

Name: \_\_\_\_\_

1. (20 points) Draw the Lewis dot structure (including resonance structures where appropriate) for the following organic species. You may use a line for each bonding pair of electrons, but make certain to include lone pairs and any formal charges. Indicate the orbital hybridization on each of the non-hydrogen atoms.

A. Benzylic cation,  $C_7H_7^+$

B. Acetylide ion,  $C_2H^-$

C. Isopropyl cyanide,  $C_4H_7N$

2. (60 points) Multiple Choice: Circle the **best** possible answer.

- A. Cyclopentadiene is unusually acidic for a hydrocarbon. Why?
- a) Cyclopentadiene is aromatic.
  - b) The conjugate base of cyclopentadiene is aromatic.
  - c) The double bonds in cyclopentadiene can accept  $H^+$ .
  - d) Cyclopentadiene is an unstable diradical.

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B. What is the value of  $n$  from Huckel's rule for the 18-annulene shown below?

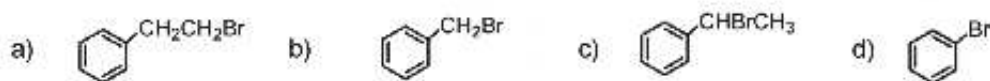


- a)  $n = 3$                       b)  $n = 4$                       c)  $n = 5$                       d)  $n = 9$

C. Compound X,  $C_8H_{10}$ , forms benzoic acid when reacted with potassium dichromate in sulfuric acid.  
Compound X is:

- a) *p*-xylene                      b) propylbenzene                      c) ethylbenzene                      d) styrene

D. Which one of the following bromides reacts fastest in  $S_N1$  hydrolysis in aqueous acetone?



E. Identify the most stable carbocation.

- a)  $CH_3CH_2-\overset{+}{C}=CH_2$   
b)  $H_2C=CH-\overset{+}{CH_2}CH_3$   
c)  $CH_3CH=\overset{+}{CH}-CH_3$   
d)  $CH_3\overset{+}{C}HCH_2CH_3$

F. An alkyne which gives only one organic product on ozonolysis followed by hydrolysis is

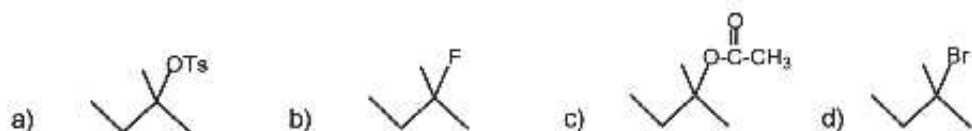
- a) 2-hexyne                      b) 2-heptyne                      c) 3-hexyne                      d) 3-heptyne

G. Which one of the following compounds has the highest heat of combustion per mole of substance?

- a) 2-Methylpropene                      b) 1-Butene  
c) *trans*-2-Butene                      d) *cis*-2-Butene

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H. Which one of the following undergoes  $S_N1$  solvolysis in ethanol/water at the fastest rate?



I. Identify the strongest base.



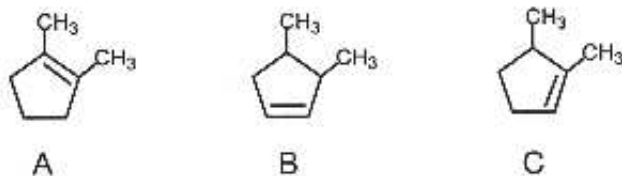
J. Identify the major organic product expected from the acid-catalyzed dehydration of 2-methyl-2-pentanol?

