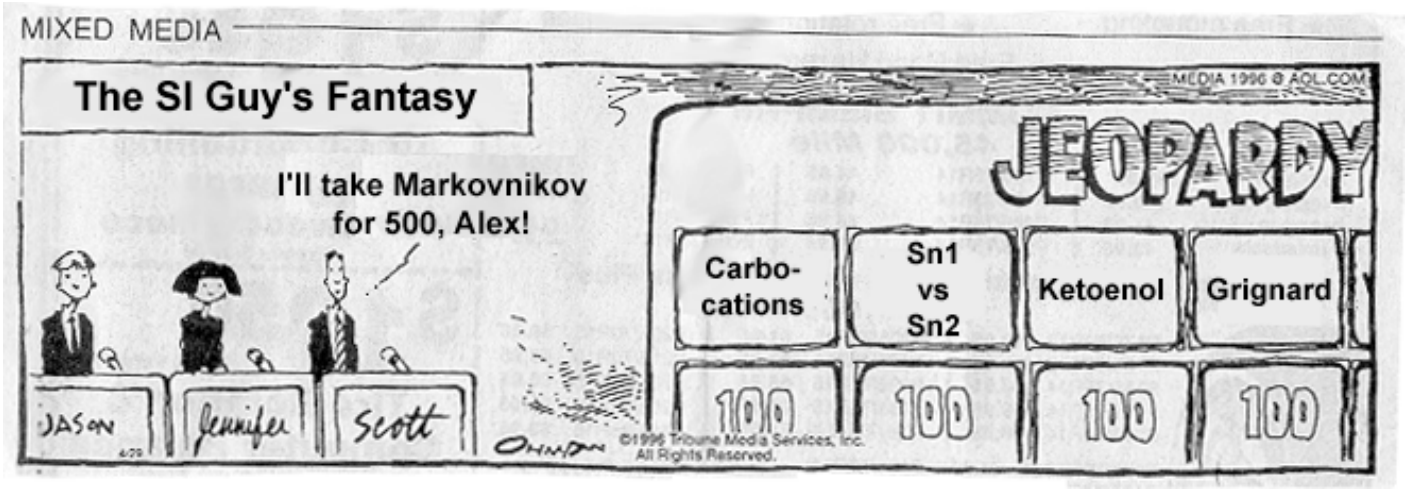
CHEMISTRY 341

Final Exam

Wednesday, December 16, 1998

Name_____

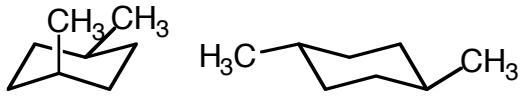


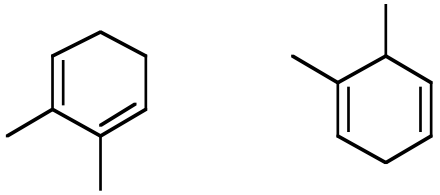
Please read through each problem carefully. Enter your answers in the spaces provided. If you need additional scratch paper, you can use the back of the test pages.

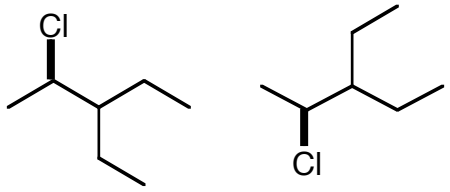
Problem 1	15 pts _____	Problem 8	6 pts _____
Problem 2	9 pts _____	Problem 9	9 pts _____
Problem 3	27 pts _____	Problem 10	33 pts _____
Problem 4	9 pts _____	Problem 11	24 pts _____
Problem 5	9 pts _____	Problem 12	22 pts _____
Problem 6	3 pts _____	Problem 13	15 pts _____
Problem 7	6 pts _____	Problem 14	10 pts _____
		given	3 pts **3**

