

Answers to the Final Exam  
CHM 333 December 12, 2008

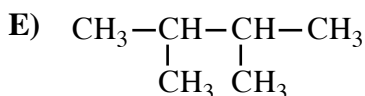
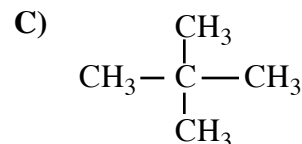
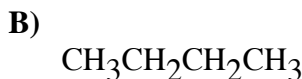
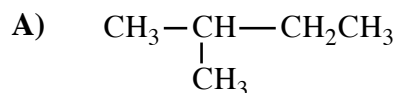
Print Name \_\_\_\_\_

Sign Name \_\_\_\_\_

Student I.D. # \_\_\_\_\_

1. (60 pts) Multiple choice/fill in the blanks. Put your answer in the space provided.

D a) Which of the following has the greatest Van der Waal's interaction between molecules of the same kind?



C b) Ethyne ( $\text{H}-\equiv-\text{H}$ ) does not show IR absorption in the region 2000-2500  $\text{cm}^{-1}$  because:

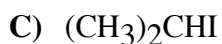
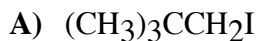
A) C-H stretches occur at lower energies.

B) CC stretches occur at about 1640  $\text{cm}^{-1}$ .

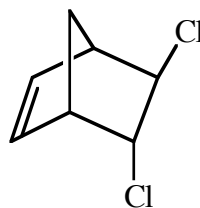
C) There is no change in the dipole moment when the CC bond in ethyne stretches.

D) There is a change in the dipole moment when the CC bond in ethyne stretches.

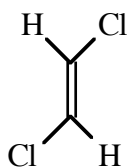
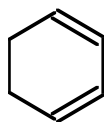
E c) Which of the following compounds will undergo an  $\text{S}_{\text{N}}2$  reaction most readily?



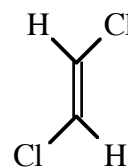
D d) What diene and what dienophile would be used to synthesize the following compound?



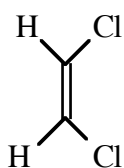
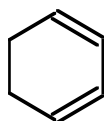
A)



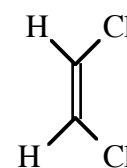
D)



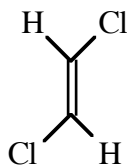
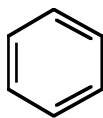
B)



E)



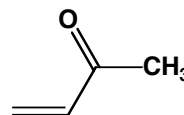
C)



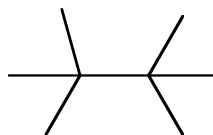
C e) Which compound would be expected to show intense IR absorption at 2710 and 1705  $\text{cm}^{-1}$ ?



D)



A f) How many distinct monochlorinated products, including stereoisomers, can result when the alkane below is heated in the presence of  $\text{Cl}_2$ ?



A) 1

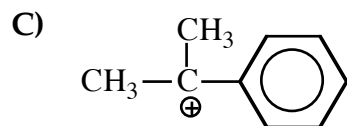
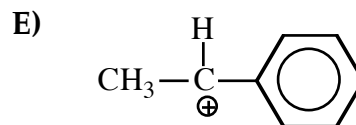
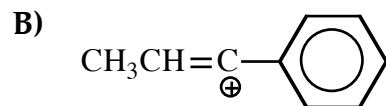
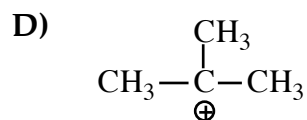
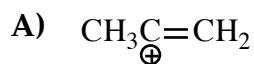
B) 2

C) 3

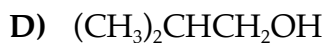
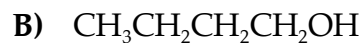
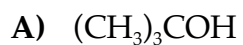
D) 4

E) 5

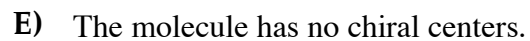
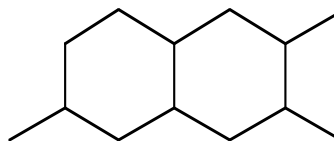
C g) Which of the following is the most stable cation?



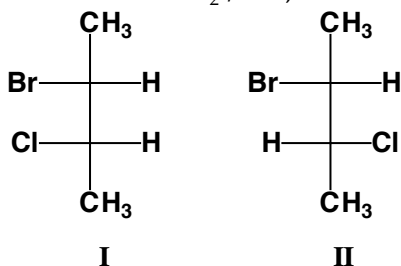
A h) Which of the following alcohols will react most rapidly with the Lucas reagent (HCl,  $\text{ZnCl}_2$ )?



D i) How many chiral centers are in this molecule?

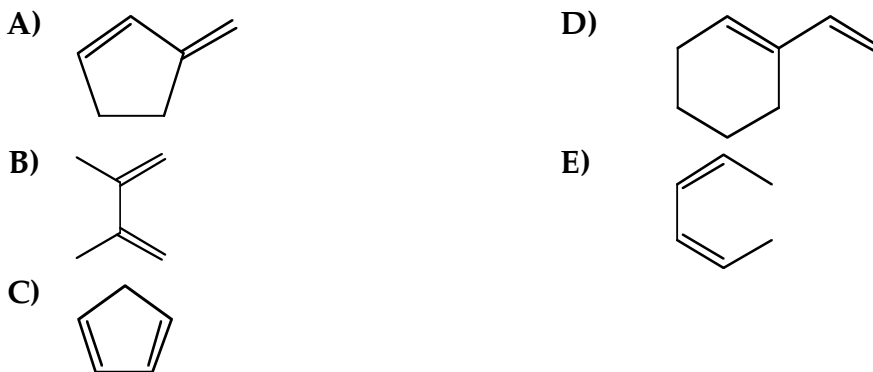


D j) When (R)-2-bromobutane reacts with  $\text{Cl}_2 / h\nu$ , which of the following is true?

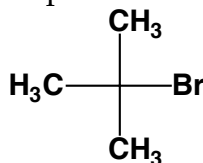


- A) Only I is formed                      B) Only II is formed.  
C) I and II are formed in equal amounts.                      D) I and II are formed in unequal amounts.  
E) I and II could never form under these conditions

C k) Which of the following dienes is the most reactive in a Diels-Alder reaction?

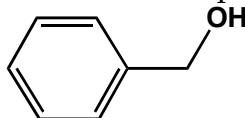


D l) Which of the following is the base peak for the compound below?



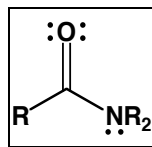
- A) 77                      B) 92  
C) 15                      D) 57  
E) 43

C m) Which of the following m/z values is the base peak for benzyl alcohol?



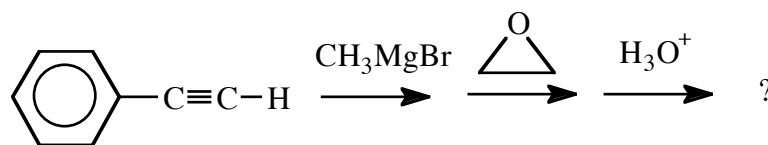
- A) 77                      B) 108  
C) 91                      D) 17  
E) 52

B n) What are the approximate bond angles about the nitrogen atom in an amide?



- A) 180°
- B) 120°
- C) 109°
- D) 90°

D o) What is the product of the following reaction sequence?

