#3

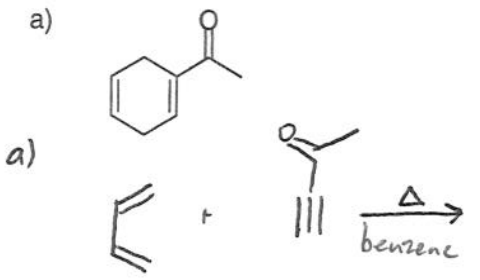
PES 317 c.1

Name: Key
Perm. #:

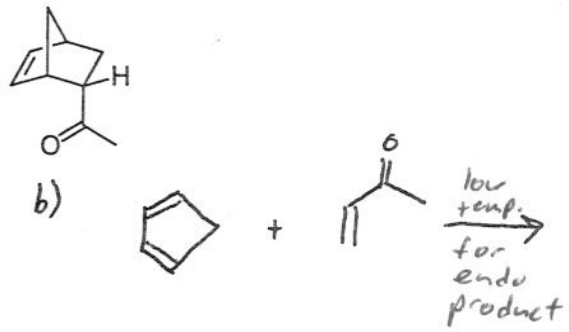
Quiz 3

1) Give the two components and conditions necessary to synthesis the following compounds in one step.

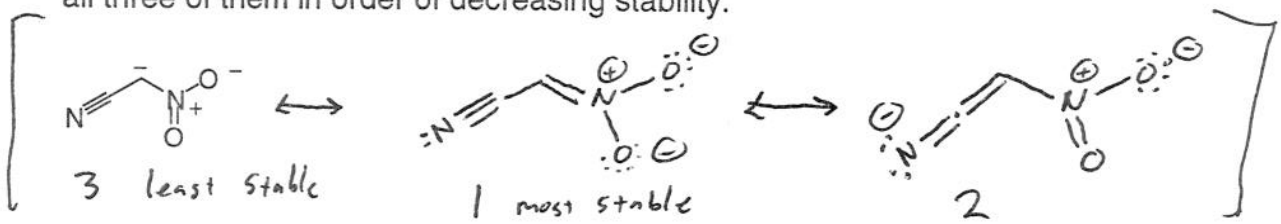
a)



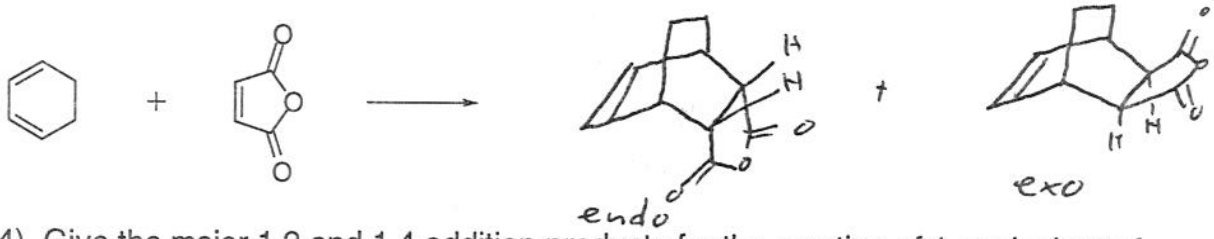
b)



2) Draw the other two major resonance structures for the following anion. Rank all three of them in order of decreasing stability.

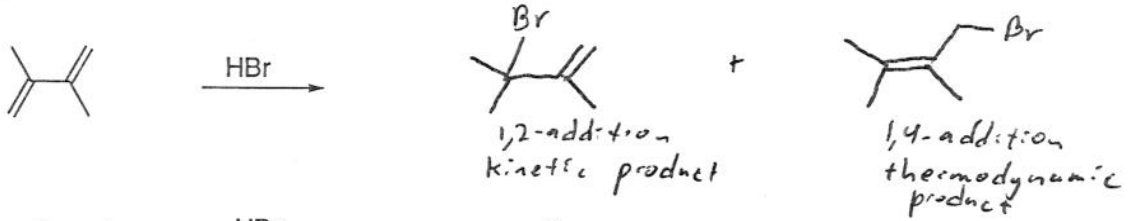


3) Draw and label the *endo* and *exo* products of the following Diels Alder reaction. Which is generally the kinetically favored product?



The endo product is generally kinetically favored.

4) Give the major 1,2 and 1,4 addition products for the reaction of 1 equivalent of HBr across the following dienes. Label them as the thermodynamic or kinetic product.



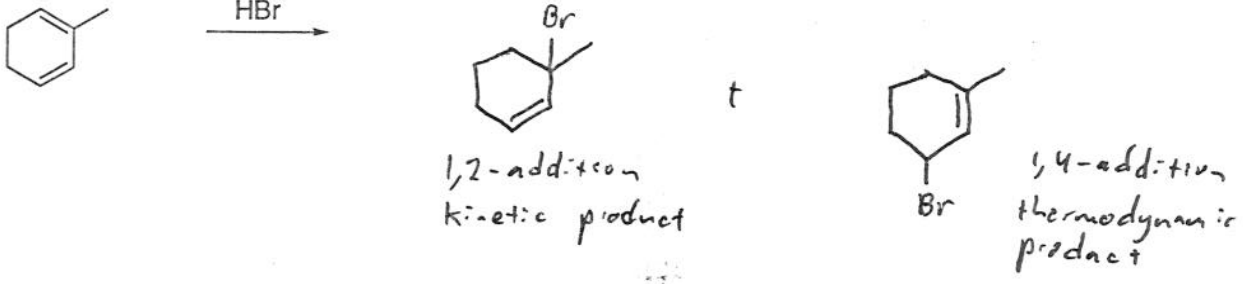
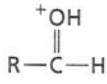
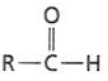
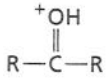
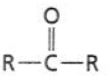
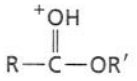
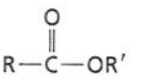
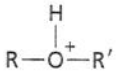
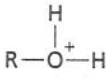
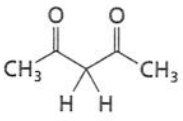
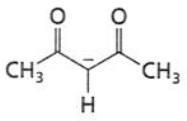
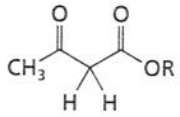
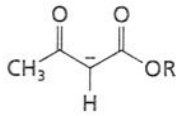
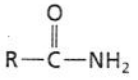
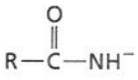
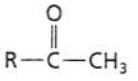
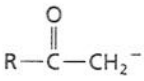
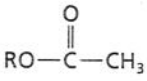
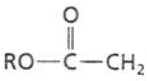
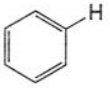


Table 6.3
Acidities of molecules and ions commonly encountered in organic chemistry.[a]

Acid	*Conjugate base*	pK_a
$HClO_4$	ClO_4^-	−10
HI	I^-	−10
		−10
H_2SO_4	HSO_4^-	−10
HBr	Br^-	−9
HCl	Cl^-	−7
		−7
$ArSO_3H$	$ArSO_3^-$	−6.5
		−6
	$R-O-R'$	−3.5
	$R-O-H$	−2
H_3O^+	H_2O	−1.7
HNO_3	NO_3^-	−1.4
HSO_4^-	SO_4^{2-}	2
HF	F^-	3.1
$ArNH_3^+$	$ArNH_2$	4
RCOOH	$RCOO^-$	5
H_2CO_3	HCO_3^-	6.4
H_2S	HS^-	7
ArSH	ArS^-	7
		9

Acid	*Conjugate base*	pK_a
HCN	CN^-	9.2
NH_4^+	NH_3	9.2
ArOH	ArO^-	10
$R-CH_2NO_2$	$R-\bar{C}H-NO_2$	10
RNH_3^+	RNH_2	11
RSH	RS^-	11
		11
CH_3OH	CH_3O^-	15.2
H_2O	HO^-	15.7
RCH_2OH	RCH_2O^-	16
R_2CH-OH	R_2CH-O^-	17
R_3C-OH	R_3C-O^-	17
		17
		20
		24
$R-CH_2CN$	$R-\bar{C}H-CN$	25
$H-C\equiv C-H$	$H-C\equiv C^-$	25
H_2	H^-	35
NH_3	NH_2^-	38
$Ph-CH_3$	$Ph-CH_2^-$	40
		43
$CH_2=CH_2$	$CH_2=CH^-$	44
CH_4	CH_3^-	48

[a] pK_a values from J. March, *Advanced Organic Chemistry*, 4th ed., John Wiley & Sons, New York, 1992, pp. 250–252. Abbreviations: Ar = aryl; Ph = phenyl; R = alkyl.

(#1)

PE. 317 c.1

Name:
Perm. #:

Quiz 1

1) a) Draw a 3d orbital picture of formaldehyde (embalming fluid), H_2CO, showing the position of all σ and π bonds, lone pairs, and atoms.
   b) Give the hybridization of each atom in formaldehyde.
   c) What are the formal charges on C and O?
   d) What are the approximate bond angles in formaldehyde?

