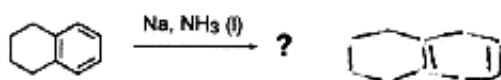
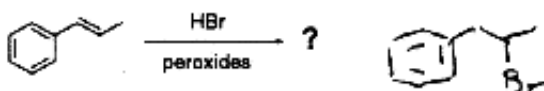


1. (20 points) Provide the missing reagents or products for the following reactions. Carefully show the stereochemistry of each product (if relevant) using wedges and dashes.

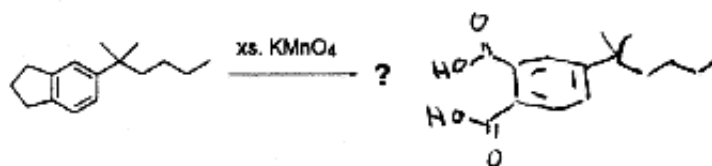
a.



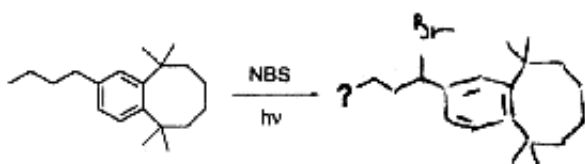
b.



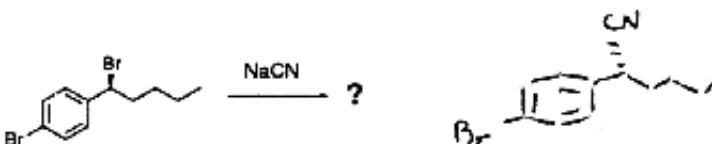
c.



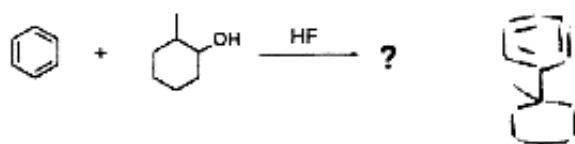
d.



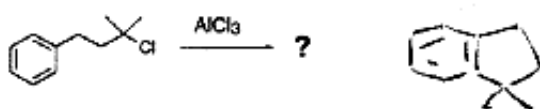
e.



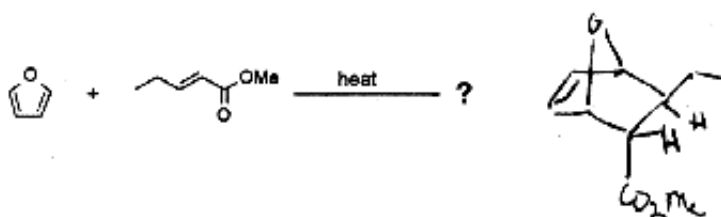
f.



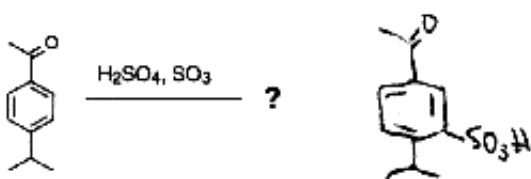
g.



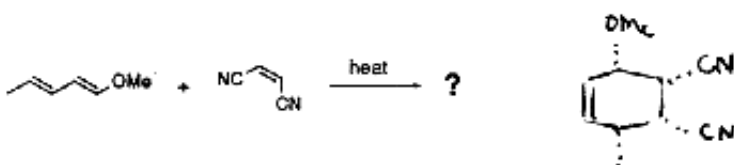
h.



i.

