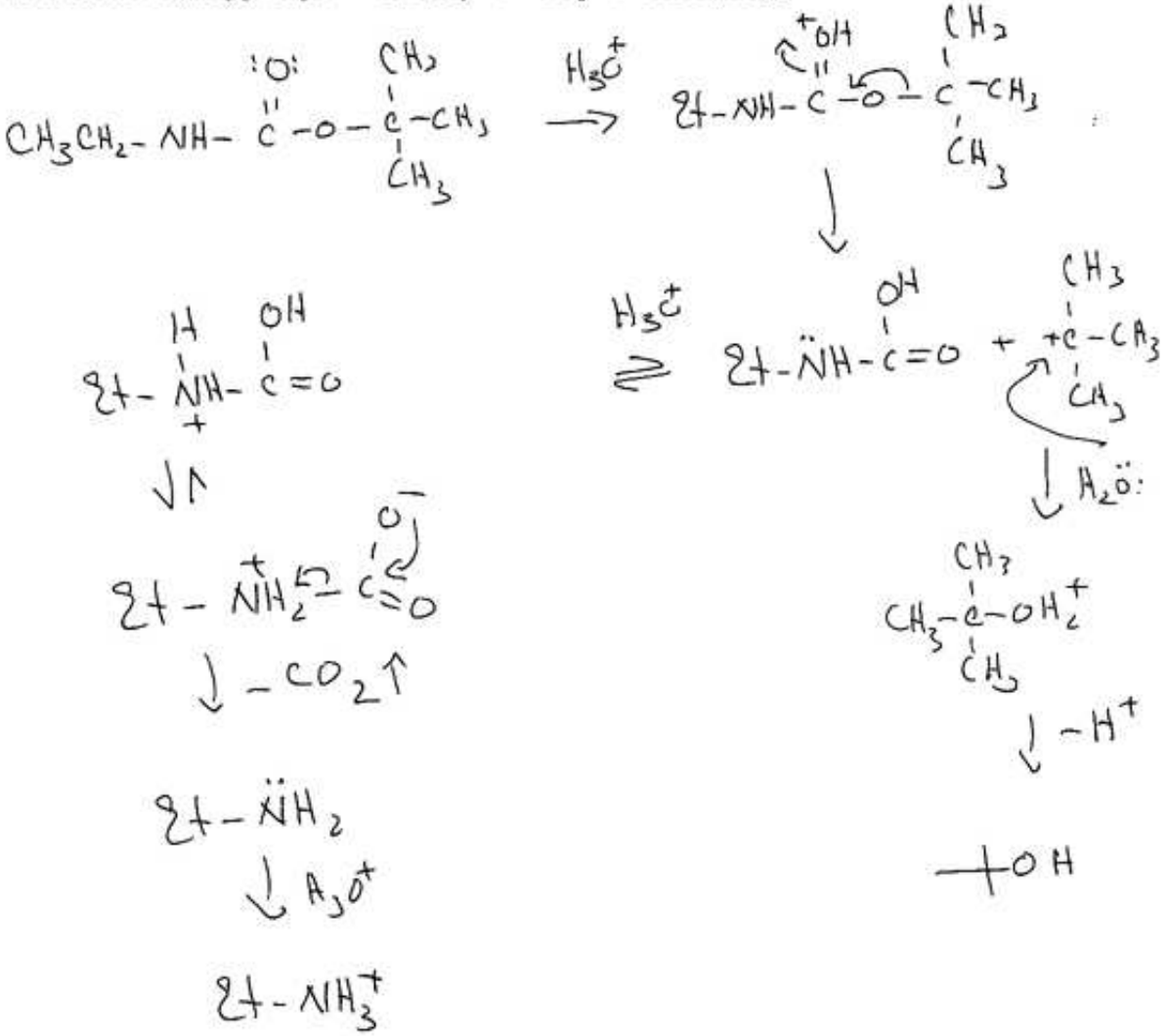
Chemistry 3331-100
Organic Chemistry/Dr. Barney Ellison
Thursday: Nov. 17th **@ 7:00pm → 9:00**/3rd Exam/Chem 142

Name: Key (please print)

1. (10 pts) Write a mechanism for the removal of the protecting group *t*-BOC from an amino group. (remember that a tertiary carbocation is exceptionally stable).

