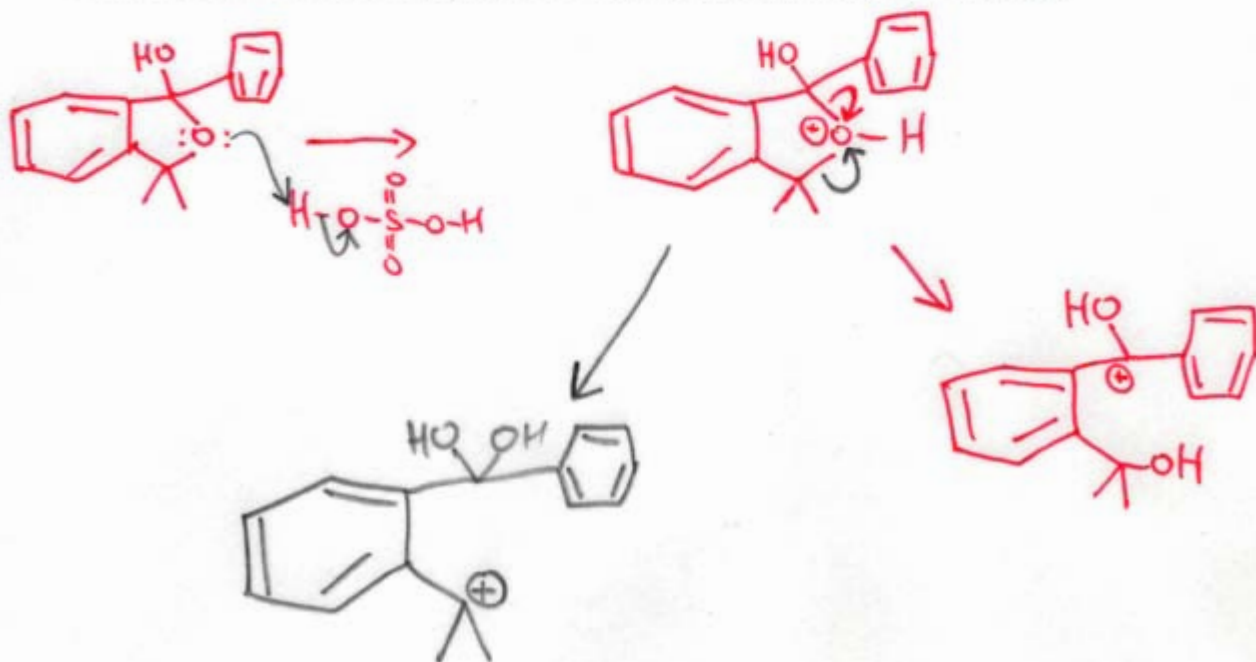
4 pairs

iii) is this reaction performed under *acidic*, *basic*, or *neutral* reaction conditions?