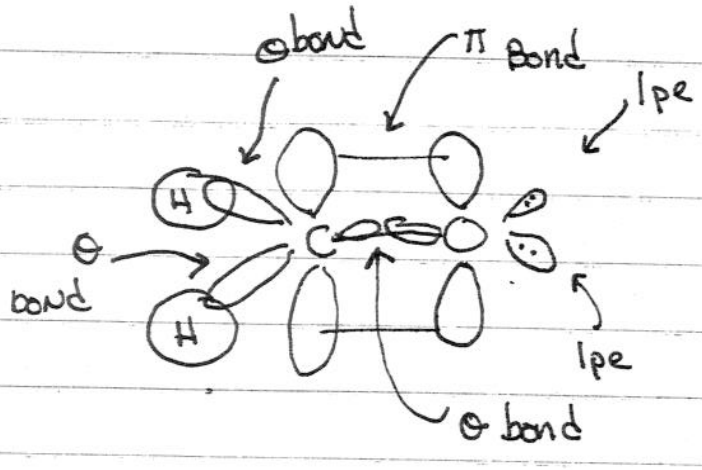
2) The pK_a of CH_3NO_2 is 10. The pK_a of ArSH is 7. Given this information, to which side, the left or the right, does the equilibrium lie in the following equation? For every mole of reagents on the disfavored side of the equilibrium, how many moles of reagents are present on the other side of the equilibrium.

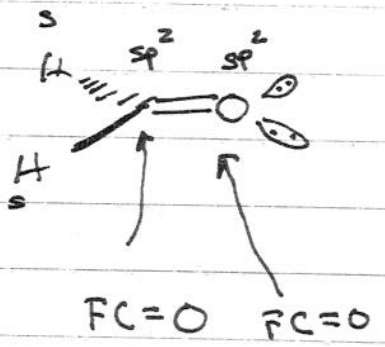
$$CH_3NO_2 + ArS^- \rightleftharpoons {}^-CH_2NO_2 + ArSH$$

3) **Using pictures and arrows only**, why is CH_3NO_2 (pK_a is 10) such a relatively strong acid? (Hint: show a picture with inductive/dipole effects in the starting material and 2 pictures with curly arrows showing resonance effects in the conjugate base.)

Quiz 1 Answer Key

Problem 1





Bond angles are 120°

4-(0+4)
0

6-(4+2)
0

Problem 2

$CH_3NO_2 + ArS^{\ominus} \rightleftharpoons \bar{C}H_2NO_2 + ArSH$

10 ← 7

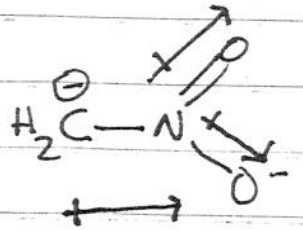
lies on the left

$10^{10-7} = 10^3$ moles of products

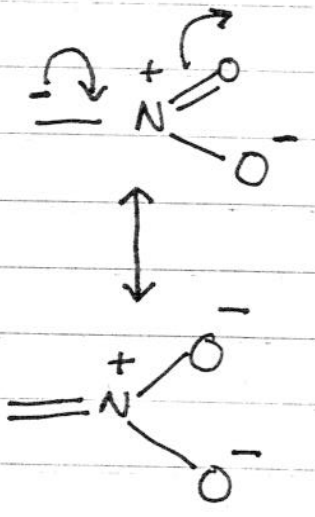
For 10^0 1 reactant moles of

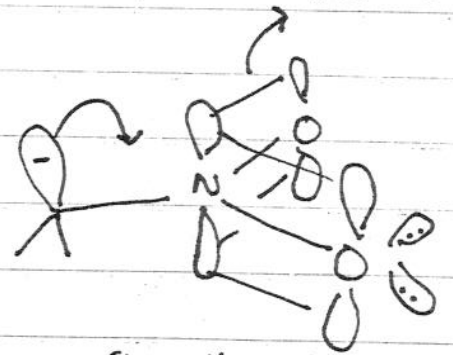
Problem 3

$\bar{C}H_2NO_2$

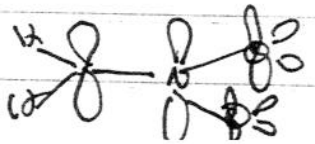


inductive effects through the σ system





sp^3 "anion" becomes sp^2 so it can delocalize over vicinal π system

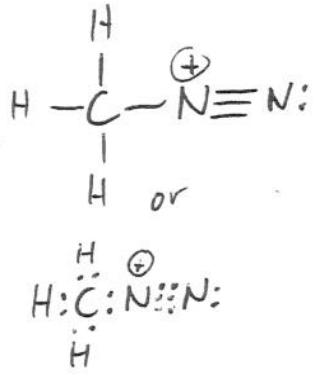


PES 319E c.1 1/5

1) Draw the Lewis structures for the following species. (Be sure to show all lone pairs and atoms with their formal charge unless 0). (10 points)

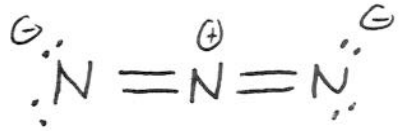
a) $[CH_3N_2]^+$ b) N_3^- (arranged NNN)

a)

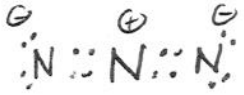


or

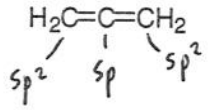
b)

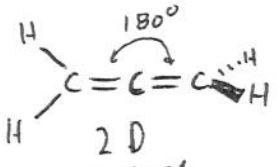


or



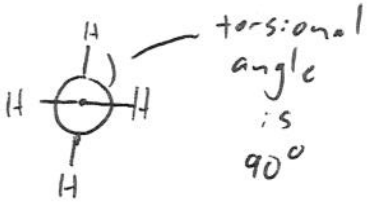
2) Draw a 3-d orbital picture for the molecule shown below. Give the hybridization of each carbon atom in the structure and give the C-C-C bond angle. What is the torsional angle between the H-CCC-H? (hint: This molecule's carbon framework resembles carbon dioxide.) (20 points)



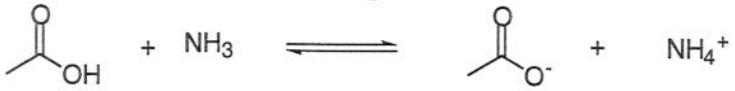


2D picture

C-C-C angle is 180° (linear)



3) If the pk_a of CH_3CO_2H is 5 and the pk_a of NH_4^+ is 9.2, where does the equilibrium lie for the following equation? (right or left) (8 points)

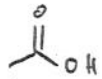


right

For every 1 mole of reagents on the disfavored side, how many moles are on the favored side? (6 points)

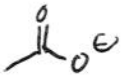
$K_{eq} = 10^{9.2-5} = 10^{4.2} = 15{,}850$

Label each reagent in the above equilibrium as a Lewis acid or Lewis base (8 points)



Lewis acid

Lewis base

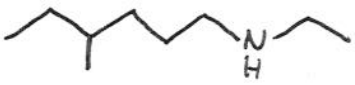


Lewis base

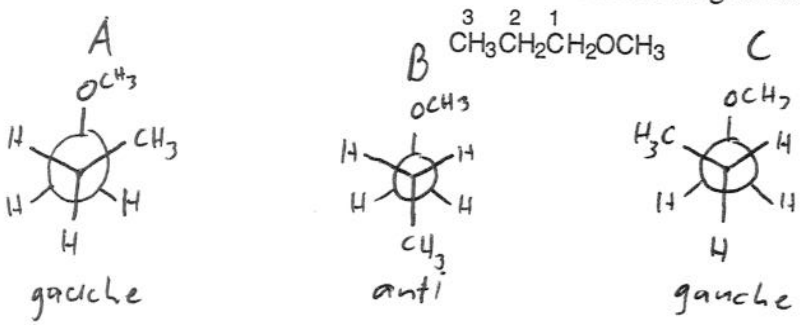
Lewis Acid

4) Draw the skeletal structures of the following molecules: (10 points)

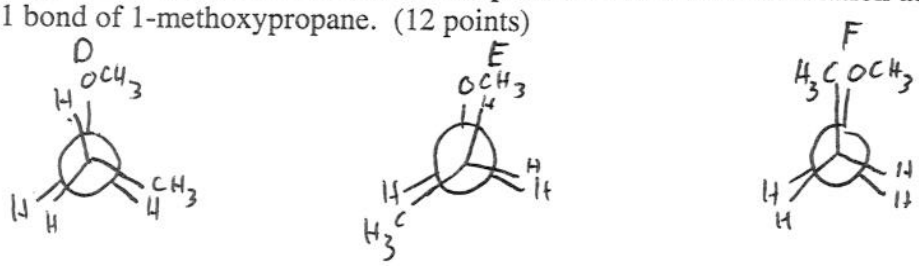
a) 1-ethyl-4-*t*-butylcyclohexene b) 4-methyl-N-ethylhexan-1-amine



