Exam 4 Test Prep Worksheet

Alkenes			
Reaction	**Reagents**	**Regioselectivity**	**Stereoselectivity**
Hydrohalogenation	HX	Markovnikov	racemic mixture
Hydrohalogenation with peroxide	HX / ROOR	Anti-markovnikov	racemic mixture
Acid-Catalyzed Hydration	H_2SO_4, H_2O	Markovnikov	racemic mixture
Oxymercuration-Demurcuration	1. $Hg(OAc)_2$, H_2O 2. $NaBH_4$	Markovnikov	Anti
Hydroboration- oxidation	1. $BH_3 \cdot THF$ 2. H_2O_2, $NaOH$	Anti-markovnikov	Syn
Halogenation	X_2 / CCl_4	N/A	Anti
Halohydrination	X_2 / H_2O	Markovnikov -OH priority	Anti
Catalytic Hydrogenation	H_2 / Pt	N/A	syn
Syn-Dihydroxylation	1. OsO_4, pyridine 2. $NaHSO_3/H_2O$	E → racemic mixture Z → meso	Syn
Oxidative Cleavage with hot potassium permanganate	$KMnO_4$, ^-OH, H_2O / heat	N/A	N/A
Ozonolysis	O_3 / DMS	N/A	N/A

Alkenes			

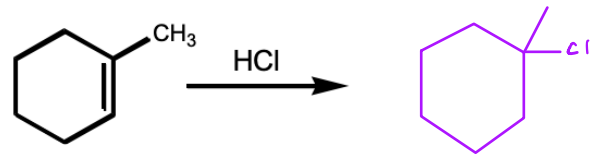
Alkynes			
Reaction	**Reagents**	**Regioelectivity**	**Stereoselectivity**
Halogenation	xs X_2, CCl_4	N/A	trans
Hydrohalogenation	xs HX	Markovnikov	trans
Hydrogenation	H_2, Pt	N/A	cis
Hydrogenation with Lindlar's	H_2, $Pd/CaCO_3$, Pb	N/A	cis
Ozonolysis	O_3, DMS	N/A	N/A
Oxidative Cleavage with hot potassium permanganate	$KMnO_4$, OH, H_2O, heat	N/A	N/A
Formation of Acetylide	$NaNH_2$	N/A	N/A
Dissolving Metal Reduction	Na, $NH_3(l)$	N/A	trans

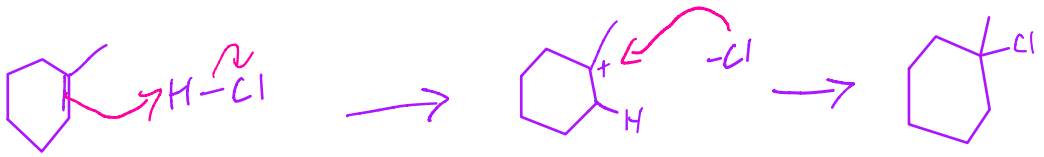
Alkynes			

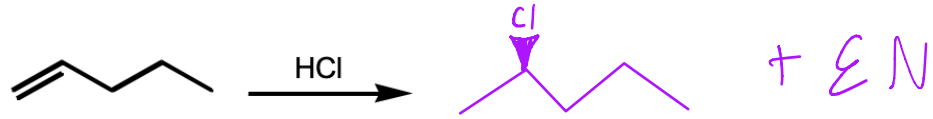
Given the reactions below:

1. Name the reaction
2. Predict the major product of the reaction
3. Draw the mechanism (if needed)

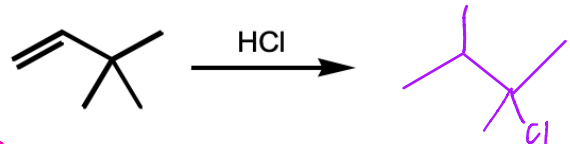
Hydrohalogenation



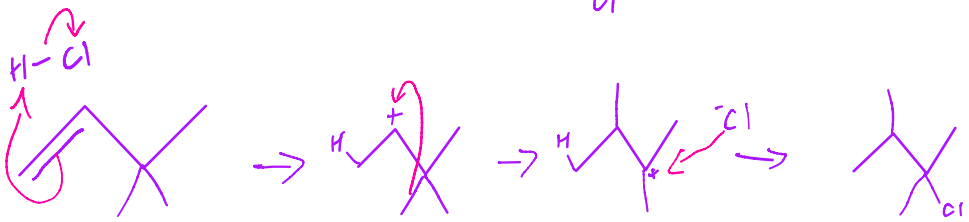




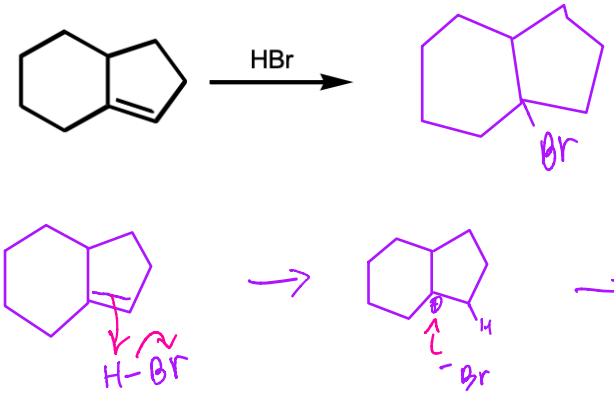
Hydrohalogenation

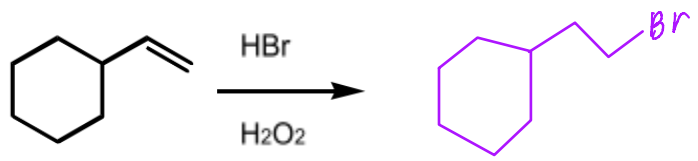


Hydrohalogenation



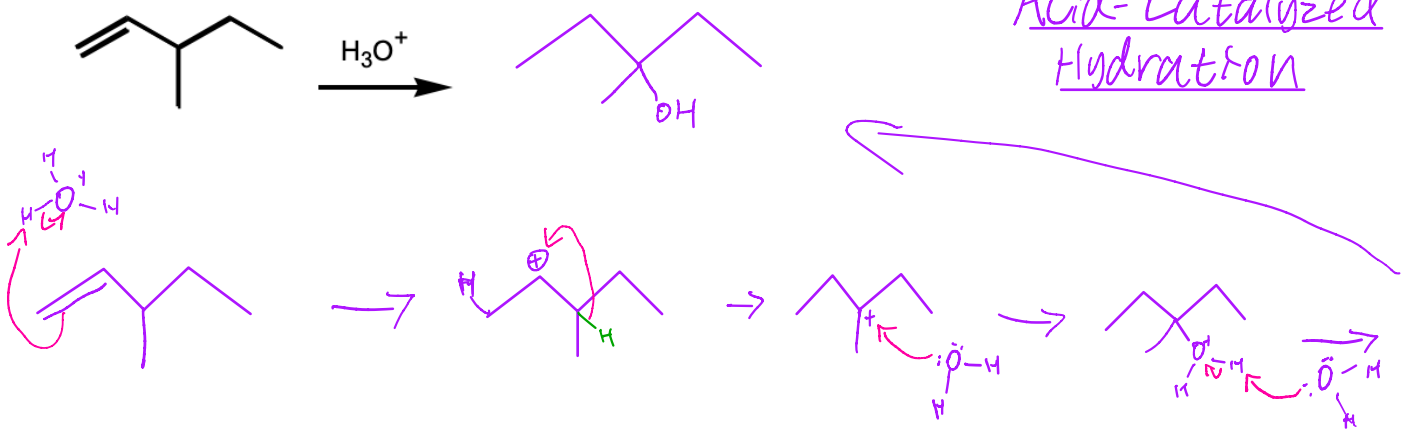