acidic

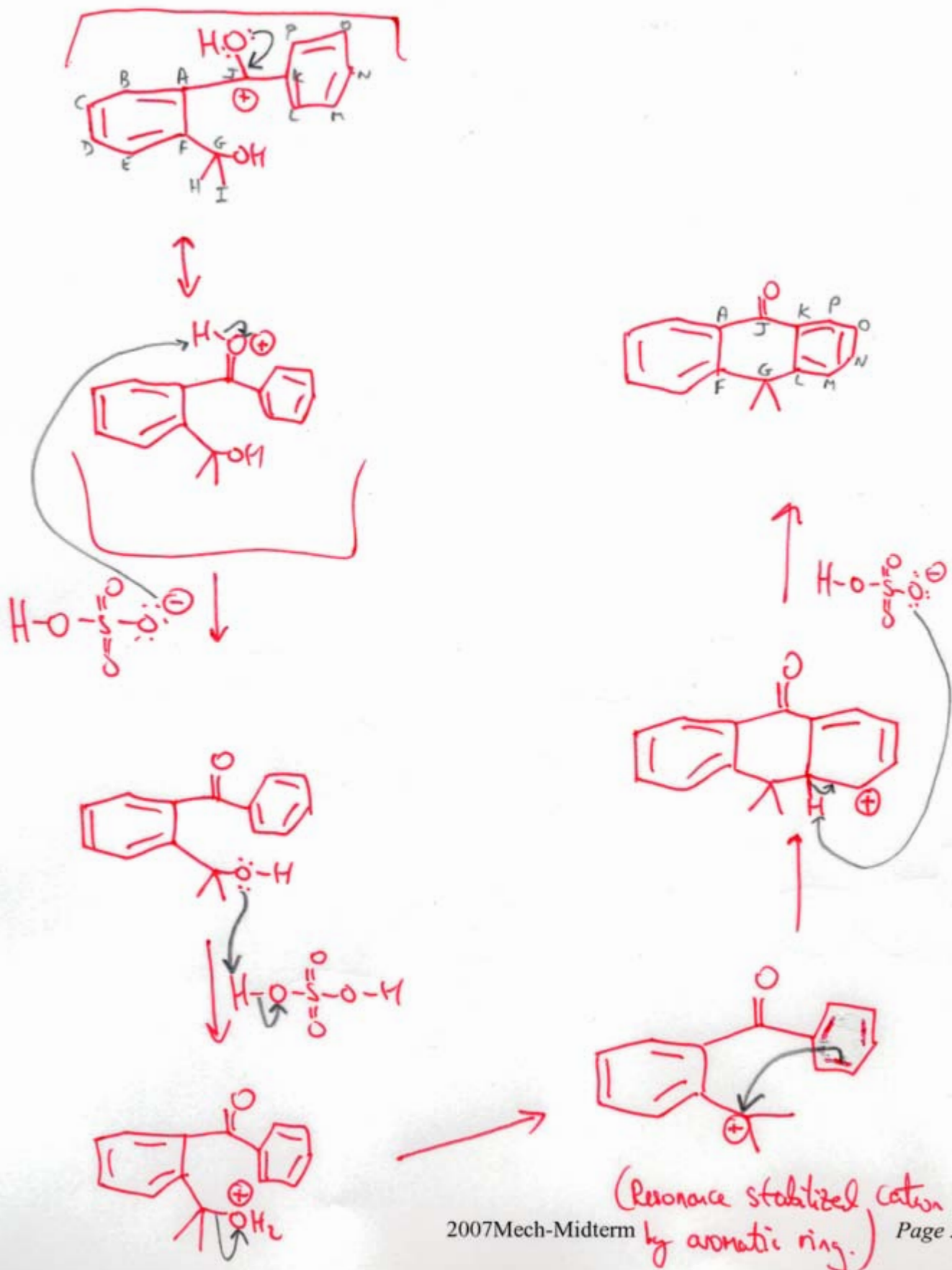
iv) Protonation of one of the oxygens, followed by ring opening can produce the two different cations shown in Question 4 part e.

Write mechanisms showing the formation of both of these cations.





v) Starting at the more stable cation that you chose, write the rest of the mechanism for this transformation.



6) (10pts) The cyanide ion ( $\text{CN}^-$ ) is a strong nucleophile but a weak base.