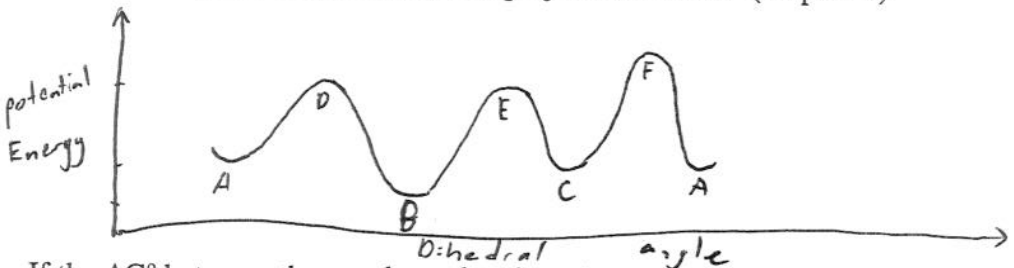
5) Using Newman Projections draw three conformations for 1-methoxypropane looking down the C2 to C1 bond. Label the three conformations gauche or anti. (12 points)



Using Newman projections draw all eclipsed conformations for rotation about the C2 to C1 bond of 1-methoxypropane. (12 points)



Sketch an energy diagram for rotation about the C2 to C1 bond of 1-methoxypropane. Label the diagram with the Newman projections above. (12 points)



If the ΔG° between the gauche and anti conformations is 0.4 kcal/mol, what is the ratio of anti conformers to gauche conformers? (8 points)

$\Delta G^\circ = -RT \ln K_{eq}$

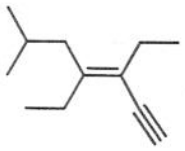
$\Delta G^\circ = 1.4 \log K_{eq}$

$K_{eq} = 10^{\Delta G^\circ / 1.4} = 10^{0.4/1.4} = 10^{0.286} = 1.9$

anti : gauch = 1.9 : 1

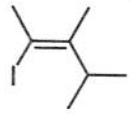
6) Label the following alkenes as Z or E. (10 points)

a)



E

b)

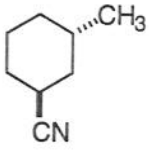


Z

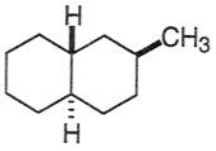
7) Draw the most stable conformation of the following molecules. (24 points)

a)

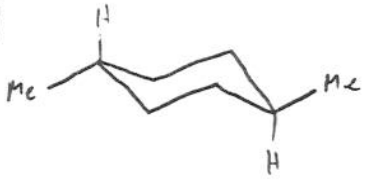
b)



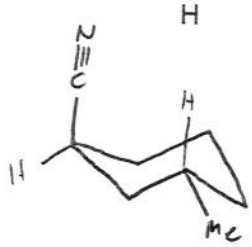
c)



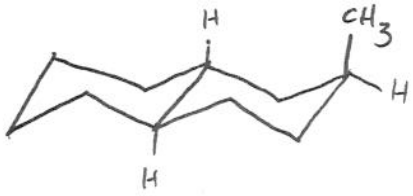
a)



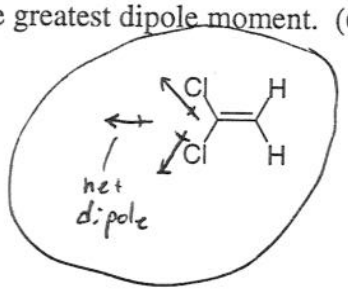
b)

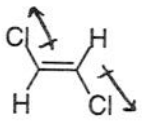


c)



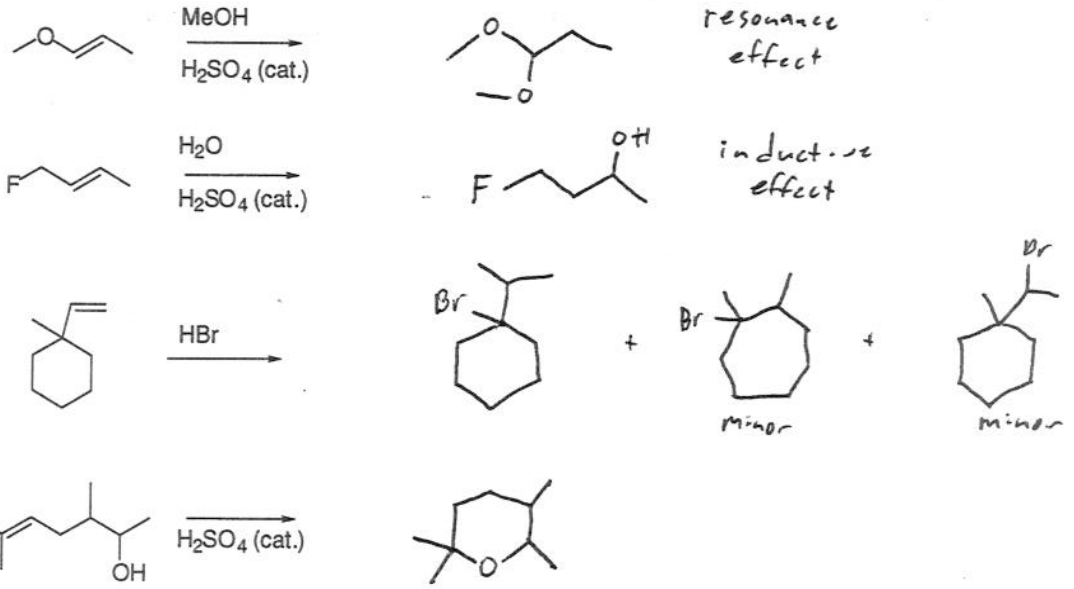
8) Draw the dipole vectors for the carbon-chlorine bonds and the net dipole moment of the molecules (added vectors) using the arrow with a [+] on one side. Circle the molecule with the greatest dipole moment. (6 points)



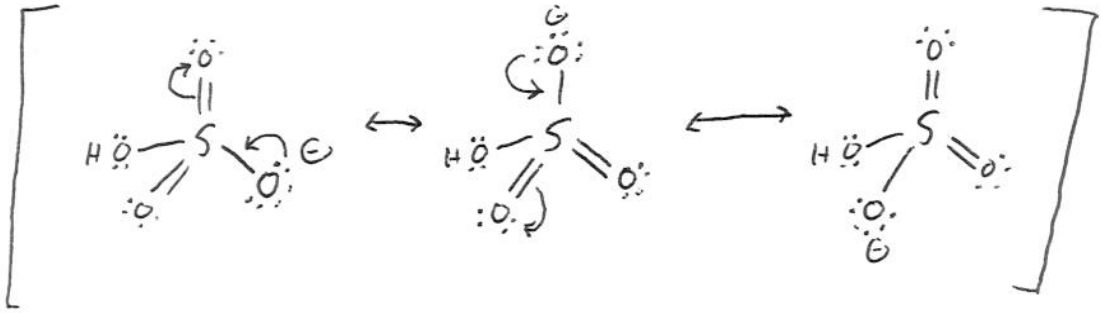


O net dipole

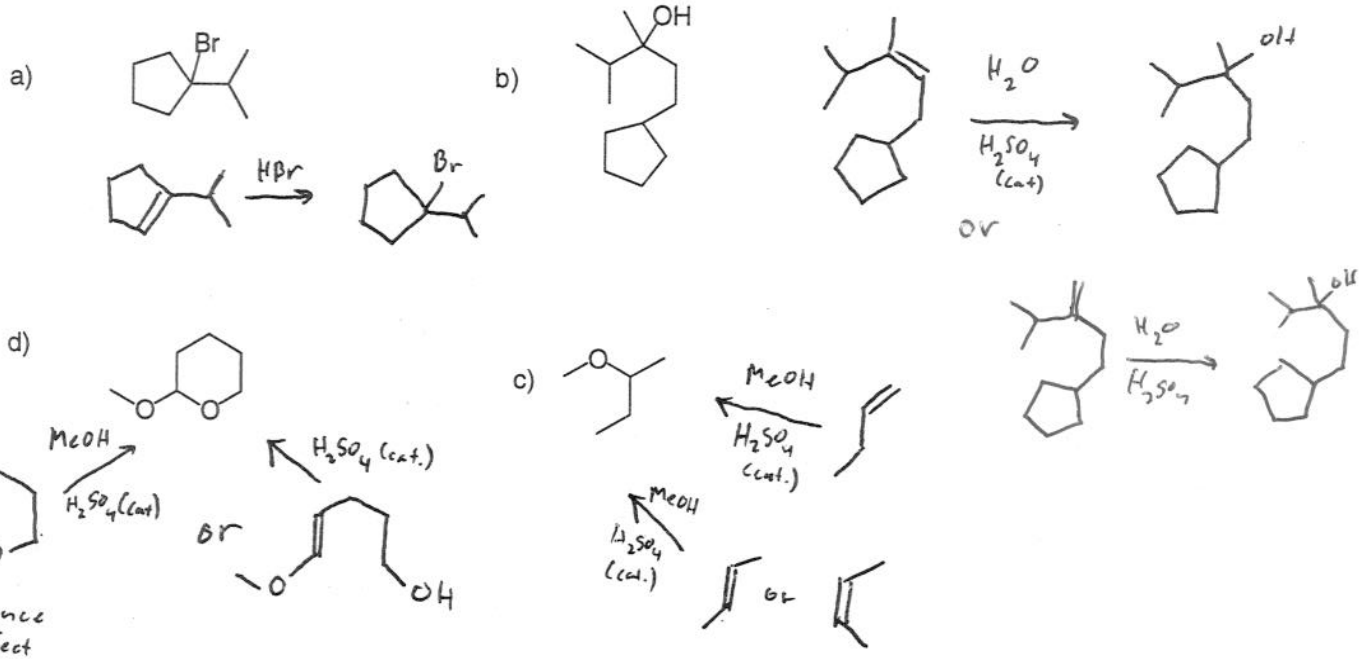
9) Draw the major product you would expect from the following reactions. (28 points)