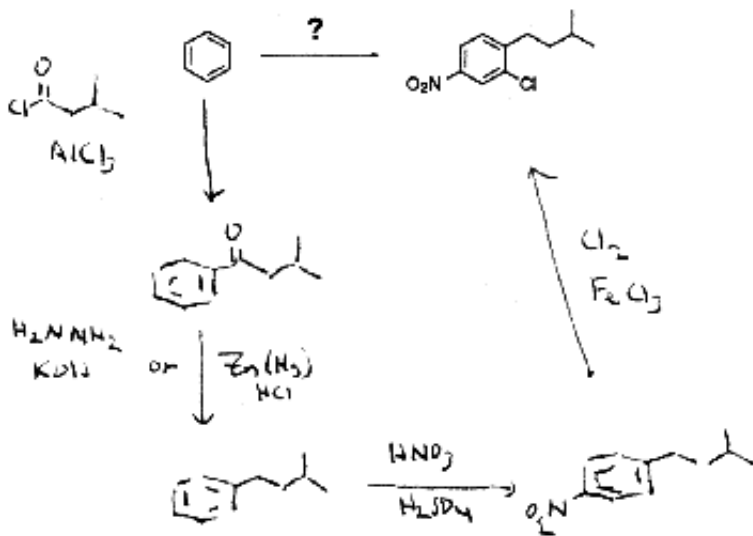


j.

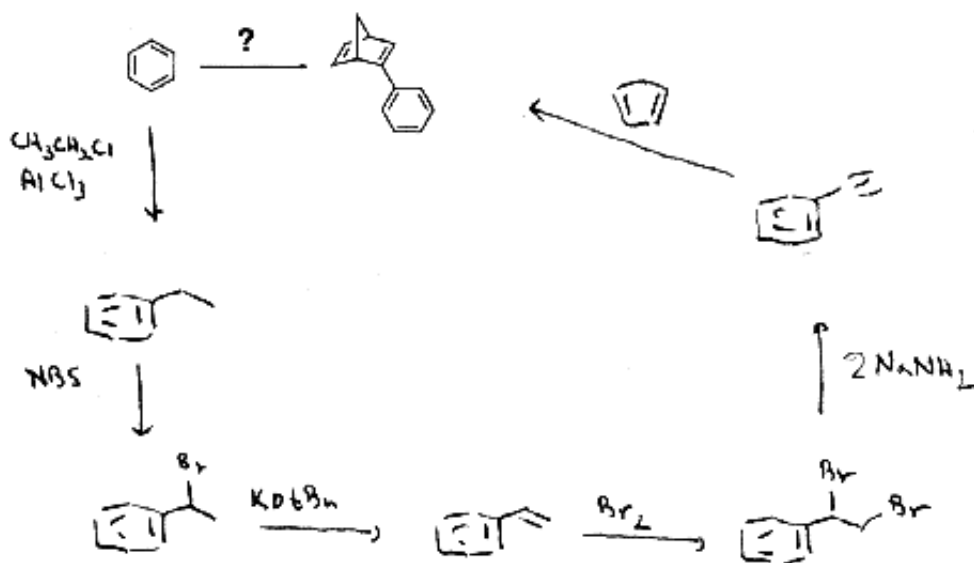


2. (30 points) Propose a synthesis of the target compounds starting with the substrate provided and any other chemical reagents. Several steps are required in each case. You do not have to show mechanisms for each of the individual steps, but do show the products formed from each of the reactions you perform.

A.

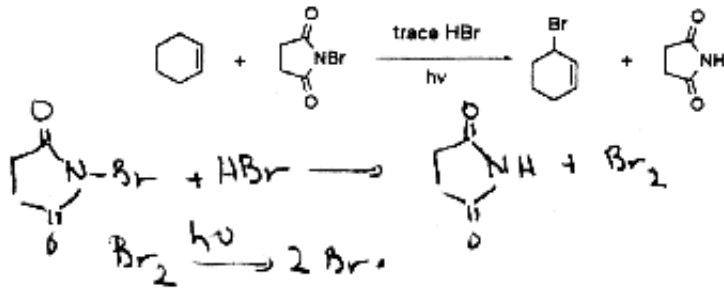


B.