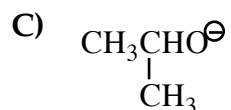
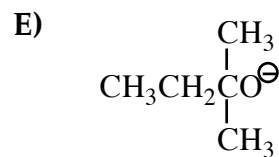
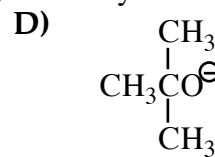


- A)
- B)
- C)
- D)
- E)

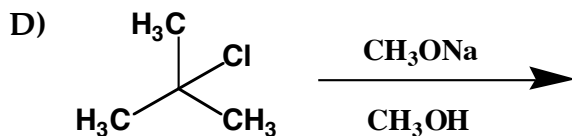
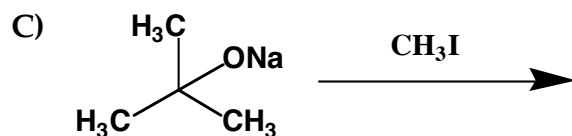
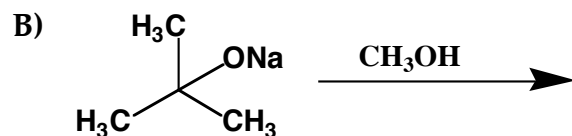
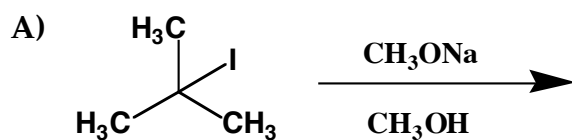
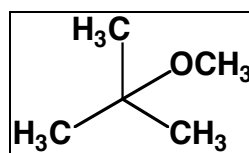
A p) An acylium ion is often produced as a fragment in the MS of which of the following class of organic compounds?

- A) Ketones
- B) Ethers
- C) Alkyl Halides
- D) Alcohols
- E) Peroxides

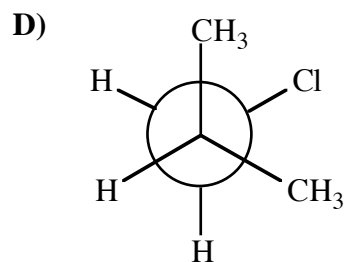
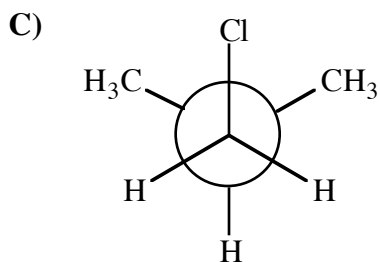
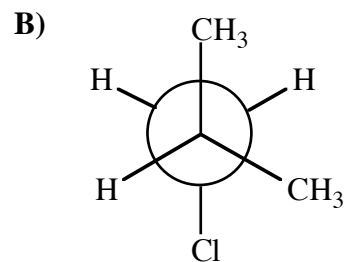
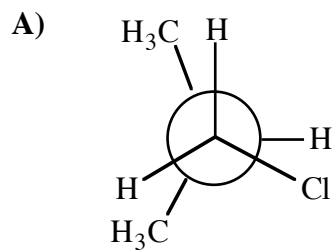
E q) Which of the following nucleophiles gives the highest anti-Zaitsev (Hofmann) product in E2 reactions when reacted with 2-bromo-2,3-dimethylbutane?



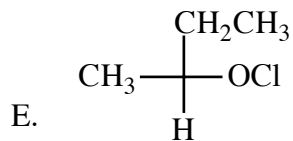
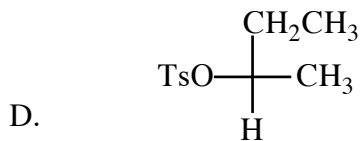
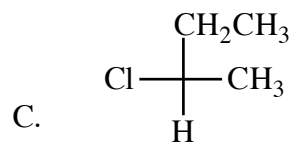
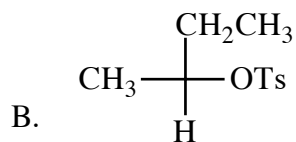
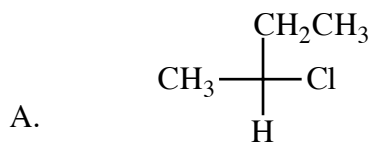
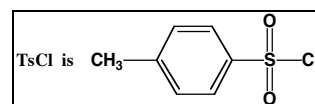
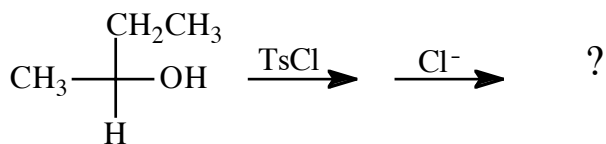
C r) Which reaction provides the highest yield of this ether?



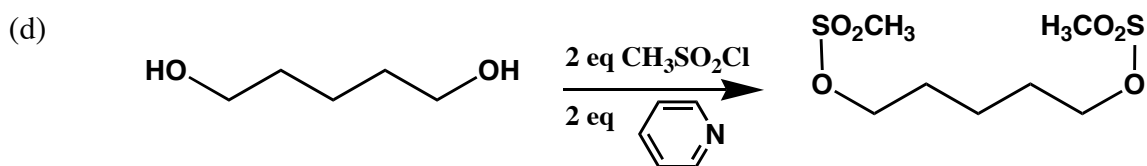
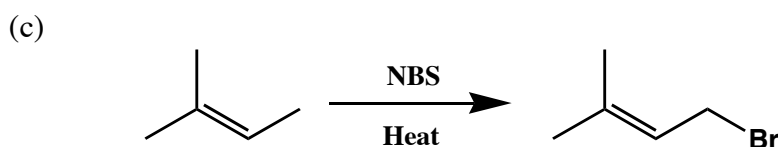
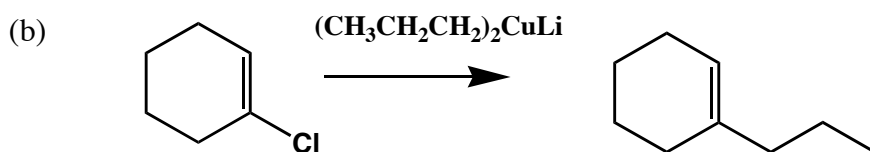
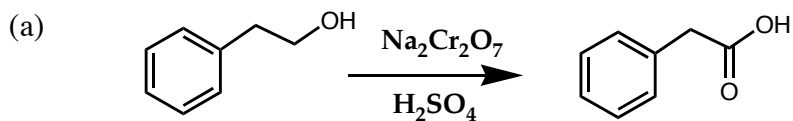
**B** s) Which of the following conformers of isobutyl chloride is the most stable?



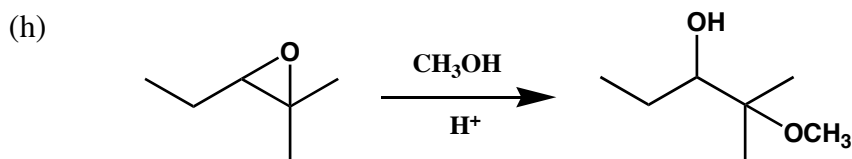
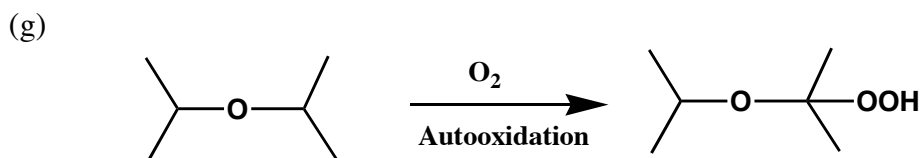
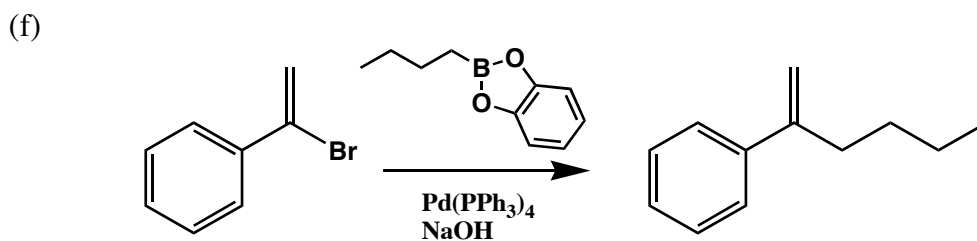
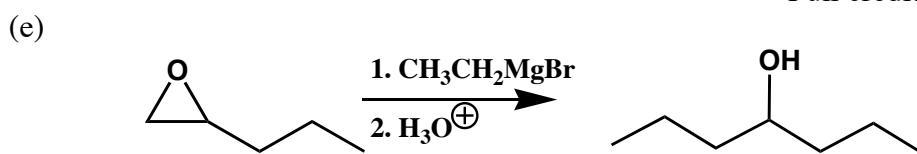
**C** t) What is the product of the following reaction?