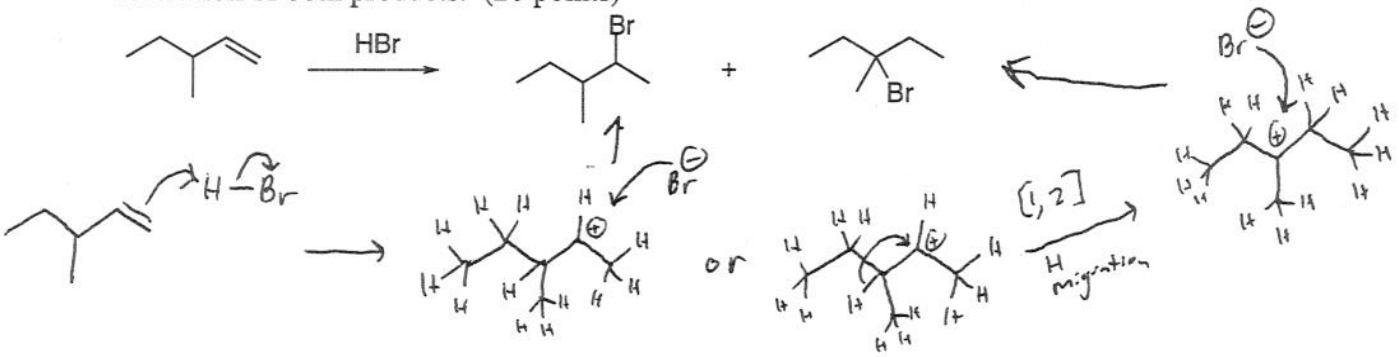
10) Using three resonance structures with curly arrows, explain why $[HSO_4]^-$ is a relatively stable anion. (6 points)



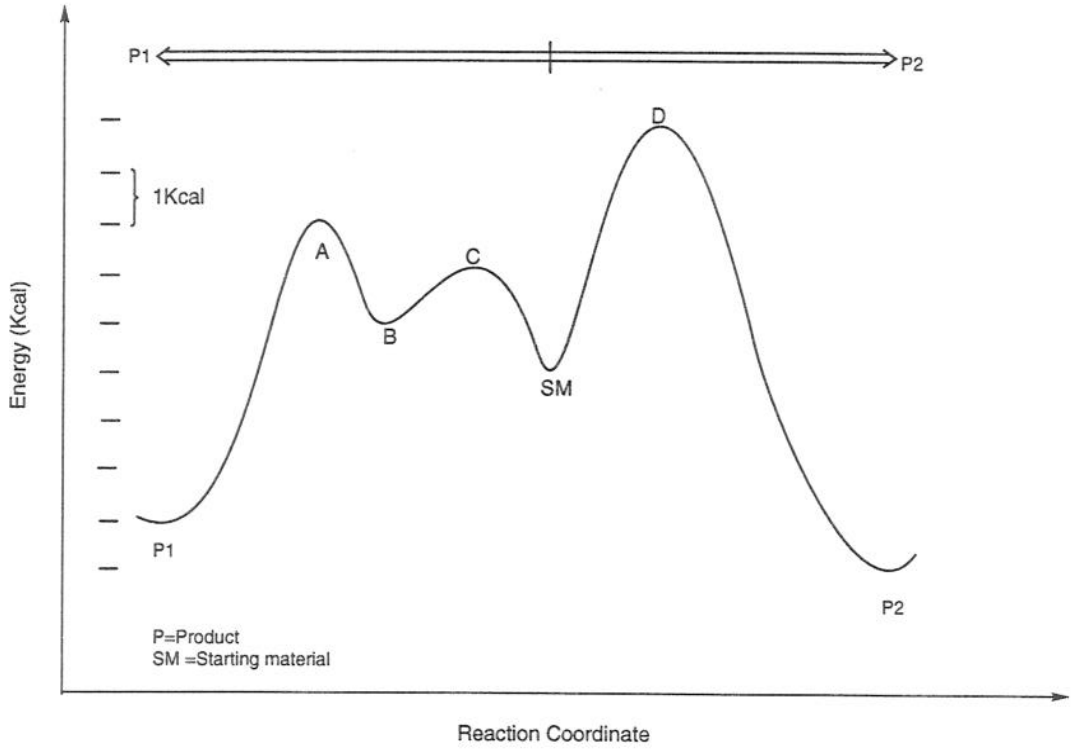
11) Give the alkene and the reaction conditions needed to yield each of the following as the major product. (28 points)



12) Give a curly arrow pushing mechanism for the following reaction explaining the formation of both products. (20 points)



13) Given the following reaction coordinate diagram, answer the following questions.



a) Label whether or not the following transformations are exergonic or endergonic: SM→B, SM→P1, SM→P2 (9 points)

endergonic, exergonic, exergonic (respectively)

b) If the reaction is under thermodynamic control, which is the primary product? If the reaction is under kinetic control, which is the primary product? (6 points)

thermodynamic control => P_2 major product kinetic control => P_1 major product

c) What is the product ratio, if the reaction is under thermodynamic control? (7 points)

$K_{eq} = 10^{\Delta G^\circ / 1.4} = 10^{1/1.4} = 5.2$

$P_2 : P_1 = 5.2 : 1$

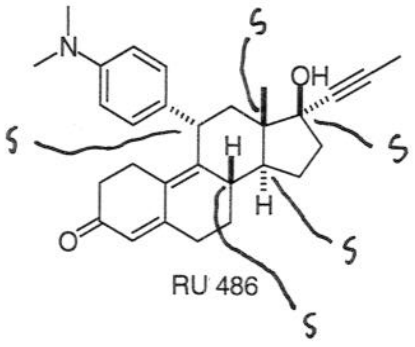
#2

PES 317 c.1

Name:
Perm. #: Key

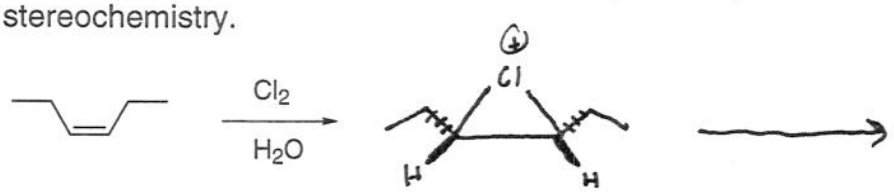
Quiz 2

1) RU 486, the primary active ingredient in the abortion pill, is shown below. How many chiral centers does RU 486 have? Label each stereocenter as R or S. 5 chiral centers



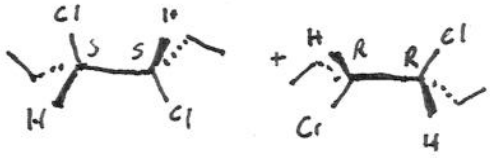
Explanation for how to determine R or S on the last page.

2) Draw the intermediate of the following reaction. Label this intermediate along the reaction coordinate as chiral or meso. How many possible product stereoisomers are formed? Draw all these possible products showing stereochemistry.



meso intermediate

2 possible product stereoisomers are formed



3) (S)-(-)-Proline has a specific rotation of -84°. If the observed optical rotation of a mixture of (R) and (S)-Proline is -40°, what is the enantiomeric excess of the mixture. What percent of the Proline is present as the S enantiomer and what percent is the R isomer?

$$ee = \frac{-40^\circ}{-84^\circ} = 47.6\%\ ee$$

$$47.6 + \left(\frac{100 - 47.6}{2}\right) = 73.8\%\ S$$

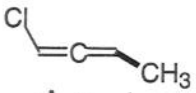
$$26.2\%\ R$$

Check:

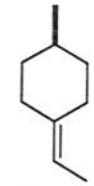
$$\frac{73.8 - 26.2}{73.8 + 26.2} = 47.6\%\ ee$$

Turn Over

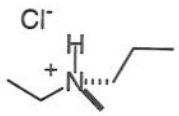
4) Indicate if the following molecules are chiral, achiral, or meso.

a) 

chiral

b) 

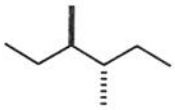
chiral

c) 

chiral

d) 

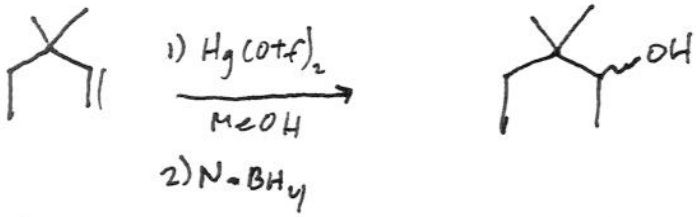
achiral

e) 