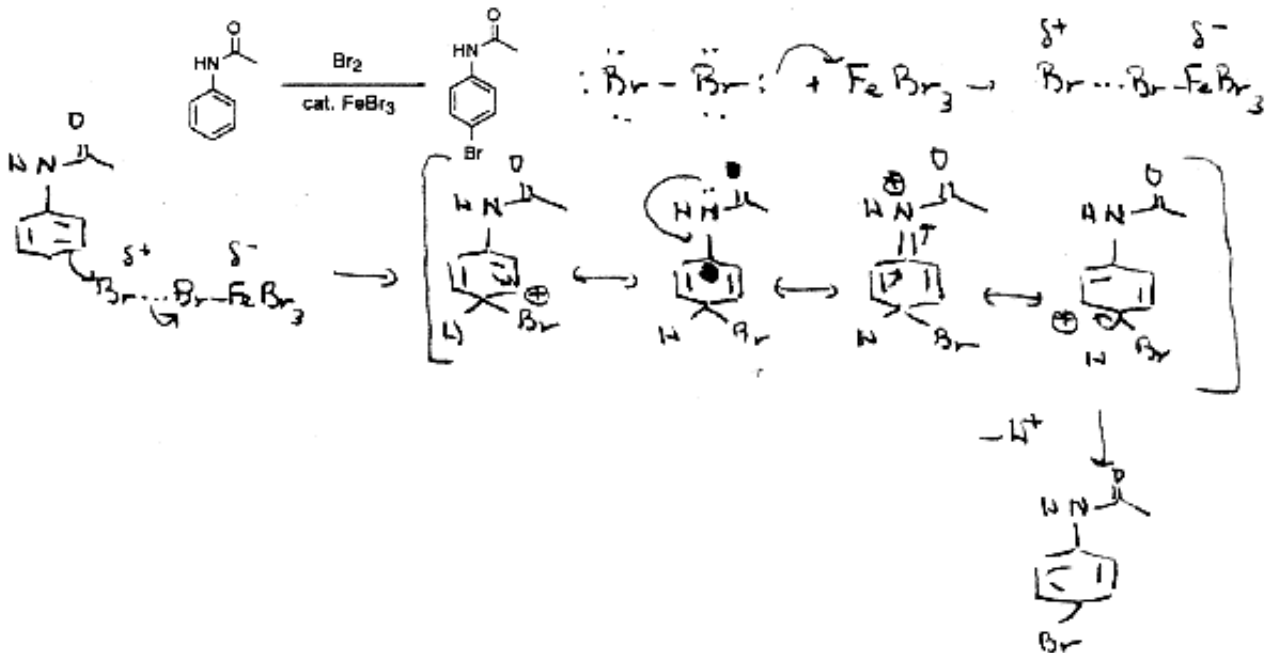


3. (30 points) Write out a detailed, stepwise mechanism for the following transformations. Draw all reasonable resonance structures for any intermediates along the reaction pathway.

a.

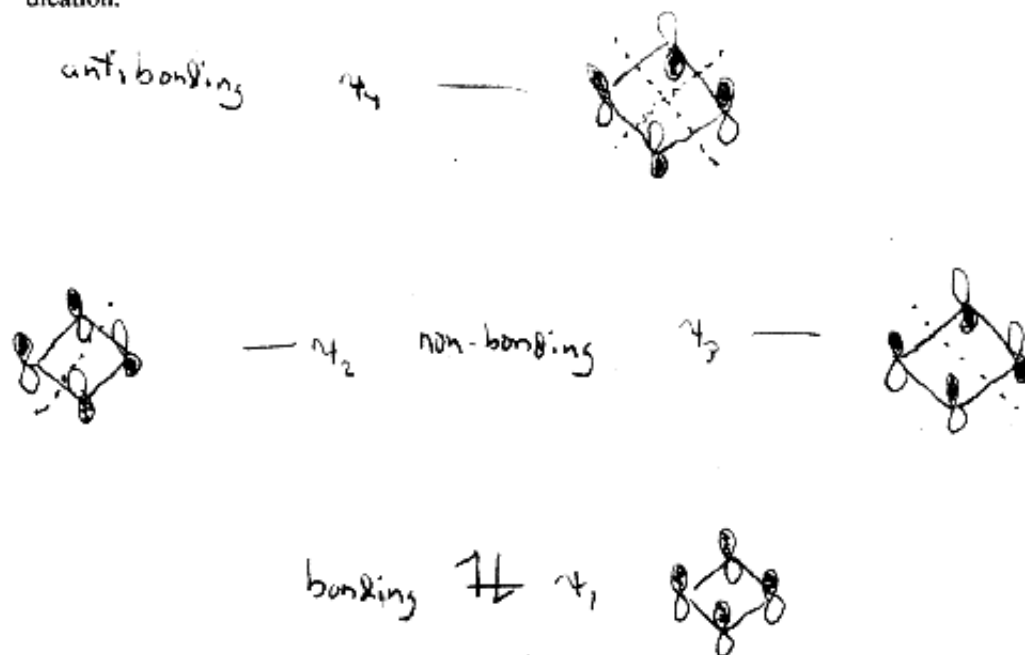


b.

