

NAME (Print): _____

Chemistry 310M/318M

Dr. Brent Iverson

Final exam

December 7, 2011

SIGNATURE: _____

Please print the
first three letters
of your last name
in the three boxes

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Please Note: This test may be a bit long, but there is a reason. I would like to give you a lot of little questions, so you can find ones you can answer and show me what you know, rather than just a few questions that may be testing the one thing you forgot. **I recommend you look the exam over and answer the questions you are sure of first**, then go back and try to figure out the rest. Also make sure to **look at the point totals** on the questions as a guide to help budget your time.

You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK will be regraded.

Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.

FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

Page	Points
1	(29)
2	(22)
3	(14)
4	(15)
5	(-)
6	(-)
7	(-)
8	(16)
9	(19)
10	(21)
11	(-)
12	(22)
13	(25)
14	(42)
15	(35)
16	(30)
17	(17)
18	(22)
19	(16)
20	(12)
21	(8)
22	(8)
Total	(373)
%	
T Score	
HW	
Total Grade	

(HW score + Exam Grade) \Longrightarrow

Honor Code

The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.

(Your signature)

The first semester of Organic Chemistry is a journey that begins with a review of material you have seen, transitions to the study of organic molecules, then settles in with a long discussion of reactions and their mechanisms. The pace accelerates through the chapters until we finish with the chemistry of epoxides. Solving organic synthesis problems requires not only a firm command of the many reactions and mechanisms we have presented, but also high level problem solving skills and a spark of creativity. You have all come a long way since late August when you first came to class. It is my sincere hope that this final serves to affirm that you have completed this journey successfully and caught the Organic Chemistry wave!

As you go through the test, use good test taking strategy by:

- 1) Remaining as relaxed and calm as possible
- 2) Working problems worth the most points first
- 3) Concentrate on finishing all the problems you are most certain about
- 4) Leave the ones you have doubts about for last
- 5) Do not second guess yourself

*Have a safe holiday and remember to exercise every chance you get.
If you stay in shape throughout your life, you will thank yourself
more than you can imagine!!!*

Brent Iverson

Use this page to write down your roadmap if you would like.

Use this page for scratch if you would like. For your reference, here are the Golden Rules of Chemistry:

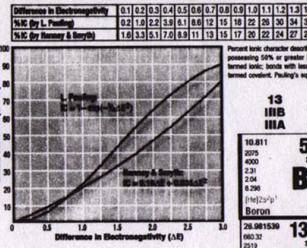
1. Atoms prefer filled valence shells. 2. The most important question in chemistry is "[Where are the electrons?](#)" 3. Nature hates unpaired electrons. 4. Nature hates localized charges. 5. Most reactions involve nucleophiles (molecules with a location of particularly high electron density) attacking electrophiles (molecules with a location of particularly low electron density). 6. Steric interactions (atoms bumping into each other) can prevent reactions by keeping the reactive atoms away from each other. 7. Pi electrons prefer to be delocalized over as many adjacent sp^2 hybridized atoms (or sp^1 hybridized atoms in some cases) as possible, and aromaticity is the most stable form of pi electron delocalization.

PERIODIC TABLE OF THE ELEMENTS

Elementary Subatomic Particles

Particle	Electron	Proton	Neutron	Photon	Neutrino
Symbol	e ⁻	p ⁺	n ⁰	γ	ν
Rest mass (kg)	9.1093897(1) × 10 ⁻³¹	1.672621(1) × 10 ⁻²⁷	1.674927(1) × 10 ⁻²⁷	0	0
Rest mass (g/mol)	5.48579909(4) × 10 ⁻⁴	1.007276467(1) × 10 ⁻³	1.008664916(4) × 10 ⁻³	0	0
Particle-electron mass ratio	1	1836.15267(25)	1838.68366(49)	0	0
Particle-proton mass ratio	5.44617013(1) × 10 ⁻⁴	1	1.001378404(9)	0	0
Particle-neutron mass ratio	5.4559726(1) × 10 ⁻⁴	0.99864615(1)	1	0	0
Electric charge (C)	-1.602176634(8) × 10 ⁻¹⁹	1.602176634(8) × 10 ⁻¹⁹	0	0	0
Spin (h)	1/2	1/2	1/2	0	1/2
Spin quantum number	1/2	1/2	1/2	0	1/2
Compton wavelength (m)	2.42631024(1) × 10 ⁻¹²	1.32140987(1) × 10 ⁻¹³	1.31959110(1) × 10 ⁻¹³	—	—
Magnetic moment (J/T)	9.2847601(1) × 10 ⁻²⁴	1.4106076(1) × 10 ⁻²⁶	0.96623707(4) × 10 ⁻²⁶	0	0
In Bohr magneton, μ _B	1.001158652(1818)	1.52100220(15) × 10 ⁻⁴	1.041873632(9) × 10 ⁻⁴	0	0
In nuclear magneton, μ _N	1836.26983(60)	1.83626983(60)	1.83626983(60)	0	0

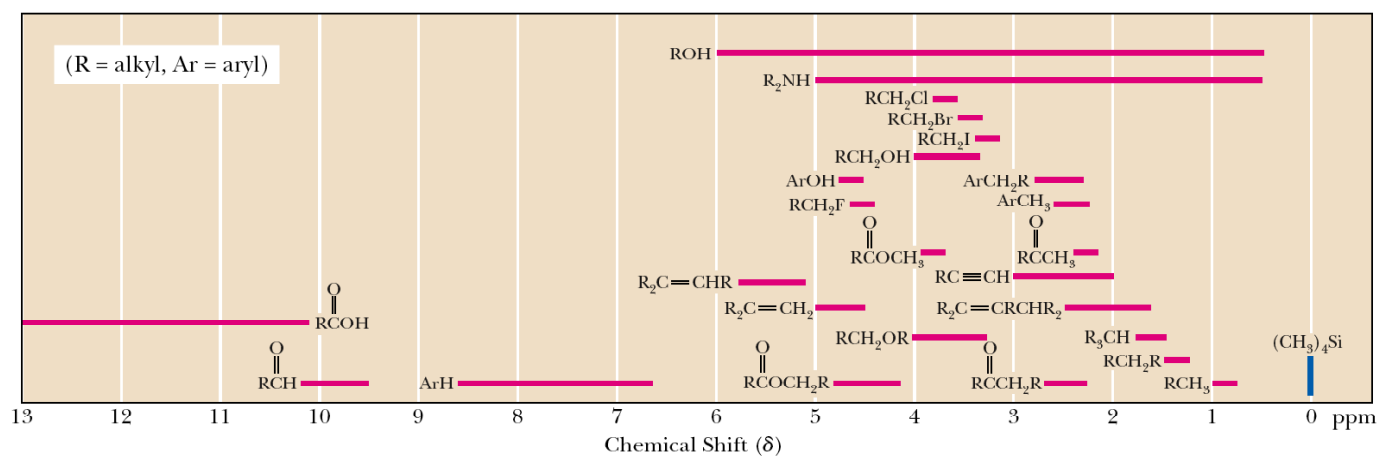
% Ionic Character of a Single Chemical Bond



