Chemistry 210
"Organic Chemistry I"
Winter Semester 2001
Dr. Rainer Glaser

Examination #5
"Reactions of Alcohols and Related Reactions, NMR & IR."

The Final Learning Experience

Saturday, May 19, 2001, 1:00 - 3:00 pm

Name:

Answer Key

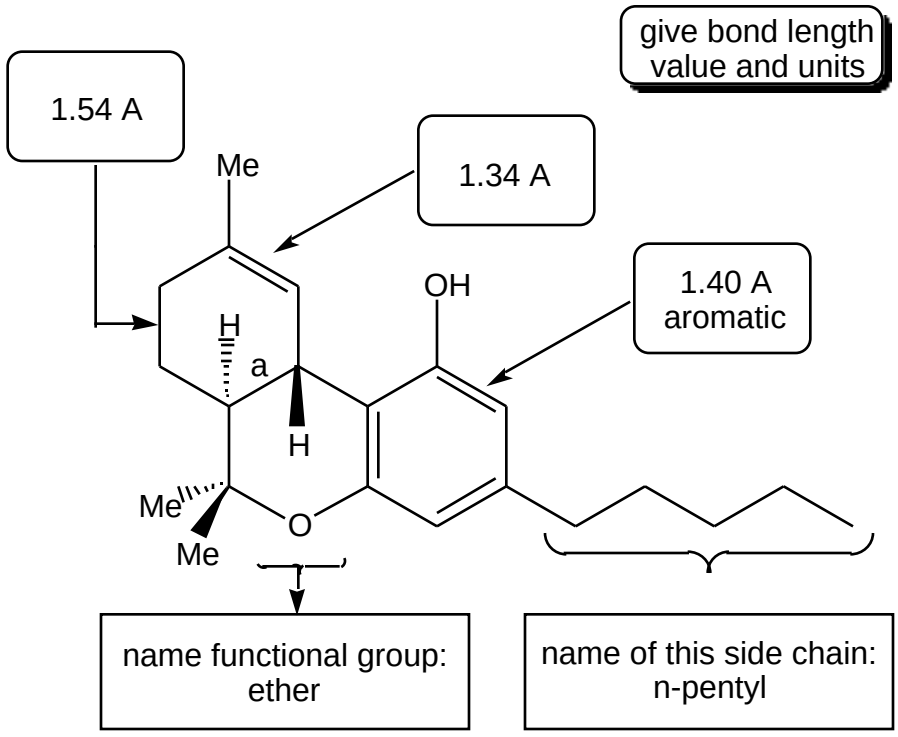
Question 1. Marijuana Structure. (Today's News!)	20	
Question 2. Diels-Alder Reactions & Carbene Chemistry.	20	
Question 3. Syntheses of Alcohols: Grignards& Reductions & more	40	
Question 4. Reactions of Alcohols.	20	
Question 5. Oxidation of Alcohols. NMR & IR.	50	
Question 6. Reactions of Alcohols. Aspartame. (News #11)	30	
Question 7. IR-Spec. & Greenhouse Effect (News #12 and VC #12)	40	
Total	220	

Question 1. Marijuana Structure. (20 points)

"SUPREME COURT SAYS NO TO MEDICAL MARIJUANA USE"
The Los Angeles Times, May 15, 2001.

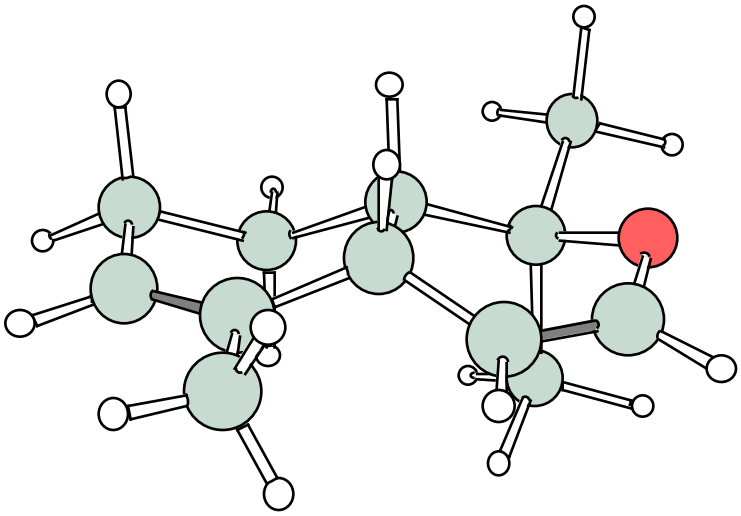
WASHINGTON--The Supreme Court dealt a defeat Monday to the medical marijuana movement, ruling that federal law prohibits dispensing the drug to seriously ill patients to relieve their pain and nausea. As a legal matter, the 8-0 ruling all but invalidates the measures adopted in California and eight other states that give sick people a "right" to obtain marijuana for medical purposes. Because federal law trumps state laws, Monday's ruling makes clear that the distribution of marijuana is illegal throughout the United States. However, it is not clear that federal authorities will be able to enforce their prohibition on marijuana. Advocates of medical marijuana said they are confident that jurors in California and the other states will not convict those who are charged with giving marijuana to sick people. …

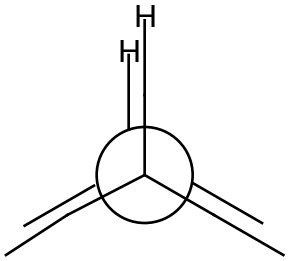
(a) The active ingredient of marijuana is **tetrahydrocannabinol**, or **THC** for short, and its structure is shown. In the five boxes, please provide the information requested. (10 p., 2 points each).



(b) Now let's take a look at the bond that is marked by "a". The models **A** and **B** are simplified versions of THC. The simplification consists in the omission of the entire benzene ring. Consider the Lewis structure of THC on the previous page and decide whether Model **A** or Model **B** more closely mimics the fused ring system in THC. The better model is _____Model **B**____. On the right, draw Newman projections of the "a" bond for Model **A** and for Model **B**. (Focus only on the "a" bond" and abbreviate the attached groups simply as R, R', R", …) For each model state whether the conformation is *staggered* or whether it is *eclipsed*. For each model state whether the two hydrogen atoms are *cis* or whether they are *trans*. (10 points)