- a) 2-Methyl-1-pentene      b) 2-Methyl-2-pentene  
c) 3-Methyl-1-pentene      d) *Cis*-3-methyl-2-pentene

K. Predict which one of the following alkenes reacts the fastest with HCl.

- a) 1-Hexene  
b) *Cis*-3-hexene  
c) *Trans*-3-hexene  
d) 2-Methyl-2-pentene

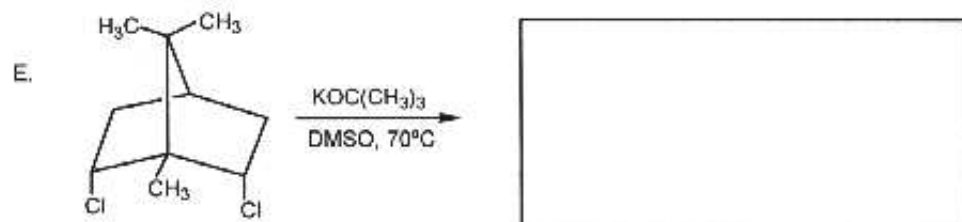
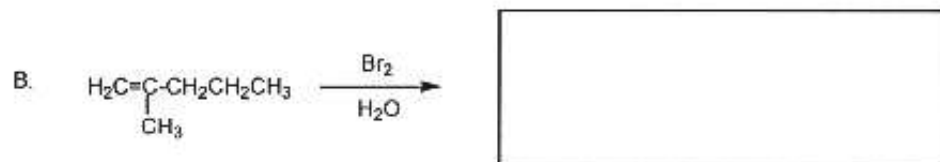
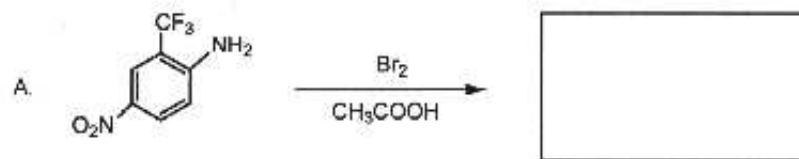
L. Rank the following alkenes in order of decreasing reactivity with  $Br_2$  in  $CCl_4$ .

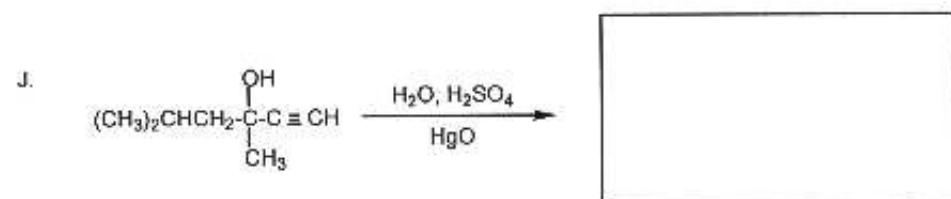
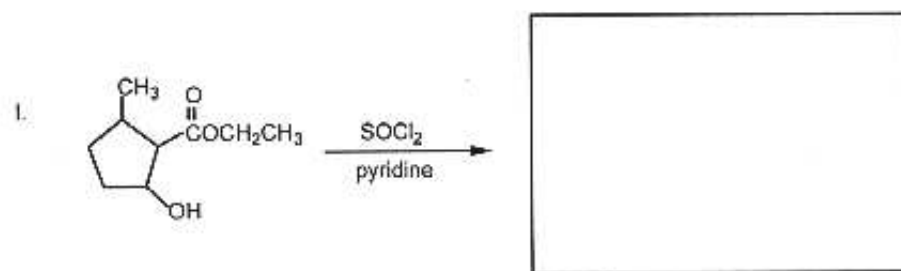
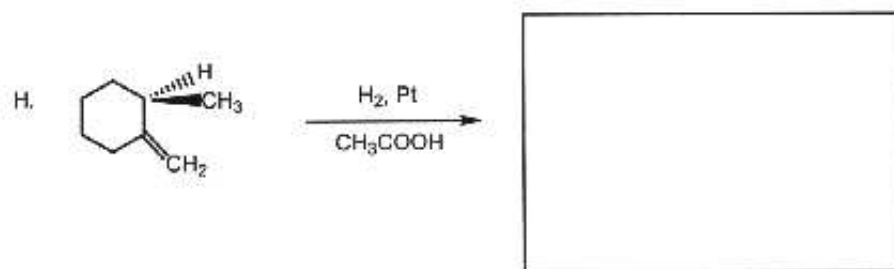
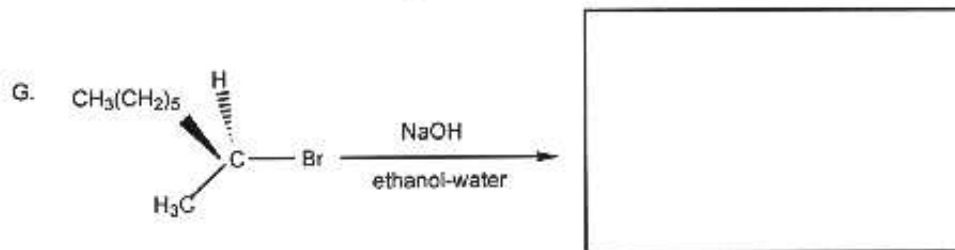
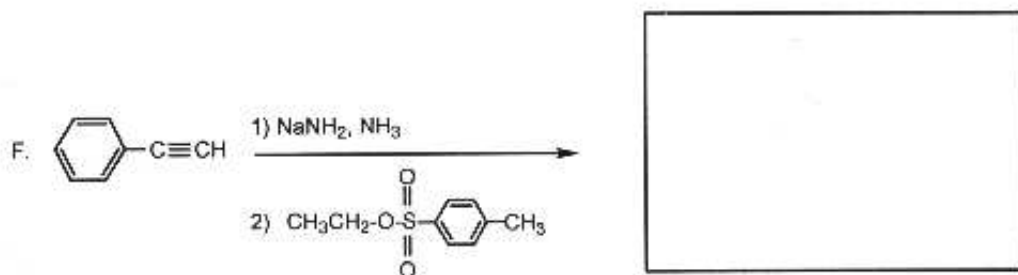