1 IA 1 H 1.00794 1.008 1.009 1.010 1.011 1.012 1.013 1.014 1.015 1.016 1.017 1.018 1.019 1.020 1.021 1.022 1.023 1.024 1.025 1.026 1.027 1.028 1.029 1.030 1.031 1.032 1.033 1.034 1.035 1.036 1.037 1.038 1.039 1.040 1.041 1.042 1.043 1.044 1.045 1.046 1.047 1.048 1.049 1.050 1.051 1.052 1.053 1.054 1.055 1.056 1.057 1.058 1.059 1.060 1.061 1.062 1.063 1.064 1.065 1.066 1.067 1.068 1.069 1.070 1.071 1.072 1.073 1.074 1.075 1.076 1.077 1.078 1.079 1.080 1.081 1.082 1.083 1.084 1.085 1.086 1.087 1.088 1.089 1.090 1.091 1.092 1.093 1.094 1.095 1.096 1.097 1.098 1.099 1.100 1.101 1.102 1.103 1.104 1.105 1.106 1.107 1.108 1.109 1.110 1.111 1.112 1.113 1.114 1.115 1.116 1.117 1.118 1.119 1.120 1.121 1.122 1.123 1.124 1.125 1.126 1.127 1.128 1.129 1.130 1.131 1.132 1.133 1.134 1.135 1.136 1.137 1.138 1.139 1.140 1.141 1.142 1.143 1.144 1.145 1.146 1.147 1.148 1.149 1.150 1.151 1.152 1.153 1.154 1.155 1.156 1.157 1.158 1.159 1.160 1.161 1.162 1.163 1.164 1.165 1.166 1.167 1.168 1.169 1.170 1.171 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1.836 1.837 1.838 1.839 1.840 1.841 1.842 1.843 1.844 1.845 1.846 1.847 1.848 1.849 1.850 1.851 1.852 1.853 1.854 1.855 1.856 1.857 1.858 1.859 1.860 1.861 1.862 1.863 1.864 1.865 1.866 1.867 1.868 1.869 1.870 1.871 1.872 1.873 1.874 1.875 1.876 1.877 1.878 1.879 1.880 1.881 1.882 1.883 1.884 1.885 1.886 1.887 1.888 1.889 1.890 1.891 1.892 1.893 1.894 1.895 1.896 1.897 1.898 1.899 1.900 1.901 1.902 1.903 1.904 1.905 1.906 1.907 1.908 1.909 1.910 1.911 1.912 1.913 1.914 1.915 1.916 1.917 1.918 1.919 1.920 1.921 1.922 1.923 1.924 1.925 1.926 1.927 1.928 1.929 1.930 1.931 1.932 1.933 1.934 1.935 1.936 1.937 1.938 1.939 1.940 1.941 1.942 1.943 1.944 1.945 1.946 1.947 1.948 1.949 1.950 1.951 1.952 1.953 1.954 1.955 1.956 1.957 1.958 1.959 1.960 1.961 1.962 1.963 1.964 1.965 1.966 1.967 1.968 1.969 1.970 1.971 1.972 1.973 1.974 1.975 1.976 1.977 1.978 1.979 1.980 1.981 1.982 1.983 1.984 1.985 1.986 1.987 1.988 1.989 1.990 1.991 1.992 1.993 1.994 1.995 1.996 1.997 1.998 1.999 2.000 2.001 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2.168 2.169 2.170 2.171 2.172 2.173 2.174 2.175 2.176 2.177 2.178 2.179 2.180 2.181 2.182 2.183 2.184 2.185 2.186 2.187 2.188 2.189 2.190 2.191 2.192 2.193 2.194 2.195 2.196 2.197 2.198 2.199 2.200 2.201 2.202 2.203 2.204 2.205 2.206 2.207 2.208 2.209 2.210 2.211 2.212 2.213 2.214 2.215 2.216 2.217 2.218 2.219 2.220 2.221 2.222 2.223 2.224 2.225 2.226 2.227 2.228 2.229 2.230 2.231 2.232 2.233 2.234 2.235 2.236 2.237 2.238 2.239 2.240 2.241 2.242 2.243 2.244 2.245 2.246 2.247 2.248 2.249 2.250 2.251 2.252 2.253 2.254 2.255 2.256 2.257 2.258 2.259 2.260 2.261 2.262 2.263 2.264 2.265 2.266 2.267 2.268 2.269 2.270 2.271 2.272 2.273 2.274 2.275 2.276 2.277 2.278 2.279 2.280 2.281 2.282 2.283 2.284 2.285 2.286 2.287 2.288 2.289 2.290 2.291 2.292 2.293 2.294 2.295 2.296 2.297 2.298 2.299 2.300 2.301 2.302 2.303 2.304 2.305 2.306 2.307 2.308 2.309 2.310 2.311 2.312 2.313 2.314 2.315 2.316 2.317 2.318 2.319 2.320 2.321 2.322 2.323 2.324 2.325 2.326 2.327 2.328 2.329 2.330 2.331 2.332 2.333 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Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
R_2NH	0.5-5.0	RCH_2OH	3.4-4.0
ROH	0.5-6.0	RCH_2Br	3.4-3.6
RCH_3	0.8-1.0	RCH_2Cl	3.6-3.8
RCH_2R	1.2-1.4	$\begin{array}{c} O \\ \\ RCOCH_3 \end{array}$	3.7-3.9
R_3CH	1.4-1.7	$\begin{array}{c} O \\ \\ RCOCH_2R \end{array}$	4.1-4.7
$R_2C=CRCHR_2$	1.6-2.6	RCH_2F	4.4-4.5
$RC\equiv CH$	2.0-3.0	$ArOH$	4.5-4.7
$\begin{array}{c} O \\ \\ RCCH_3 \end{array}$	2.1-2.3	$R_2C=CH_2$	4.6-5.0
$\begin{array}{c} O \\ \\ RCCH_2R \end{array}$	2.2-2.6	$R_2C=CHR$	5.0-5.7
$ArCH_3$	2.2-2.5	$\begin{array}{c} O \\ \diagup \quad \diagdown \\ H_2C \quad CH_2 \end{array}$	3.3-4.0
RCH_2NR_2	2.3-2.8	$\begin{array}{c} O \\ \\ RCH \end{array}$	9.5-10.1
RCH_2I	3.1-3.3	$\begin{array}{c} O \\ \\ RCOH \end{array}$	10-13
RCH_2OR	3.3-4.0		

* Values are relative to tetramethylsilane. Other atoms within the molecule may cause the signal to appear outside these ranges.

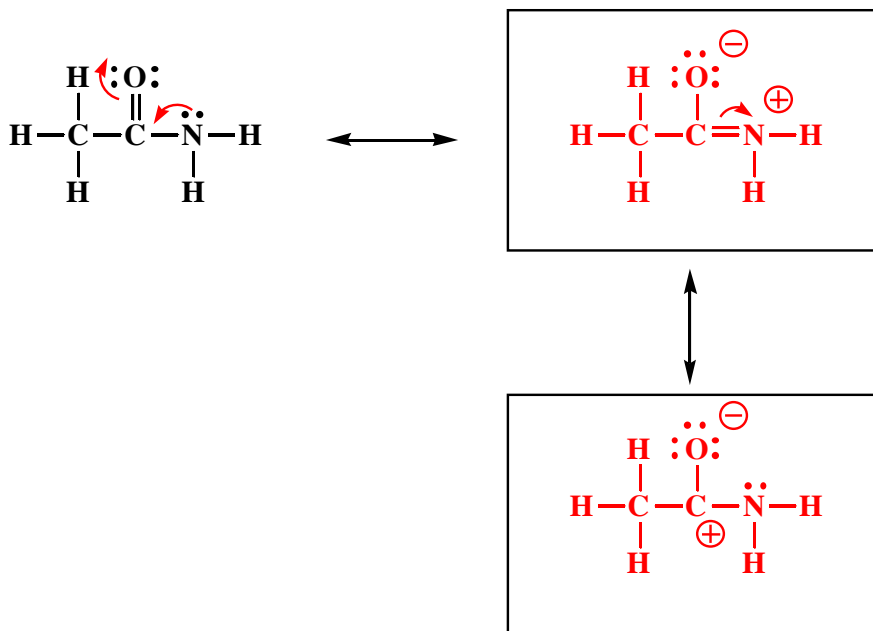


Compound		pK _a
Hydrochloric acid	$\text{H}-\text{Cl}$	-7
Protonated alcohol	$\text{RCH}_2\text{O}^+\text{H}_2$	-2
Hydronium ion	H_3O^+	-1.7
Acetic acid	$\text{CH}_3\text{C}(=\text{O})-\text{H}$	4.8
Ammonium ion	H_4N^+	9.2
Thiols	$\text{RCH}_2\text{S}-\text{H}$	10-12
β-Dicarbonyls	$\text{RC}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})\text{R}'$	10
Ethyl ammonium ion	$\text{H}_3\text{N}^+-\text{CH}_2\text{CH}_3$	10.8
β-Ketoesters	$\text{RC}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})\text{OR}'$	11
β-Diesters	$\text{ROC}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})\text{OR}'$	13
Water	$\text{HO}-\text{H}$	15.7
Alcohols	$\text{RCH}_2\text{O}-\text{H}$	15-19
Acid chlorides	$\text{RC}(=\text{O})-\text{H}_2-\text{CCl}$	16
Aldehydes	$\text{RC}(=\text{O})-\text{H}_2-\text{CH}$	18-20
Ketones	$\text{RC}(=\text{O})-\text{H}_2-\text{CR}'$	18-20
Esters	$\text{RC}(=\text{O})-\text{H}_2-\text{COR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\text{H}$	25
LDA	$\text{H}-\text{N}(i\text{-C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\text{C}-\text{H}$	44
Alkanes	$\text{CH}_3\text{CH}_2-\text{H}$	51

1. (5 pts) What is the most important question in organic chemistry?