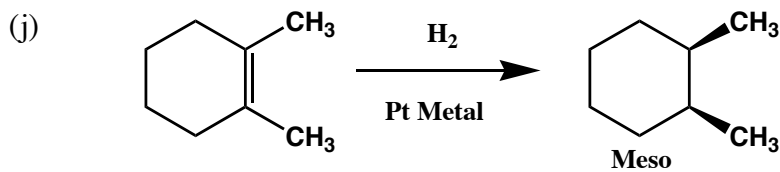
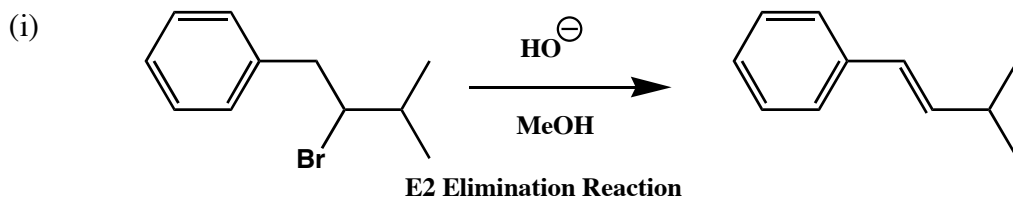


2. (50 pts.) For each of the following reactions state the principle product. If there is no reaction, state NR. Specify stereochemistry where appropriate.

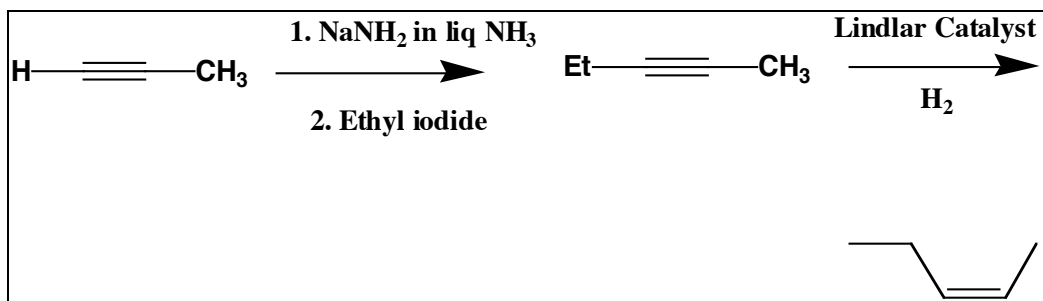
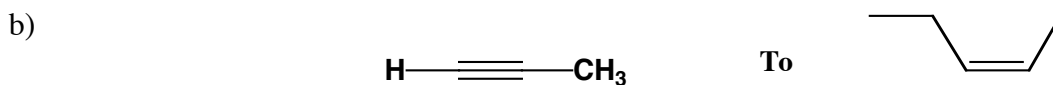
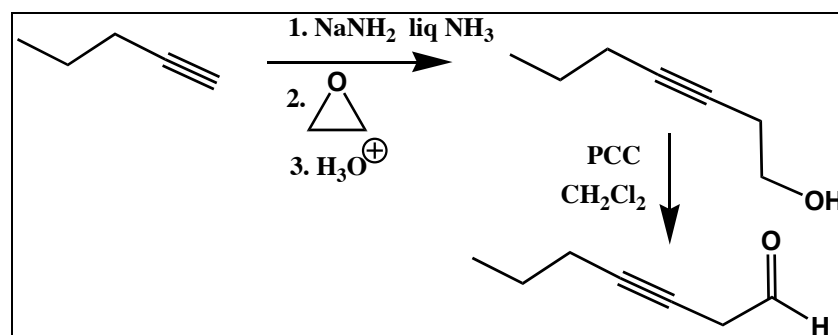
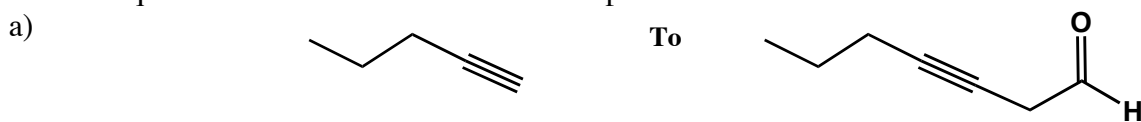


Full credit for dichloro

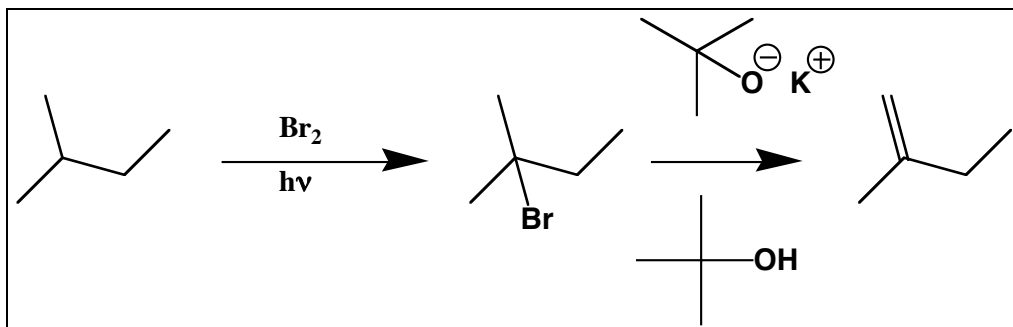
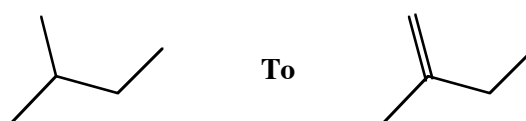




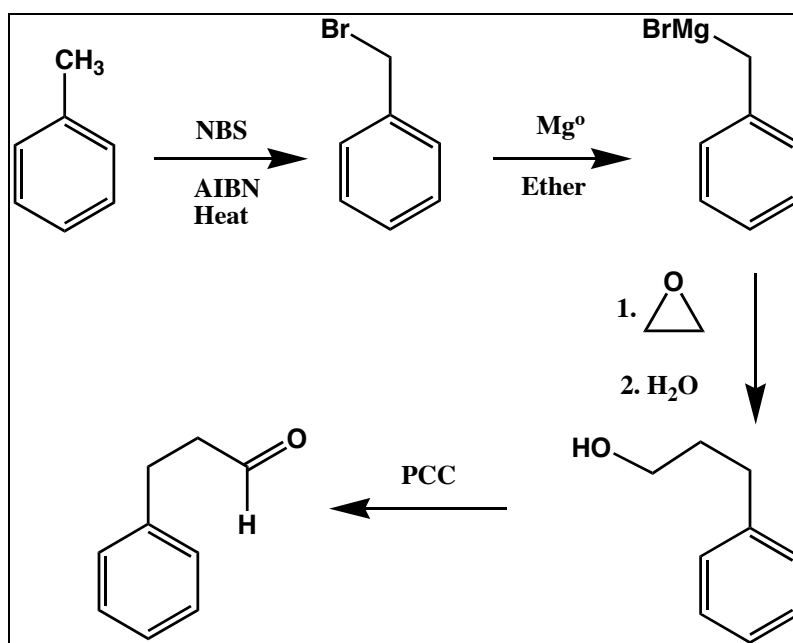
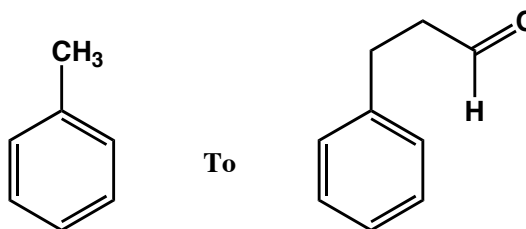
3. (40 pts.) For each of the following starting materials, provide a short, high yield synthetic sequence that would afford the desired product.