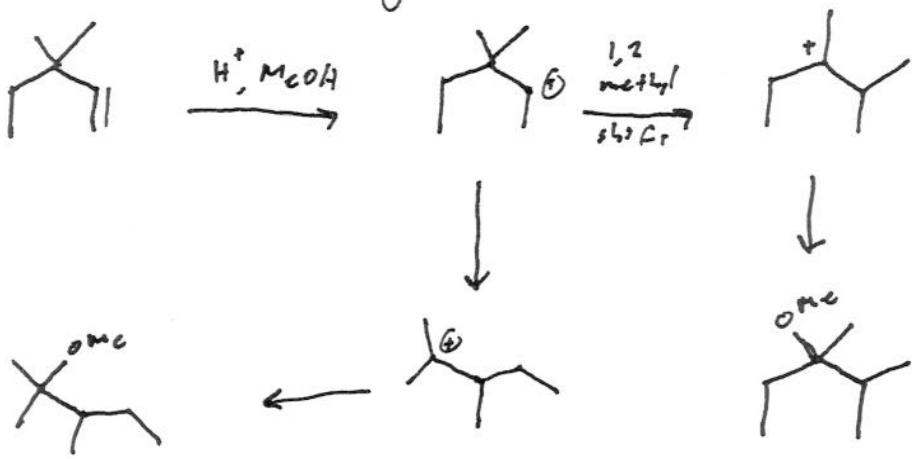
meso

5) Give all reagents necessary to achieve the following transformation:

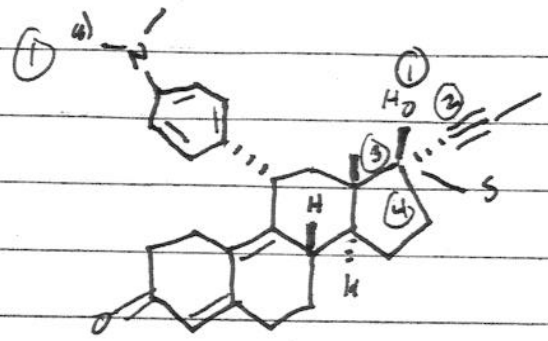
note: The squiggly line indicates both possible stereoisomers at that center are present.

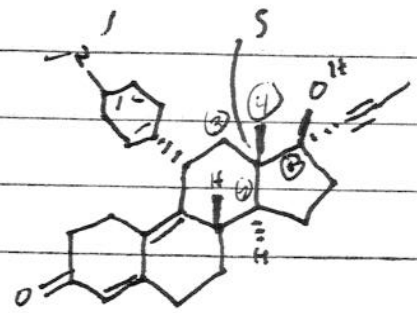


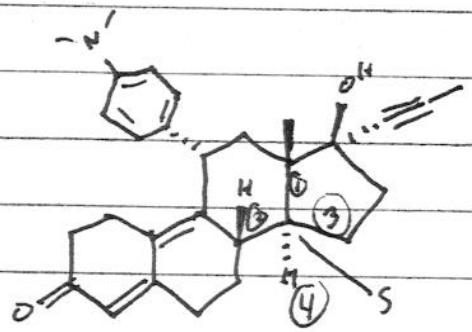
not will H⁺ and MeOH because the cation rearrange

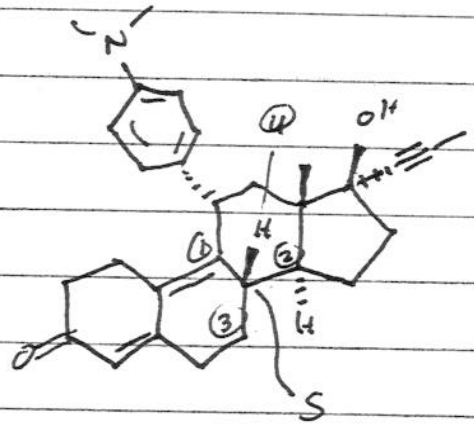


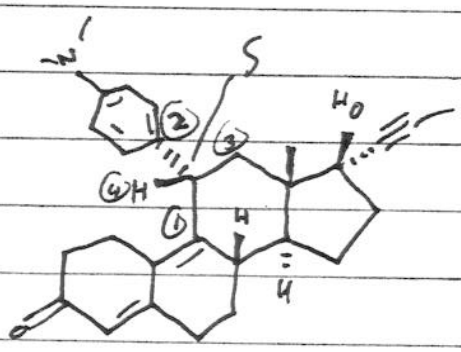
Priority of groups





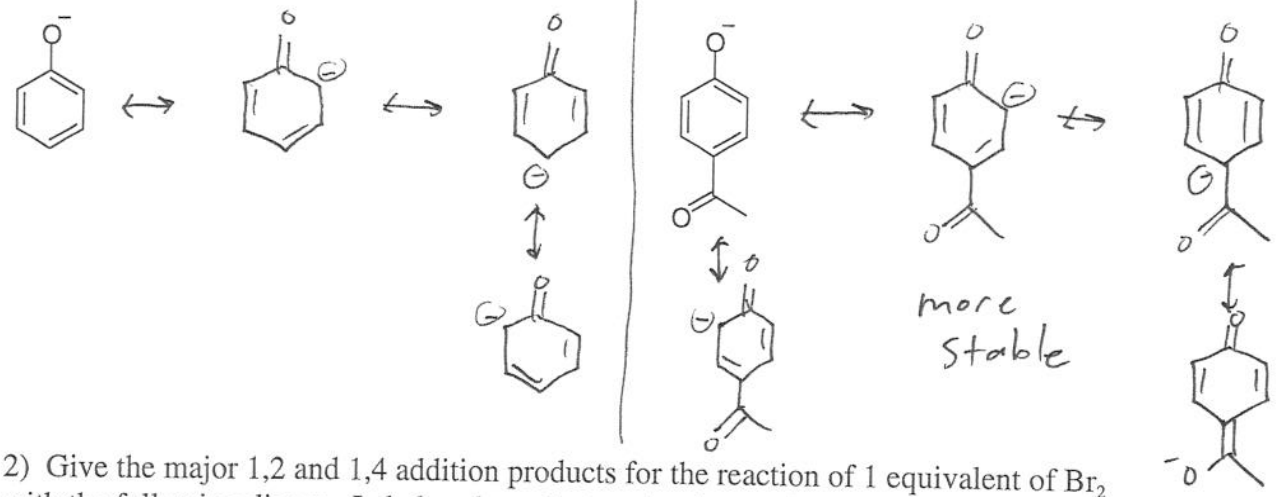




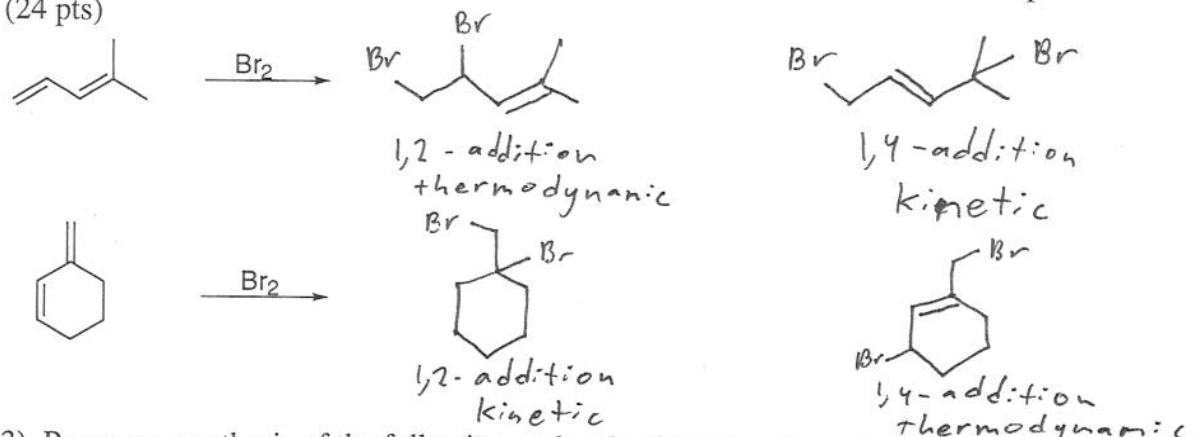


PES
3218
c.1
1/5

1) Draw all the resonance forms of the two anions shown below. Which of the two is the more stable anion? (20 pts)