Where are the electrons?

2. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges. For the two structures on the left in each problem, use arrows to indicate the movement of electrons to give the structures you drew. There is no need to draw any circles around any of these contributing structures. You might want to read these directions again to make sure you know what we want

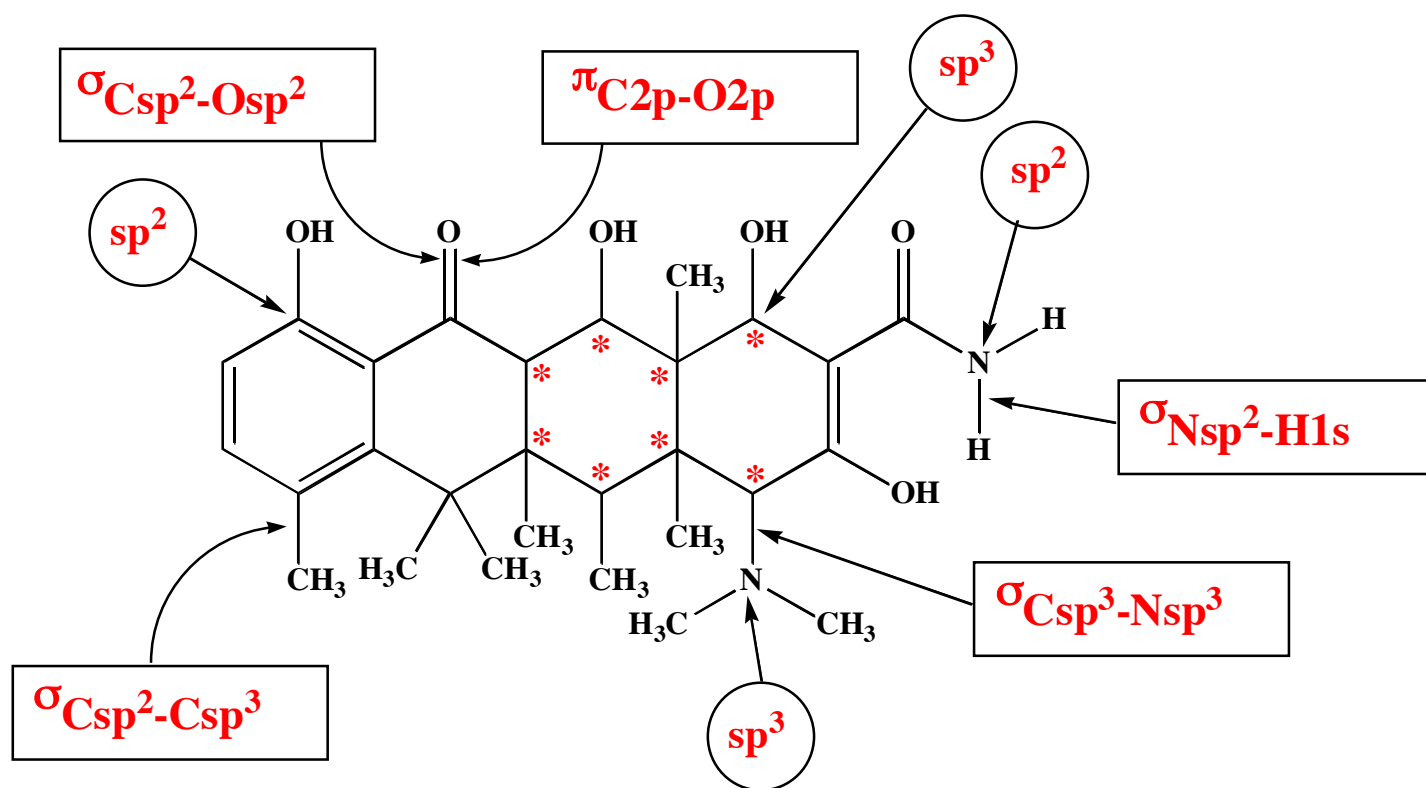


3. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here and your answer should match a recent Rule of the Day.

The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on the **same principles as NMR**, namely the **flipping (i.e. resonance) of nuclear spins of protons** by **radio frequency irradiation** when a patient is placed in a **strong magnetic field**. **Magnetic field gradients** are used to gain imaging information, and **rotation of the gradient around the center of the object** gives imaging in an entire plane (**i.e. slice inside patient**). In an MRI image, you are looking at **individual slices that when stacked make up the three-dimensional image of relative amounts of protons, especially the protons from water and fat, in the different tissues.**

4. (1 pts each) Below is the structure of the antibiotic tetracycline. **In the rectangles provided, indicate the type of bond** and the hybridized orbitals that overlap to form the bond. For example, one answer could be: $\sigma_{\text{Csp}^3-\text{H}1s}$

Next, in the circles provided, write the hybridization state of the atoms indicated with the arrows.



5. (1 pt each) On the above structure of tetracycline, the stereochemistry is not indicated. On the above structure indicate **EACH CHIRAL CENTER WITH AN ASTERISK (*)**.

6. (5 pts). Tetracycline is sold as a single stereoisomer. How many possible stereoisomers are there for tetracycline? It is OK to leave your answer in the form of an exponential. No need to multiply it out.

$$2^8 = 256$$

7. (1 pt each) **Circle all the True statements.** (Do not circle any false statements) You may notice these resemble Rules of the Day! These are worth a significant number of points, so read them carefully and do not second guess yourself. We are not trying to trick you into the wrong answer.

A. For organic chemistry, it is best to think of electron density as particles, described by particle equations such as Kepler's laws of motion, which were recently passed as part of the economic bailout legislation.

B. For organic chemistry, it is best to think of electron density as waves, described by wave equations (NOT discrete particles orbiting the nucleus!)

C. The preferred staggered conformation of butane is referred to as "gotcha", rather than the "anti" or "eclipsed" conformation.

D. Diastereomers are stereoisomers that are not enantiomers.

E. There is an absolute link between "R" and "S", "D" and "L" and "+" and "-", because "R" is always "D" and "+", while "S" is always "L" and "-".

F. Substituted cyclohexanes prefer (i.e. are lower in energy) to have as many substituents in equatorial positions as possible, with the larger substituents dominating.

G. Samples of enantiomers rotate the plane of plane polarized light to an equal extent, but in opposite directions.

H. Anti stereochemistry of addition means that the atoms add to either side of a C=C double bond, syn means they add to the same side, and mixed means they add both syn and anti in the same reaction.

I. Bulky groups (who obviously used performance enhancing steroids) on the back of an alkyl halide increase non-bonded interaction strain, and thereby accelerate an S_N2 reaction.

J. Because of the electron density of the pi bond, alkenes react as nucleophiles to make new bonds with molecules containing high partial positive charge (electrophiles).

K. If electromagnetic energy of the precise energy difference between the +1/2 and -1/2 spins states is used to irradiate the sample, the energy is absorbed as the spin "flips" from the +1/2 state to the -1/2 state.