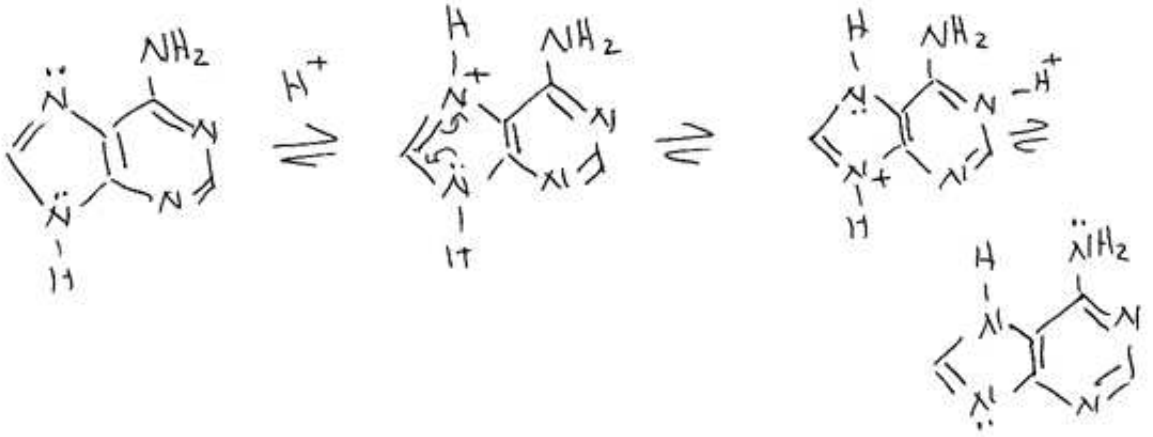
$Et\text{-}NH\text{-}COO\text{-}C(CH_3)_3 + H_3O^+ \rightarrow Et\text{-}NH_3^+ + CO_2 + HOC(CH_3)_3$

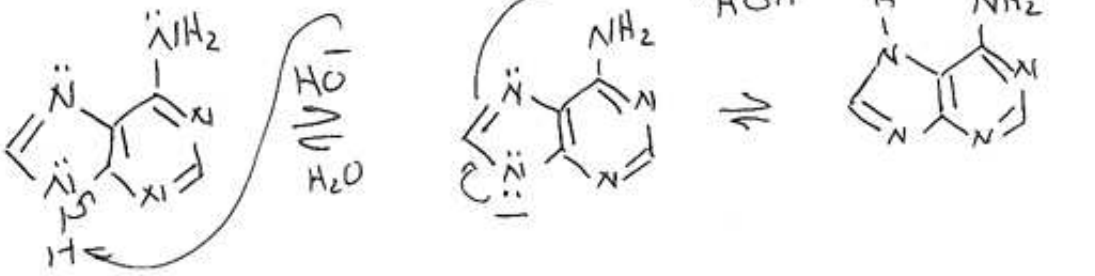


2. (10 pts) Write mechanisms for the interconversion of the two tautomers of adenine under acidic and basic conditions.

a) $H_3O^+/H_2O$

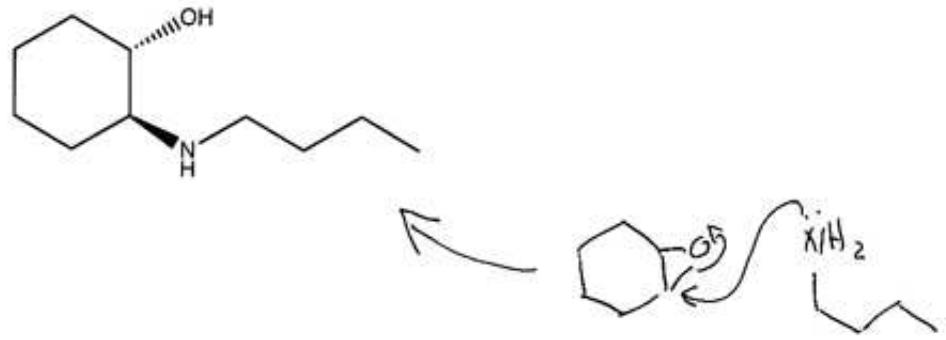
b) $OH^-/H_2O$





3. (15 pts) Each of the following aminoalcohols can be prepared by the reaction of an amine with an epoxide. Suggest appropriate starting materials that can produce each product.