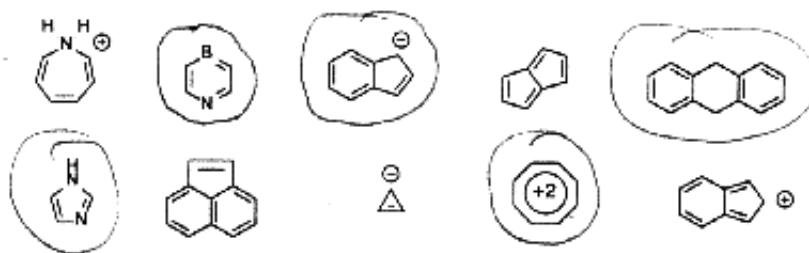


4. (20 points)

A. Draw the Hückel π molecular orbitals for the cyclobutadiene system and arrange them in order of increasing energy. Label the molecular orbitals as bonding, nonbonding, and antibonding as appropriate for their energy levels. Finally, on this diagram show the electron distribution for cyclobutadienyl dication.

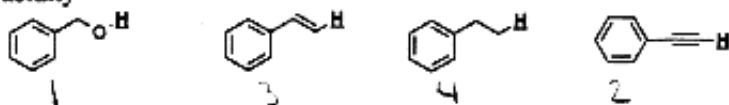


B. Circle the molecules that are aromatic according to Hückel's theory.

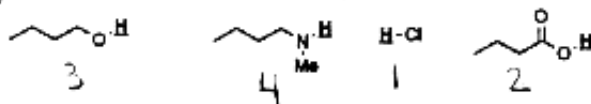


5. (25 points) Rank the following [1→4 (5), 1 = greatest or most] according to the indicated criteria.