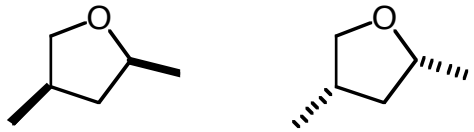
TOTAL 200 pts_____

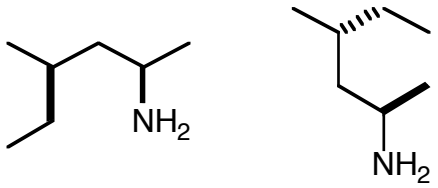
1) Use the best term to describe the relationship between the following pairs of molecules. (conformers, enantiomers, diastereomers, identical, constitutional isomers) (15 points)

a) 

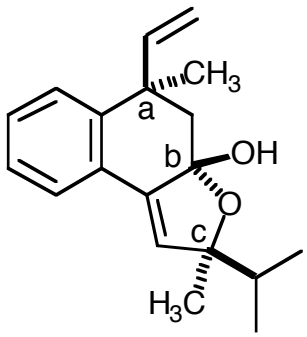
b) 

c) 

d) 

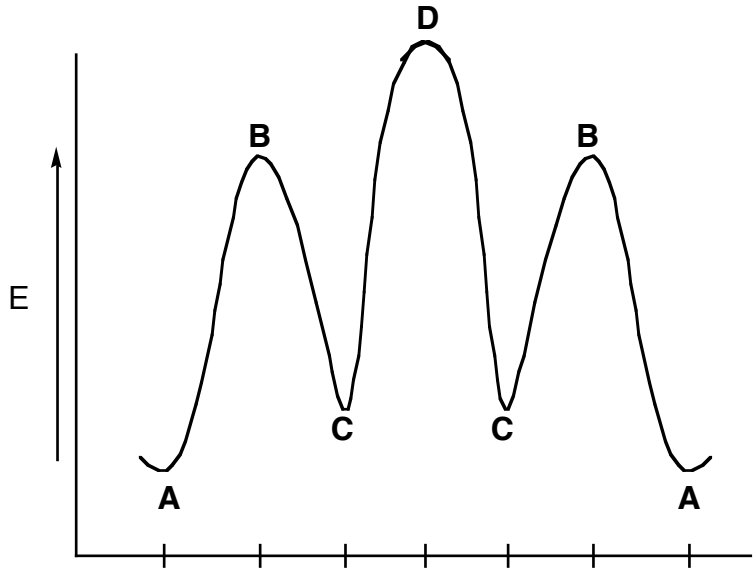
e) 

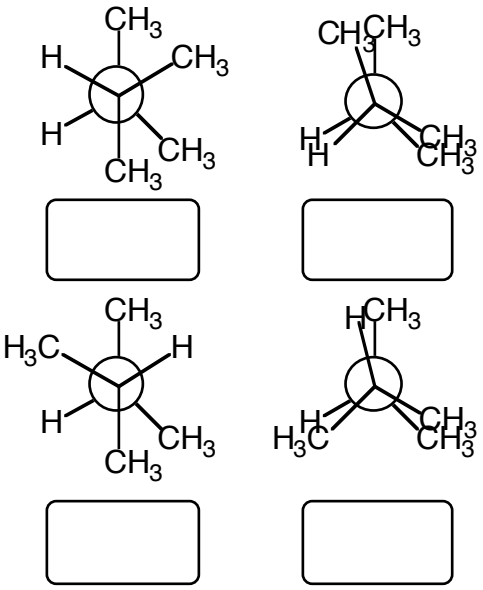
2) Determine the (R) or (S) configuration for the following stereogenic centers. (9 points)