- a)  $A > B > C$   
b)  $B > A > C$   
c)  $C > A > B$   
d)  $A > C > B$

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3. (33 points) Provide the missing reagents or products for the following reactions. Carefully show the stereochemistry of each product (if relevant) using wedges and dashes. If a mixture of products is produced, indicate the major and minor products.

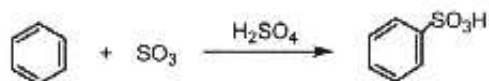




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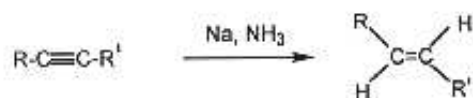
4. (27 points) Write out a detailed, stepwise mechanism for the following transformations. Draw all reasonable resonance structures for any intermediates along the reaction pathway. Please write each step in the boxes provided (the number of boxes may or may not correspond to the number of steps).

A.



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- B. Write out a detailed, stepwise mechanism for the following transformation. Draw all reasonable resonance structures for any intermediates along the reaction pathway. Please write each step in the boxes provided (the number of boxes may or may not correspond to the number of steps).



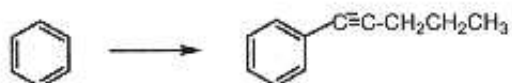
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5. (30 points) Show that the Diels-Alder reaction between 1,3-butadiene and ethylene is a symmetry-allowed cycloaddition reaction. Draw the  $\pi$  molecular orbitals of (i) 1, 3-butadiene and (ii) ethylene, and label them as bonding or antibonding orbitals. Select the appropriate frontier orbitals (HOMO and LUMO) involved in sigma bond formation, and label your diagrams very clearly for the orbital interaction leading to sigma bond formation. Either use color (or some other code) to designate the signs of p orbital wave functions or use plus (+) and minus (-) signs. Using two sentences or less, explain clearly which frontier orbitals of the diene and the dienophile are involved in sigma bond formation, as well as the details of orbital overlap (how do the orbitals overlap?) and direction of electron flow (from ? to ?).

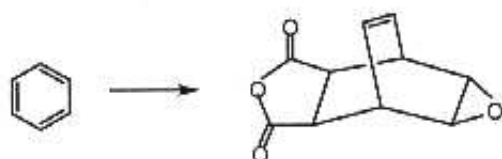
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6. (30 points) Propose a synthesis of the target compounds starting with the substrate provided and any other chemical reagents. Several steps are required in each case. You do not have to show mechanisms for each of the individual steps, but do show the products formed from each of the reactions you perform.