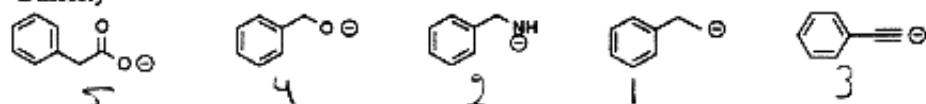
a. Proton acidity



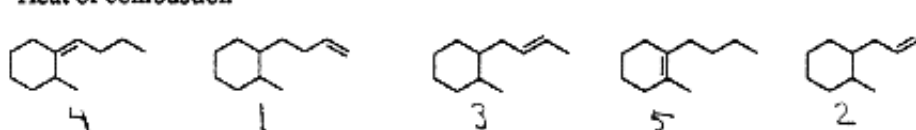
b. Proton acidity



c. Basicity



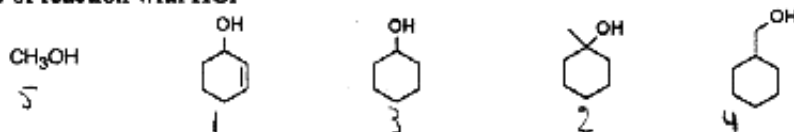
d. Heat of combustion



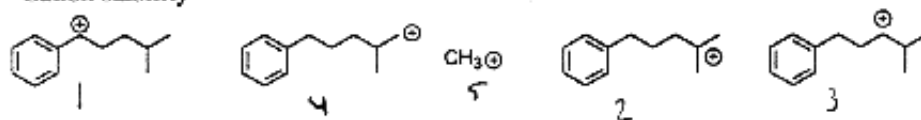
e. Rate of reaction with *tert*-butanol



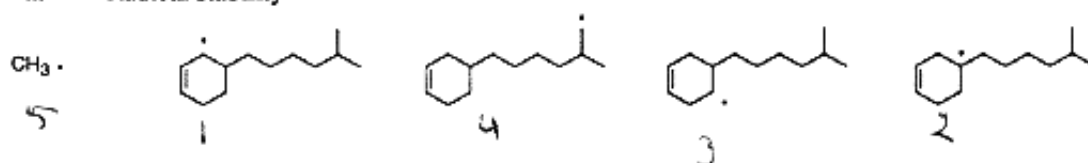
f. Rate of reaction with HCl



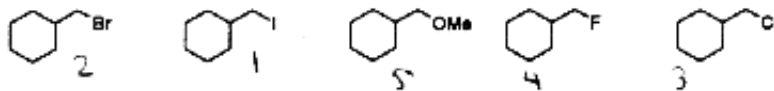
g. Cation stability



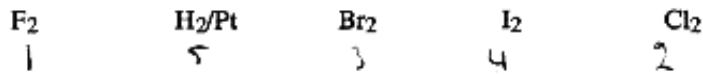
h. Radical stability



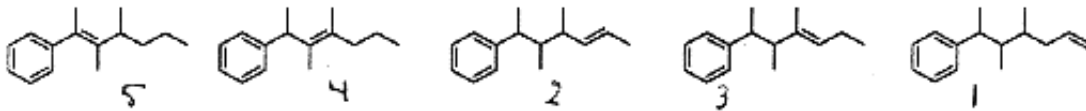
i. Rate of reaction with NaCN



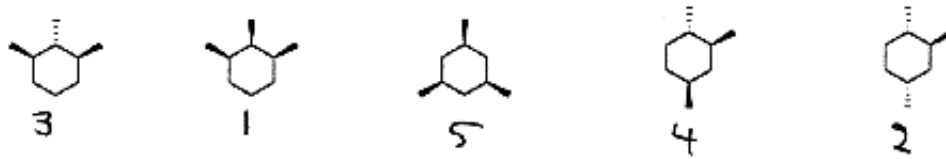
j. Rate of reaction with cyclohexene



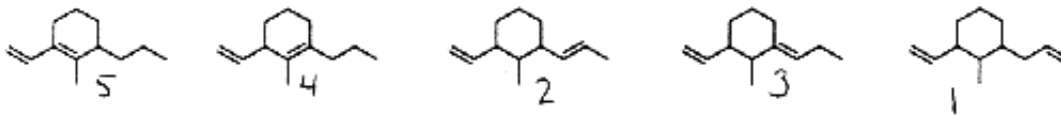
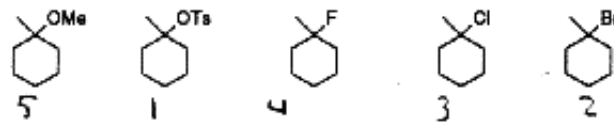
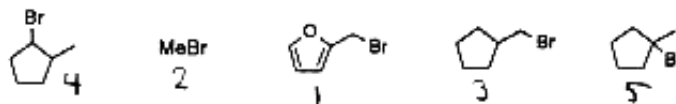
k. Heat of hydrogenation



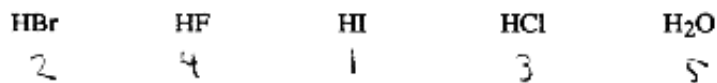
l. Heat of combustion



m. Heat of hydrogenation

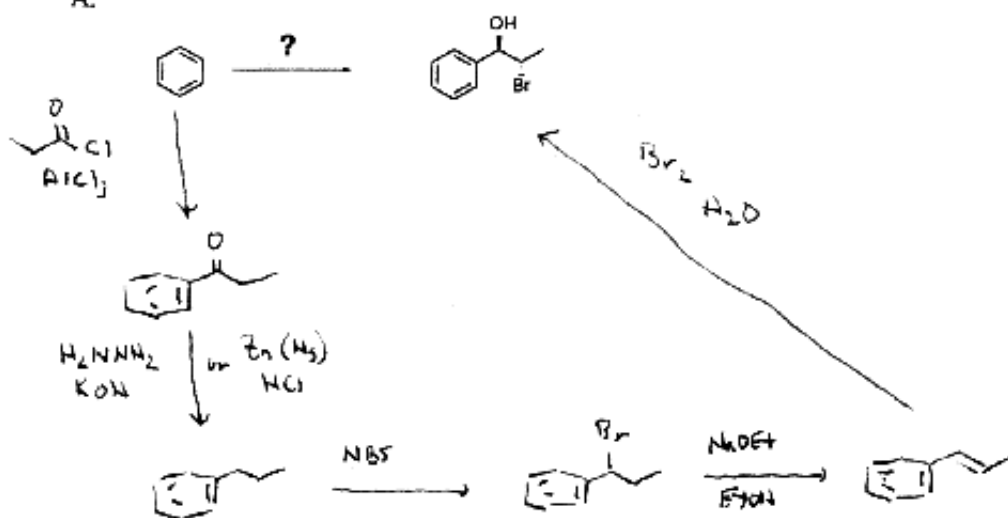
n. Rate of reaction with potassium *tert*-butoxideo. Rate of S_N2 reaction with sodium acetylide