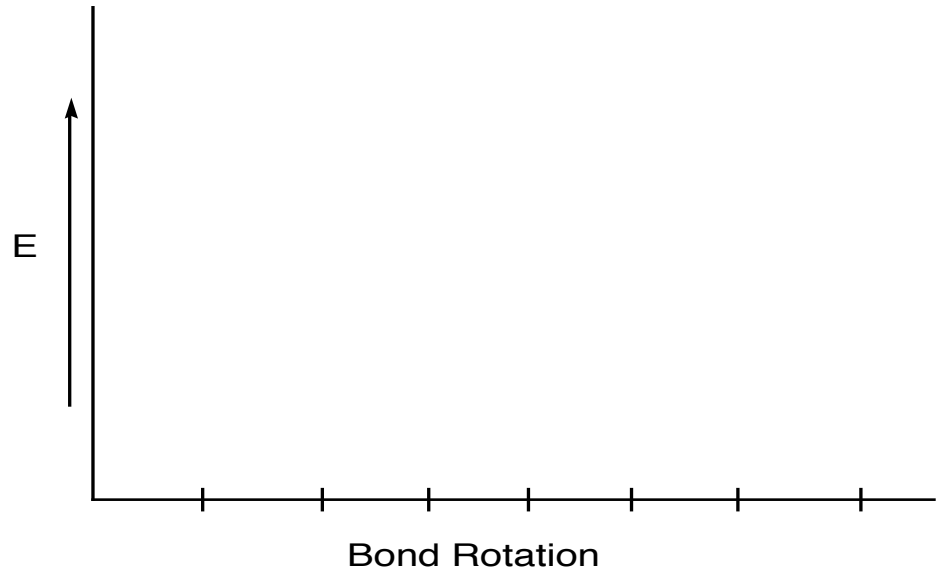
a b c

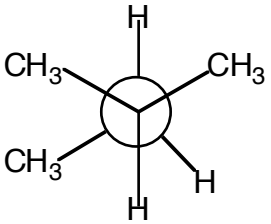
3) a) The energy diagram below shows the energy change in the conformations of 2,3-dimethylbutane as the C2-C3 bond is rotated. Each extreme in energy is marked with a letter. In the box below each conformation place the letter that corresponds to that extreme. (12 points)



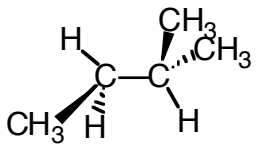


b) On the diagram below, sketch the energy change as the molecule shown below, 2-methylbutane, undergoes bond rotation for 360° (one full circle). Your sketch should start with the energy of the conformation shown, and show in a relative sense what is equal in energy, and what is higher or lower in energy. Please make your drawing clear! (15 points)



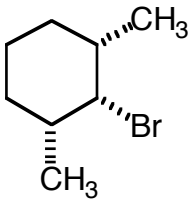


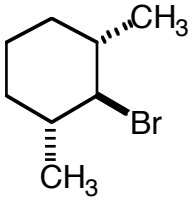
Newman projection



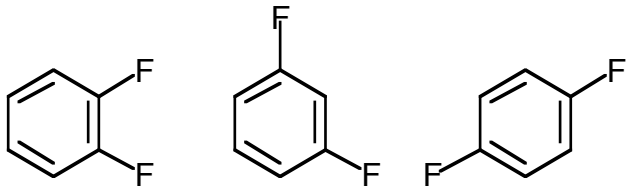
Sawhorse view

4) One of the following isomers of 2-bromo-1,3-dimethylcyclohexane cannot undergo an E2 elimination reaction. Circle the structure that cannot and explain why. (9 points)





5) The ^{13}C NMR data were recorded for the following three difluorobenzene derivatives. Match the structure with the correct spectral data. (9 points)



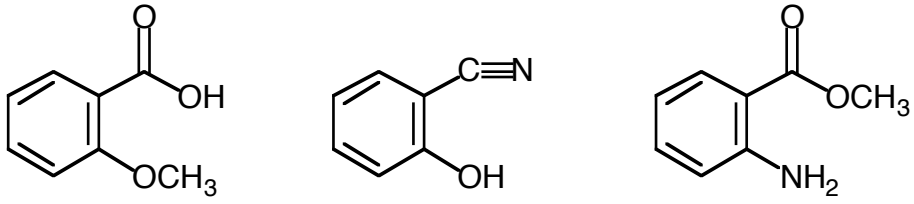
A **B** **C**

Spectrum 1: 116, 159 ppm

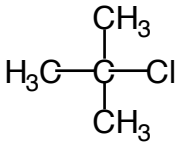
Spectrum 2: 127, 129, 131, 135 ppm

Spectrum 3: 128, 131, 133 ppm

6) The IR spectrum of a molecule which is known to be one of the following three structures was recorded. Characteristic absorbances appear at 3350 (broad and strong), 3050, and 2210 cm^{-1}. Circle the structure which is most consistent with this data. (3 points)