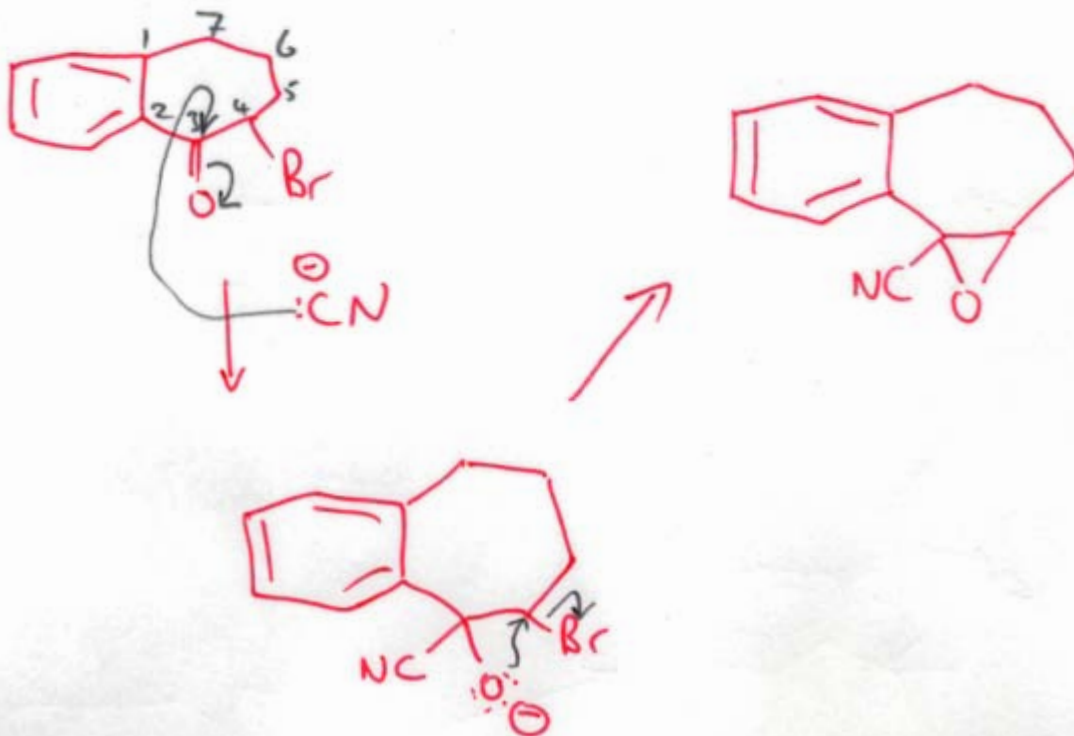
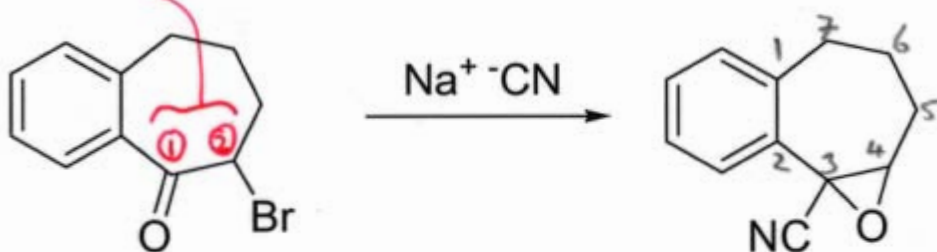
i) draw a correct Lewis structure for the cyanide ion.



ii) the organic starting material has two electrophilic centers – indicate where these two sites are.

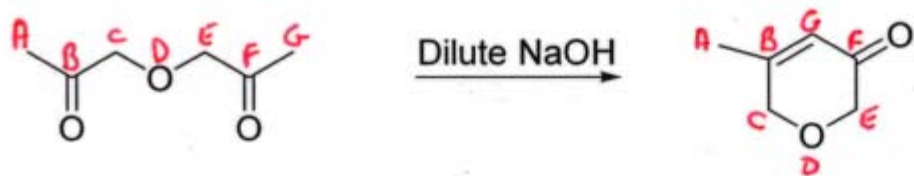


iii) Write the mechanism for this transformation.