(A)



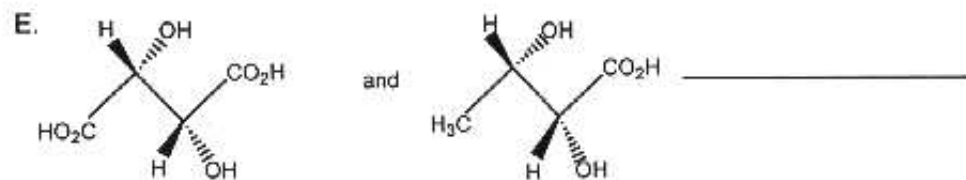
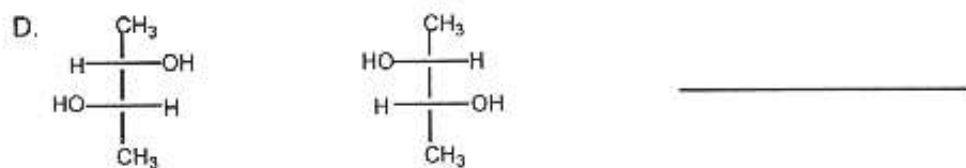
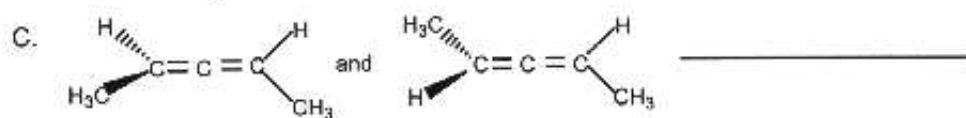
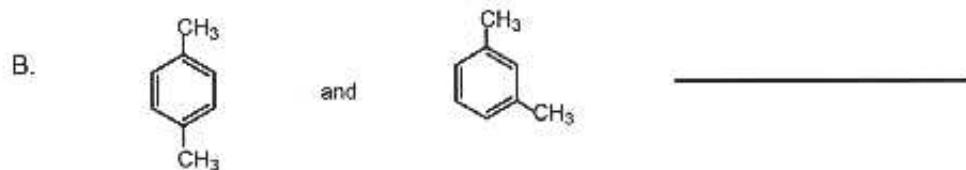
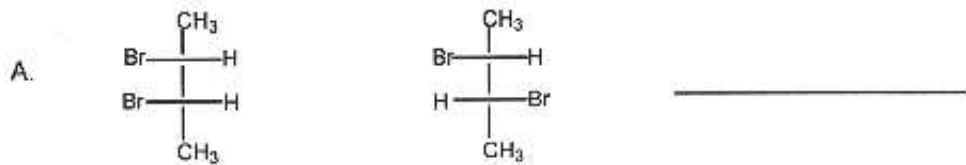
(B)





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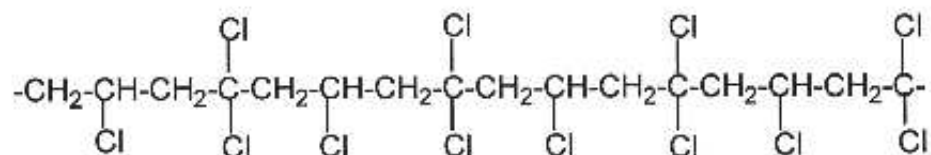
7. (25 points) Label the following pairs of structures as one of the following:  
identical, constitutional isomers, not related, enantiomers, or diastereomers.



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8. (25 points) Answer the following:

(A) The structure of a segment of an **addition polymer** (copolymers are possible, and arise from two different monomers) is shown below:



Briefly outline your reasoning in identifying the monomer(s).

The IUPAC name(s) of the monomer(s) is(are):

- (B) *Cis*-2-methylcyclohexyl tosylate when treated with KOt-Bu in DMSO gives 1-methylcyclohexene (59%) and 3-methylcyclohexene (41%). *Trans*-2-methylcyclohexyl tosylate, under identical reaction conditions, gives 3-methylcyclohexene (100%). Using appropriate structures, explain why:
- the *trans*-isomer gives only one product, and
  - the *cis*-isomer forms 1-methylcyclohexene as the major product.