The first 12 questions are 5 point multiple choice questions and should be answered by filling in the appropriate bubble for each question.

Questions 13-16 are 10 point short answer questions and should be answered in the space provided on the front and back of the answer form.

^{1}H-NMR Chemical Shifts

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)
$(CH_3)_4Si$	0 (by definition)	RCH_2OH	3.4–4.0
R_2NH	0.5–5.0	RCH_2Br	3.4–3.6
ROH	0.5–6.0	RCH_2Cl	3.6–3.8
RCH_3	0.8–1.0	$RCOCH_3$	3.7–3.9
RCH_2R	1.2–1.4	$RCOCH_2R$	4.1–4.7
R_3CH	1.4–1.7	RCH_2F	4.4–4.5
$R_2C{=}CRCHR_2$	1.6–2.6	$ArOH$	4.5–4.7
$RC{\equiv}CH$	2.0–3.0	$R_2C{=}CH_2$	4.6–5.0
$RCCH_3$	2.1–2.3	$R_2C{=}CHR$	5.0–5.7
$RCCH_2R$	2.2–2.6	ArH	6.5–8.5
$ArCH_3$	2.2–2.5	RCH	9.5–10.1
$ArCH_2R$	2.3–2.8	$RCOH$	10–13
RCH_2I	3.1–3.3		
RCH_2OR	3.3–4.0		

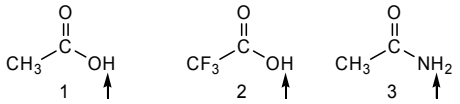
Infrared Absorption Frequencies

Bonding		Frequency (cm^{-1})	Intensity*
C—H	alkane	2850–3000	m
	—CH_3	1375 and 1450	w–m
	—CH_2—	1450–1475	m
	alkene	3000–3100	w–m
		650–1000	s
	alkyne	3300	m-s
	arene	3030	w-m
		690–900	s
	aldehyde	2720	w
C=C	alkene	1600–1680	w–m
	arene	1450 and 1600	m
C≡C	alkyne	2100–2250	w
C—O	alcohol, ether, ester, carboxylic acid	1000–1100 (sp^3 C—O)	s
		1200–1250 (sp^2 C—O)	s
	anhydride	900–1300	s

Bonding		Frequency (cm^{-1})	Intensity*
C=O	amide	1630–1680	s
	carboxylic acid	1700–1725	s
	ketone	1630–1820	s
	aldehyde	1630–1820	s
	ester	1735–1800	s
	anhydride	1740–1760 and 1800–1850	s
	acid chloride	1800	s
O—H	alcohol, phenol		
	free	3600–3650	w
	hydrogen bonded	3200–3500	m
	carboxylic acid	2500–3300	s
N—H	amine and amide	3100–3550	m–s
C≡N	nitrile	2200–2250	m

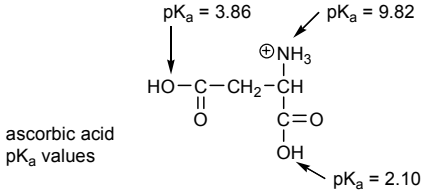
Multiple Choice Questions. 60 points

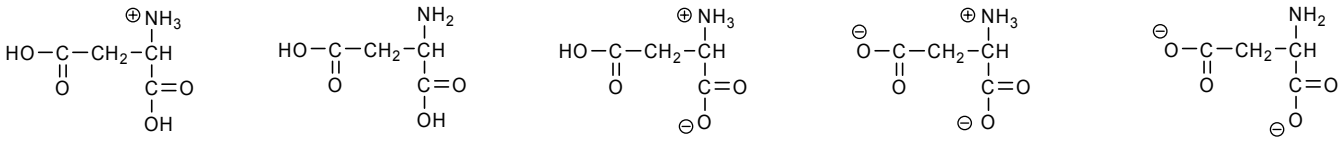
1. Choose the correct order of acidity for the following compounds (most acidic on right).