a)

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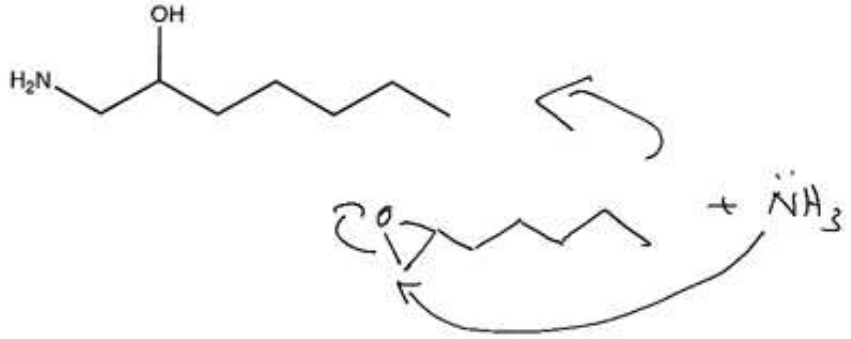
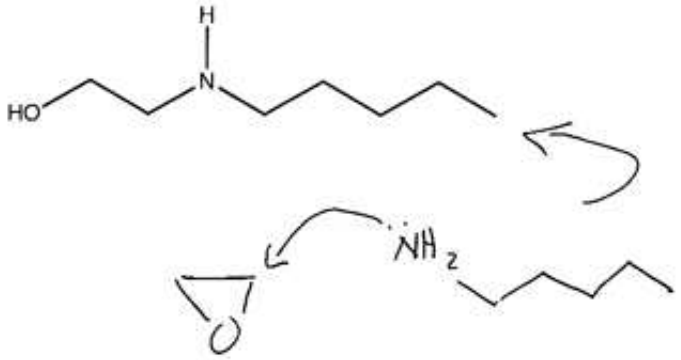
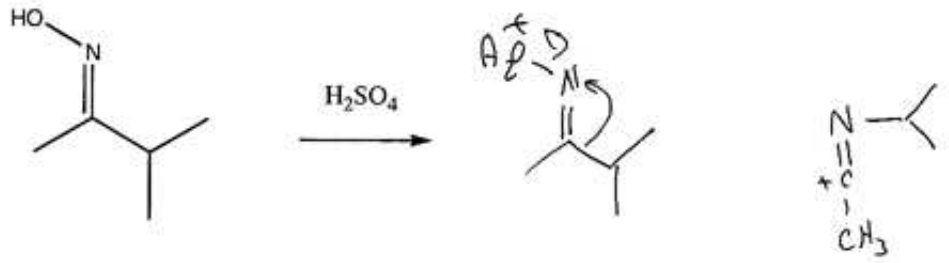



c)



4. (15 pts) Show the structure of the product that would be obtained from the Beckmann rearrangement of each of the following oximes. Be sure the consider the regiochemistry.

a)

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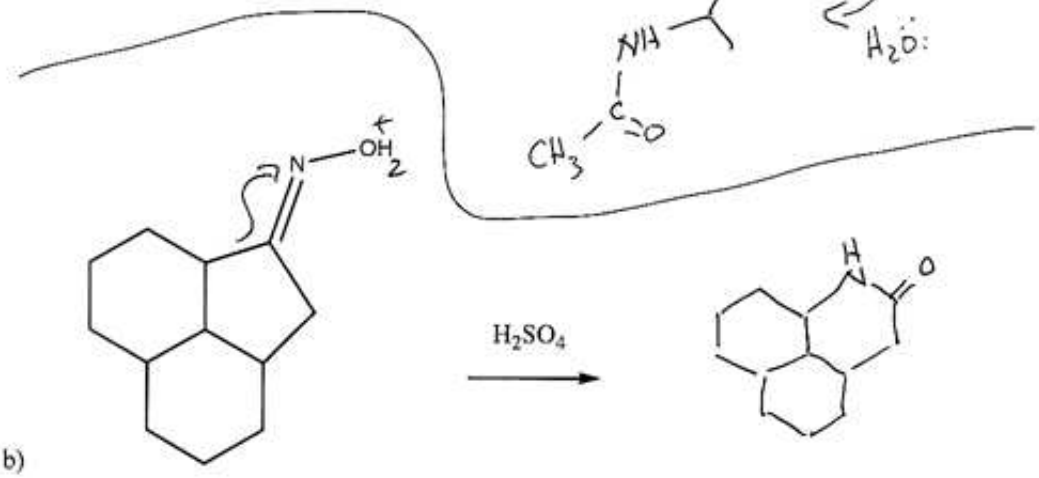