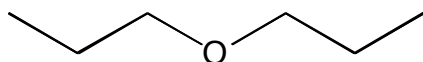
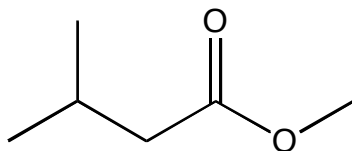
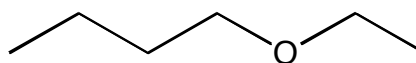
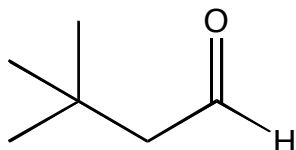
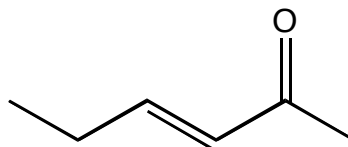
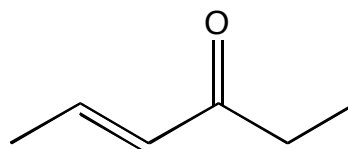
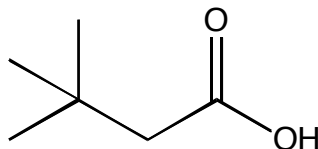
L. A ¹H nucleus surrounded by greater electron density is considered to be more shielded and comes into resonance (absorbs electromagnetic radiation) at a higher frequency (larger ppm).

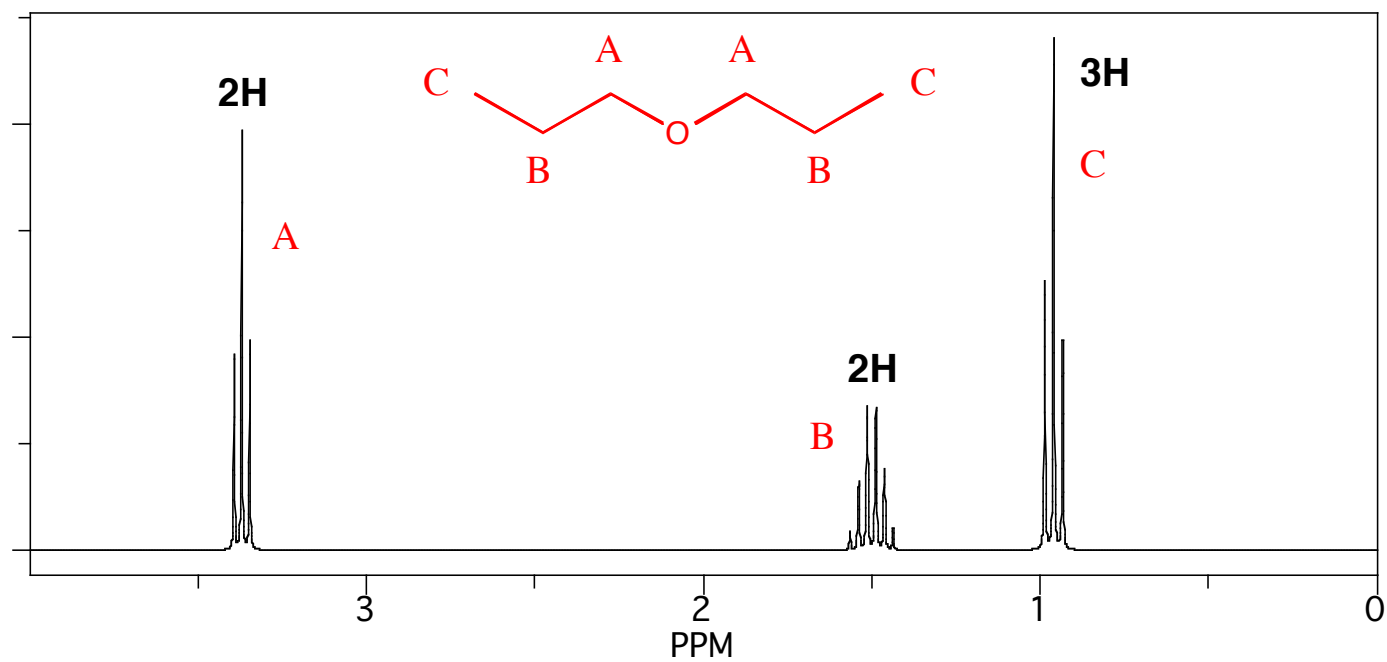
M. A ¹H nucleus surrounded by greater electron density is considered to be more shielded and comes into resonance (absorbs electromagnetic radiation) at a lower frequency (smaller ppm).

N. "Resonance" in NMR refers to the phenomenon of absorption of energy when a nuclear spin "flips".

O. Running 3-5 miles a week EVERY WEEK as an adult dramatically increases your fitness level and improves your health throughout your life. Doing this and enjoying a healthy life is even more important than getting an A on this organic final!

8. (15 pts total) On the following three pages there are NMR spectra. The relative integrations are given above each signal. Assign each spectra to the appropriate structure out of the following possibilities. Each NMR spectrum has a letter on it. **Write the appropriate letter underneath the molecules in the space provided.** Notice that not all of the molecules below will have letters underneath them, as there are only three spectra but seven molecules.