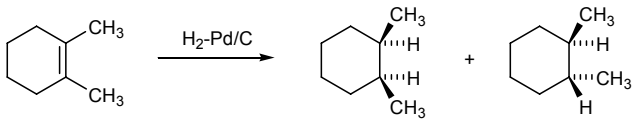
A. 3<1<2 B. 1<3<2 C. 2<3 <1 D. 3<2<1 E. 1<2<3

2. The pK_a values of aspartic acid, a naturally occurring amino acid are shown to the right. Choose from below, the structure of the major species present at a pH of 7.2.





3. Choose the *incorrect* statement about the following catalytic hydrogenation.



(A) The *syn* addition of hydrogen gives the *cis* isomer as the major product.

(B) The minor product occurs as the result of a catalyzed isomerization of the reactant..

(C) The catalyst (Pd/C) speeds up the reaction by stabilizing the major product of the reaction.

(D) The minor *trans* isomer is actually present as a racemic mixture.

(E) The reduction of 3,3,6,6-tetramethylcyclohexene would be predicted to occur at a slower reaction rate.

4. Choose the *incorrect* statement about the following acid/base reactions involving propyne and its anion propynide.

(i) $CH_3C\equiv CH + OH^- \rightleftharpoons CH_3C\equiv C^- + H_2O$

(ii) $CH_3C\equiv CH + NH_2^- \rightleftharpoons CH_3C\equiv C^- + NH_3$

	pK_a
H_2O	16
$CH_3C\equiv CH$	25
NH_3	34

(A) The equilibrium in equation (i) lies to the left.

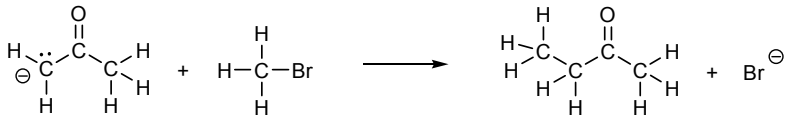
(B) The equilibrium in equation (ii) lies to the right.

(C) You can prepare propynide, $CH_3C\equiv C^-$, salts in NH_3. .

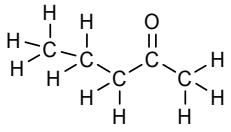
(D) Propyne, $CH_3C\equiv CH$, is a stronger acid than ammonia, NH_3.

(E) In reaction (ii) ammonia, NH_3, acts as a base.

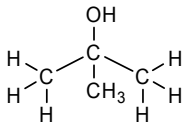
5. In addition to 2-butanone, a second product is formed in the following acid-base reaction. Choose the structure for this second product.



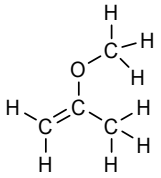
acetonate ion methyl bromide 2-butanone



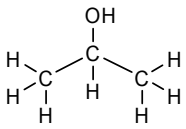
(A)



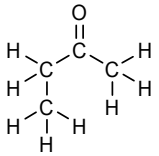
(B)



(C)

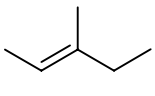


(D)

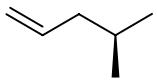


(E)

6. Choose the *incorrect* statement about the following two alkenes.



(i)



(ii)

(A) Alkene (i) is more stable than alkene(ii).

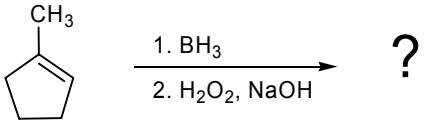
(B) Hydrogenation of achiral alkene (i), will give chiral products.

(C) Hydrogenation of chiral alkene, (ii), will give a chiral product.

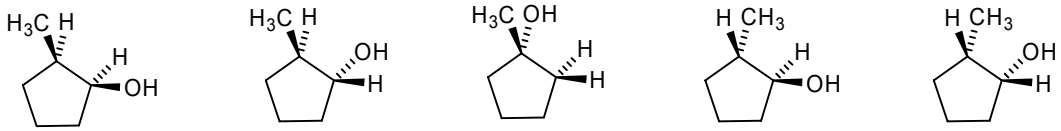
(D) Hydrogenation of alkene (ii) will yield more heat than will hydrogenation of alkene (i).

(E) The two alkenes (i) and (ii) are configurational isomers.