c)

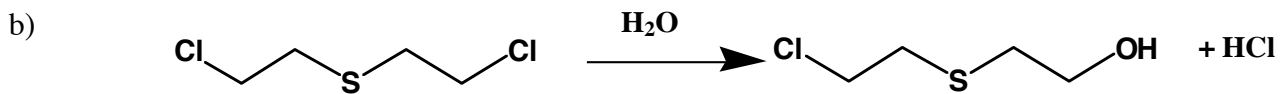
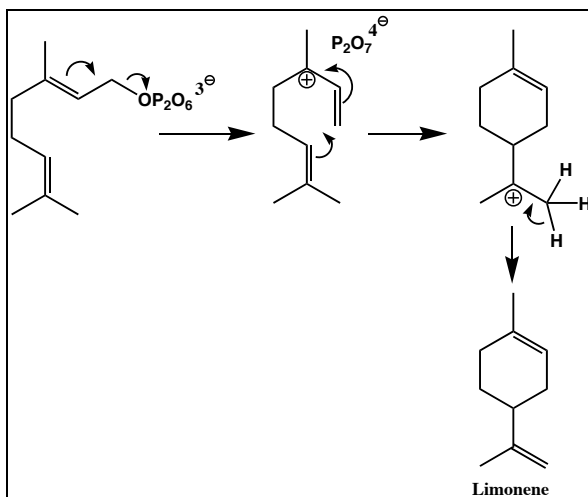
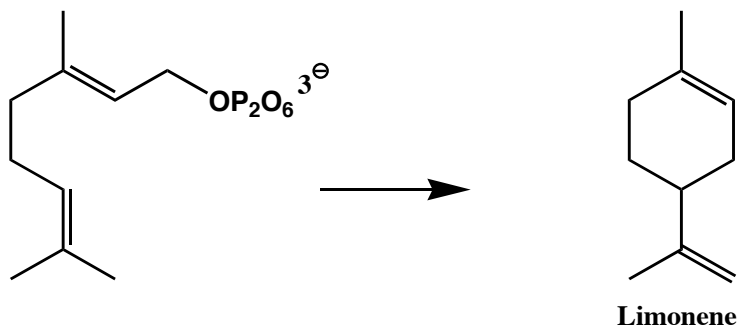


d)

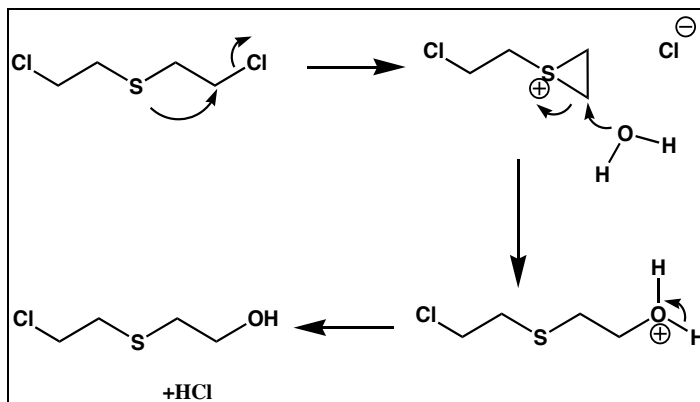


4. (40 pts.) Provide a mechanism for the following conversions using curved arrows to show electron movement.

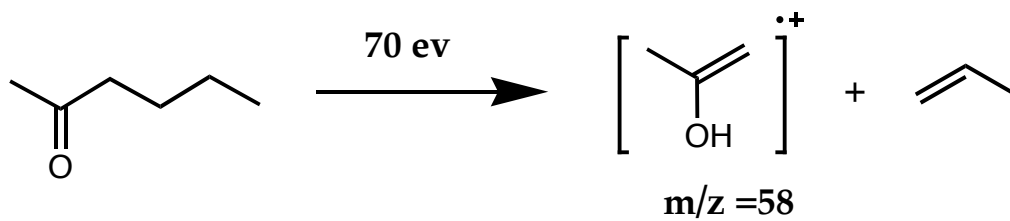
- a) Hydroxyl groups are activated as leaving groups in nature when functionalized as pyrophosphates. Geranyl pyrophosphate is converted to limonene via elimination of pyrophosphate to afford a carbocation that is eventually converted to limonene. Show a mechanism.



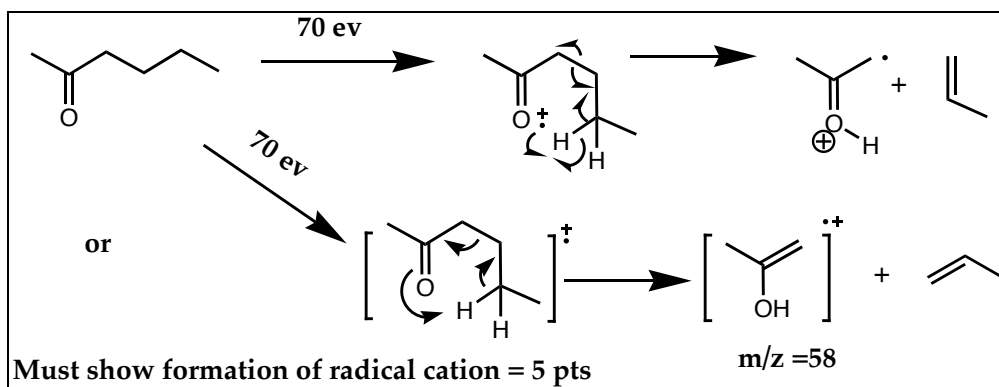
Be sure to account for the role of sulfur in the hydrolysis mechanism.



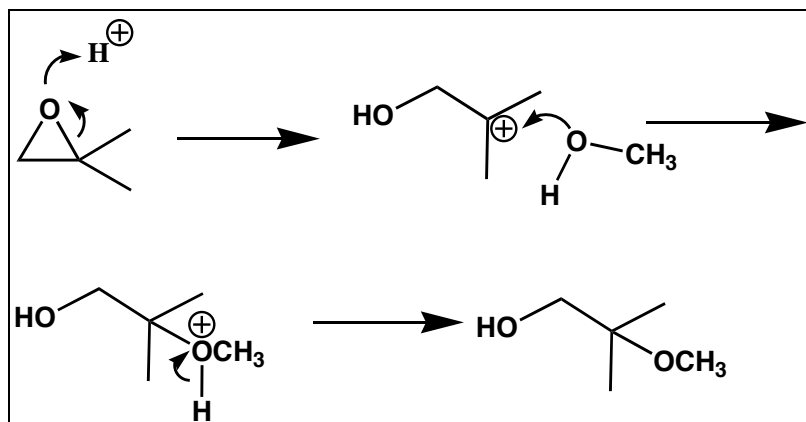
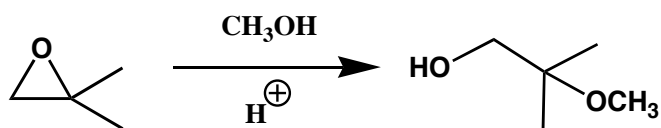
c)



Account for both fragments arising from the ketone.