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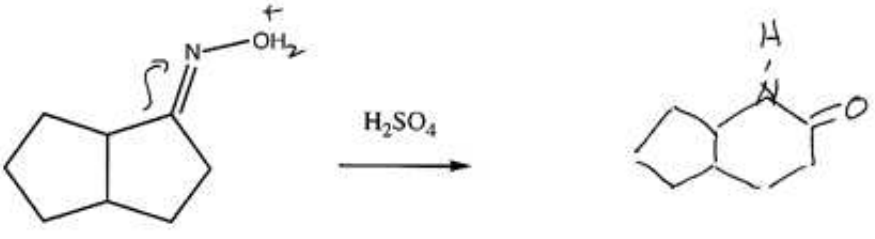
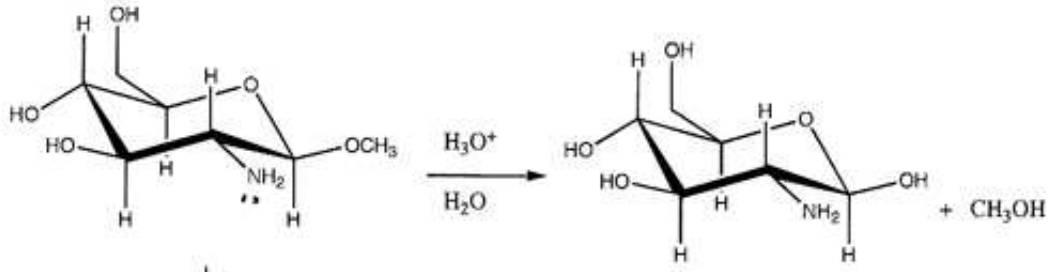
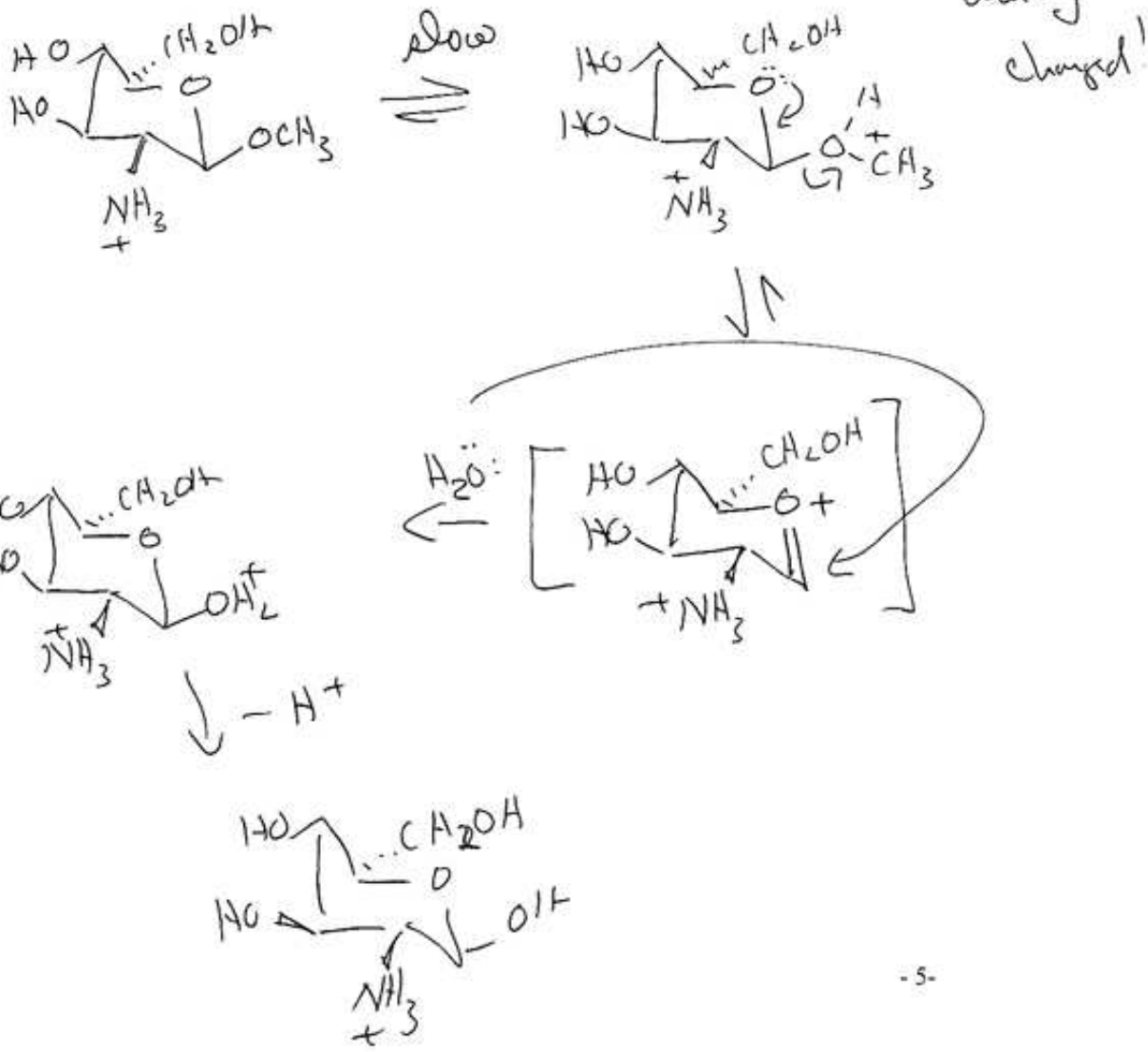
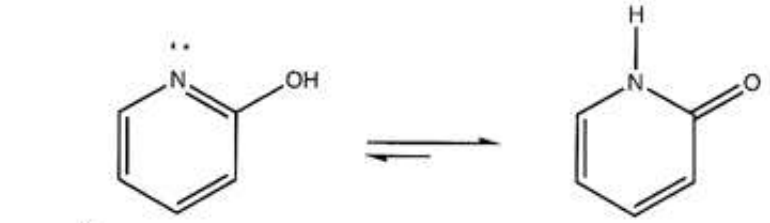