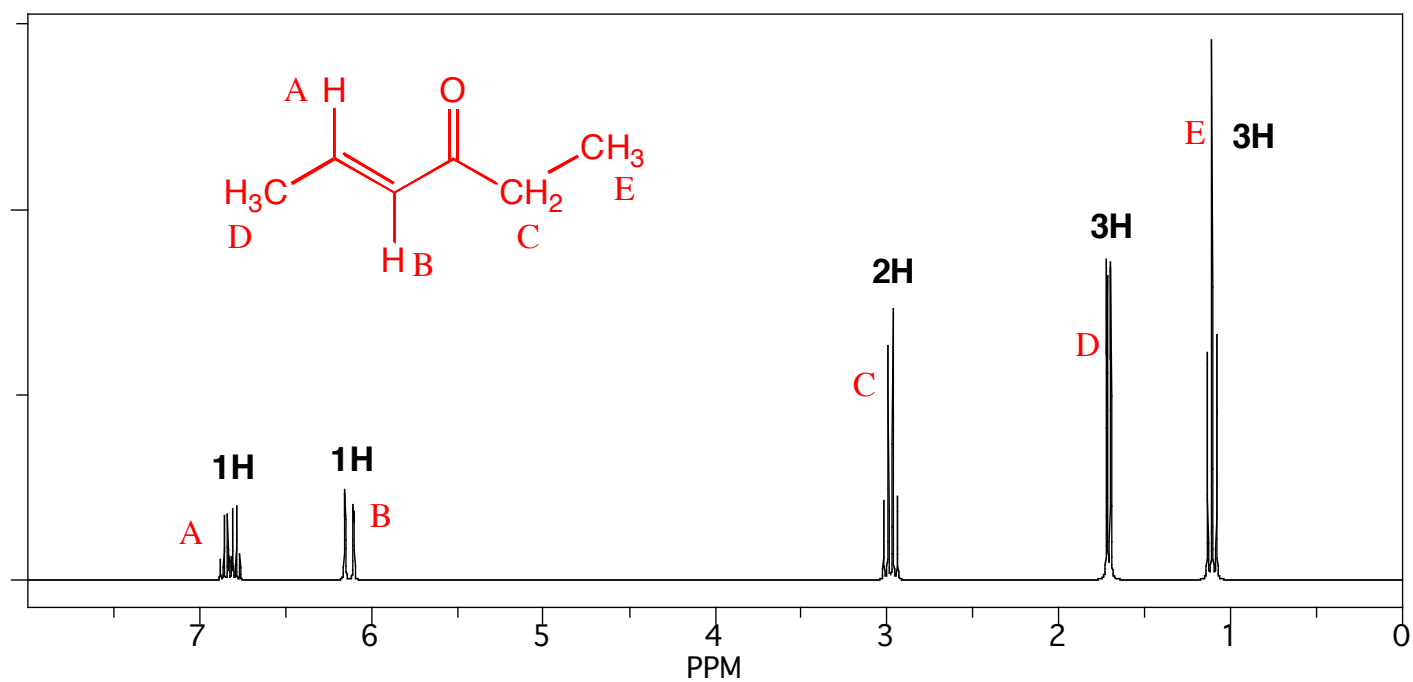
**A****C****B**

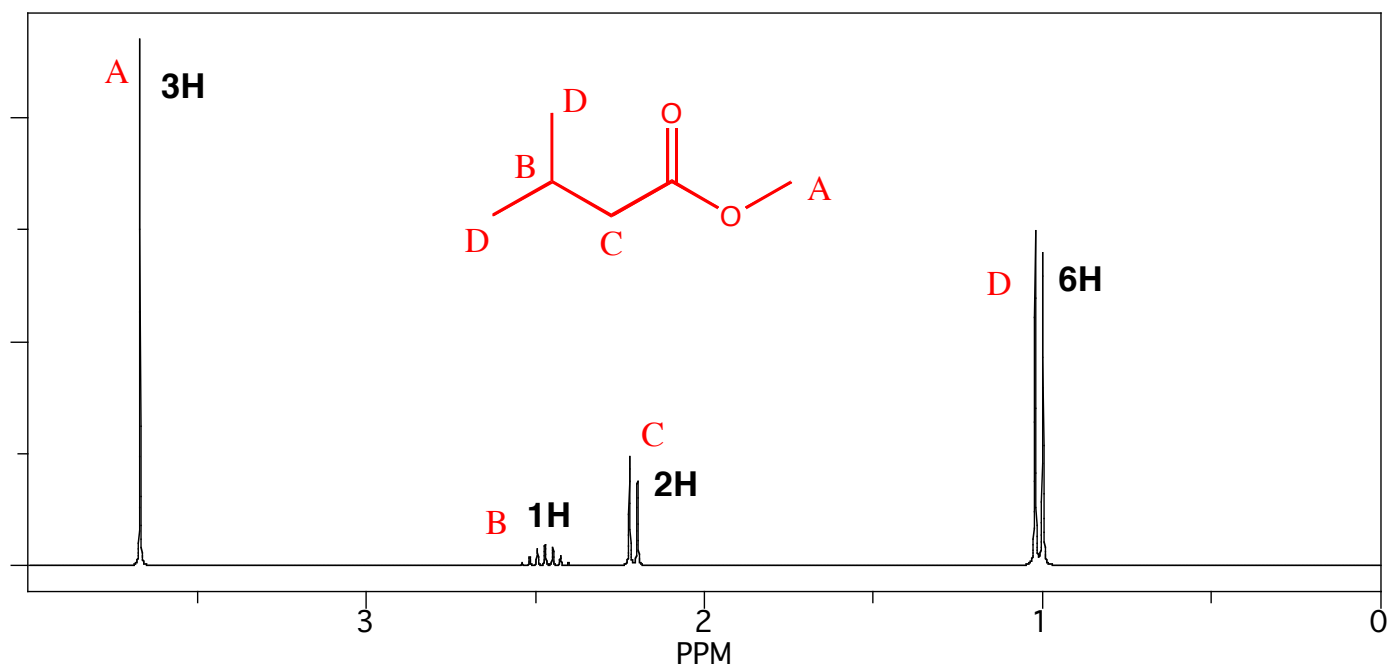
A

Signature_____

Pg 6

B

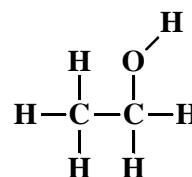
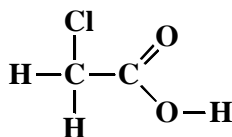
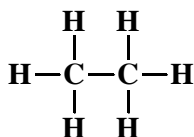
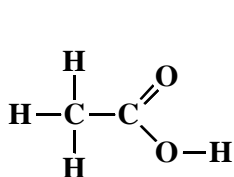


C

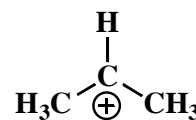
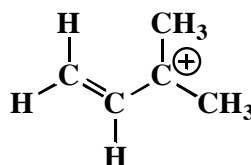
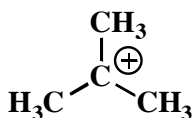
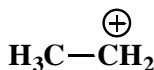
Signature _____

Pg 8 _____(16)

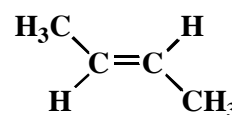
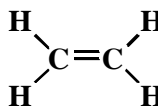
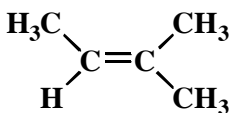
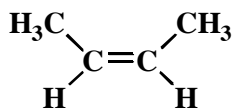
9. (4 pts) Rank the following with respect to relative acidity. Put a **1** under the molecule that is **most acidic**, and a **4** under the molecule that is **least acidic**. Remember, the **1** goes under the **MOST acidic**!

relative
rank:**2****4****1****3**

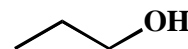
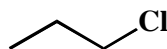
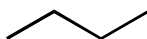
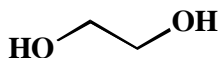
10. (4 pts total) For the following series of compounds, rank them in order of most to least stable cation by writing a **1** under the **most stable** all the way to a **4** under the **least stable**.

relative
rank:**4****2****1****3**

11. (4 pts) **Stability of alkenes:** Place a **1** under the most stable (i.e. most favored Zaitzev product) and a **4** under the least stable (least stable Zaitzev product) alkene

relative
rank:**3 (cis)****1****4****2 (trans)**

12. (4 pts total) For the following compounds, rank them in order of highest to lowest boiling point, with a **1** under the molecule with the **highest boiling point** and a **4** under the molecule with the **lowest boiling point**.

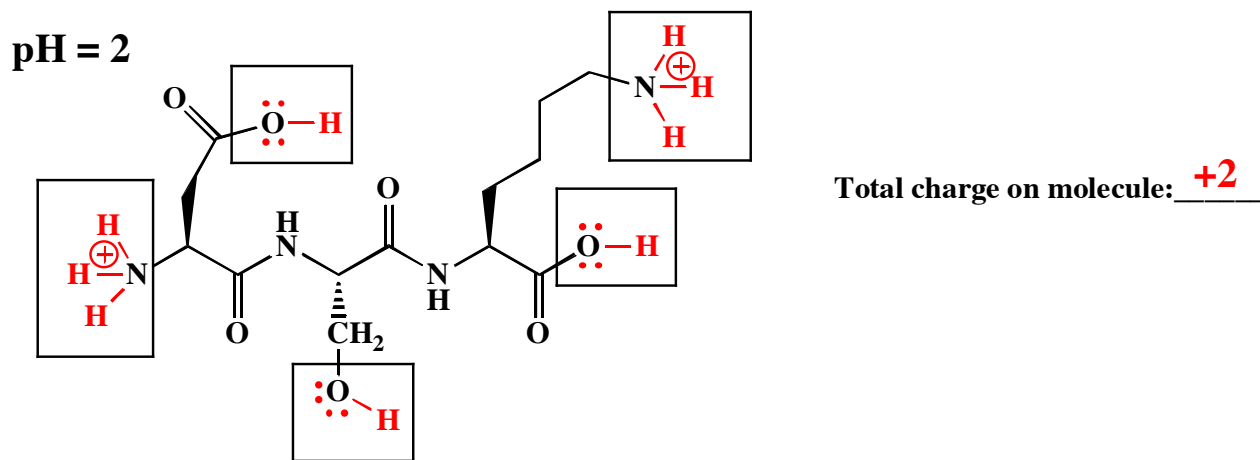
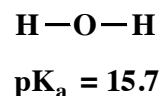
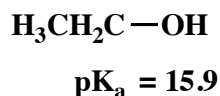
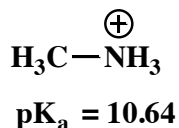
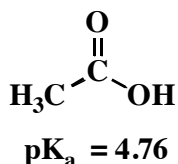
relative
rank:**1****4****3****2**

Are you sure you ranked them in the correct order according to the directions???