7. Supposed you carried out the hydroboration of 1-methylcyclopentene:



Choose the correct answer for the products formed in the above reaction.



1. 2. 3. 4. 5.

(A) An equal mixture of 1 and 5.

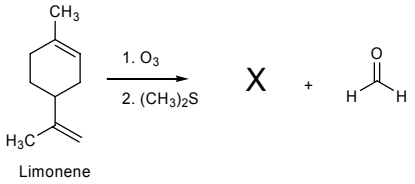
(B) An equal mixture of 1 and 2

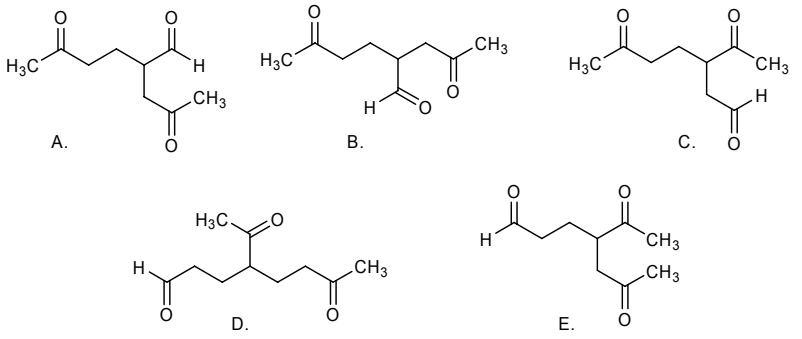
(C) An equal mixture of 2 and 4

(D) An equal mixture of 4 and 5

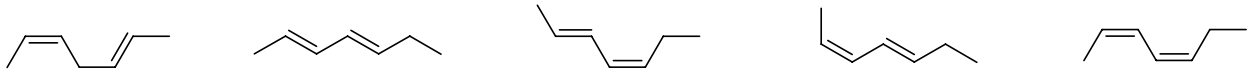
(E) Compound 3 only

8. The ozonolysis of limonene (oil of lemons) give compound X plus formaldehyde. Choose the correct structure for X.

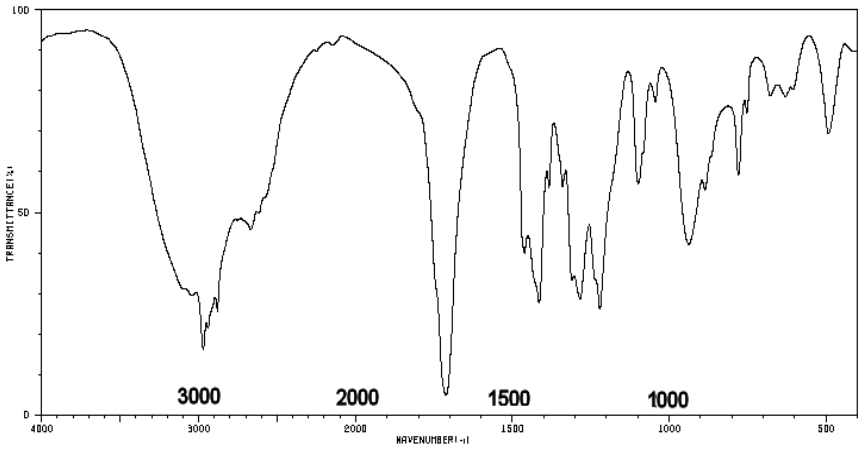


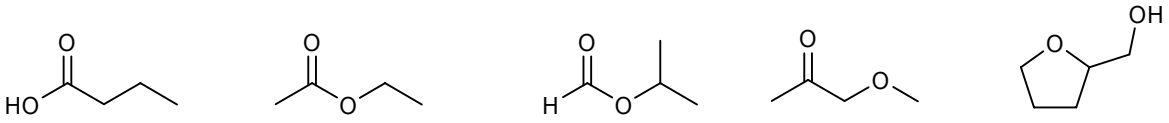


9. Which one of the following structures would be named, **(2*Z*,4*E*)-2,4-heptadiene**?