Model A

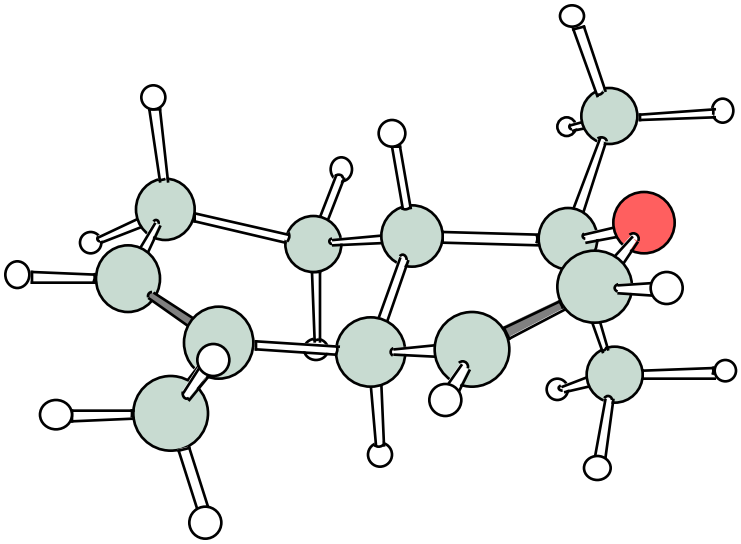


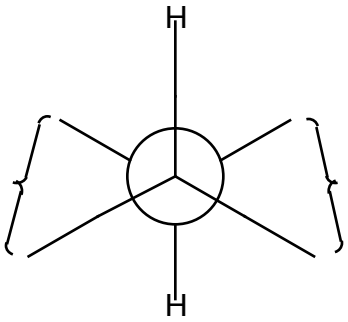


eclipsed

cis

Model B



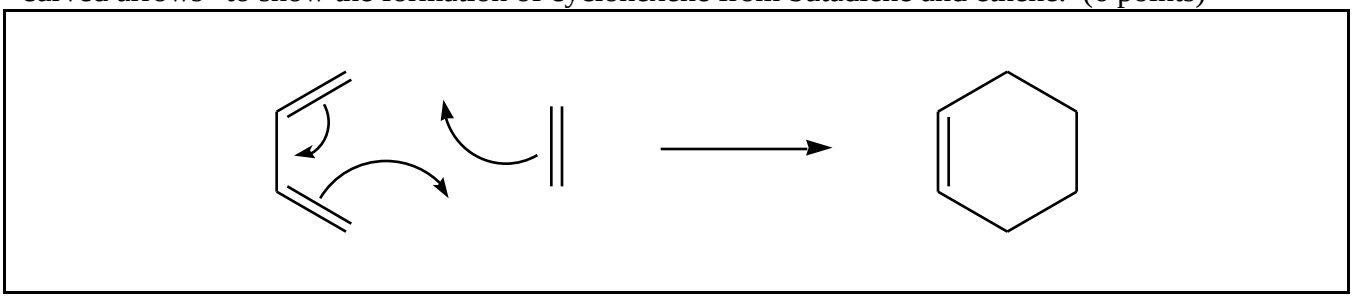


staggered

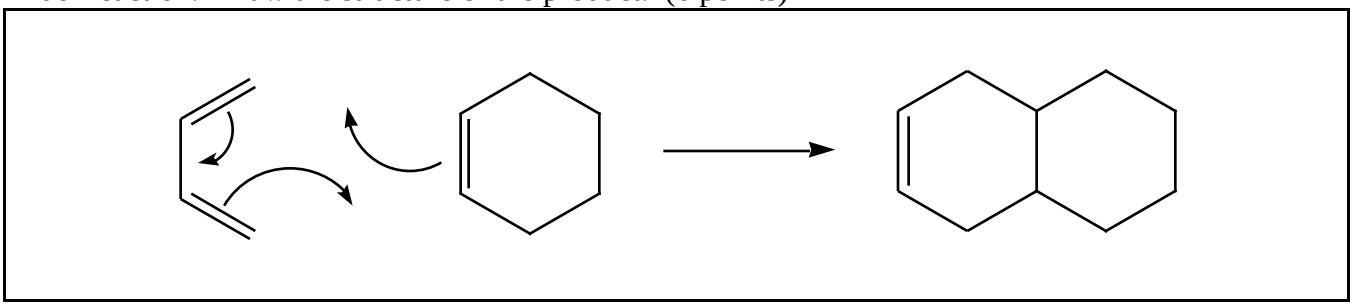
trans

Question 2. Diels-Alder Reaction & Carbene Chemistry. (20 points)

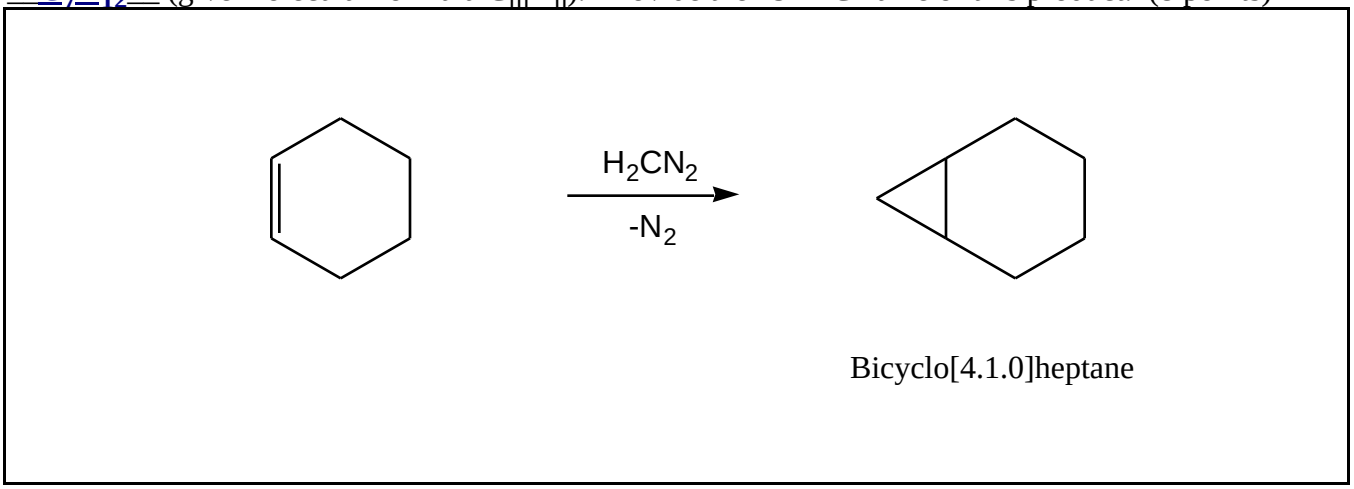
(a) The Diels-Alder reaction is the best reaction to prepare six-membered rings. The simplest Diels-Alder reaction is that between **butadiene and ethene** to form cyclohexene. Draw the substrates and use "curved arrows" to show the formation of cyclohexene from butadiene and ethene. (6 points)



(b) Many alkenes can be used as substrates in Diels-Alder reactions and that includes cyclic alkenes as well. Consider the Diels-Alder reaction between the diene **butadiene** and the dienophile **cyclohexene**. Draw the structures of the substrates and use "curved arrows" to show the electron flow in the Diels-Alder reaction. Draw the structure of the product. (6 points)



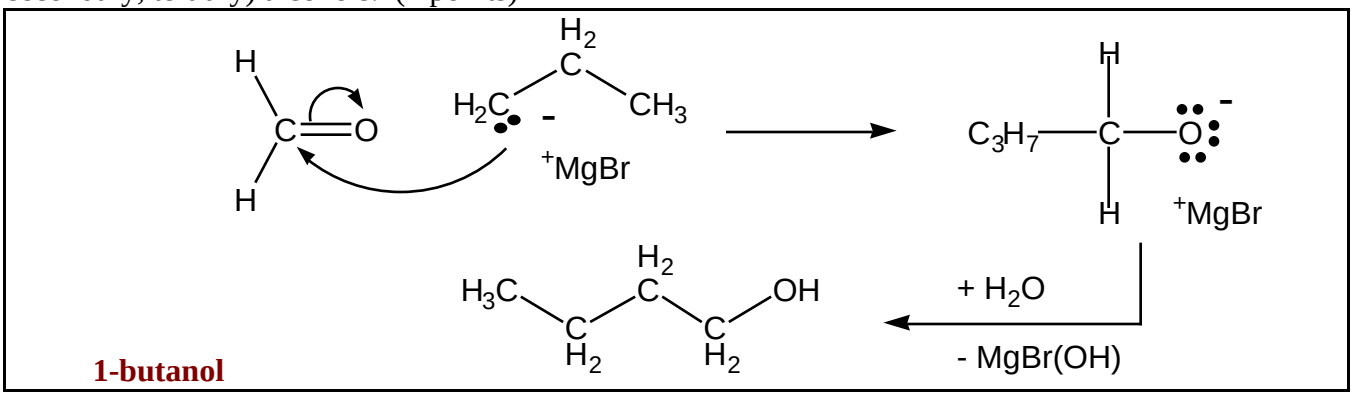
(c) Consider the photochemical reaction of **cyclohexene with diazomethane**. Draw the structure of the product. This product is a _____ (**fused**, spiro) bicyclic compound with molecular formula __C_7H_{12}__ (give molecular formula C_mH_n). Provide the IUPAC name of this product. (8 points)