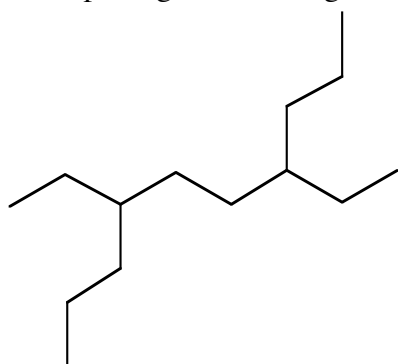


d)



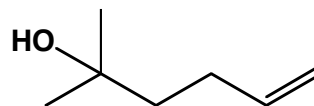
5. (45 pts.) Provide a systematic or common name for each of the following structures. Do not forget to use R, S, E, Z, cis, trans etc. where necessary. Points will be deducted for misspellings, numbering errors, wrong chain, etc.

(a)



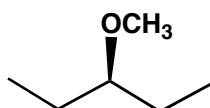
**4,7-Diethyldecane**

(b)



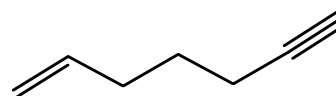
**2-Methylhex-5-en-2-ol**

(c)



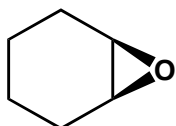
**3-Methoxypentane**

(d)



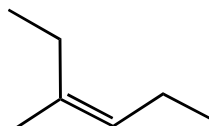
**Hept-1-en-6-yne**

(e)



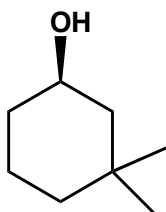
**Cyclohexene Oxide or epoxycyclohexane**

(f)



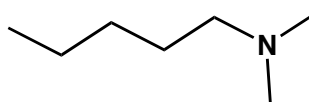
**(Z)-3-Methylhex-3-ene**

(g)



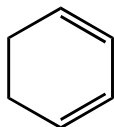
**R-3, 3-Dimethylcyclohexanol**

(h)



**N, N-Dimethyl-1-pentanamine**

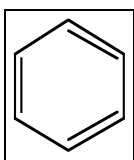
(i)



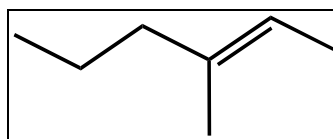
**1,3-Cyclohexadiene**

6. (40 pts) Show the structure corresponding to each of the compound names provided below. Merely showing a molecular formula is not acceptable.

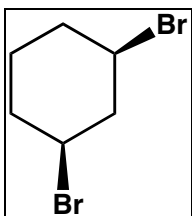
a. Benzene



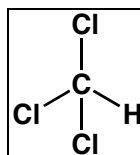
b. E)-3-Methylhex-2-ene



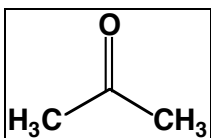
c. Meso-1, 3-Dibromocyclohexane



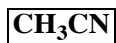
d. Chloroform



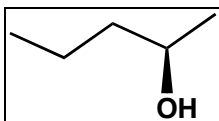
e. Acetone



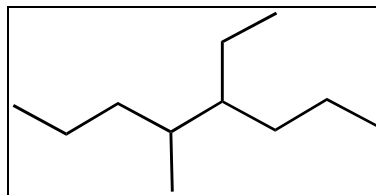
f. Acetonitrile



g. (S)-2-pentanol

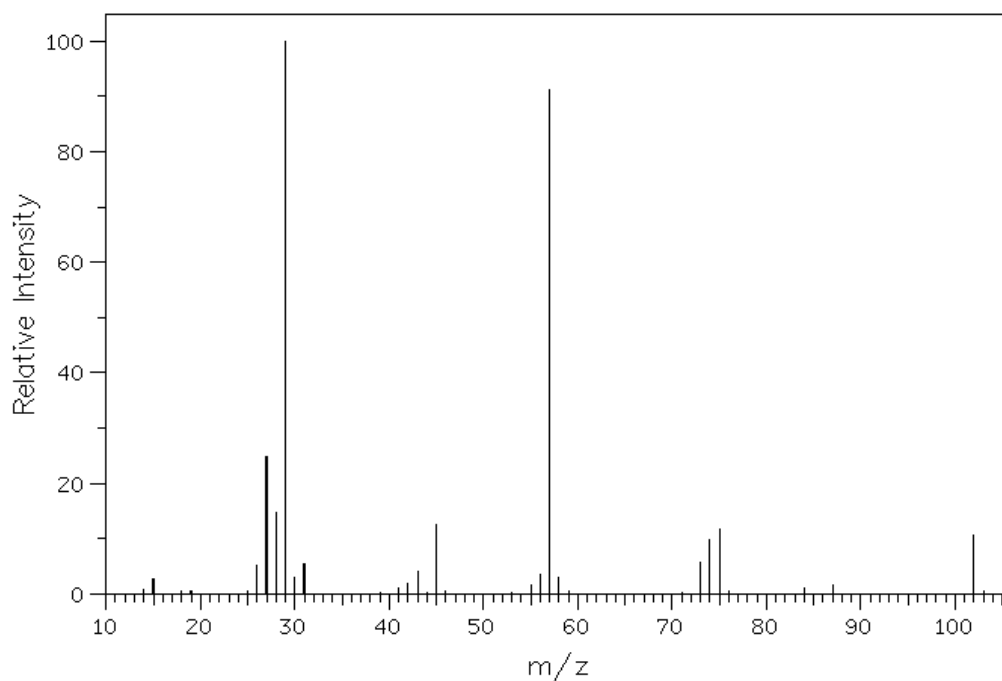
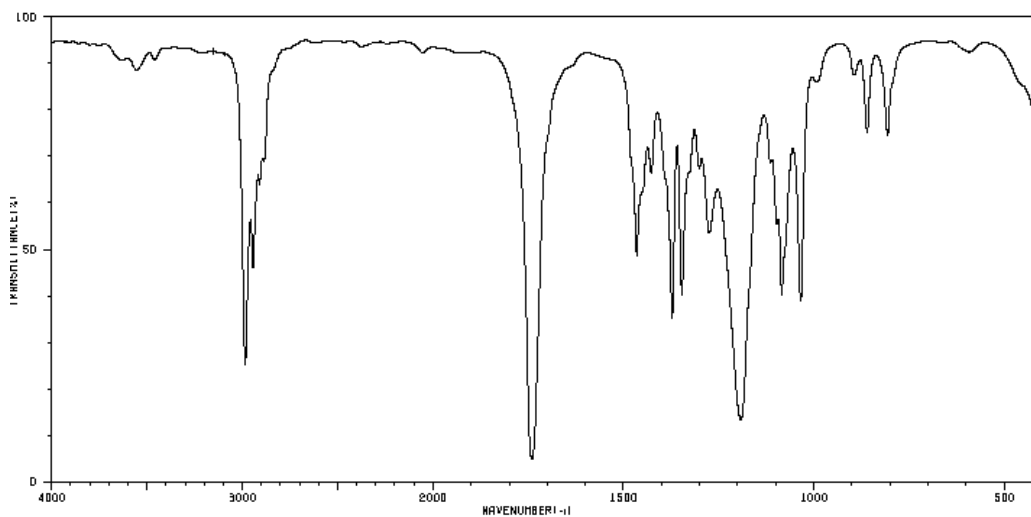


h. 4-Ethyl-5-methyloctane

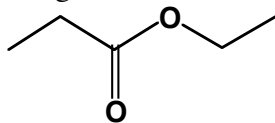


7. (20 pts) Provide the structures of the following compounds using the IR and mass spectra provided. Assign peaks that were important in making your structural assignment.

a)