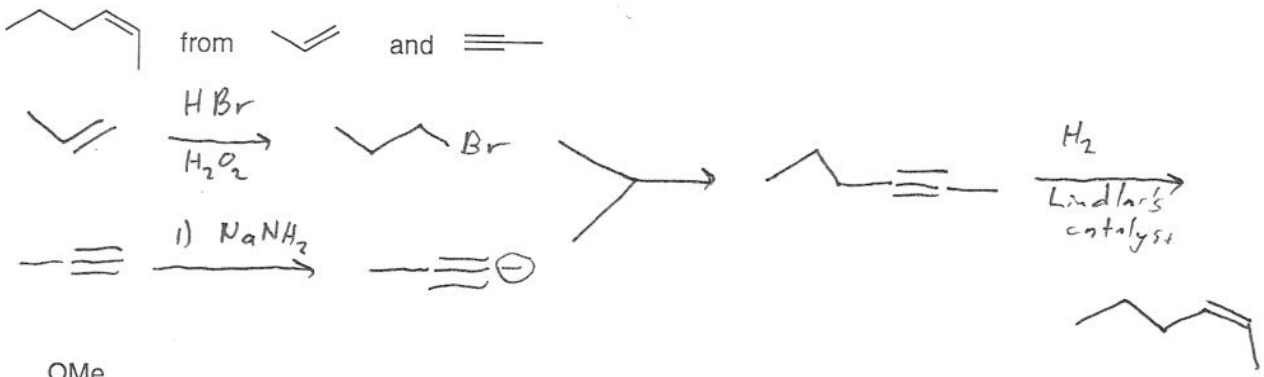


2) Give the major 1,2 and 1,4 addition products for the reaction of 1 equivalent of Br_2 with the following dienes. Label each product as the thermodynamic or kinetic product. (24 pts)

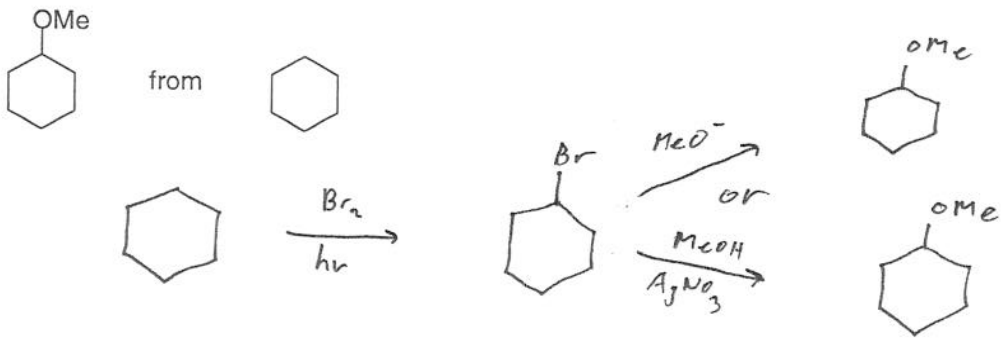


3) Propose a synthesis of the following molecules from the given starting materials. (30 pts)

a)



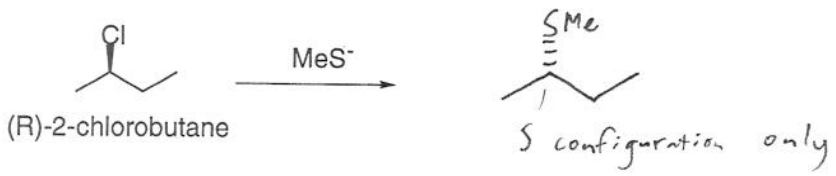
b)



4) Give the major products of the following reactions. Be sure to pay attention to stereochemistry. (Not all reactions need give a product.) (70 pts)

a)

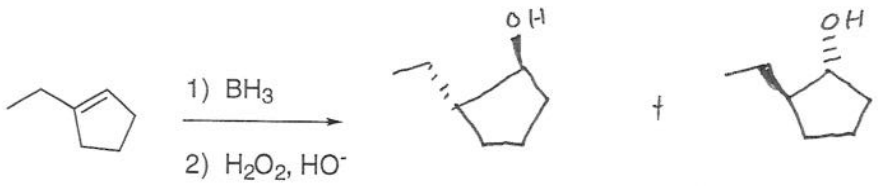
b)



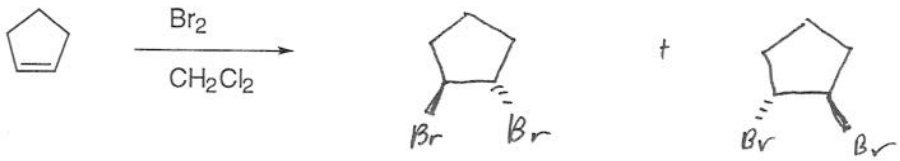
(R)-2-chlorobutane

S configuration only

c)



d)

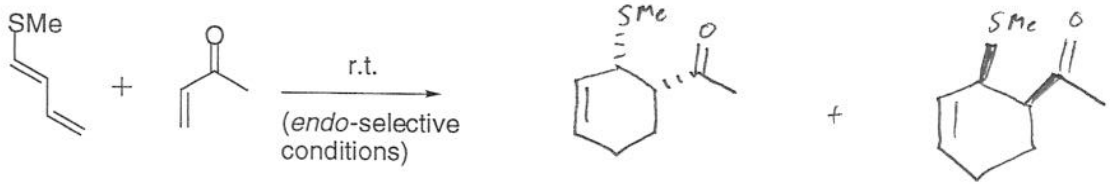


e)

no reaction

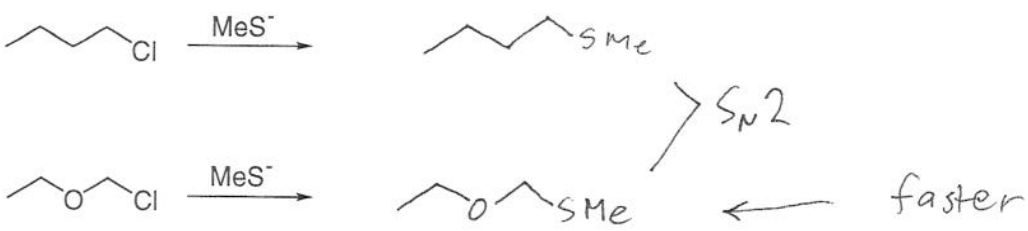
f)

g)

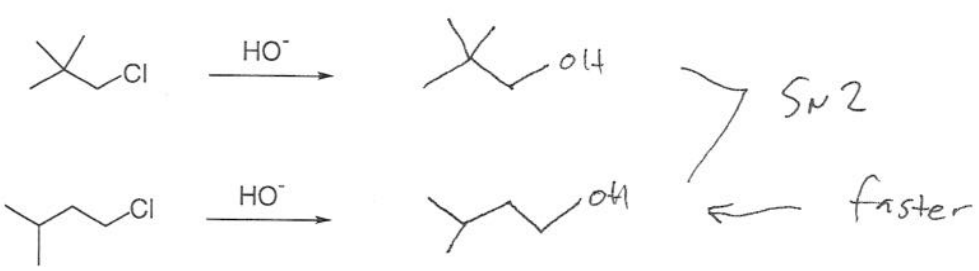


5) Give the products of the following reactions. For each pair of reactions indicate if the reactions go by an S_N1 or S_N2 type mechanism and label which reaction of the two will occur more rapidly. (56 pts)

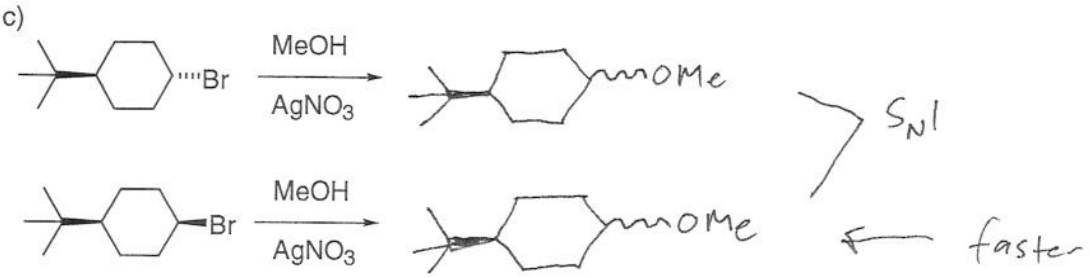
a)



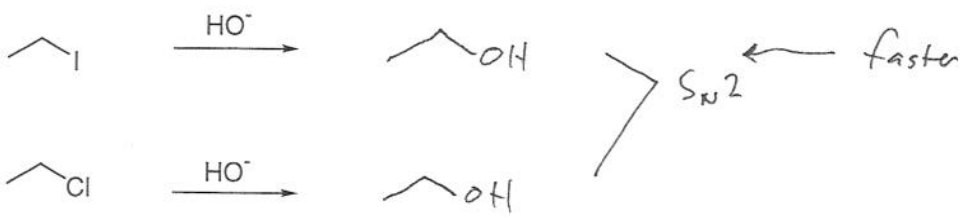
b)



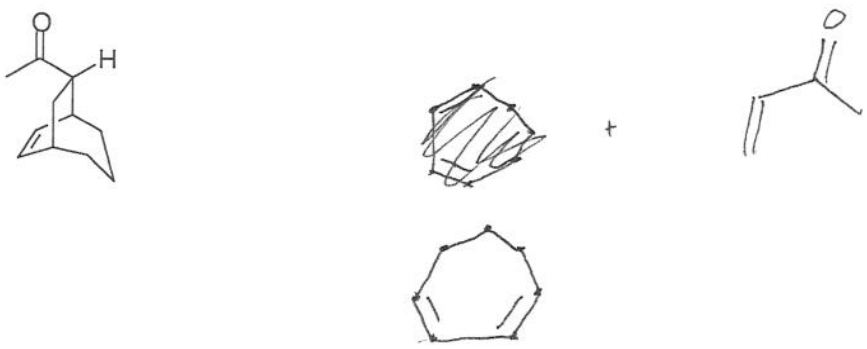
c)