Hydrohalogenation



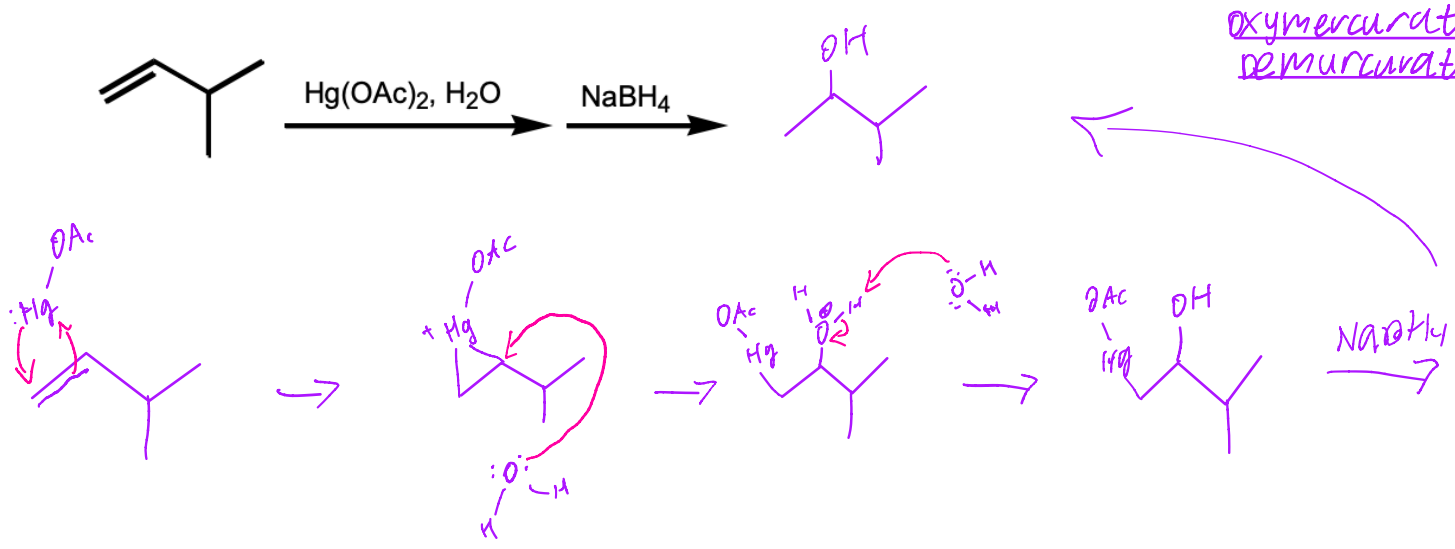


Hydrohalogenation with peroxides

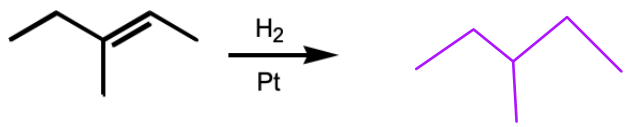
Acid-catalyzed Hydration

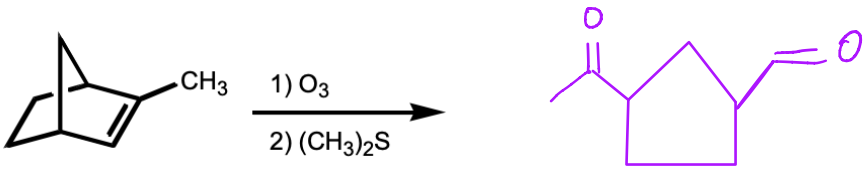


Oxymercuration demercuration

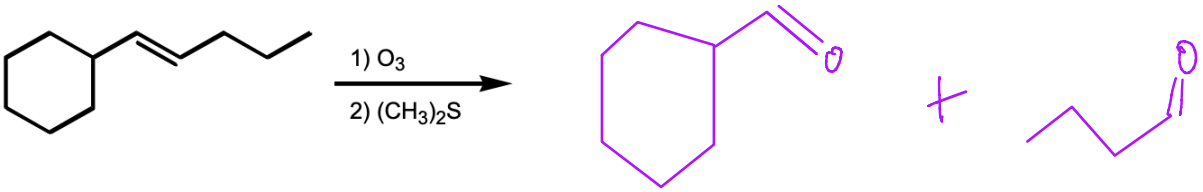


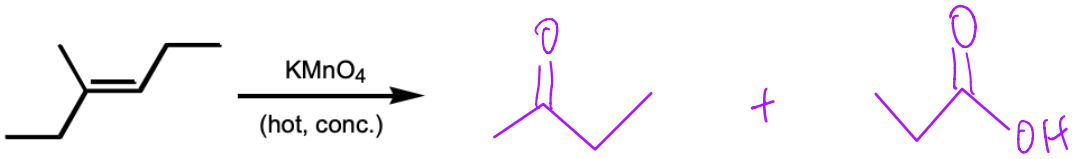
Hydrogenation



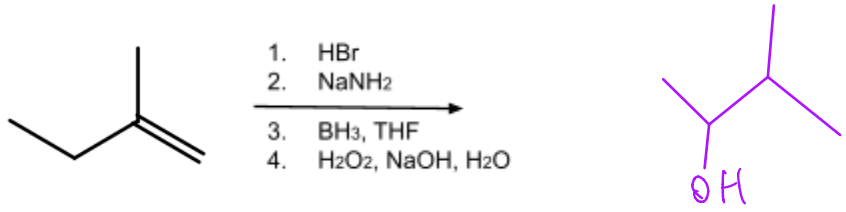