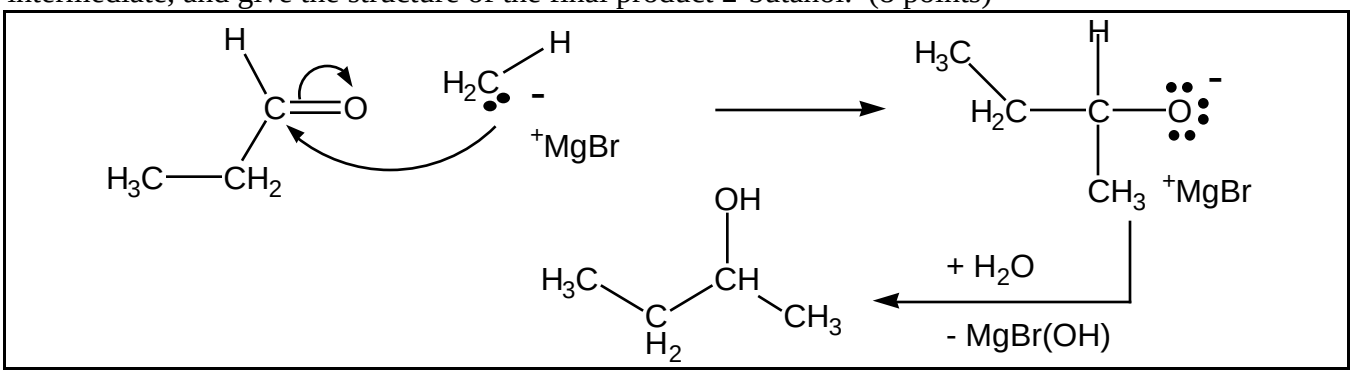
Bicyclo[4.1.0]heptane

Question 3. Syntheses of Alcohols: Grignard Reactions & Reductions & more. (40 points)

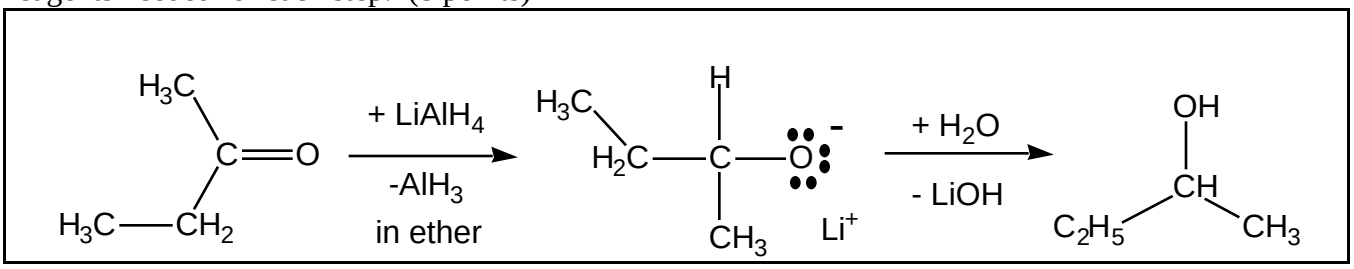
(a) Formaldehyde, $H_2C{=}O$, is reacted with n-propyl magnesium bromide, n-PrMgBr, and the initially formed intermediate is hydrolyzed. Draw the Lewis structures of the substrate, of the intermediate, and of the final product. This reaction of formaldehyde provides a synthesis of _____ (**primary**, secondary, tertiary) alcohols. (4 points)



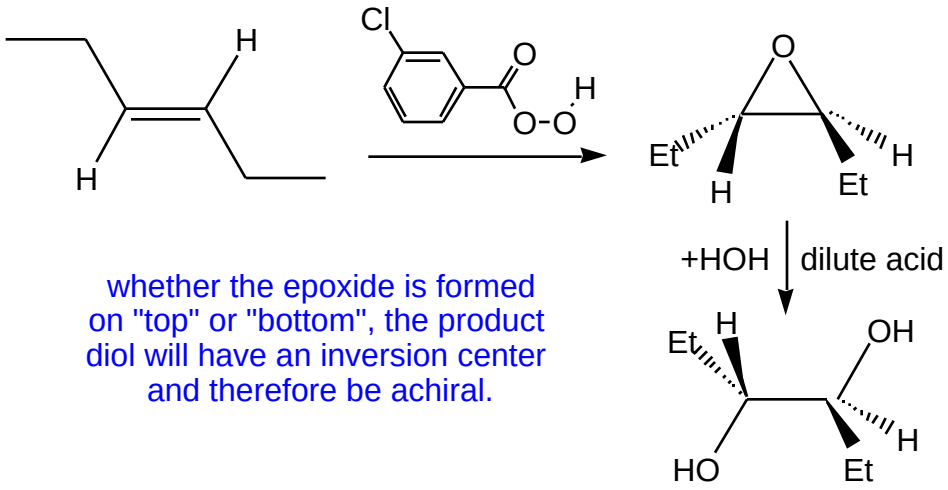
(b) Suggest a synthesis of **2-butanol** by way of a Grignard reaction starting from $H_3C\text{-}CH_2\text{-}CHO$. Draw the Lewis structures of the substrate, specify the Grignard reagent, draw the Lewis structure of the intermediate, and give the structure of the final product 2-butanol. (8 points)



(c) Suppose you wanted to prepare **2-butanol** by reduction of a ketone. What ketone would you use? What reducing reagent would you use? What solvent would you use for the reduction reaction? Provide a reaction diagram with complete Lewis structures that shows both steps of the reduction and the reagents needed for each step. (8 points)

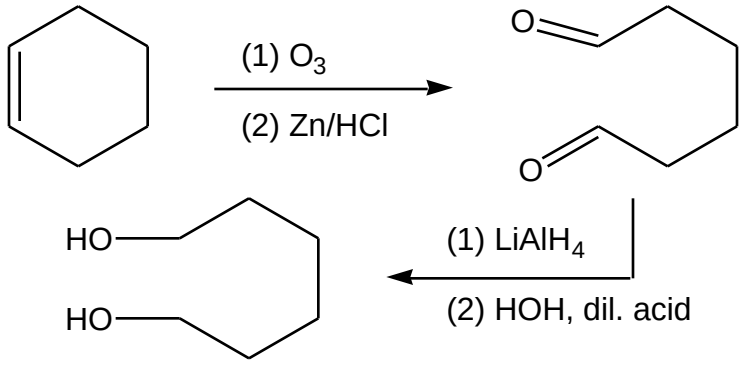


(d) Outline a synthesis of **3,4-hexanediol** starting from *trans*-3-hexene. The first step of this synthesis involves an epoxidation. Draw the structures of *trans*-3-hexene and of its epoxide. Draw the structure of the epoxidation reagent. Then specify the conditions needed to convert the epoxide into the diol and draw the structure of the diol. The product _____ (is**, is not**) chiral. (10 points)



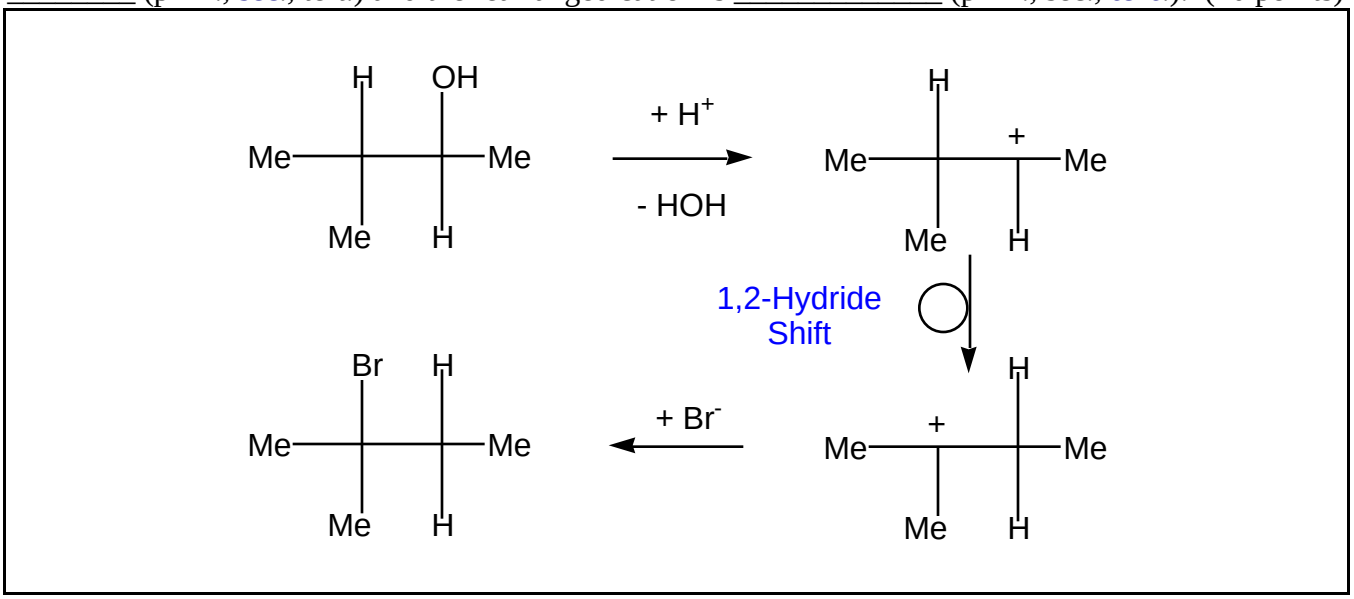
whether the epoxide is formed on "top" or "bottom", the product diol will have an inversion center and therefore be achiral.