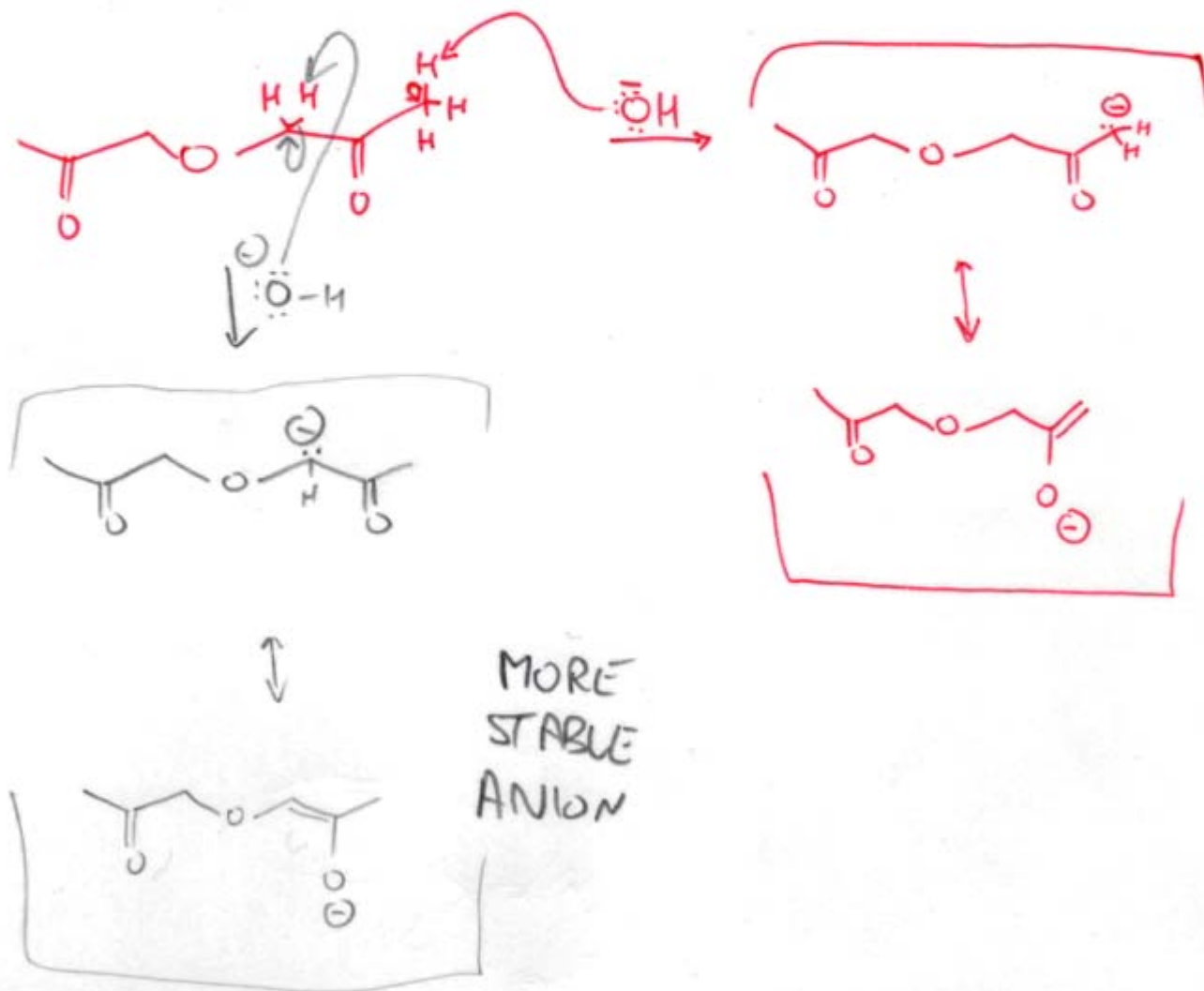


7) (15pts) The following cyclization reaction occurs in dilute Sodium Hydroxide.