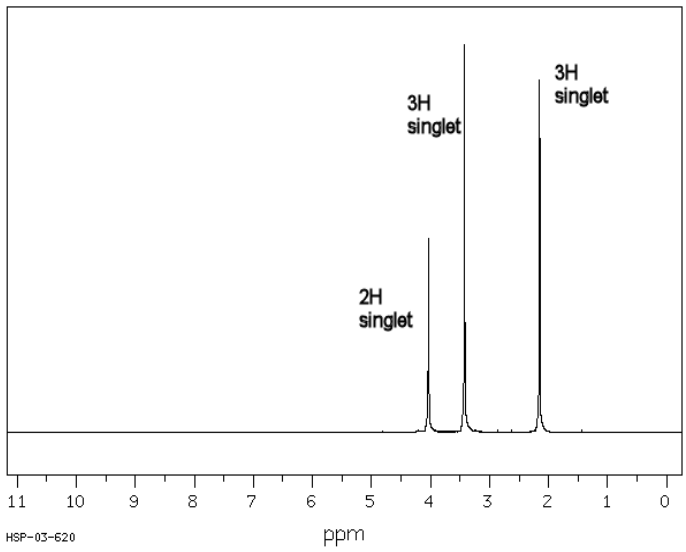
10. You have a compound of formula $C_4H_8O_2$. Which structure shown below is consistent with the following IR spectrum?

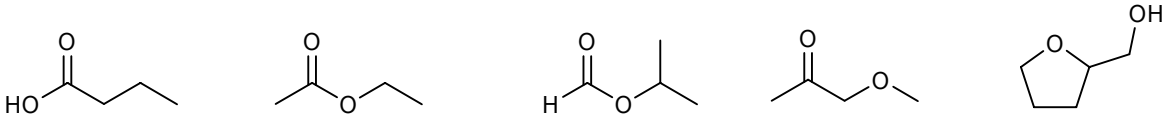




A. B. C. D. E.

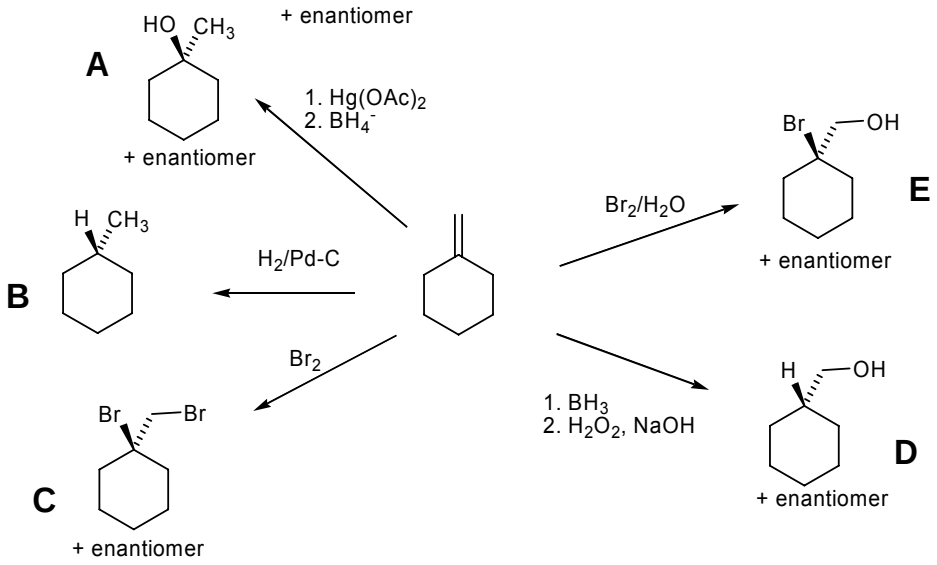
11. You have a compound of formula $C_4H_8O_2$. Which structure shown below is consistent with the following NMR spectrum?



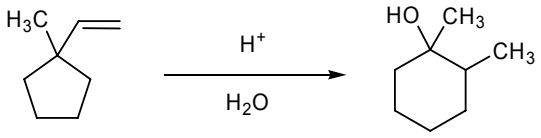


A. B. C. D. E.

12. Which of the following reactions is *incorrect*?

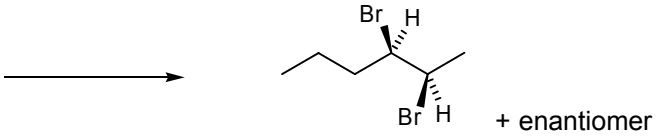


The following short answer questions are worth 10 points each.
Draw a curved arrow mechanism for the following reaction.