(e) Outline a synthesis of **1,6-hexanediol** starting from cyclohexene. Employ this strategy: Oxidize the cyclohexene such that the C=C double bond is completely broken; you know two good methods to accomplish that. Then take a look at the functional groups in the product of oxidation and convert it into the diol. Draw the structures of the substrate, the important intermediate(s) and of the product. Specify all reagents needed. (10 points)

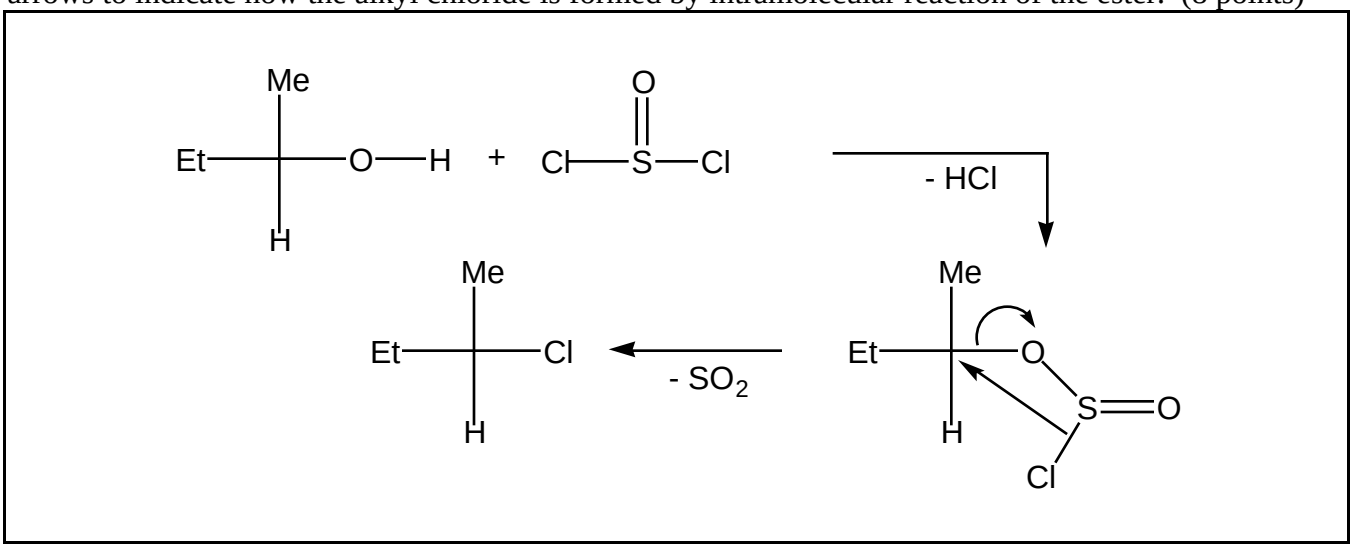


Question 4. Mechanisms of Reactions of Alcohols. (20 points)

(a) 3-Methyl-2-butanol, H_3C-CH(CH_3)-CH(OH)-CH_3, is treated with HBr and a rearranged alkyl bromide is formed as the major product. Show the mechanism for the formation of this major product, that is, draw the substrate, the intermediate cations, and the product. The initially formed cation is _____ (prim., **sec**., tert.) and the rearranged cation is _____ (prim., sec., **tert**.). (10 points)



(b) A good method for the synthesis of alkyl chlorides from alcohols involves the reaction of the alcohol with **thionyl chloride**. Outline the conversion of 2-butanol into 2-chlorobutane. Draw the structures of 2-butanol and of thionyl chloride and draw the structure of the ester formed between them. Use curved arrows to indicate how the alkyl chloride is formed by intramolecular reaction of the ester. (8 points)



Suppose you start this reaction with enantiomerically pure *R*-2-butanol. Will the final product have the *R* or *S* configuration? ***R*** (2 points)

Question 5. Oxidation of Alcohols. (50 points)

The oxidation of ethanol first leads to acetaldehyde and then to acetic acid. The H-NMR spectra and the IR-spectra of ethanol, acetaldehyde and of acetic acid are provided on the following pages.

(a) Draw the structures of ethanol, of acetaldehyde and of acetic acid. (3 points)

Ethanol: $H_3C–CH_2–OH$. Acetaldehyde: $H_3C–CH=O$. Acetic acid: $H_3C–COOH$

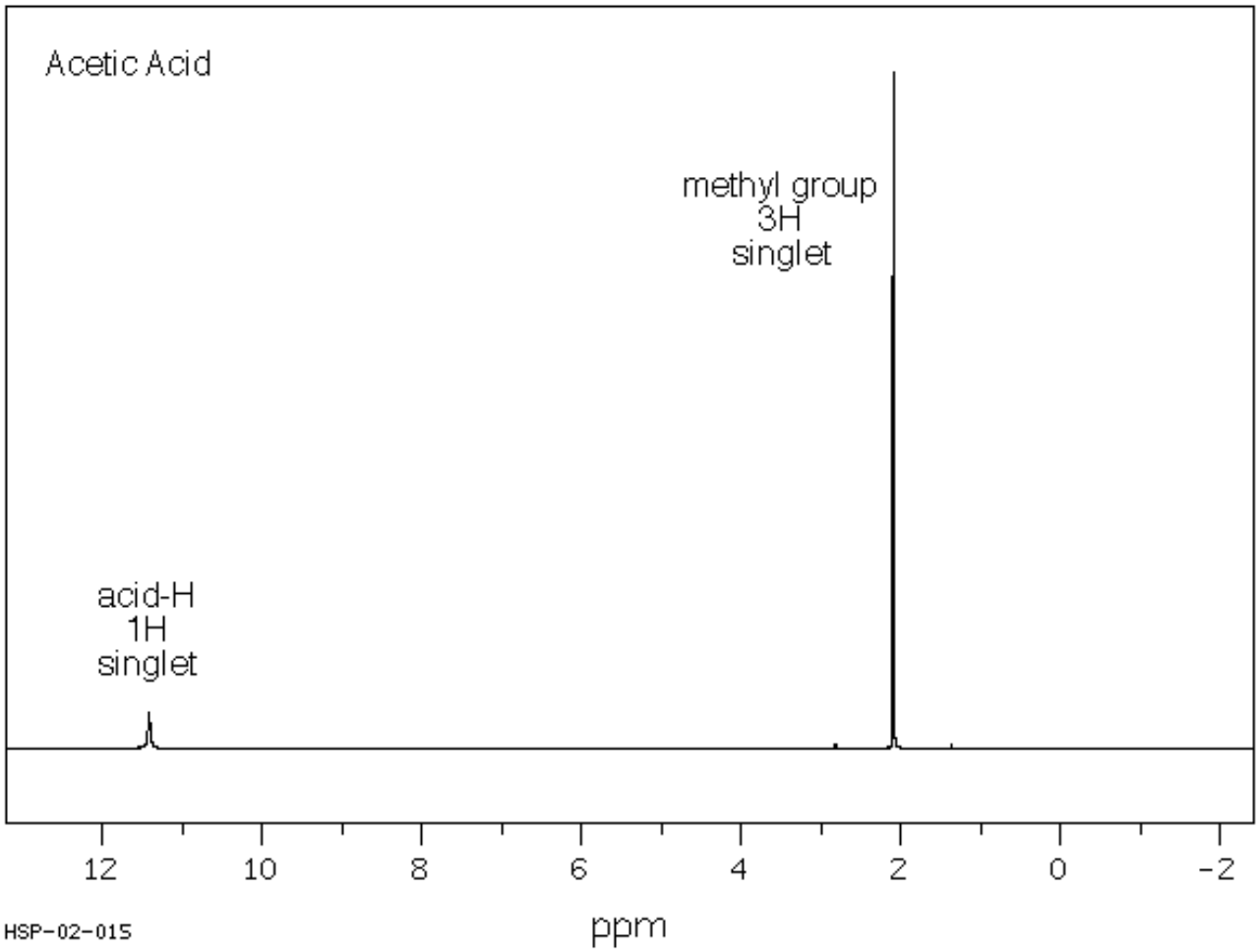
(b) Provide the name and the chemical formula of a laboratory reagent for the oxidation of ethanol all the way to acetic acid. (2 points)