p. Rate of reaction with cyclohexene

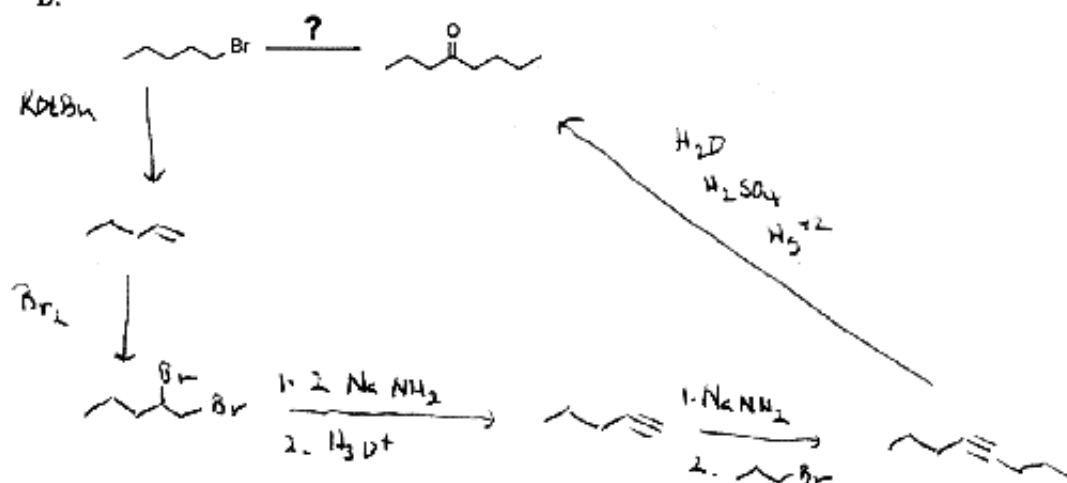


6. (20 points) Propose a synthesis of the target compounds starting with the substrate provided and any other chemical reagents. Several steps are required in each case. You do not have to show mechanisms for each of the individual steps, but do show the products formed from each of the reactions you perform.

A.

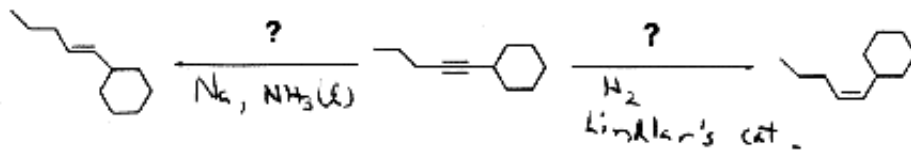


B.

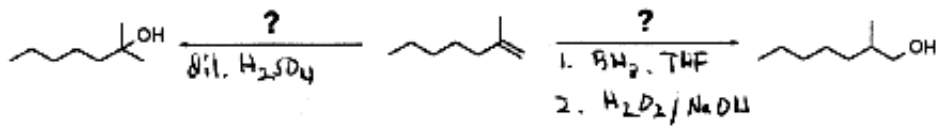


7. (25 points) Provide the missing reagents and reaction conditions where necessary for the following reactions.

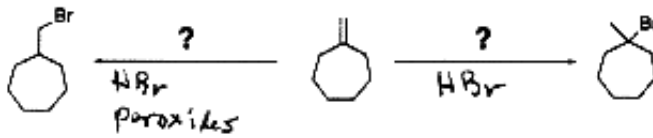
a.