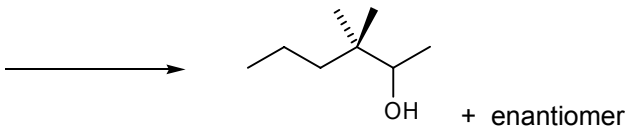


13. Complete the following reactions by supplying the missing reagents.

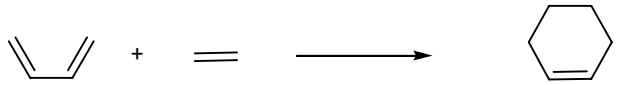
a.



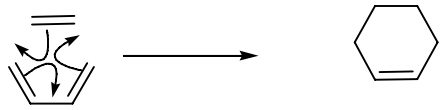
b.



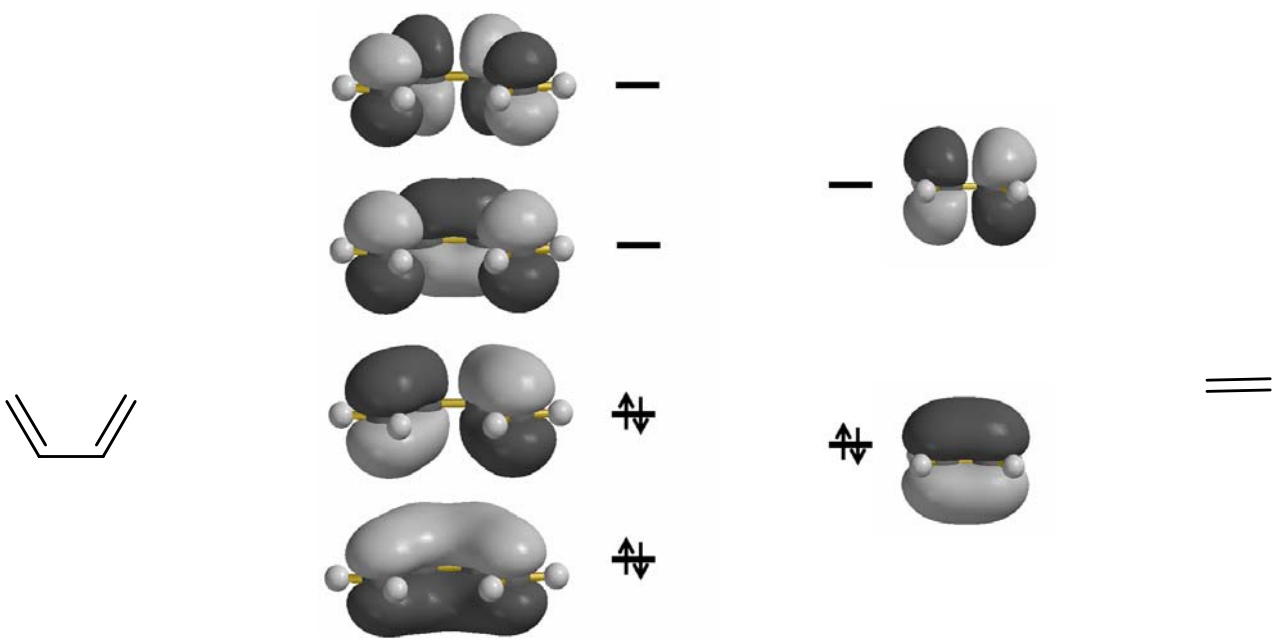
14. Here is an unusual reaction we have not yet discussed in the course. The reaction of ethylene with butadiene to give cyclohexene.



Here we show the reaction using arrows



Here are the relevant orbitals of butadiene and ethylene.