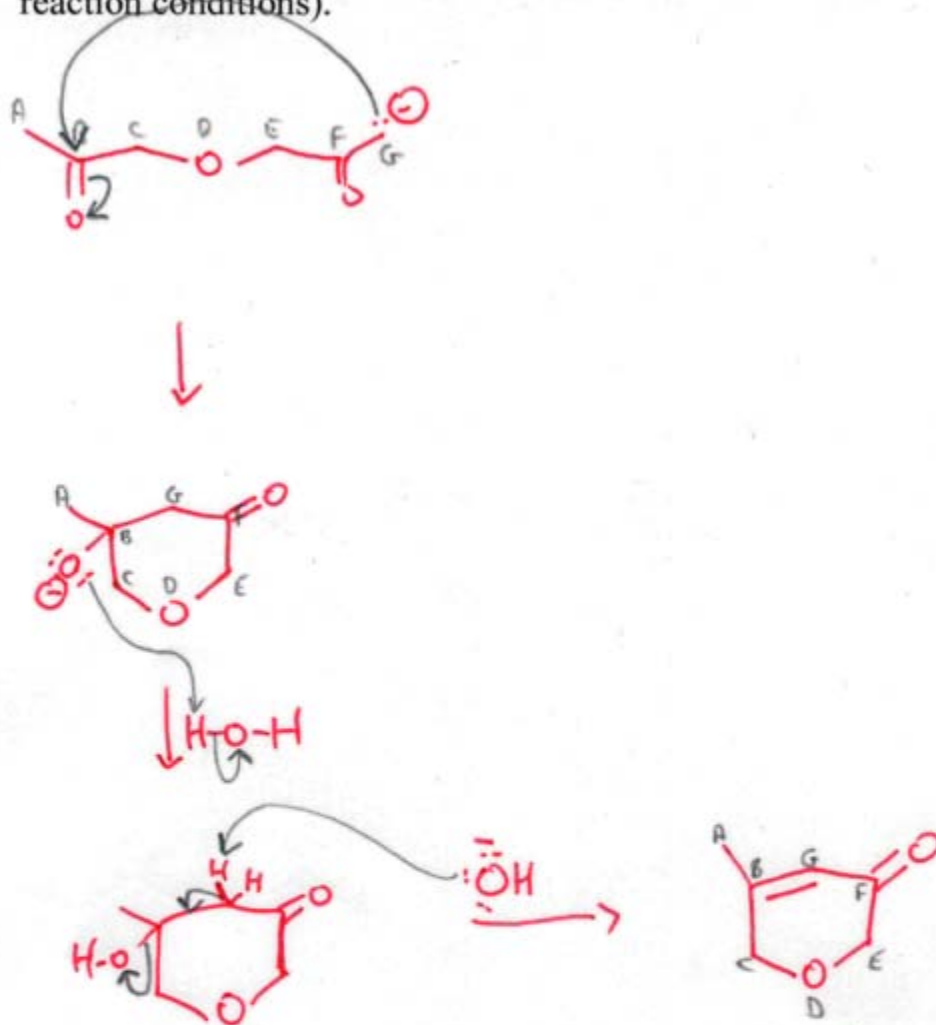


i) The organic starting material can potentially generate two different enolate anions.

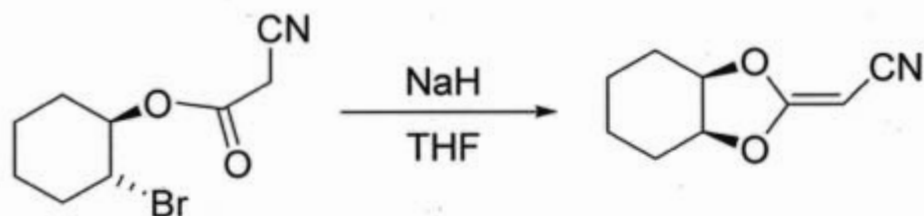
- Draw both of these different anions.
- Write the mechanisms for their formation.
- Indicate which anion is the more stable.



ii) This reaction actually *does not* proceed through the more stable anion, but the *other* enolate, which then attacks one of the ketone functionalities. This is followed by a dehydration which yields the  $\alpha, \beta$  unsaturated carbonyl product. Write the mechanism for this reaction (paying attention to the reaction conditions).