7) In the mass spectrum of tertiary butyl chloride, the M^+ peak at 92 is not observed. A peak shows up at m/z 77 with a peak at 79 which is 1/3 the height. The base peak in the spectrum is at m/z 57. What are the structures for the cations which correspond to these peaks. (atomic weights C = 12, H = 1, Cl = 35). (6 points)



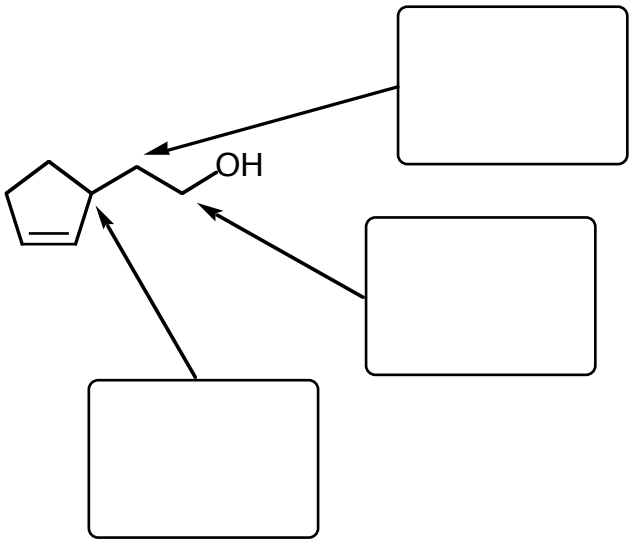
tert-butyl chloride

m/z 77

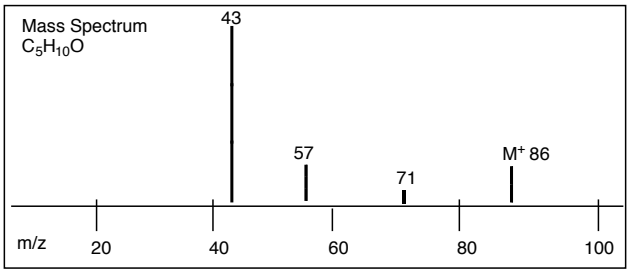
m/z 57

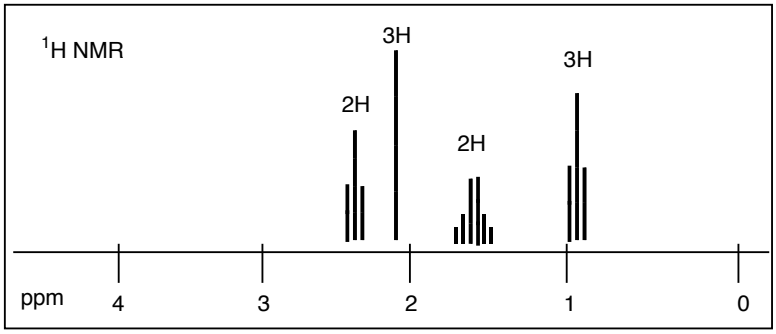
8) The ^{1}H NMR of cyclohexane shows one resonance at 25°C, however, 2 resonances appear when the NMR is taken at –90°C. Provide a brief explanation for this phenomena. (6 points)

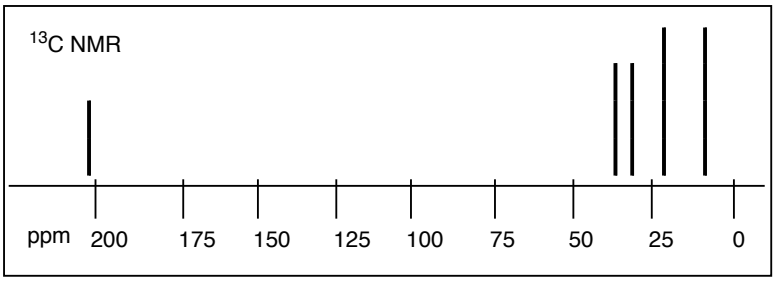
9) For hydrogens on the carbons indicated with arrows, how many peaks would the resonances be split into in the proton NMR spectrum (assume the same coupling constant for multiple neighbors)? (9 points)