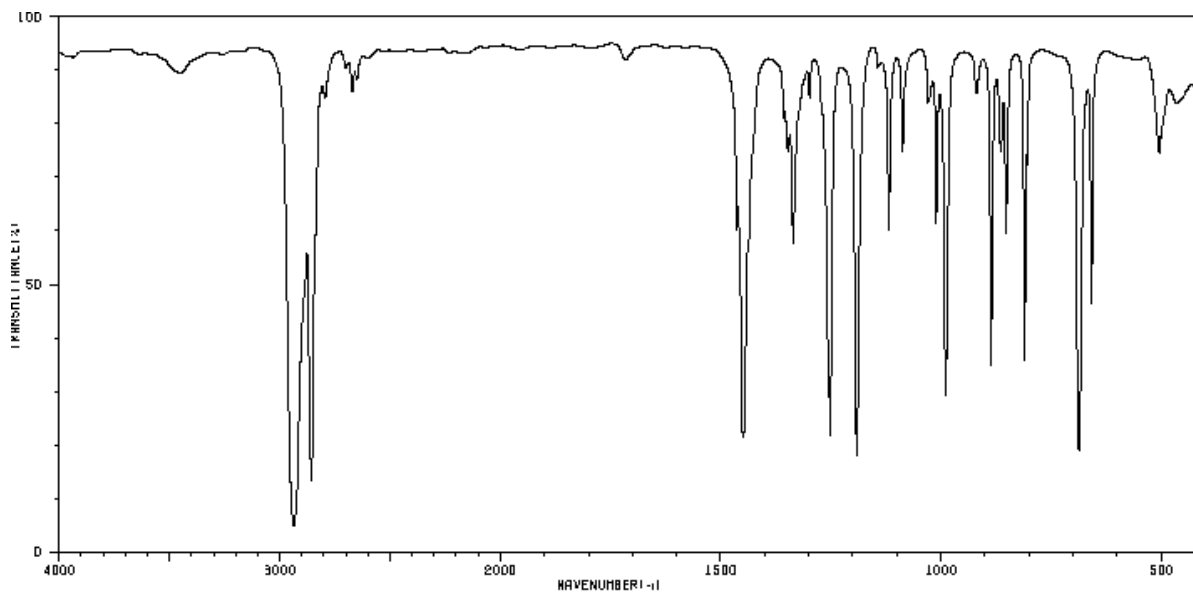
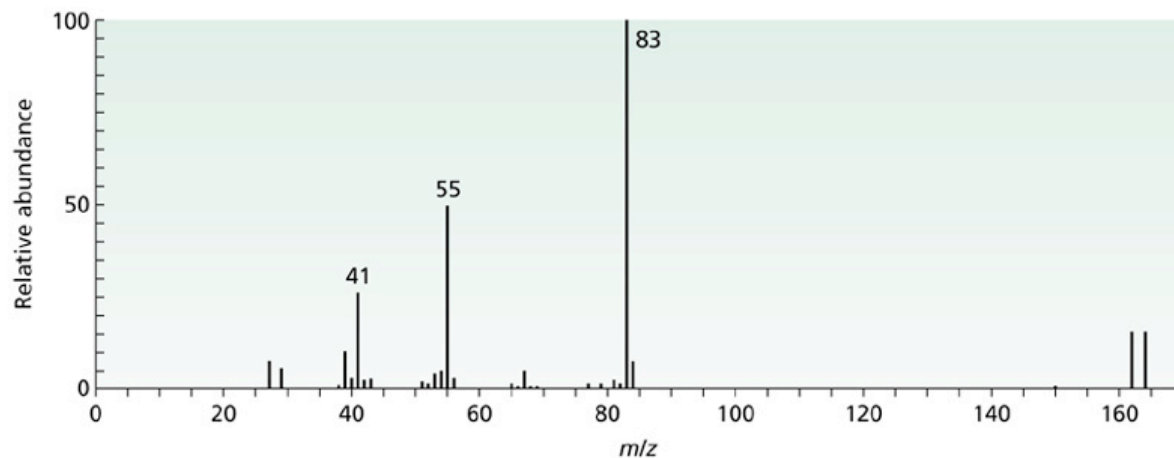


Assigned structure and peak assignments

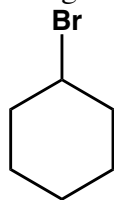


- IR shows a carbonyl and the MS clearly shows an ethyl at  $m/z$  29. These groups account for  $m/z$  57, leaving  $m/z$  45 to be accounted for.
- The IR also shows a strong band at  $1200\text{ cm}^{-1}$  for a CO stretch. Together with the carbonyl indicate the presence of an ester.
- Subtracting the mass of oxygen from  $m/z$  45 leaves  $m/z$  29, an ethyl group.
- The MS also shows  $m/z$  57, the ethyl acylium ion.

b)