8) (15 pts) The following transformation is achieved via sodium hydride in THF solvent.



i) Write a correct Lewis structure for ionic sodium hydride – paying special attention to the number of electrons associated with the Hydrogen.



ii) Is sodium hydride considered *acidic* or *basic* ?

**BASIC**

iii) why is this reaction performed in an aprotic solvent (like THF) ?

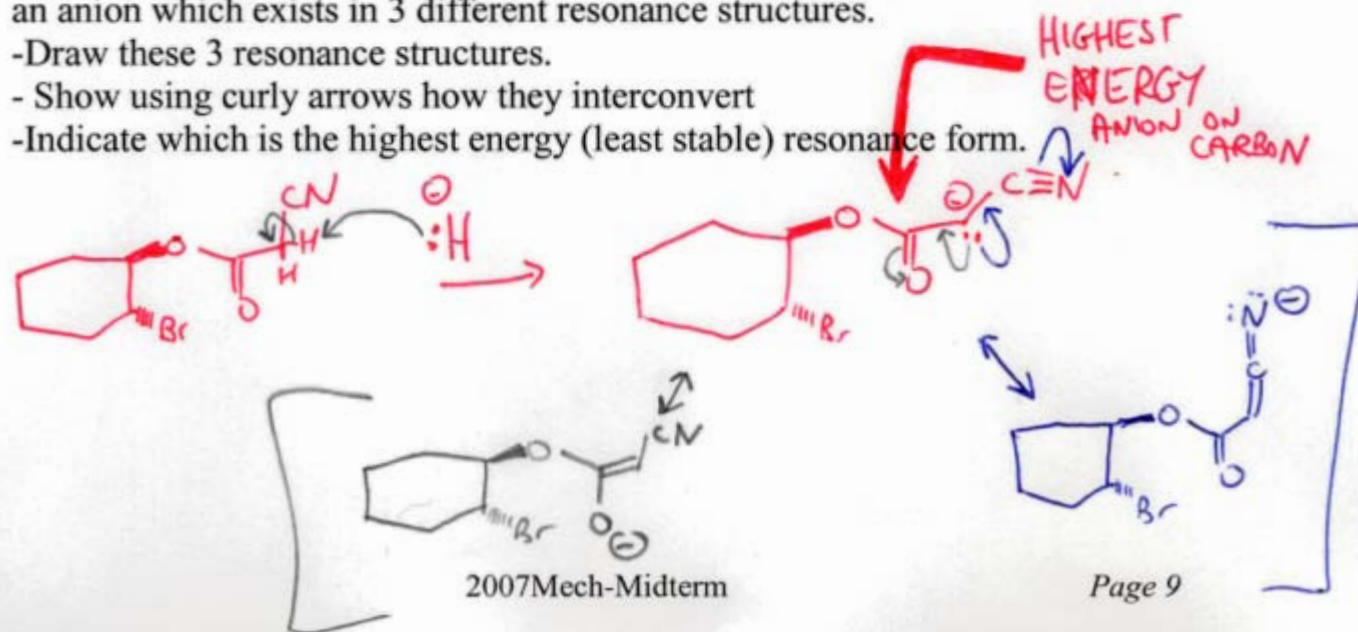
The strongly basic NaH would react with protic (acidic hydrogen) solvents.

iv) The sodium hydride reacts with the organic starting material to generate an anion which exists in 3 different resonance structures.

-Draw these 3 resonance structures.

- Show using curly arrows how they interconvert

-Indicate which is the highest energy (least stable) resonance form.



v) What scientific term (which contains zero vowels!) describes the stereochemical relationship between the two Oxygen atoms in the product?

SYN

vi) Write the mechanism for this reaction (which involves the intermediate anion performing a nucleophilic substitution).