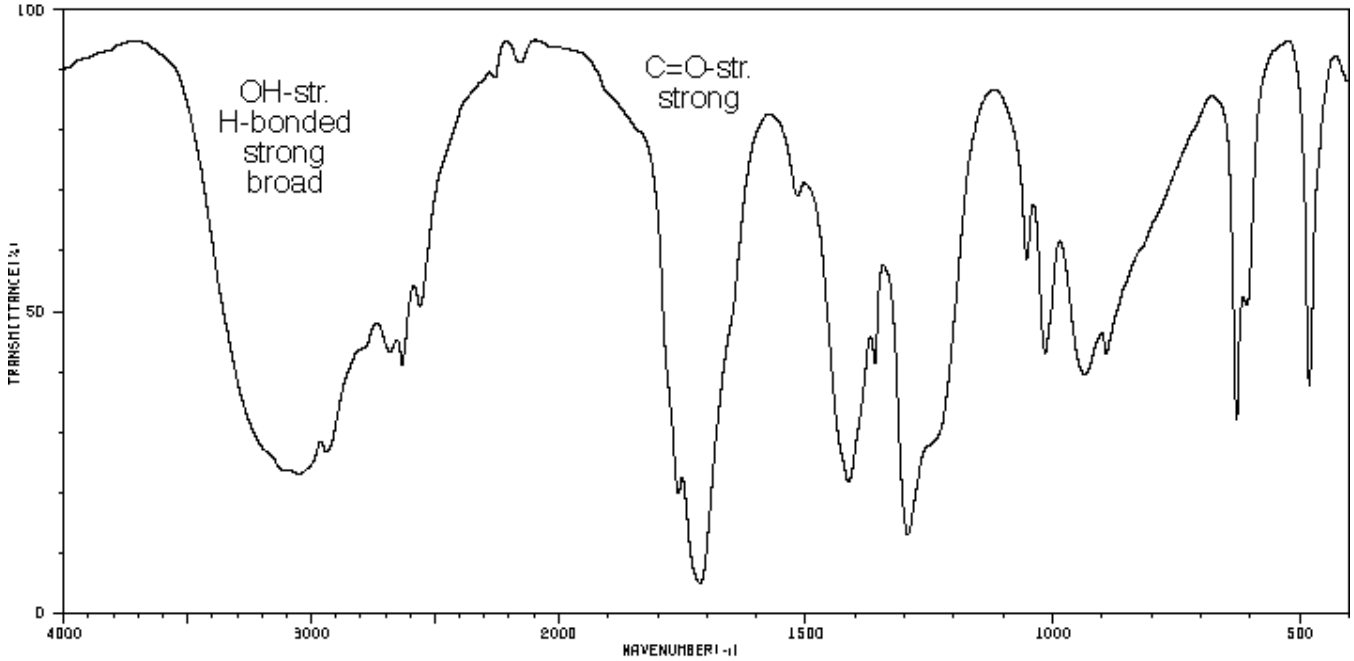
H_2CrO_4, CrO_3/H_2SO_4 or any of its derivatives including $K_2Cr_2O_7/H_2SO_4$

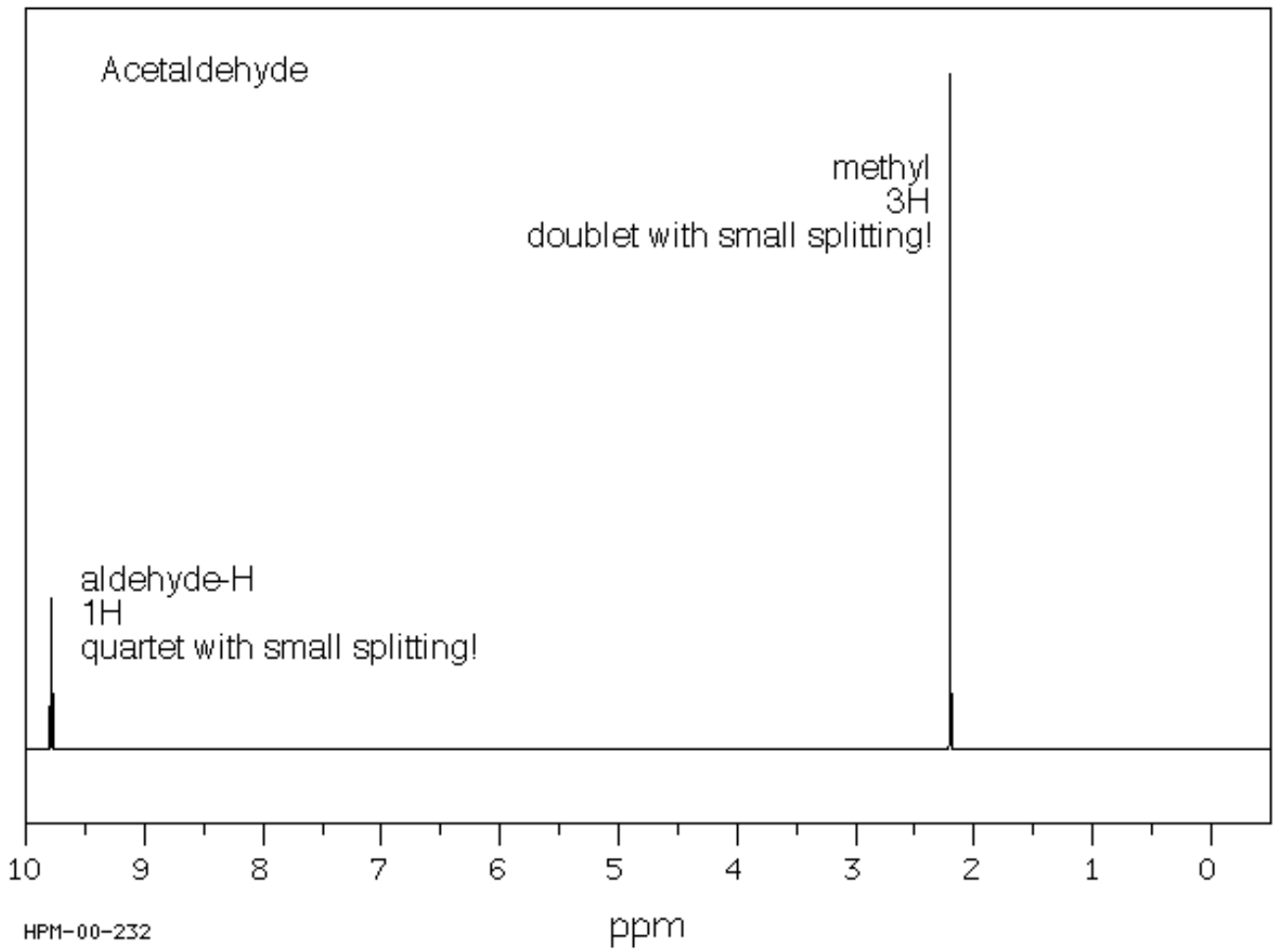
(c) Provide the name and the chemical formula of a laboratory reagent for the oxidation of ethanol to acetaldehyde only (and **not** further to acetic acid). (3 points)