10)A molecule with the formula $C_5H_{10}O$ shows a characteristic Infrared absorption at 1715 cm^{-1} and the following MS and NMR spectra. The proton spectra shows the peaks and the relative number of hydrogens that each resonance integrates. The carbon spectrum shows 5 different carbons. (33 points)







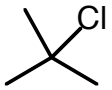
a) What functional group is present in this molecule? (3 points)

b) Draw the structure of this molecule (partial credit will be given for correct "pieces" of the molecule if they match the NMR data). (15 points)

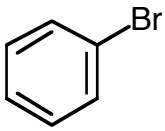
c) What is the structure for the base peak in the Mass Spectrum? Briefly explain why this fragment is particularly stable. (15 points)

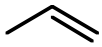
11)Provide the products for the following reactions. Indicate stereochemistry clearly if present. (24 points)

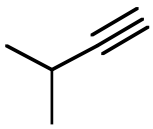
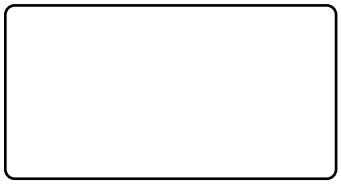
a)  1) OsO_4 2) $NaHSO_3$ → 

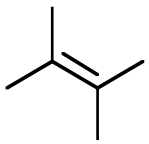
b)  KOH, CH_3CH_2OH → 

c)  NBS, H_2O → 

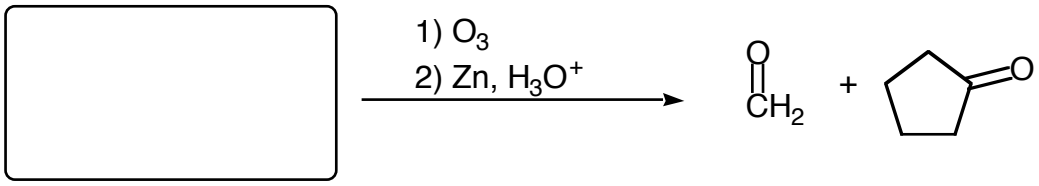
d)  1) Li 2) CuI 3) CH_3I → 

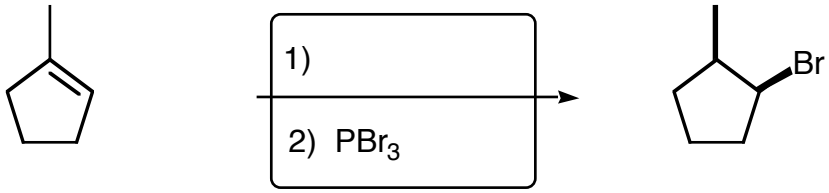
e)  1) Br_2 2) NaOH, ethanol → 

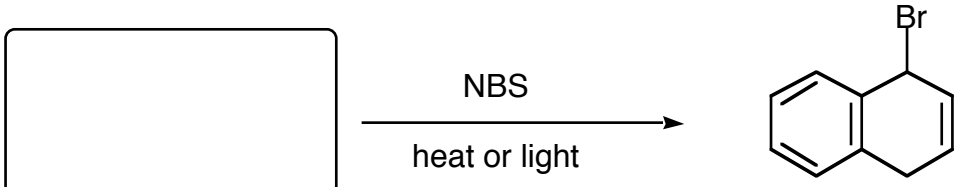
f)  1) $NaNH_2$ 2) CH_3Br 3) Li in NH_3 → 