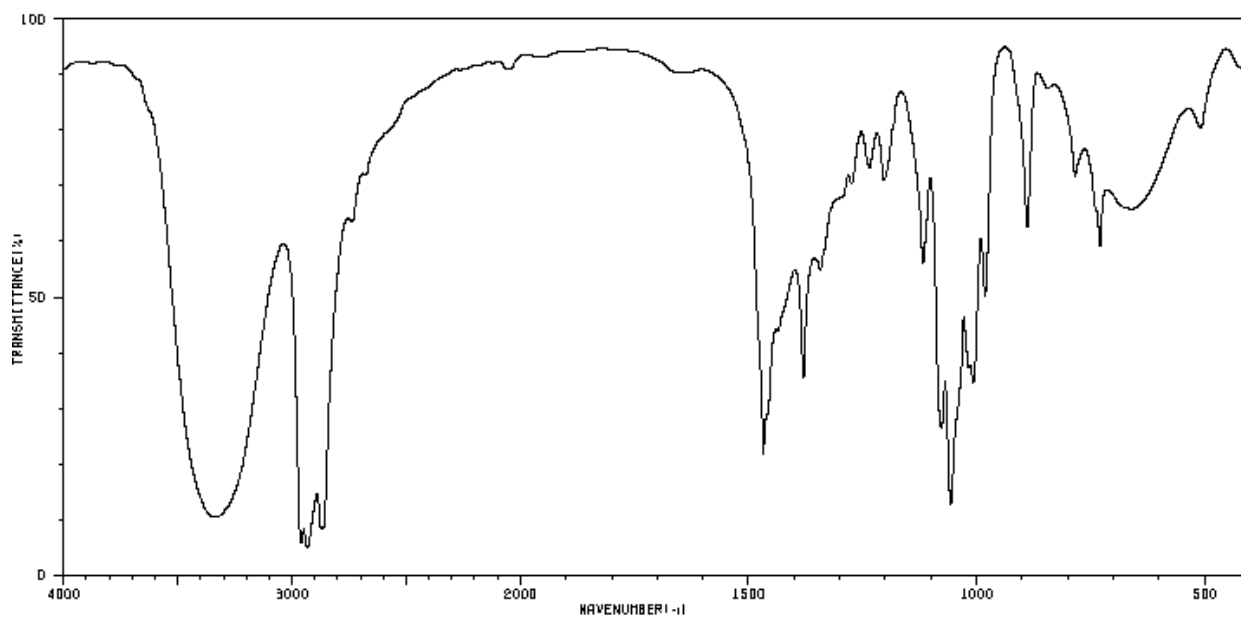


#### Assigned structure and peak assignments

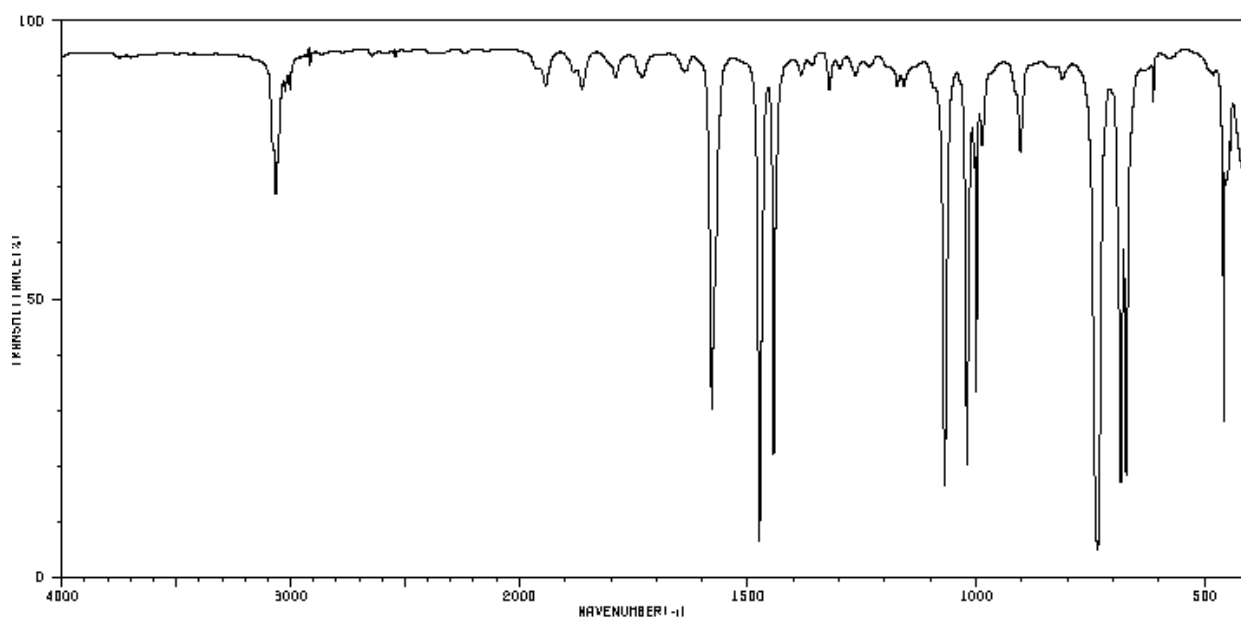


- Compound contains bromine, note  $M^+$  and  $M^+ + 2$  peaks with equal intensities.
- IR shows an alkane with no functional groups.
- No methyl and ethyl fragments, therefore not an alkyl chain.
- The loss of Br affords an  $m/z = 83$  base peak.
- A 6 – carbon chain would have  $m/z = 85$ , must have either a ring or an alkene if  $m/z = 83$ .
- The  $m/z = 83$  base peak is the cyclohexyl carbocation.

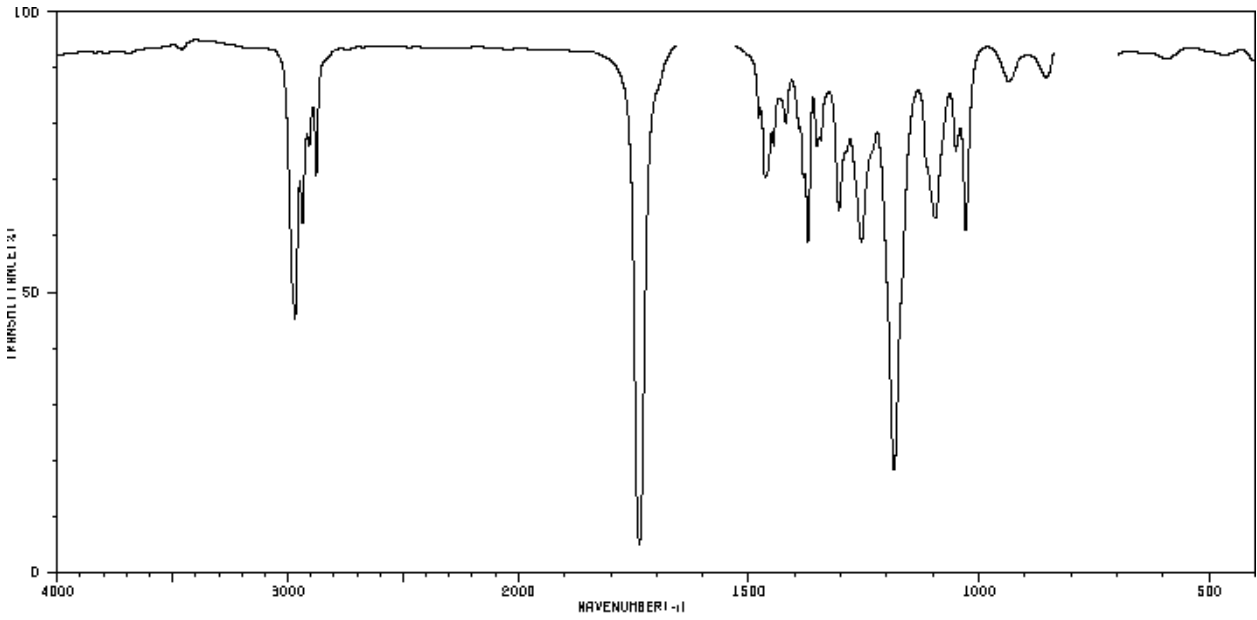
8. (20 pts) Match the following four IR spectra with the selection of compounds on the following page.



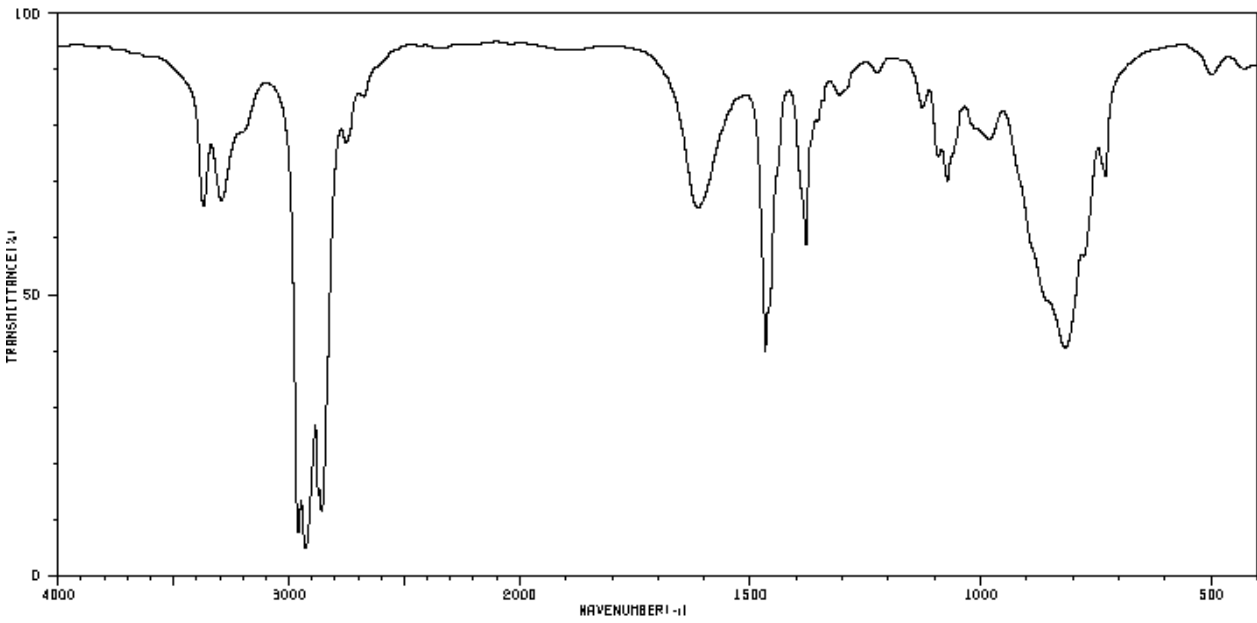
a.   A  



b.   F

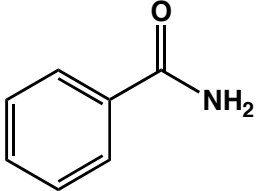
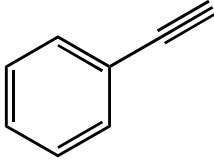
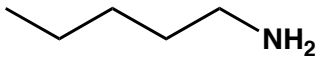
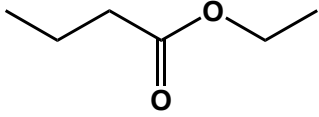
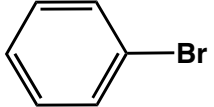


c.  D



d.  B

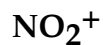
Your choices:

A. None of the above	C. 	E. 
B. 	D. 	F. 

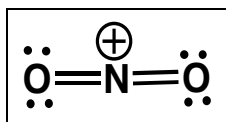
9. (45 pts) Repeat In-Class Exam questions. The score on these questions will be used to decide border-line cases (within 25 pts/1000 pts from the next higher grade).

Write a Lewis structure for each of the following compounds. You may use lines for bonds but please show all lone pairs and charges if any.

a)

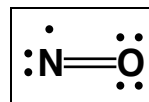


Subtract one electron for the positive charge



b)

NO, a signaling molecule in mammals

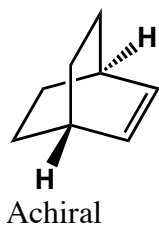


- c) Draw *trans*-1-ethyl-2-methylcyclohexane in its lowest energy chair conformation.

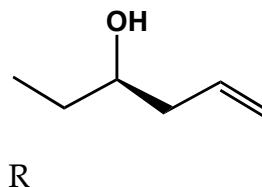


For each stereocenter in the compounds below designate as either R or S. If there are no stereocenters write achiral

d)

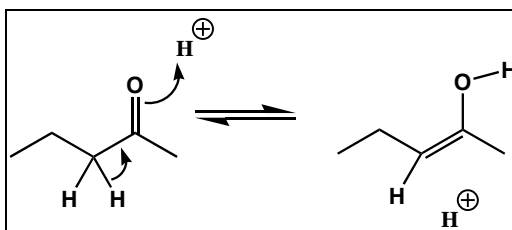


e)

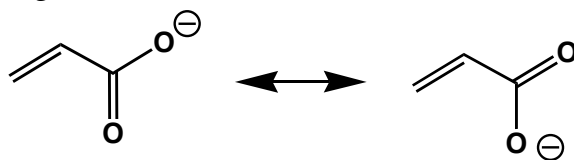


Show the curved arrows on the first structure that results in the corresponding reaction product:

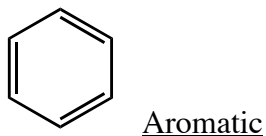
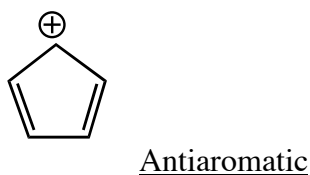
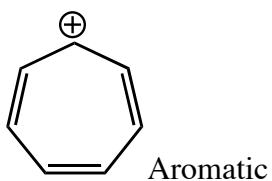
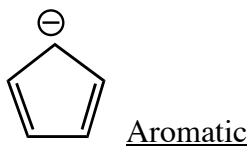
f)



- g) Show all charge delocalization structures for the following charged species. Include all degenerate structures

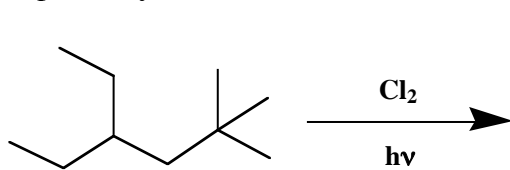


- h) Classify each of the following compounds as aromatic or antiaromatic using the Hückel rule. Assume all compounds are flat.



10. (40 pts) Answer the following questions.

- a) (15 pts) Predict all the possible monochlorination products of the alkane shown below. Which product is formed in the highest yield? Use the reactivity ratios of 1: 3.8 : 5.4 for 1° : 2° : 3° respectively.



2 pts for each structure and 5 pts for the major product.

A,  $1 \times 6 = 6$

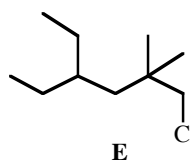
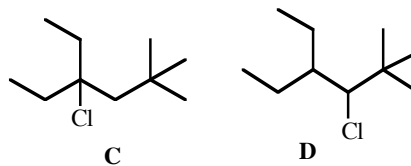
B,  $4 \times 3.8 = 15.2$

C,  $1 \times 5.4 = 5.4$

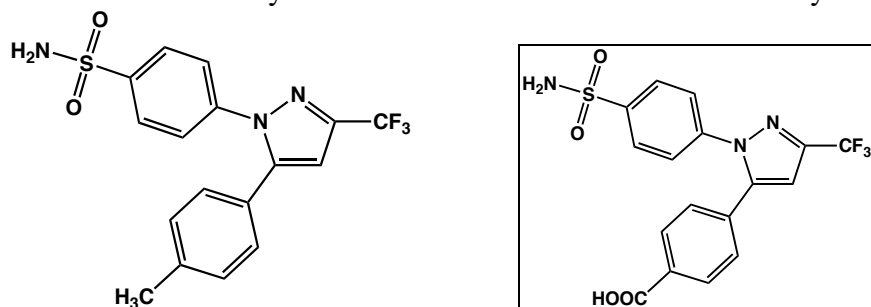
D,  $2 \times 3.8 = 7.6$

E,  $9 \times 1 = 9$

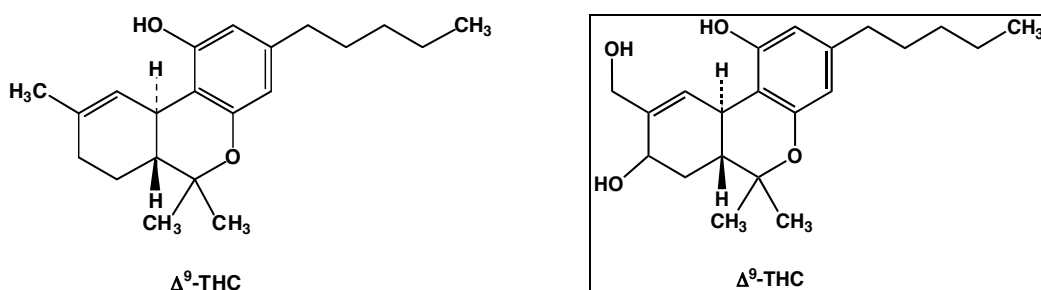
B is the major product



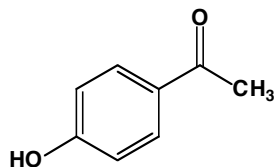
b) (5 pts) The COX-2 inhibitor Celebrex shown below is hydroxylated by a P<sub>450</sub> enzyme and then oxidized to a carboxylic acid. Show the structure of the carboxylic acid.



c) (5 pts) The active constituent of marijuana shown below undergoes allylic hydroxylation at two positions upon P<sub>450</sub> metabolism. Show the structure of this dihydroxy metabolite.



d) (15 pts) Methylparaben is a broad-spectrum preservative usually added to cosmetics. You will find methylparabene listed in the ingredients of any hand or facial cream. Explain how the methylparabene structure shown below could act as a preservative (5 pts). Show all relevant resonance structures as part of your answer to get full credit (10 pts).



Methylparaben

Methylparaben is a radical chain terminator that prevents rancidity. The methylparaben radical is stabilized by resonance and will not propagate.