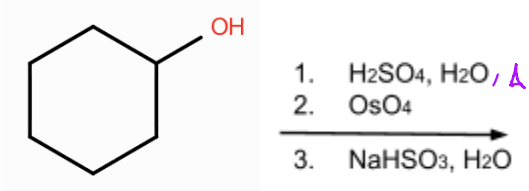
Ozonolysis

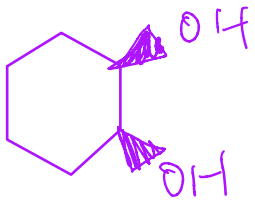




Predict the major product of the multi-step problems below:

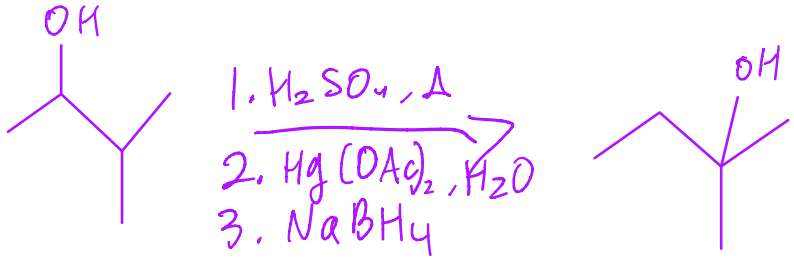


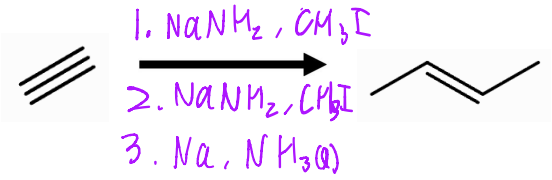




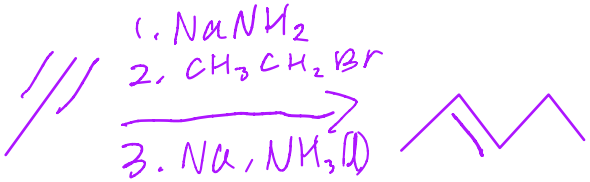
Provide the forward synthesis reagents for the problems below:

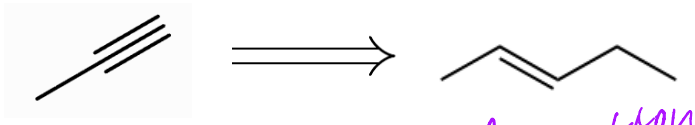
3-methyl-2-butanol to 2-methyl-2-butanol

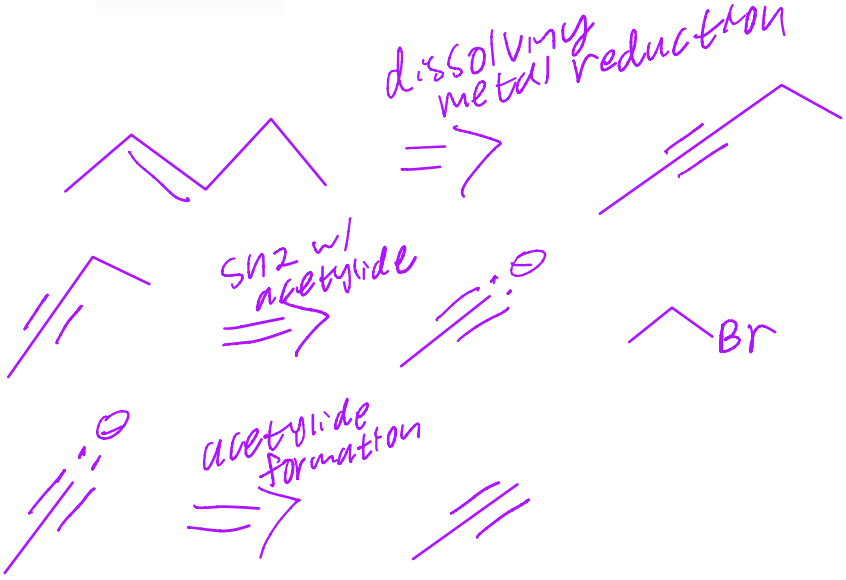


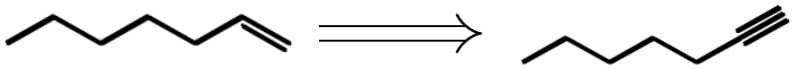


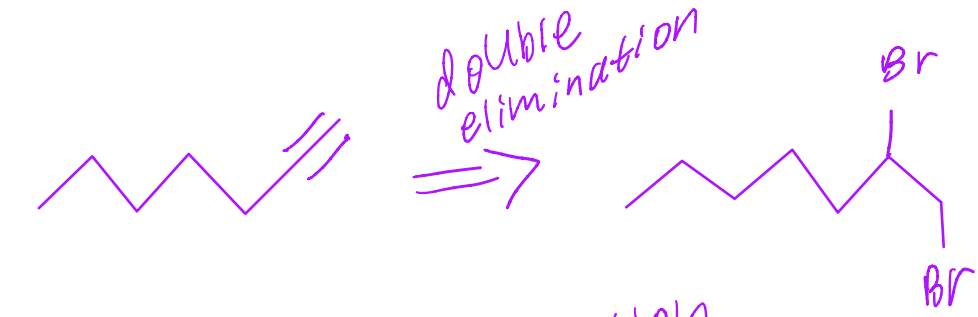
Provide a retrosynthesis for the scenarios below:

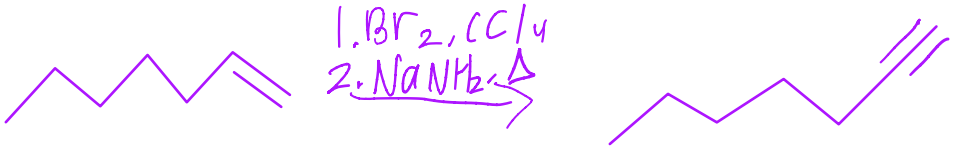












Multiple-choice questions

1. Addition of Br2 to (E)-hex-3-ene produces

   A) a meso dibromide
   B) a mixture of enantiomeric dibromides which is optically active
   C) a mixture of enantiomeric dibromides which is optically inactive
   D) (Z)-3,4-dibromo-3-hexene
   E) (E)-3,4-dibromo-3-hexene

2. Which of the following additions to alkenes occur(s) specifically in an anti fashion?

   A) hydroboration-oxidation
   B) addition of Br2
   C) addition of H2
   D) addition of H2O in dilute acid
   E) both A and B

3. HBr can be added to an alkene in the presence of peroxides (ROOR). What function does the peroxide serve in this reaction?