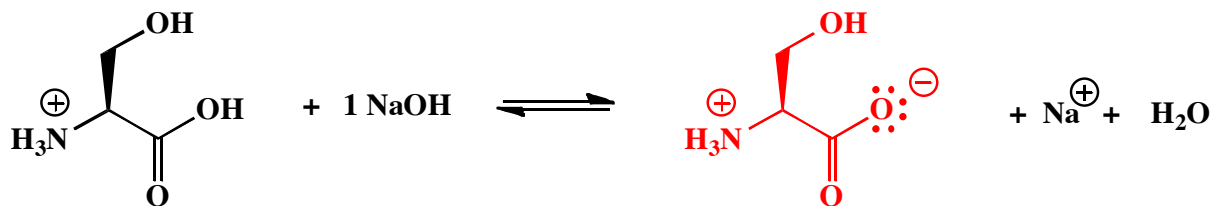
Signature _____

Pg 9 _____ (19)

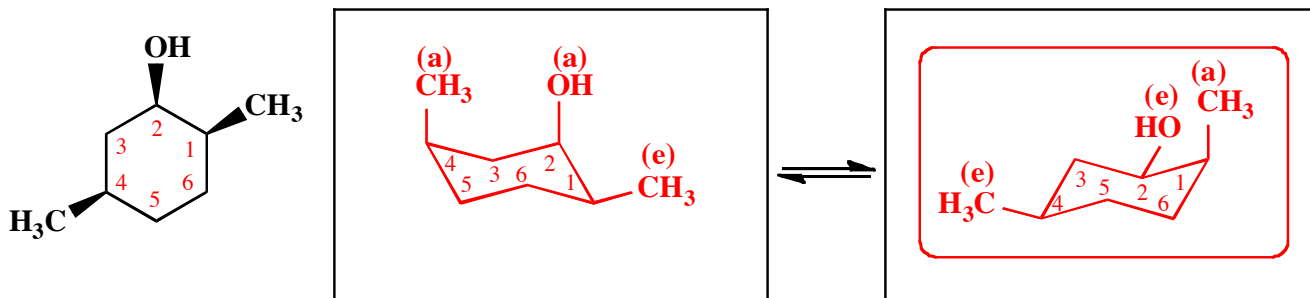
13. (7 pts) Complete the following structure by adding appropriate numbers of lone pair electrons, H atoms, and formal charges to the atoms in the boxes. You must adjust your answers to indicate the predominant species at pH 2. This problem is testing your understanding of the relationship of protonation state to pH to pK_a values for certain functional groups we have discussed. Next, in the space provided, write the overall charge on the molecule at pH 2. For your reference, here are the relevant pK_a values:



14. (4 pts) Using the pK_a information from above (Problem 13), draw the predominant form of the following molecule (the amino acid serine) when it is mixed with exactly one equivalent of NaOH. In other words, when equal numbers of each kind of molecule are mixed.

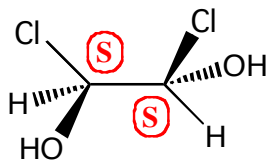
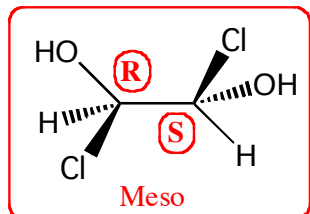


15. (8 pts) In the two spaces below, draw the two equilibrating chair structures for the following cyclohexane derivative. Circle the one that predominates at equilibrium.

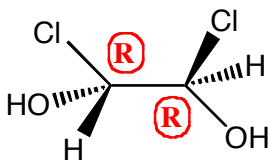
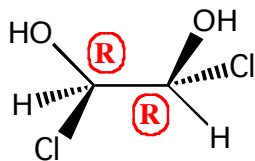


16. (8 pts) On the line provided, state the stereochemical relationship between each pair of molecules: **enantiomers, diastereomers, or the same molecule**. I recommend you assign R and S to each chiral center to help answer this question. **Circle all meso compounds.**

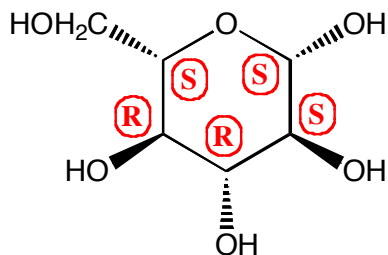
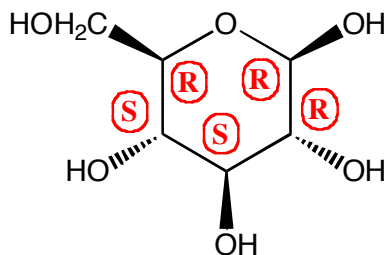
Relationship



Diastereomers

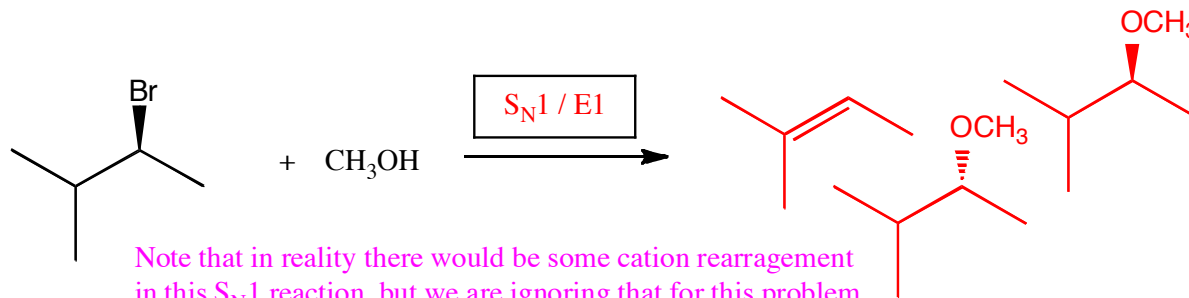
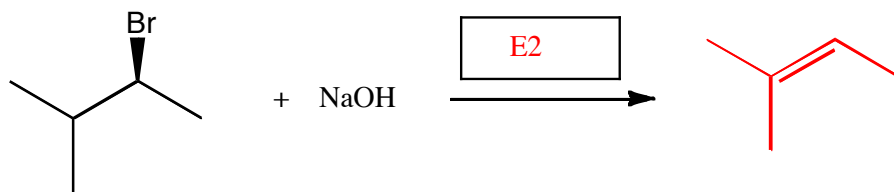
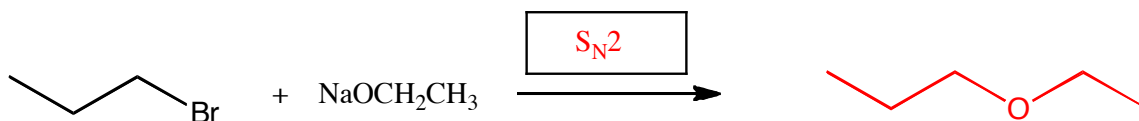


Same Molecule



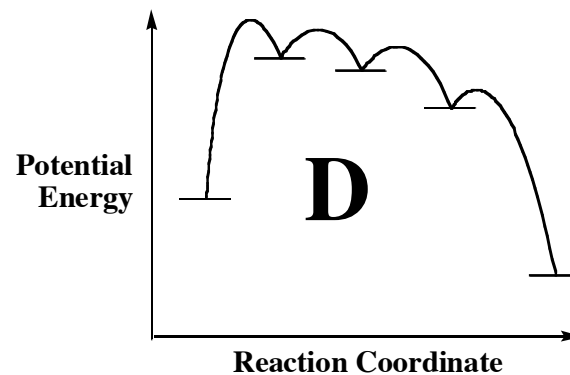
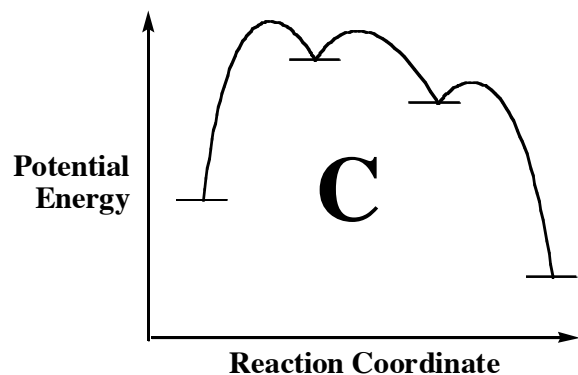
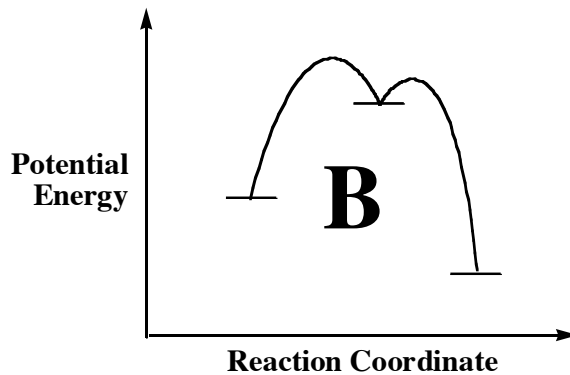
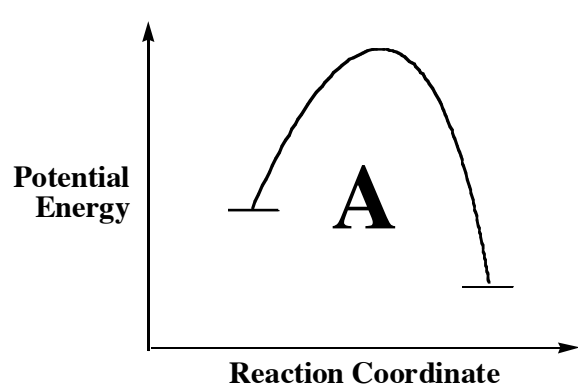
Enantiomers