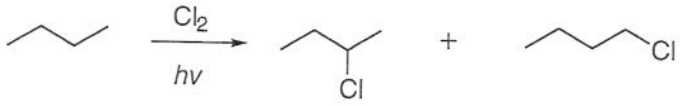
d)



6) Propose a synthesis of the following molecule. (Hint: one of the starting materials should be a seven membered ring.) (12 pts)



6) The reaction of excess n-butane with Cl_2 in the presence of light produces two *mono*-chlorinated products in the ratio given below. Show the two propogation steps leading to each of the two products for this free radical reaction. Using the bond enthalpies given below, calculate the $\Delta H°$ for each step. Draw a reaction coordinate diagram leading to each product. (There should be two humps for each product in your diagram) ($\Delta H°$(H-Cl)=103; $\Delta H°$(Cl-Cl)=58; $\Delta H°$(primary C-H)=101; $\Delta H°$(secondary C-H)=99; $\Delta H°$(primary C-Cl)=82; $\Delta H°$(secondary C-Cl)=81; all bond energies in kcal/mol) (15 pts)



rxn coordinate diagrams are on the next page

1° product — 71% — 29% — $\Delta H°$(kcal/mol)

$Cl\cdot + CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2\dot{C}H_2 + HCl$ — 101-103 = -2

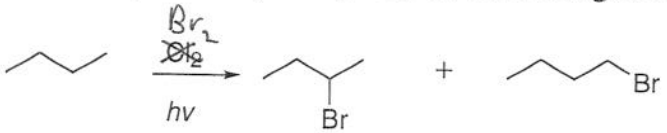
$Cl_2 + CH_3CH_2CH_2\dot{C}H_2 \longrightarrow CH_3CH_2CH_2CH_2Cl + Cl\cdot$ — 58-82 = -24

2° product — $\Delta H°$(kcal/mol)

$Cl\cdot + CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2\dot{C}HCH_3 + HCl$ — 99-103 = -4

$Cl_2 + CH_3CH_2\dot{C}HCH_3 \longrightarrow CH_3CH_2\underset{Cl}{C}HCH_3 + Cl\cdot$ — 58-81 = -23

The reaction of excess n-butane with Br_2 in the presence of light produces two *mono*-brominated products in the ratio given below. Show the two propogation steps leading to each of the two products for this free radical reaction. Using the bond enthalpies given below, calculate the $\Delta H°$ for each step. Draw a reaction coordinate diagram leading to each product. (There should be two humps for each product in your diagram) ($\Delta H°$(H-Br)=87; $\Delta H°$(Br-Br)=46; $\Delta H°$(primary C-H)=101; $\Delta H°$(secondary C-H)=99; $\Delta H°$(primary C-Br)=69; $\Delta H°$(secondary C-Br)=68; all bond energies in kcal/mol) (15 pts)



1° product — 98% — 2% — $\Delta H°$

$Br\cdot + CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2\dot{C}H_2 + HBr$ — 101-87 = 14

$Br_2 + CH_3CH_2CH_2\dot{C}H_2 \longrightarrow CH_3CH_2CH_2CH_2Br + Br\cdot$ — 46-69 = -23

2° product

$Br\cdot + CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2\dot{C}HCH_3 + HBr$ — 99-87 = 12

$Br_2 + CH_3CH_2\dot{C}HCH_3 \longrightarrow CH_3CH_2\underset{Br}{C}HCH_3 + Br\cdot$ — 46-68 = -22

Refering to the reaction coordinate diagrams you've drawn, explain why free radical bromination is more selective then free radical chlorination. Be sure to state the postulate crucial to this argument as well as give the name associated with it. (8 pts)

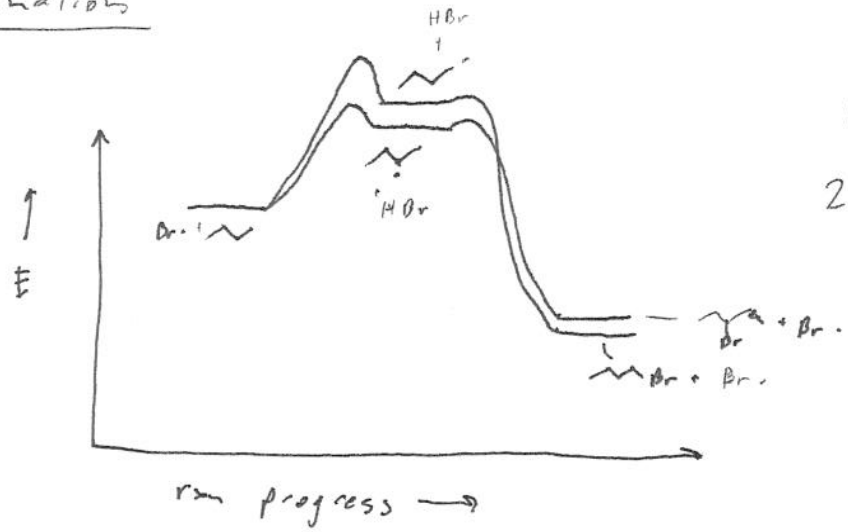
answer on next page

Chlorination

1st step exothermic

2nd step exothermic

bromination



1st step endothermic

2nd step exothermic

Explanation

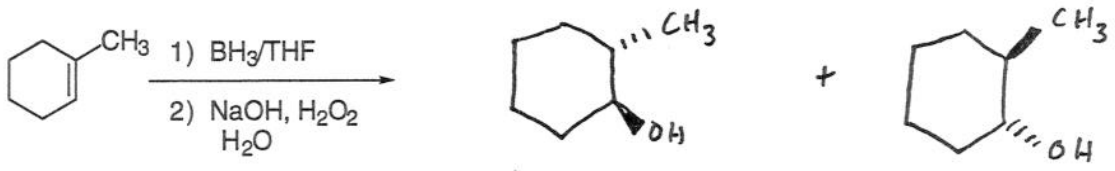
radical and by a bromine radical ...

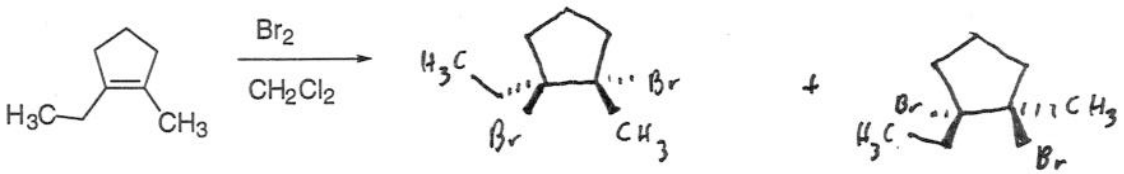
Because the reaction of a chlorine radical with an alkane to form a primary, secondary, or tertiary radical is exothermic, the transition states resemble the reactants more than the products (the Hammond postulate, Section 3.11). The reactants all have approximately the same energy, so there will be only a small difference in the activation energies for removal of a hydrogen atom from a primary, secondary, or tertiary carbon. In contrast, the reaction of a bromine radical with an alkane is endothermic, so the transition states resemble the products more than the reactants. Because there is a significant difference in the energies of the product radicals, depending on whether they are primary, secondary, or tertiary, there is a significant difference in the activation energies.

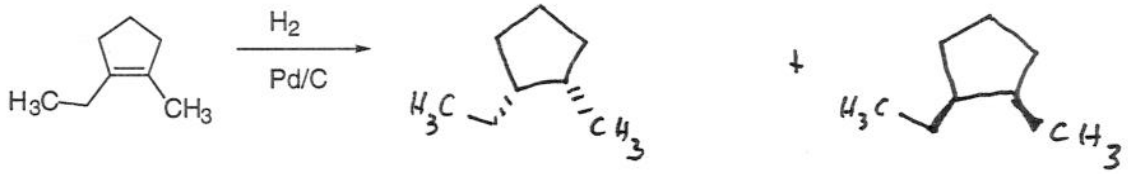
Figure 8.1 shows that a chlorine radical makes primary, secondary, and tertiary rad-

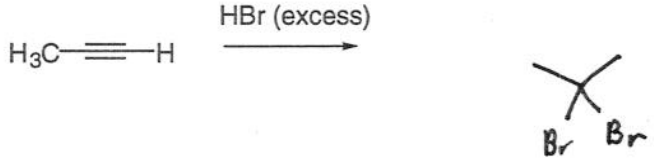
PES
320E
c.1
1/4

1) Give the products that would be obtained from the following reactions. Be sure to indicate stereochemistry where necessary drawing all enantiomers, diastereomers, and regioisomers as required. (50 points)



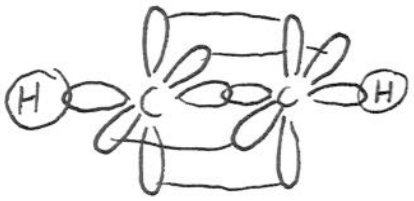






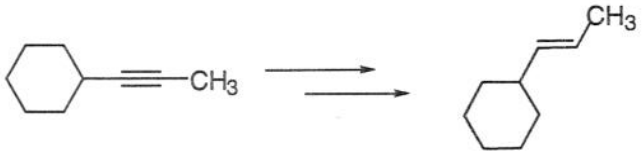
2) Draw a 3-d orbital picture for ethyne, shown below. Give the hybridization of each carbon atom in the structure and give the C-C-H bond angle. (18 points)