   A) nucleophile
   B) electrophile
   C) radical chain initiator
   D) acid catalyst
   E) solvent

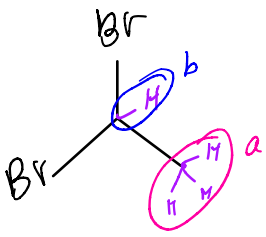
^{1}H NMR

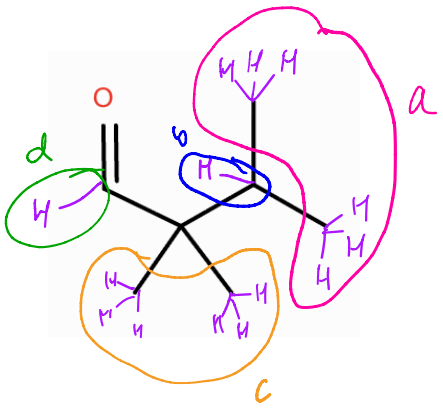
In the compounds below, circle and label the unique hydrogen environments, their splitting pattern, and intergration (except the last one)

$CHBr_2CH_3$

a. doublet 3H

b. quartet 1H





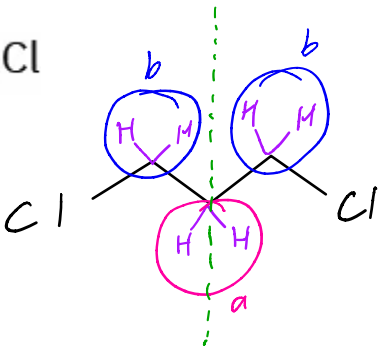
a. doublet 6 H

b. septet 1 H

c. singlet 6 H

d. singlet 1 H

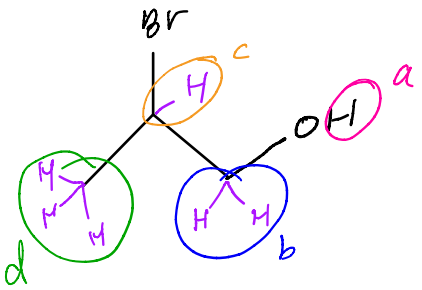
$ClCH_2CH_2CH_2Cl$



a. quintet 2 H

b. triplet 2 H

2-Bromo–1–propanol

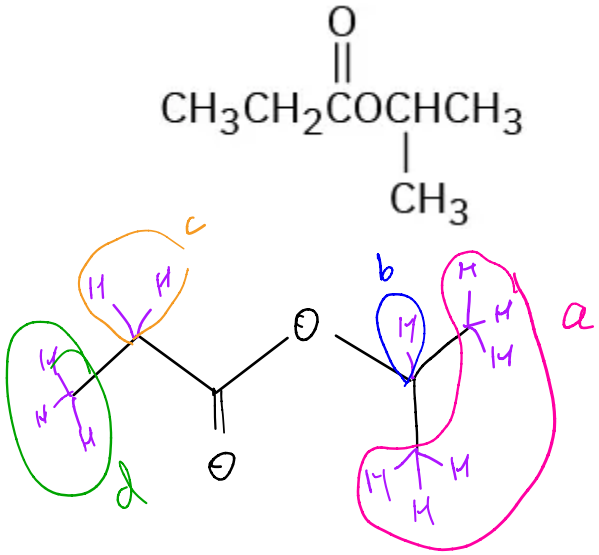


a. Singlet 1H

b. doublet 2H

c. sextet 1H

d. doublet 3H

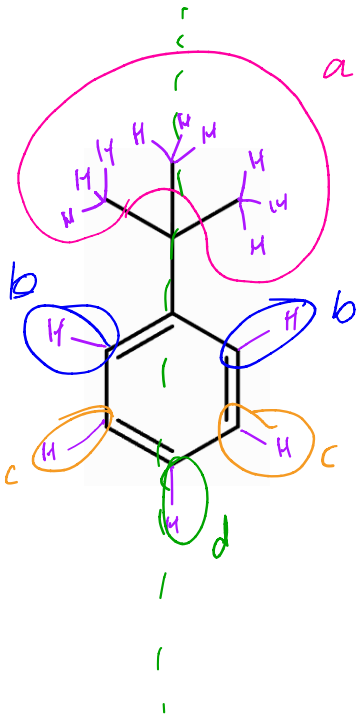


a. doublet 6 H

b. septet 1 H

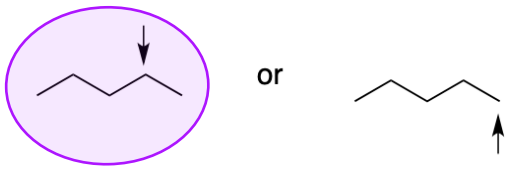
c. quartet 2 H

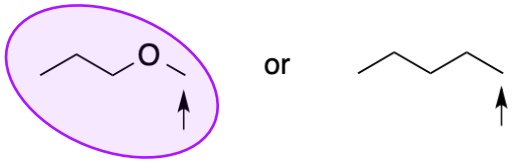
d. triplet 3 H

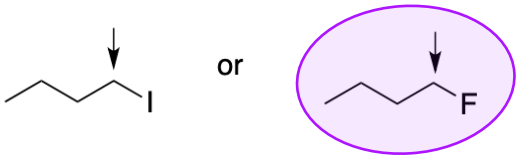


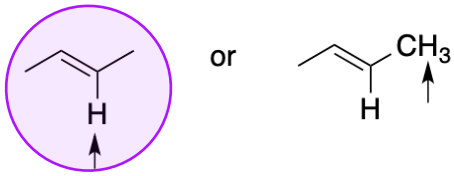
only label H-environments

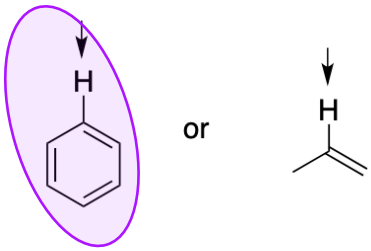
Which of the indicated protons in each pair will show up farther downfield?