17. (13 pts) For the following reactions, draw the predominant product(s), and in the box over the arrow, write the predominant mechanism(s) (S_N2 , E2 or $S_N1/E1$)

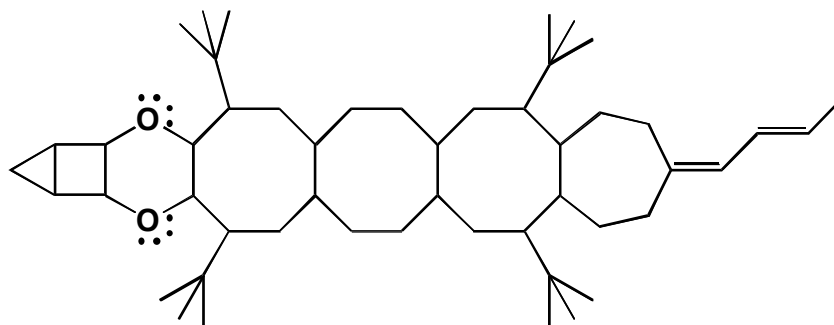
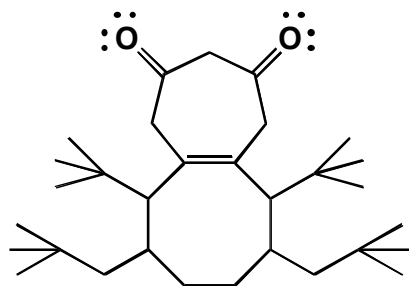


Note that in reality there would be some cation rearrangement in this S_N1 reaction, but we are ignoring that for this problem.

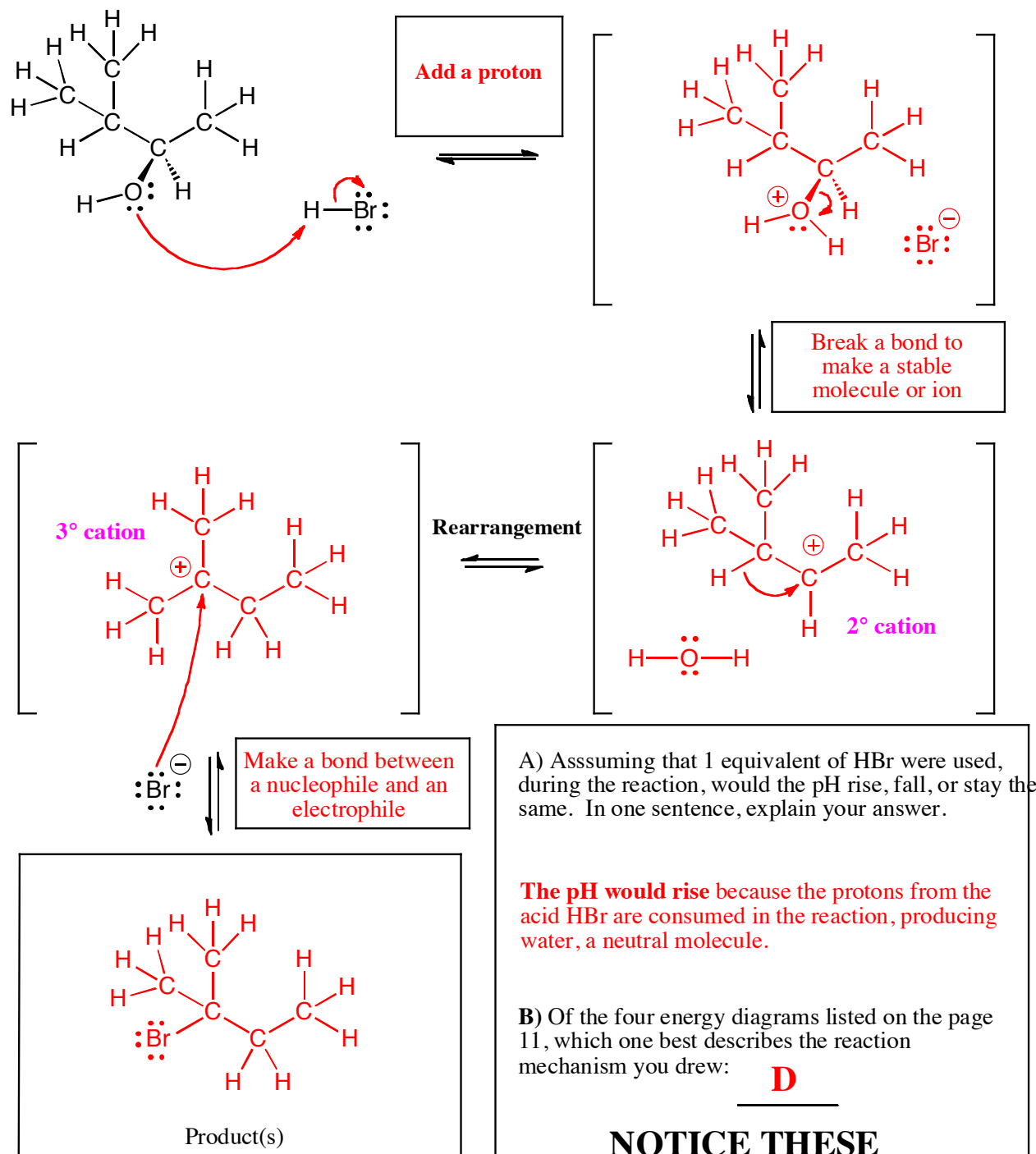
18. Shown below are four different energy diagrams. Each is labeled with a letter. Use these letters to answer questions at the bottom of the next two mechanism questions.