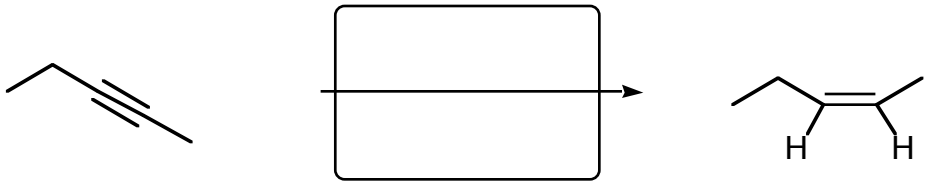
g)  CH_2I_2 Zn(Cu) → 

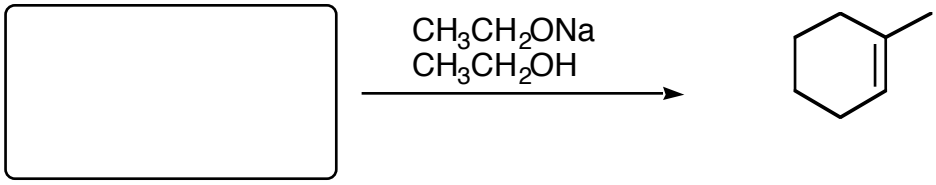
12)Provide the appropriate starting material or reagents for the following reactions. Indicate stereochemistry clearly where applicable. (22 points)

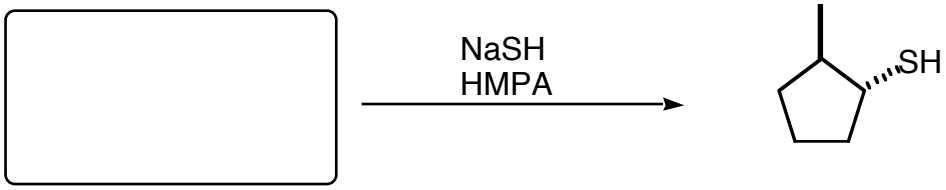
a) 

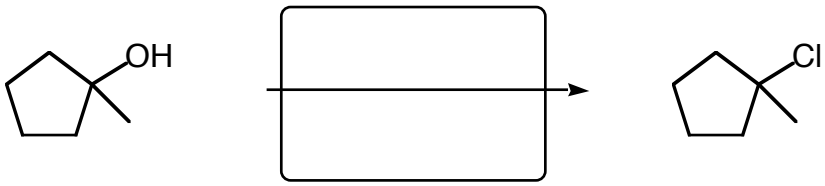
b) 

c) 

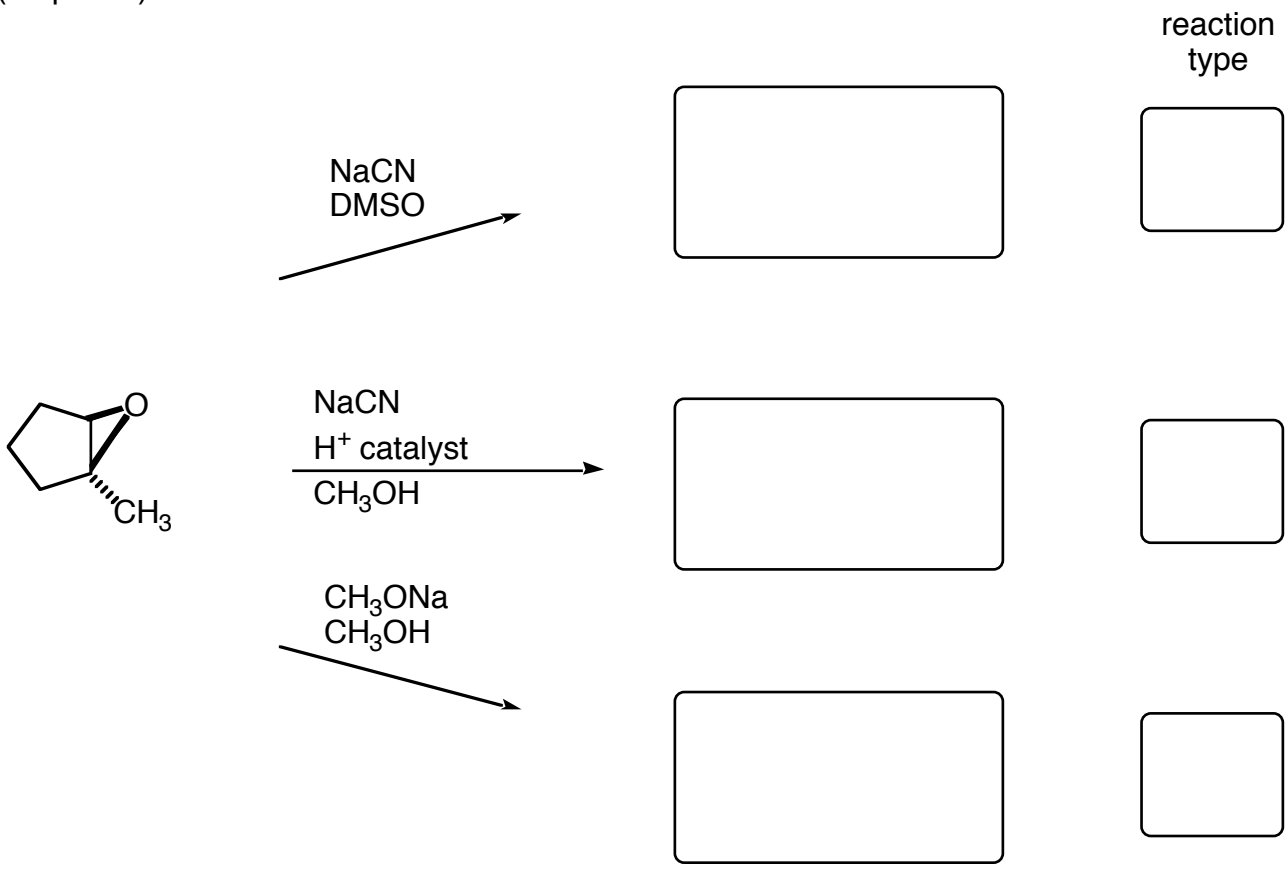
d) 