5. (10 pts) Acetal linkages formed from aminosugars are much more resistant to acid-catalyzed cleavage than are typical carbohydrates. Why?



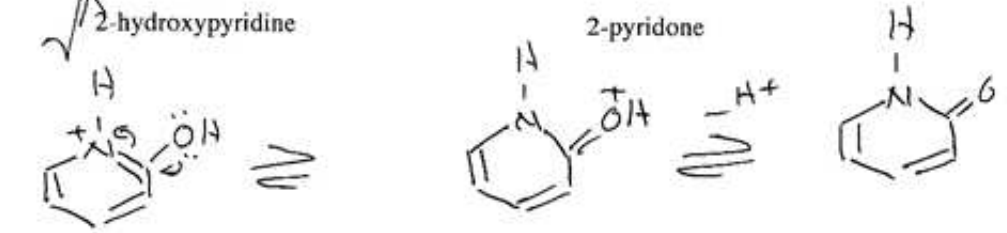



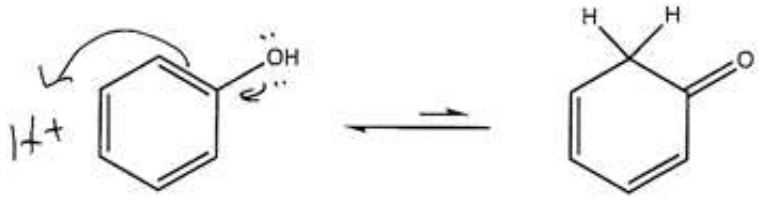
6. (10 pts) Several heterocyclic systems exist as equilibrium mixtures of hydroxyaromatic and a ketonic form. Write mechanisms for the acid catalyzed conversion for each of these conversions.