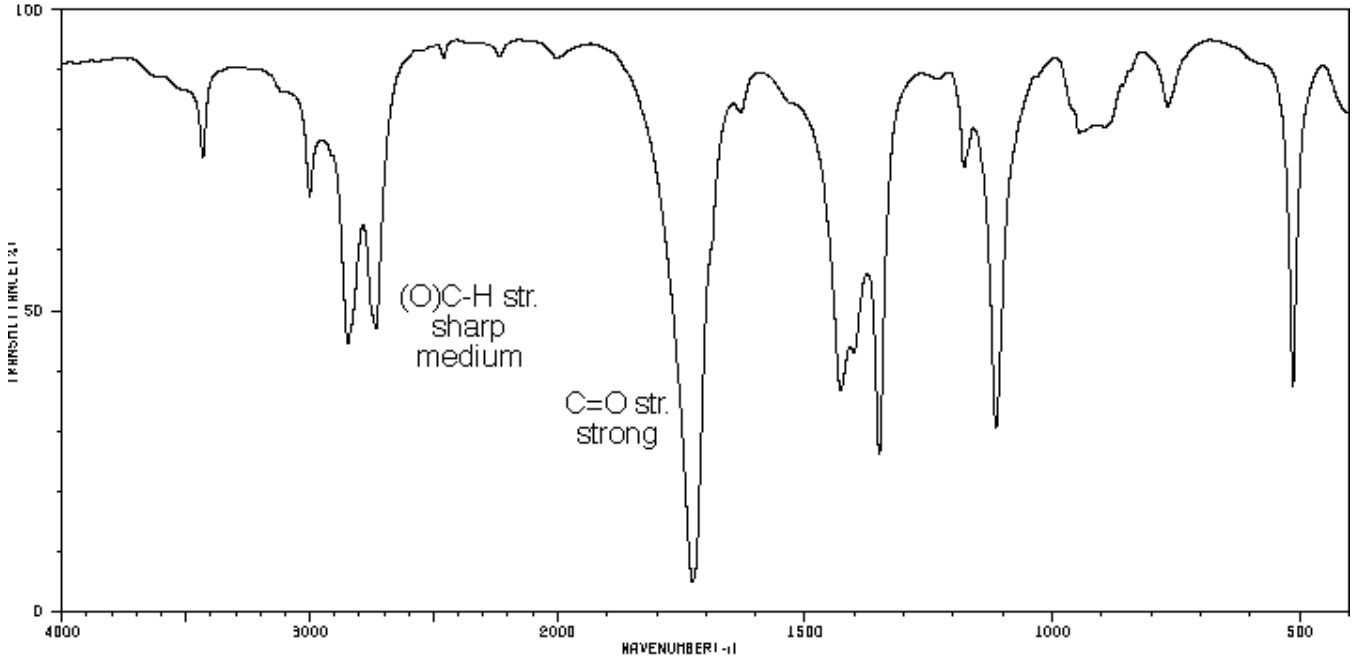
PCC, pyridinium chlorochromate: CrO_3/HCl/pyridine (= C_5H_5N) used in non-aq. solvent

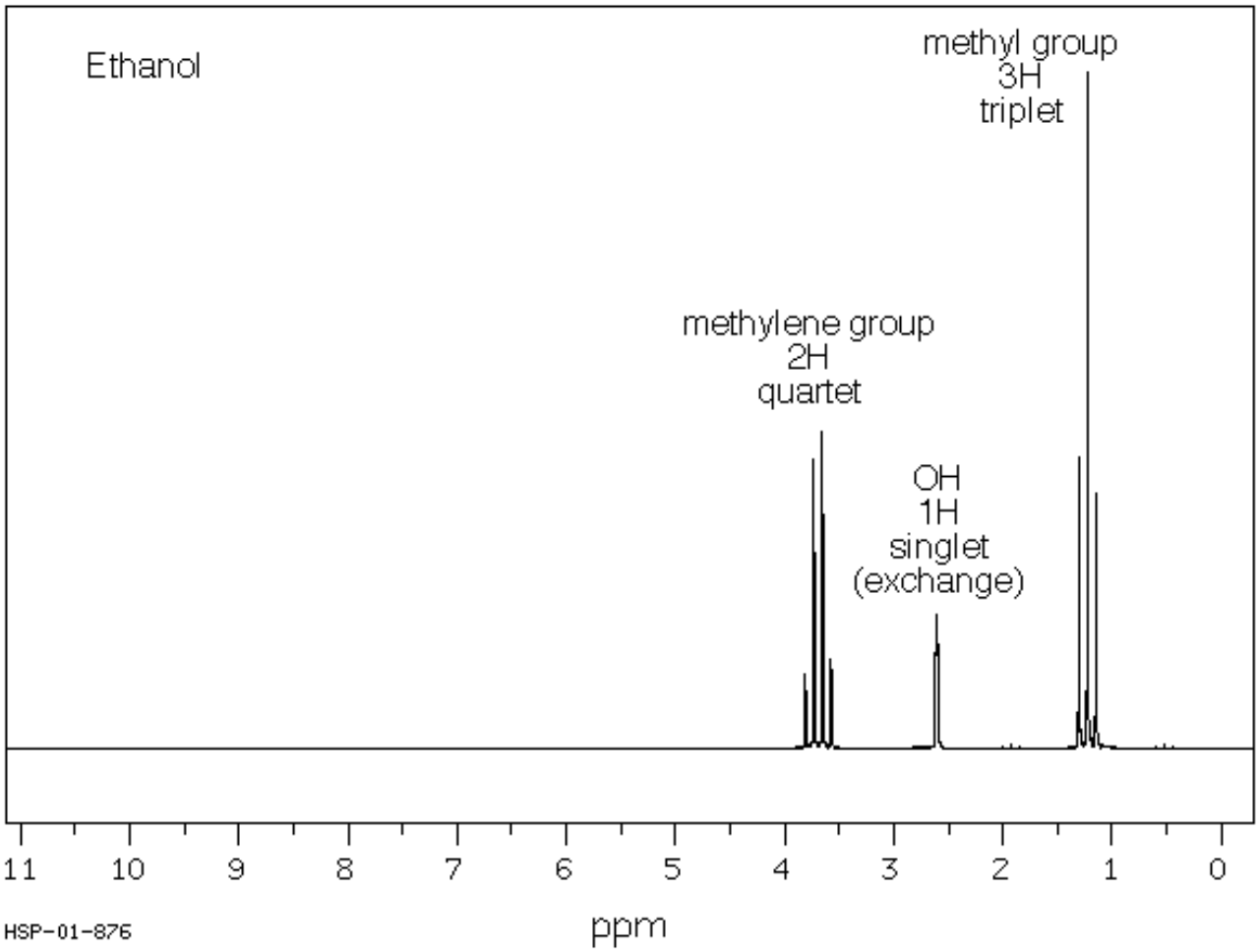
(d) For each of the three compounds—ethanol, acetaldehyde and acetic acid—the H-NMR and the IR-spectra are given the following pages. The H-NMR and the IR-spectra given on one page belong to the same compound. Which page shows the spectra of which compound is for you to find out. Write the name of the compound on the top of the page. Assign all peaks in the H-NMR spectra <u>exactly</u> in this way: Write next to each peak which H-atom causes the peak, state how many H-atoms cause the peak (write 1H, 2H, 3H, …), and write next to the peak what its splitting pattern is (e.g. singlet, doublet, triplet, …). Assign the important peaks in the IR spectra. Assign <u>only</u> the important peaks. Simply write down on each spectrum what bonds cause the important peaks. (42 points, 2 points each for the correct assignment of each spectra page to one of the three compounds, 3 points for each of 7 NMR peaks, 3 points for each of 5 important IR peaks)