Specify the symmetry of each of the following molecular orbitals

Butadiene HOMO	A	or	S	(circle your choice)
Butadiene LUMO	A	or	S	
Ethylene HOMO	A	or	S	
Ethylene LUMO	A	or	S	

The reaction is allowed by orbital symmetry True or False

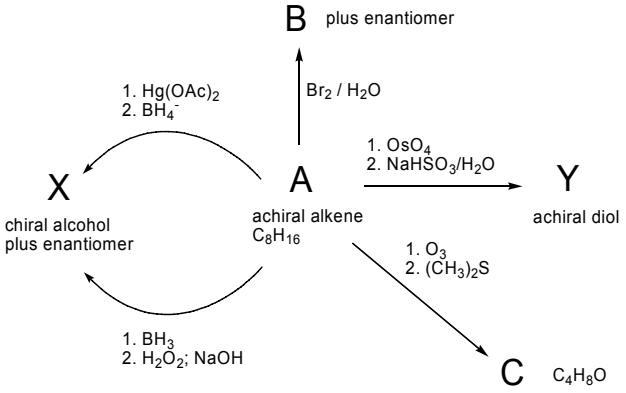
16. Compound **A** is an achiral alkene of formula C_8H_{16}. The NMR of **A** is shown below.

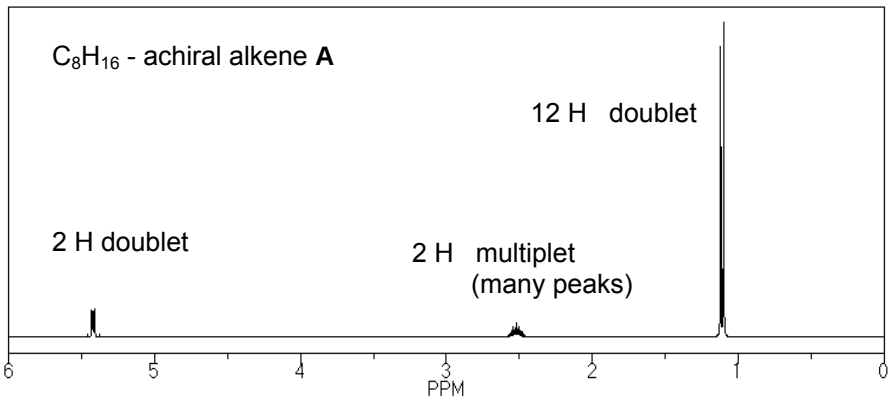
Oxymercuration of **A** gives a chiral alcohol, **X,** plus its enantiomer. Hydroboration gives the same products, **X**, as does the oxymercuration reaction.

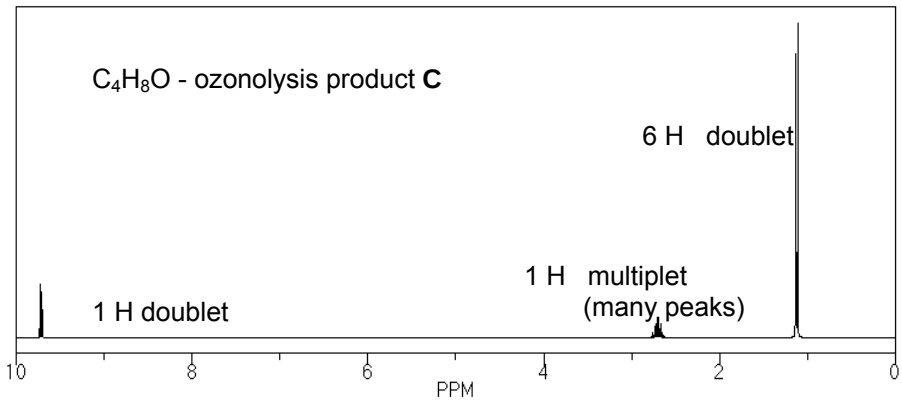
Bromine addition in H_2O gives compound, **B,** and its enantiomer.

Oxidation of **A** by OsO_4 gives an achiral diol, **Y**.

Ozonolysis of **A** gives a single compound **C,** with formula C_4H_8O. **C** has the NMR shown below.







Draw structures for **A, B, and C** on your answer sheet. (You do not need to give structures for X and **Y**)