2-hydroxypyridine

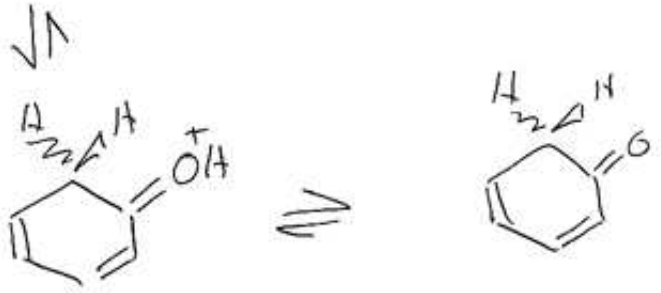
2-pyridone





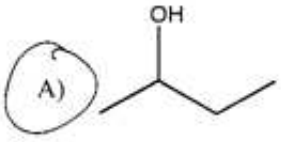

phenol

trace



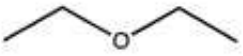
7. (10 pts) In each of the following pairs, predict which isomer is expected to have the higher solubility in water. Explain your choice.

a)



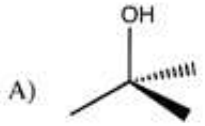

good H-bond donation & accepter

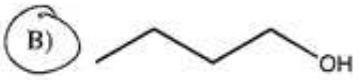
B)




can only be H bond accepter

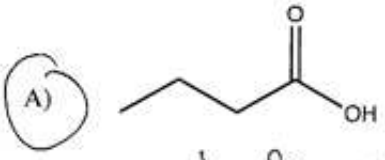
b)



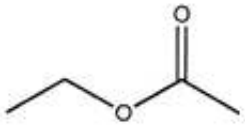

less hindered — better H bonding — entropically favored

c)



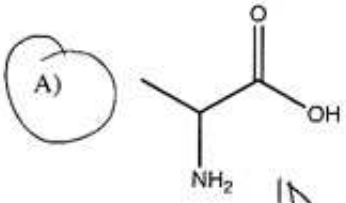

carboxylic acid is H bond accepter & donation

B)

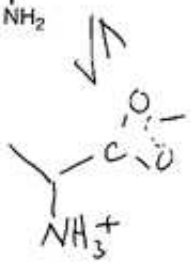



H bond accepter

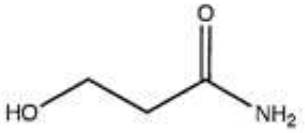
d)




Zwitter ion

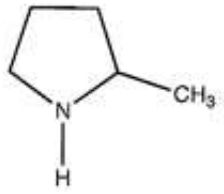



B)

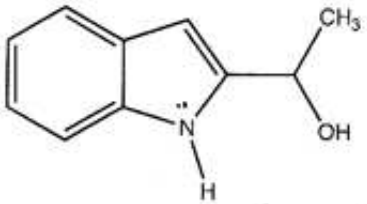



Neutral

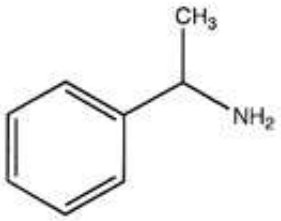
8. (10 pts) For which of the following amines is it possible to carry out a resolution into separate enantiomers by forming a salt with a chiral carboxylic acid?



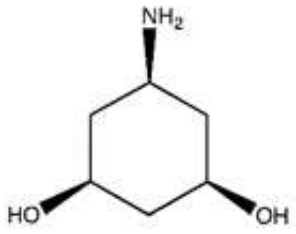

yes, can resolve




no, cannot resolve aromatic ring won't protonate

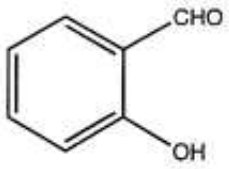


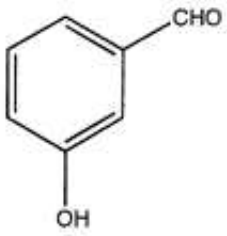

yes can resolve

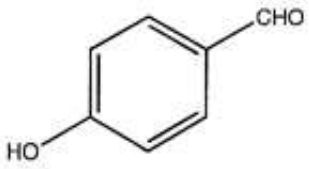


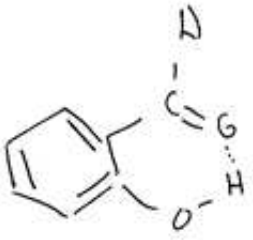

meso-compound cannot resolve

9. (10 pts) One of the three isomers of hydroxybenzaldehyde is much less soluble in water and has a lower boiling point than the other two. Identify this isomer and explain why it is "special".



less soluble
since we have
internal H bonding.

won't complex with $H_2O$ → low solubility

won't complex with itself → low boiling