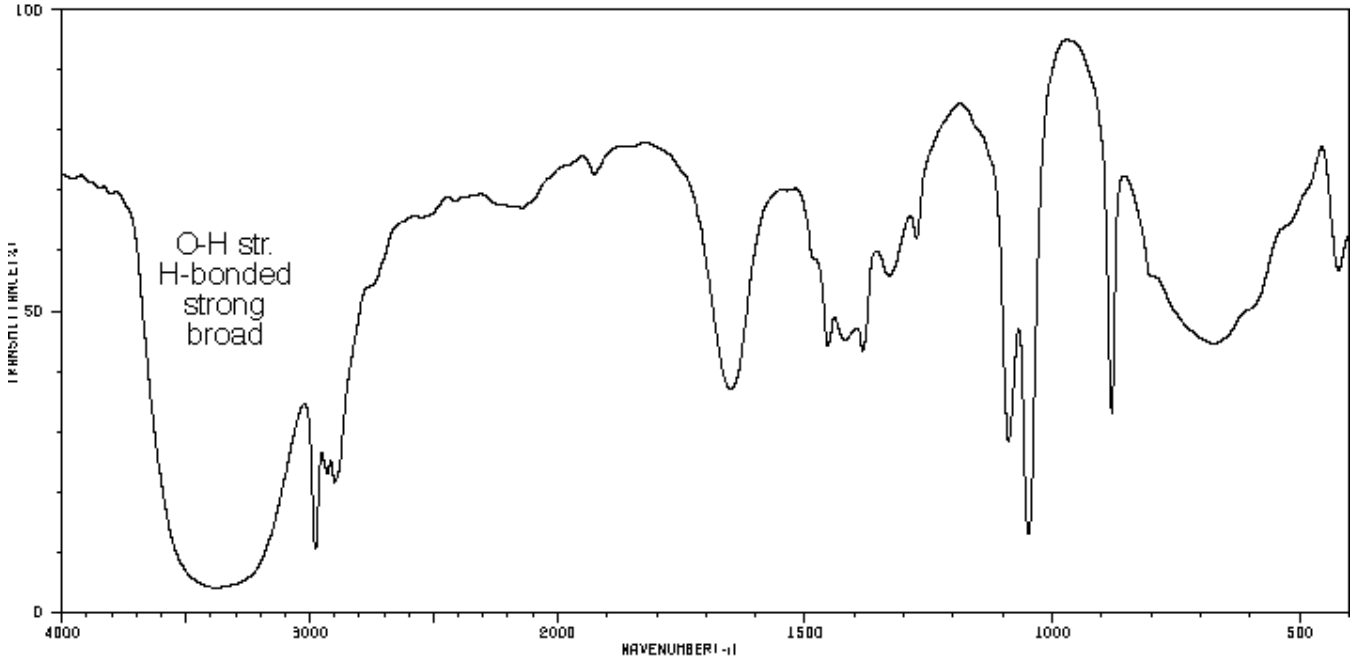

Acetic Acid
methyl group
3H
singlet
acid-H
1H
singlet
12
10
8
6
4
2
0
-2
ppm
HSP-02-015


OH-str.
H-bonded
strong
broad
C=O-str.
strong
100
50
0
4000
3000
2000
1500
1000
500


Acetaldehyde
methyl
3H
doublet with small splitting!
aldehyde-H
1H
quartet with small splitting!
10
9
8
7
6
5
4
3
2
1
0
HPM-00-232
ppm

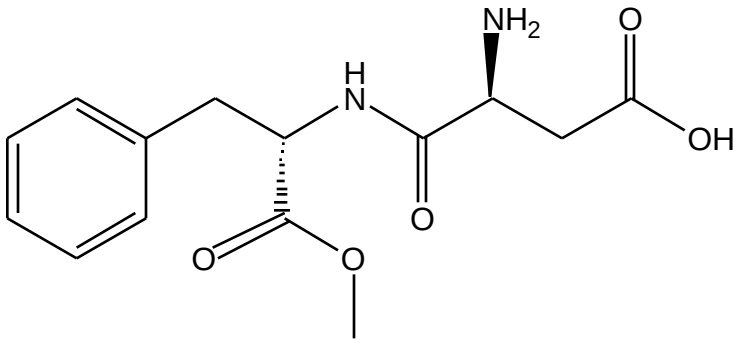

100
50
0
(O)C-H str.
sharp
medium
C=O str.
strong
4000
3000
2000
1500
1000
500


Ethanol
methyl group
3H
triplet
methylene group
2H
quartet
OH
1H
singlet
(exchange)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
HSP-01-876


100
50
0
O-H str.
H-bonded
strong
broad
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)

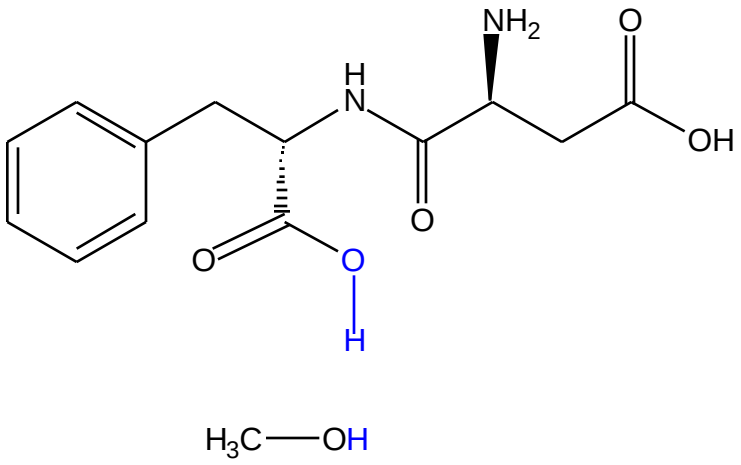
Question 6. Reactions of Alcohols. Aspartame. (30 points)

Recognize this molecule? Ever eaten it?



This is aspartame drawn exactly as it appears in *ChemFinder*. The *ChemFinder* shows that aspartame is also known as Equal®, Nutrasweet®, L-Aspartyl-L-phenylalanine methyl ester, or L-alpha-aspartyl-L-phenylalanine-methylester.

(a) Aspartame is a "methyl ester." Circle the methyl ester functionality in the structural drawing. Then draw the products of the ester hydrolysis in the following box. In other words, I am asking you to draw the structures of the alcohol and of the acid that need to combine to form the methyl ester. Of course, this ester is an _____ (**organic**, inorganic) ester because the _____ (**acid**, alcohol) from which it is formed is _____ (**organic**, inorganic). (10 points, 2 each structure, 2 each blank)

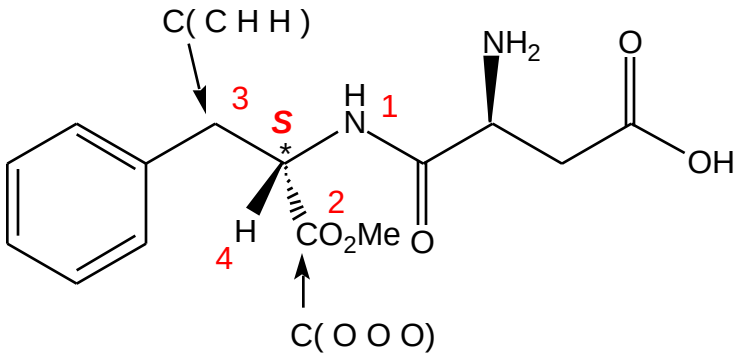


(b) Some people consider aspartame is a health risk. These claims are mostly distributed on the internet and a good starting point for your own browsing might be the *Aspartame Toxicity Info Center* at http://www.tiac.net/users/mgold/aspartame/aspartame.html. The claim basically is that aspartame results in methanol poisoning.

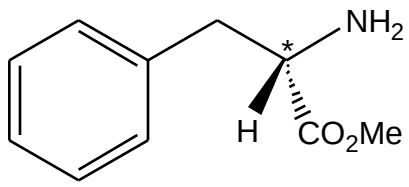
Now, in our studies of chapter 11 we read a news item on "NALTREXONE IS ALTERNATIVE TO ALCOHOLISM. WHY IS IT SO LITTLE USED?" (The Arizona Republic, February 19, 1998). Central to this story was the alcohol metabolism in the body. You learned that alcohol is first oxidized to acetaldehyde with the help of the enzyme "alcohol dehydrogenase" and that acetaldehyde is then oxidized further to acetic acid with the help of the enzyme "aldehyde dehydrogenase." These enzymes also metabolize methanol but—and this is different from ethanol—while the metabolism of ethanol produces chemicals less toxic to the body than alcohol the metabolism of methanol results in rather toxic compounds. These compounds attack nerve cells, especially the optic nerve and can damage the liver and kidneys. Most people who have drunk methanol die of severe and sudden kidney and liver failure. What are the structures of these two toxic products of methanol metabolism? (2 points each).