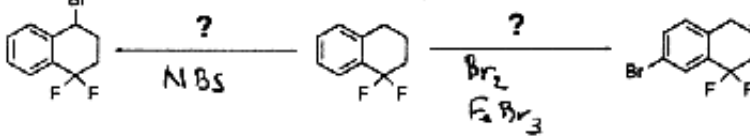
b.



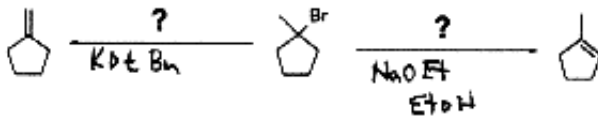
c.



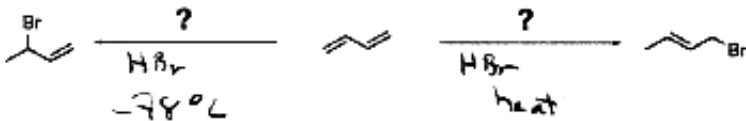
d.



e.

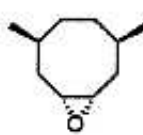

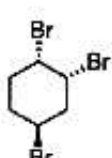
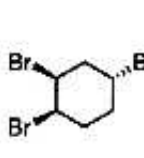
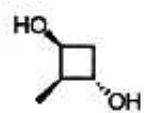
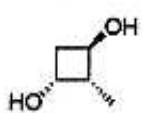
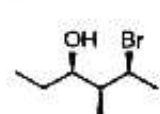
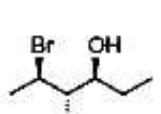


f.

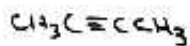
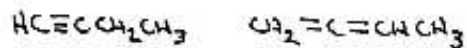


8. (30 points)

a. Label each of the following pairs of structures as homomers, enantiomers, diastereomers, or constitutional isomers, and indicate whether each compound is chiral or achiral using the check boxes.

<p style="text-align: center;"><i>Diastereomers</i></p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> $\begin{array}{c} \text{CHO} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ <input checked="" type="checkbox"/> Chiral <input type="checkbox"/> Achiral </div> <div style="text-align: center;"> $\begin{array}{c} \text{CHO} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{CH}_2\text{OH} \end{array}$ <input checked="" type="checkbox"/> Chiral <input type="checkbox"/> Achiral </div> </div>	<p style="text-align: center;"><i>Diastereomers</i></p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;">  <input type="checkbox"/> Chiral <input checked="" type="checkbox"/> Achiral </div> <div style="text-align: center;">  <input type="checkbox"/> Chiral <input checked="" type="checkbox"/> Achiral </div> </div>
<p style="text-align: center;"><i>Enantiomers</i></p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;">  <input checked="" type="checkbox"/> Chiral <input type="checkbox"/> Achiral </div> <div style="text-align: center;">  <input checked="" type="checkbox"/> Chiral <input type="checkbox"/> Achiral </div> </div>	<p style="text-align: center;"><i>Enantiomers</i></p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;">  <input checked="" type="checkbox"/> Chiral <input type="checkbox"/> Achiral </div> <div style="text-align: center;">  <input checked="" type="checkbox"/> Chiral <input type="checkbox"/> Achiral </div> </div>
<p style="text-align: center;"><i>Diastereomers</i></p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;">  <input checked="" type="checkbox"/> Chiral <input type="checkbox"/> Achiral </div> <div style="text-align: center;">  <input checked="" type="checkbox"/> Chiral <input type="checkbox"/> Achiral </div> </div>	<p style="text-align: center;"><i>Constitutional isomers</i></p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> $\begin{array}{c} \text{H} & & \text{Me} \\ & \backslash & / \\ & \text{C} = \text{C} = \text{C} \\ & / & \backslash \\ \text{Me} & & \text{H} \end{array}$ <input checked="" type="checkbox"/> Chiral <input type="checkbox"/> Achiral </div> <div style="text-align: center;"> $\begin{array}{c} \text{Me} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} = \text{C} \\ & / & \backslash \\ \text{Me} & & \text{H} \end{array}$ <input type="checkbox"/> Chiral <input checked="" type="checkbox"/> Achiral </div> </div>

b. Draw all of the isomers of C_4H_6 .



-11-