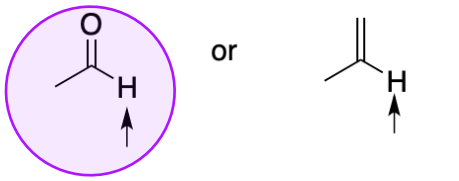






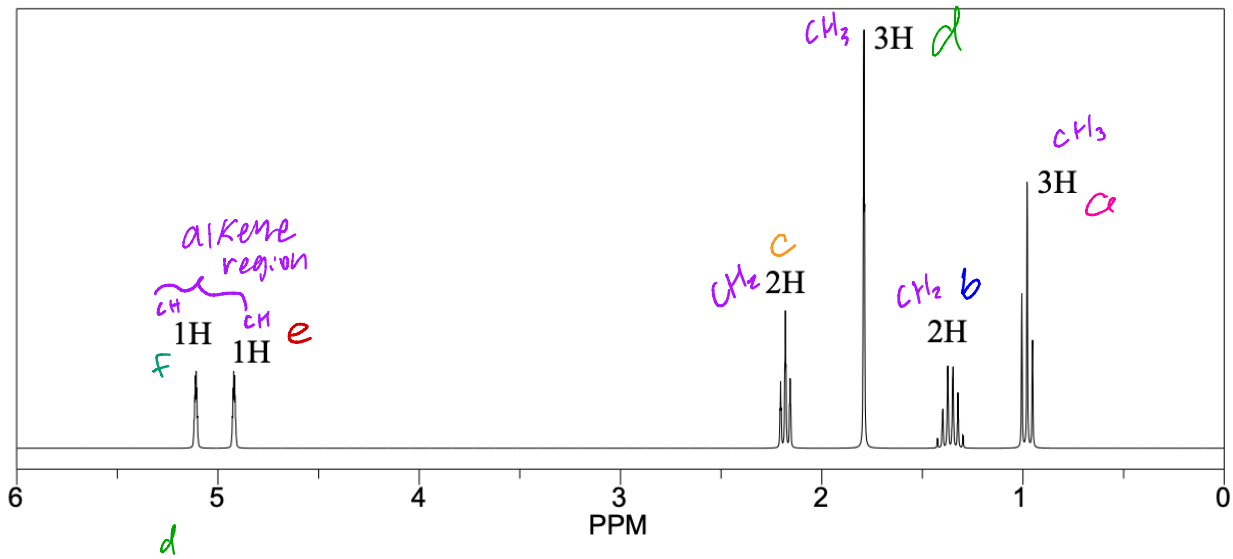


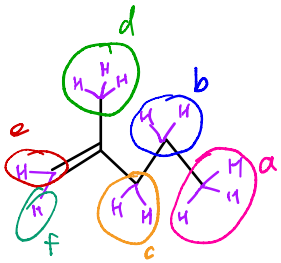


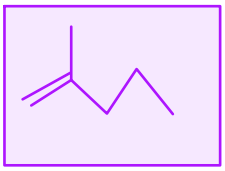


Given the molecular formula and ^{1}H NMR spectra, propose a structure

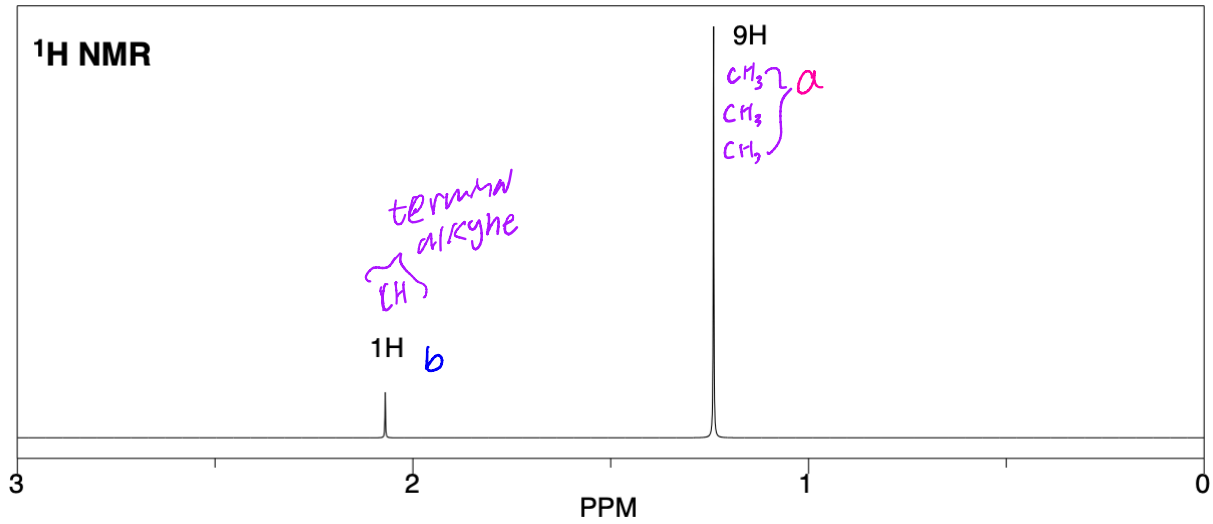
C_6H_{12}

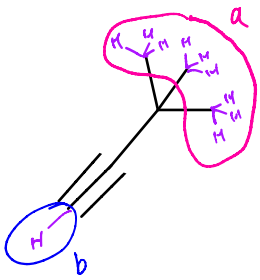


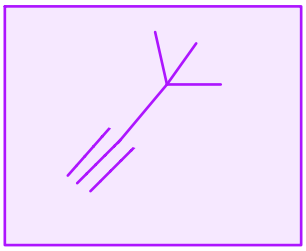




C_6H_{10}

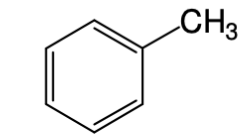




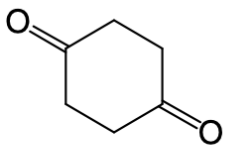


^{13}C NMR

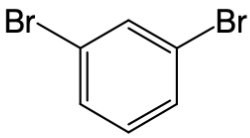
Predict how many signals you would see in the ^{13}C NMR spectrum of each of these molecules:



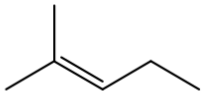
5



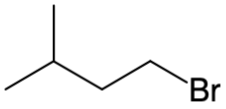
2



4

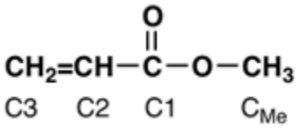


6



4

1. Which of options indicates the correct order of carbon chemical shifts of the four carbons of the following compound? Draw what the ^{13}C NMR would look like.