$H_2C{=}O$, formaldehyde	HCOOH, formic acid

(c) Now let's take a look at one of the chiral centers in aspartame. The one I want you to look at is marked in the usual fashion by a star. Write down the Cahn-Ingold-Prelog priorities of the four substituents and use the sequence rules as needed (e.g. fill in the "lists" provided). Then decide whether the chiral center is "*R*" or "*S*". (8 points)



(d) One part of aspartame is L-phenyl alanine and its structure is shown. The "L" describes the configuration of the chiral carbon center based on the Fischer projection. I will ask you a few questions whose answers all are pertinent to the creation of the Fischer projection of L-phenyl alanine. So, answer the questions and then draw the Fischer projection. (8 points)

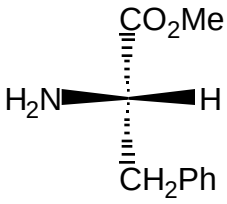
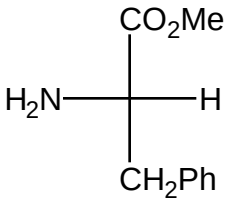


How many carbon atoms are there in the longest aliphatic chain? _____**3**_____ (1 point)

Which terminal carbon atom is most oxidized? _____**CO_2Me**_____ (1 point)

Where does one place the most oxidized carbon of the longest aliphatic chain in the Fischer projection? (2 points)

(a) **top** (b) bottom (c) left (d) right

Draw a perspective drawing of the above molecule in the orientation that is used for the projection. (2 points)	Draw the Fischer projection of the above molecule. (2 points)
	

Question 7. Infrared Spectroscopy & Greenhouse Effect. (40 points)

(a) Infrared spectroscopy measures transitions between _____ states of a molecule. (4 p)

(1) electronic **(2) vibrational** (3) rotational (4) translational

(b) What is the definition of "wavenumber"? (λ = wavelength, ν = frequency, c = light speed; 4 p)

(1) $\lambda \bullet c$ (2) λ / c **(3) $1 / \lambda$** (4) c / λ

(c) Which statement best describes in a qualitative fashion the dependencies of the vibrational frequency on the bond strength and the atomic mass of the vibrating system? The frequency increases with ... (4 p)

(1) an *increase* in bond strength and an *increase* in the mass of the vibrating system.

(2) a *decrease* in bond strength and an *increase* in the mass of the vibrating system.

(3) an *increase* in bond strength and a *decrease* in the mass of the vibrating system.

(4) a *decrease* in bond strength and a *decrease* in the mass of the vibrating system.

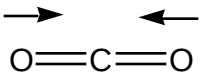
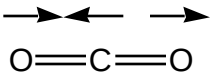
(d) Which region of the IR spectrum is called the "fingerprint region"? (Wavenumbers are given; 4 p.)

(1) 3,000 - 1,000 (2) 2,000 - 1,000 (3) 2,000 - 400 **(4) 1,400 - 400**

(e) Which one of the following carbonyl compounds shows the C=O stretching vibration with the highest wavenumber? (From VC #12; 4 p.)

(1) formaldehyde (2) formic acid (3) formyl chloride (4) formamide

(f) The symmetric stretching vibration of O=C=O is shown using small arrows to indicate the atom displacements by this vibration. In the same way, draw the arrows for the asymmetric stretching mode in the second box. (4 p.)

Symm. Stretch.	Asymm. Stretch.
	

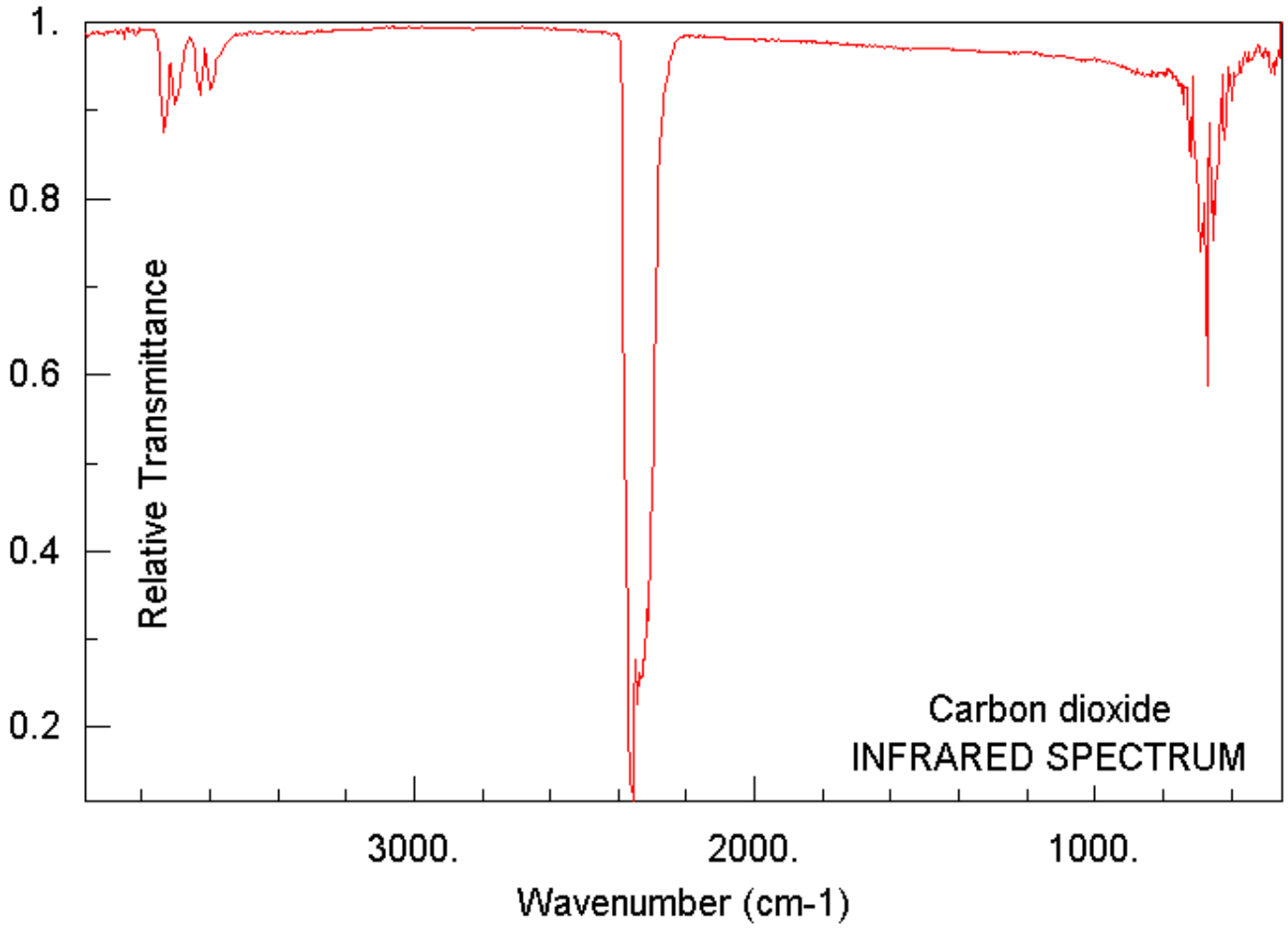
(g) Which one of the following molecules does not show any peak in the IR spectrum in the area where one would expect triple bonds to give a peak. (4 p.)

(1) N≡N (2) H–C≡N (3) H_3C–C≡N (4) N≡C–C≡N

(h) What kind of radiation occurs in the "infrared" region of the spectrum? (4 p.)

(1) visible light (2) UV light **(3) heat waves** (4) radio waves

(i) The **Greenhouse Effect** is mostly due to carbon dioxide. Well, we all know that! But now we also understand why that is so! Carbon dioxide absorbs heatwaves and thereby traps energy in the atmosphere. Carbon dioxide is *really* good at that! The peak around 2200 – 2400 1/cm is *really* broad and it is *really* strong!! This peak actually corresponds to two peaks, the symmetric and the asymmetric stretching vibrations discussed in section (f). Note that there is an additional group of peaks in the fingerprint region around __**600**__ -__**850**__ 1/cm (read the approximte wavenumber range from the spectrum and give the range). This group of peaks is due to ____**bending**___ vibrations. (4 points)



(k) Name two MAJOR anthropogenic sources of carbon dioxide that contribute to the greenhouse effect.

(1) _____**power generation**_____ (2 p.) (2) _____**home heating**_____ (2 p.)

Auf Wiedersehen! Gute Erholung im Sommer!