e) 

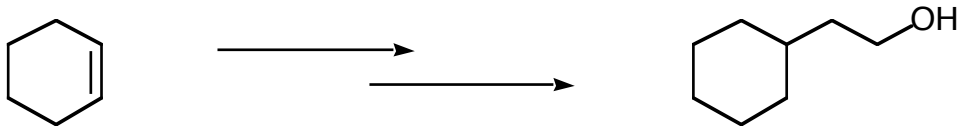
f) 

g) 

13)The carbon-oxygen bond in epoxides (three membered rings with an oxygen) are relatively weak due to the strain of the small ring and are good leaving groups. The epoxide shown below was reacted under three different conditions. Draw the product for each of these reactions and indicate what type of reaction has occurred (Sn1, Sn2, E1, or E2). (15 points)



14)Show how you would prepare vinylcyclohexane from cyclohexylethanol and any other reagents or organic molecules of 2 carbons or less that you need. Note, this is a multistep synthesis. (10 points)



USEFULL DATA

Infrared Correlations:

C-H stretches:	alkanes	2850 - 2960 cm^{-1}	medium/strong
	alkenes	3020 - 3100 cm^{-1}	medium
	alkynes	3300 cm^{-1}	strong (sharp)
O-H stretch:	alcohols	3400 - 3650 cm^{-1}	broad/strong
C=O stretch:	carbonyl	1680 - 1750 cm^{-1}	strong
CC triple bond:	alkyne	2100 2260 cm^{-1}	medium
CN triple bond	nitrile	2210 - 2260 cm^{-1}	medium

^{1}H NMR Correlations:

C-H	(alkanes)	0.5 - 1.5 ppm
allylic	(adjacent to sp^2 carbon)	1.5 - 2.5 ppm
Y-C-H	(Y = O, N, Br, Cl, etc)	2.5 - 4.5 ppm
C=C-H	(alkenes)	4.5 - 6.5 ppm
sp^2 aromatic	(benzene rings)	6.5 - 8.0 ppm
O=C-H	(aldehydes)	9.5 - 10.0 ppm
CO_2H	(acids)	11.0 - 12.0 ppm

^{13}C NMR Correlations:

C	(alkanes)	10 - 60 ppm
Y-C	(Y = O, N, Br, Cl, etc)	40 - 80 ppm
C=C	(alkenes)	100 - 150 ppm
sp^2 aromatic	(benzene rings)	120 - 160 ppm
O=C-O	(esters)	175 - 200 ppm
$O=CR_2$	(aldehydes, ketones)	200 - 220 ppm