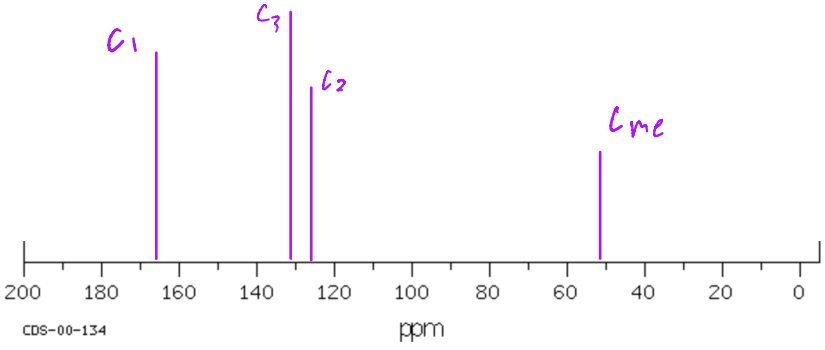


A $C_{Me} < C2 < C3 < C1$

B $C3 < C2 < C_{Me} < C1$

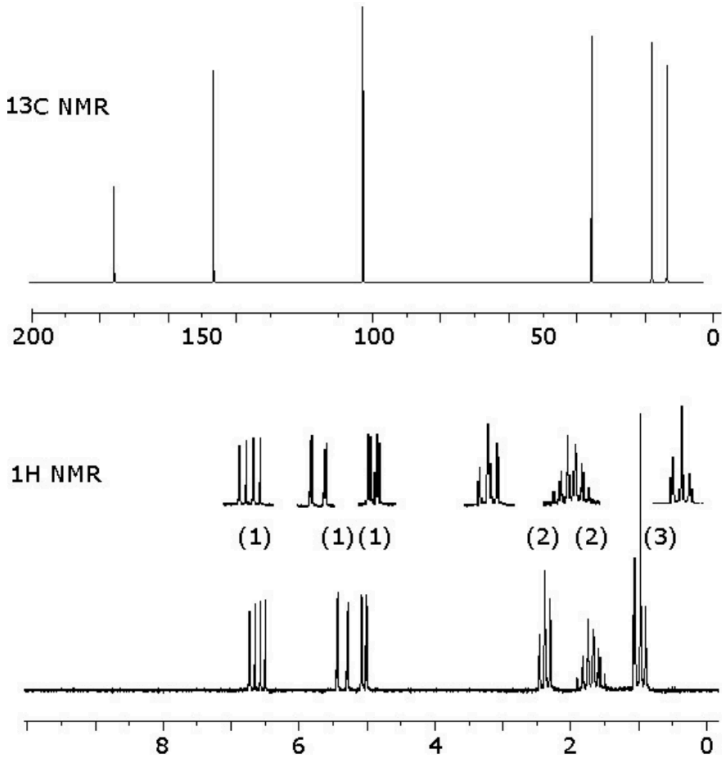
C $C1 < C3 < C2 < C_{Me}$

D $C1 < C_{Me} < C2 < C3$



Given the following molecular formula, ^{1}H NMR, ^{13}C NMR, answer the following questions:

$C_6H_{10}O_2$



1. Is there symmetry in this compound?

   no

2. In the 13C NMR, what does the chemical shift of the signal at about 105 suggest?

   sp^2 C → =C

3. In the 1H NMR, what does the chemical shift of the signal at about 5.2 suggest?

   H on an alkene

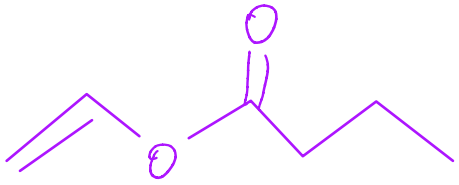
4. In the 1H NMR, what does the integration of the signal at about 2.3 suggest?

   Probably a CH_2

5. In the 1H NMR, what does the splitting pattern of the signal at about 1.0 suggest?

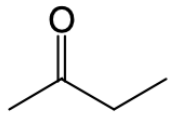
   The group is next to 2 Hs

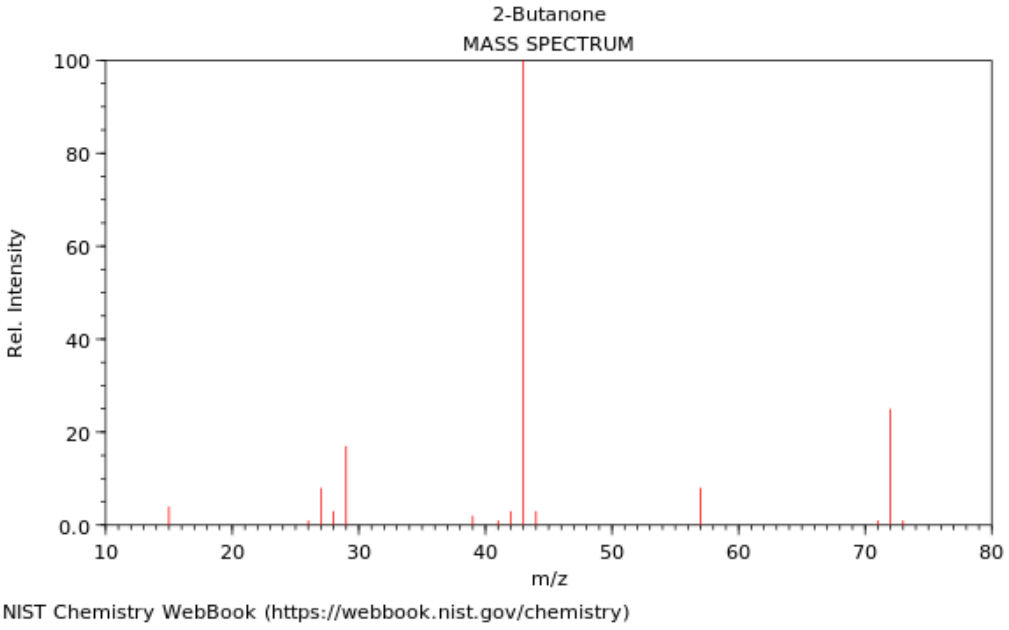
6. What is the structure of this unknown?



Mass Spectrometry

Below is the mass spectrum of 2-butanone. Explain the large peak at 43 and the small peak at 73.





- 43 m/z is the base peak, the most common fragment

- 73 m/z is the M^+ (molecular ion peak)

1. A prominent (M•-18) peak suggests that the compound might be a(n):

   A) Alkane
   B) Alcohol
   C) Ether
   D) Ketone
   E) Primary amine

2. Mass spectrometry detects:

   I. Radicals
   II. Radicals and radical cations
   III. Radical cations
   IV. Cations and Anions

   A) I and II
   B) III only
   C) IV only
   D) I, II, and III
   E) II and IV

3. What is the criteria for using mass spectrometry?

   A) To find the composition of the sample
   B) To find the relative mass of atoms
   C) To find the concentration of elements in the sample
   D) To find the properties of the sample