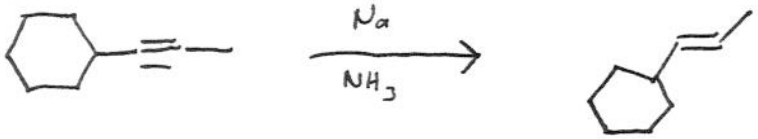
H—≡—H

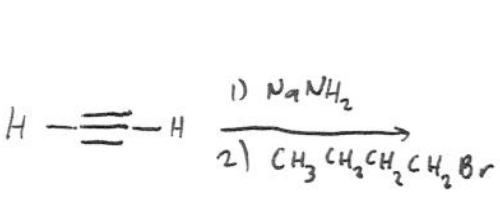


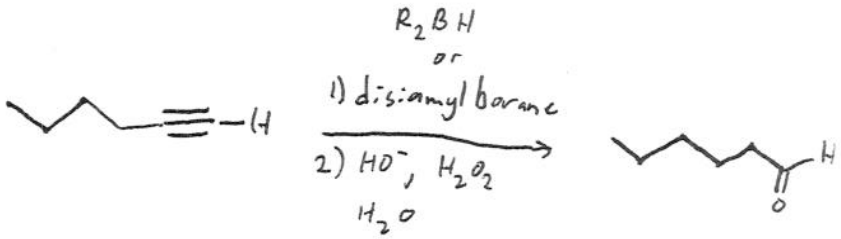
- both carbons are sp hybridized
- C-C-H bond angle is 180°

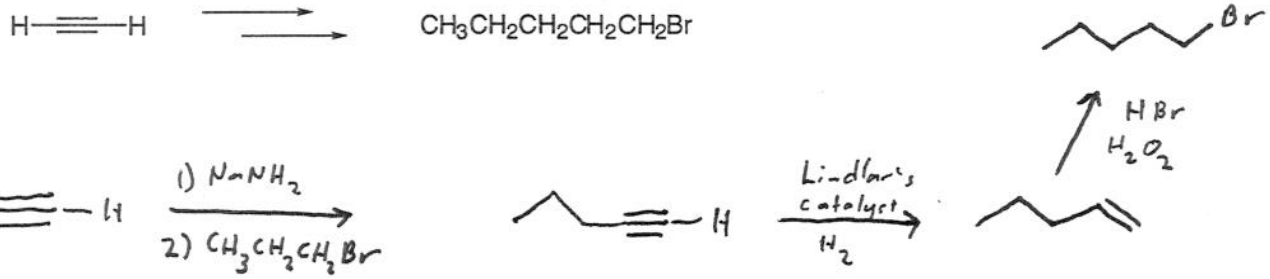
3) How could the following products be prepared from the given alkyne. Use any necessary inorganic reagents and any necessary organic compound that contains no more than four carbon atoms. (60 points)











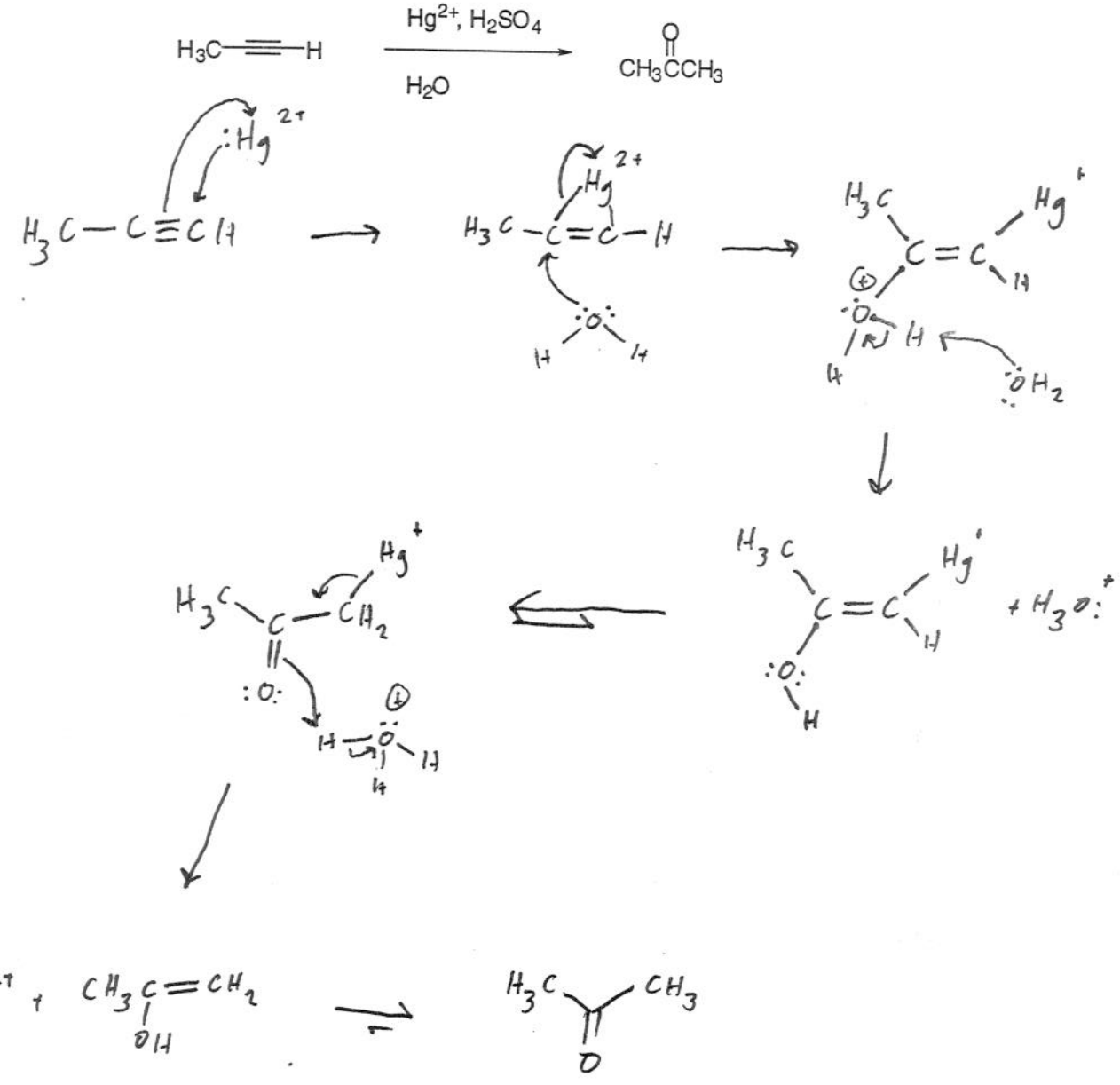
4) (R)-(+)-Limonene has a specific rotation of +123°. If the observed optical rotation of a mixture of (R) and (S)-Limonene is +80°, what is the enantiomeric excess of the mixture? What percent of the Limonene is present as the S enantiomer and what percent is the R enantiomer? (18 points)

$$ee = \frac{+80}{+123} = 65\%\ ee$$

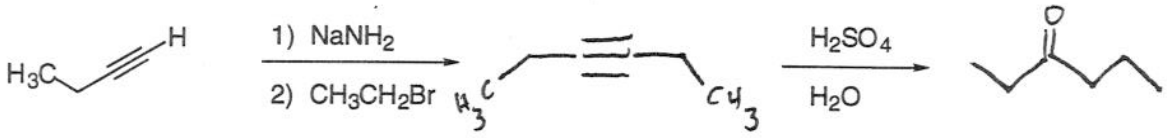
$$65 + \left(\frac{100-65}{2}\right) = 82.5\%\ R$$

$$17.5\%\ S$$

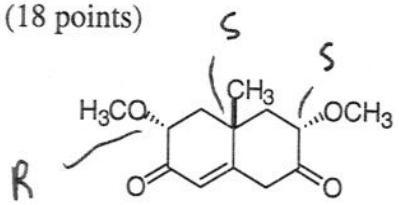
5) Give the mechanism for the mercuric-ion catalyzed hydration of an alkyne. (32 points)



6) Provide the missing products in the reaction scheme depicted below. (30 points)



7) How many chirality centers does the molecule shown below possess? Assign each chirality center as R or S. (18 points)



- The molecule contains 3 chirality centers

8) If the pk_a of HNR_2 is 36 and the pk_a of a terminal alkyne is 25, where does the equilibrium lie for the following equation? (right or left) (8points)

Equilibrium lies to the left.

For every 1 mole of reagents on the disfavored side, how many moles are on the favored side? (12 points)

For every 1 mole of reagents on the disfavored side, there are 10" moles on the favored side

Label each reagent in the above equilibrium as a Lewis acid or Lewis base. (as it is acting relative to the above equation (4 points)

Lewis base | Lewis acid | Lewis base | Lewis acid