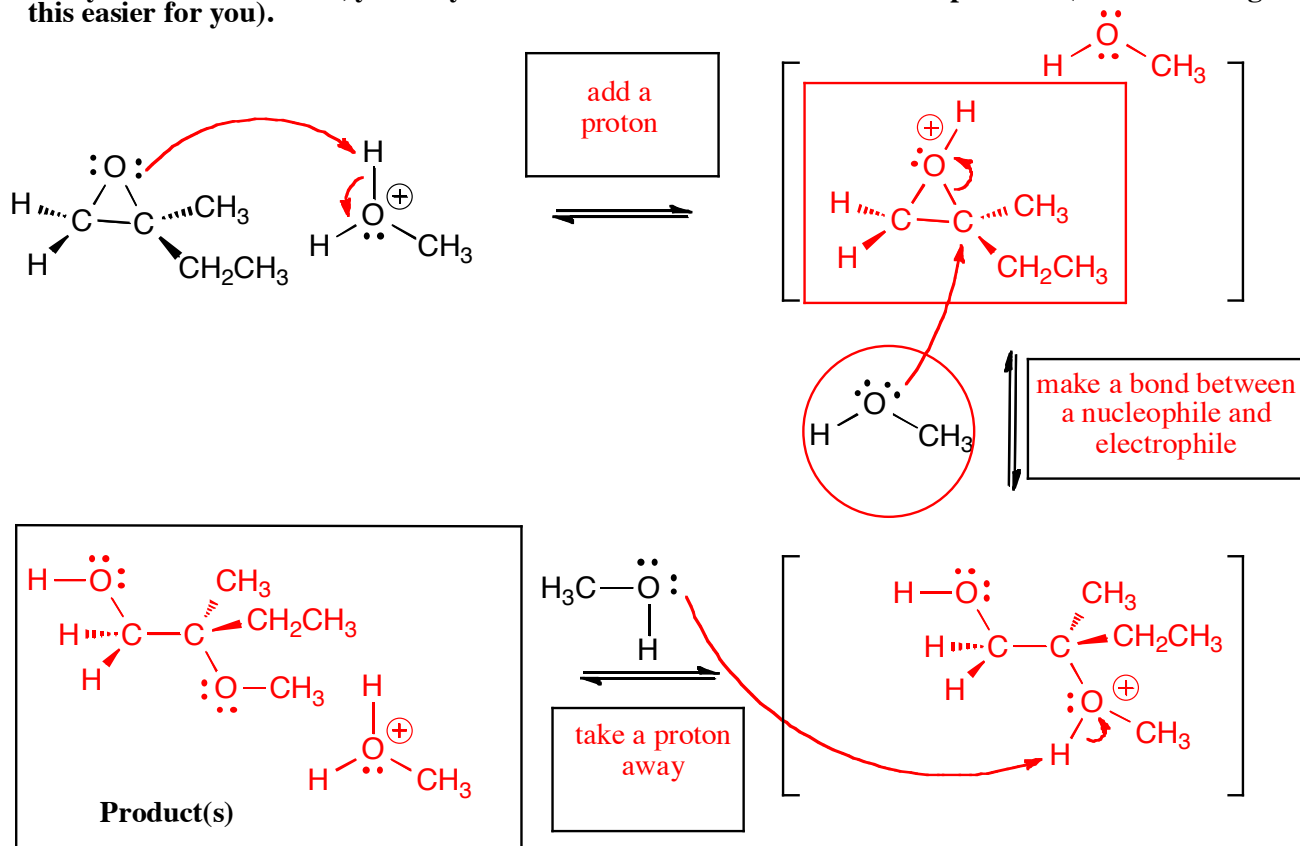
Molecular amphibians



19. (22 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) For the reaction of this alcohol with HBr, fill in the details of the mechanism. Draw the appropriate chemical structures and use an arrow to show how pairs of electrons are moved to make and break bonds during the reaction. For this question, you must draw all molecules produced in each step (yes, these equations need to be balanced!). Finally, fill in the boxes adjacent to the arrows with the type of step involved, such as "Make a bond" or "Take a proton away". MAKE SURE TO NOTICE THE QUESTIONS AT THE BOTTOM. Use wedges and dashes to indicate stereochemistry where appropriate, BUT if an intermediate or product is really a racemic mixture, you only need to draw one enantiomer for this problem (we are making this easier for you).



20. (25 pts.) For the reaction of this epoxide with methanol in acid, fill in the details of the mechanism. Draw the appropriate chemical structures and use arrows to show how pairs of electrons are moved to make and break bonds during the reaction. For this question, you must draw all molecules produced in each step (yes, these equations need to be balanced!). Finally, fill in the boxes adjacent to the arrows with the type of step involved, such as "Make a bond" or "Take a proton away". MAKE SURE TO NOTICE THE QUESTIONS AT THE BOTTOM. Use wedges and dashes to indicate stereochemistry where appropriate, BUT if an intermediate or product is really a racemic mixture, you only need to draw one enantiomer for this problem (we are making this easier for you).



A) (2 pts) During the reaction, would the pH rise, fall, or stay the same. In one sentence, explain your answer.

The pH would stay the same because acid is a catalyst here.

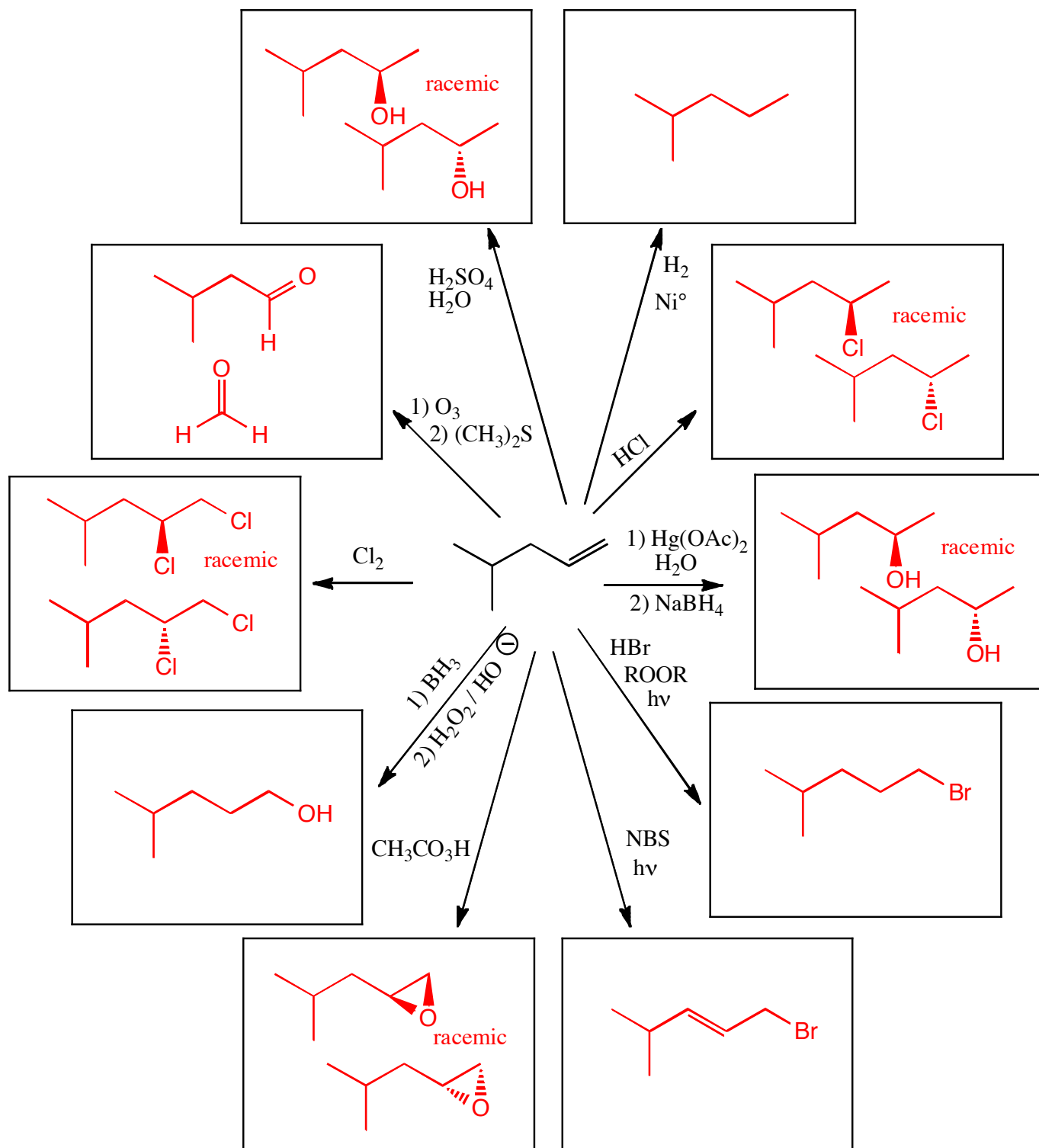
B) (2 pts) Of the four energy diagrams listed on page 11, which one best describes the reaction mechanism you drew:

C

C) (4 pts) For this part of the question, ignore all proton transfer steps. For each step that involves a nucleophile reacting with an electrophile, draw a circle around the nucleophile and a box around the electrophile.

NOTICE ALL THREE PARTS OF THIS (A-C)

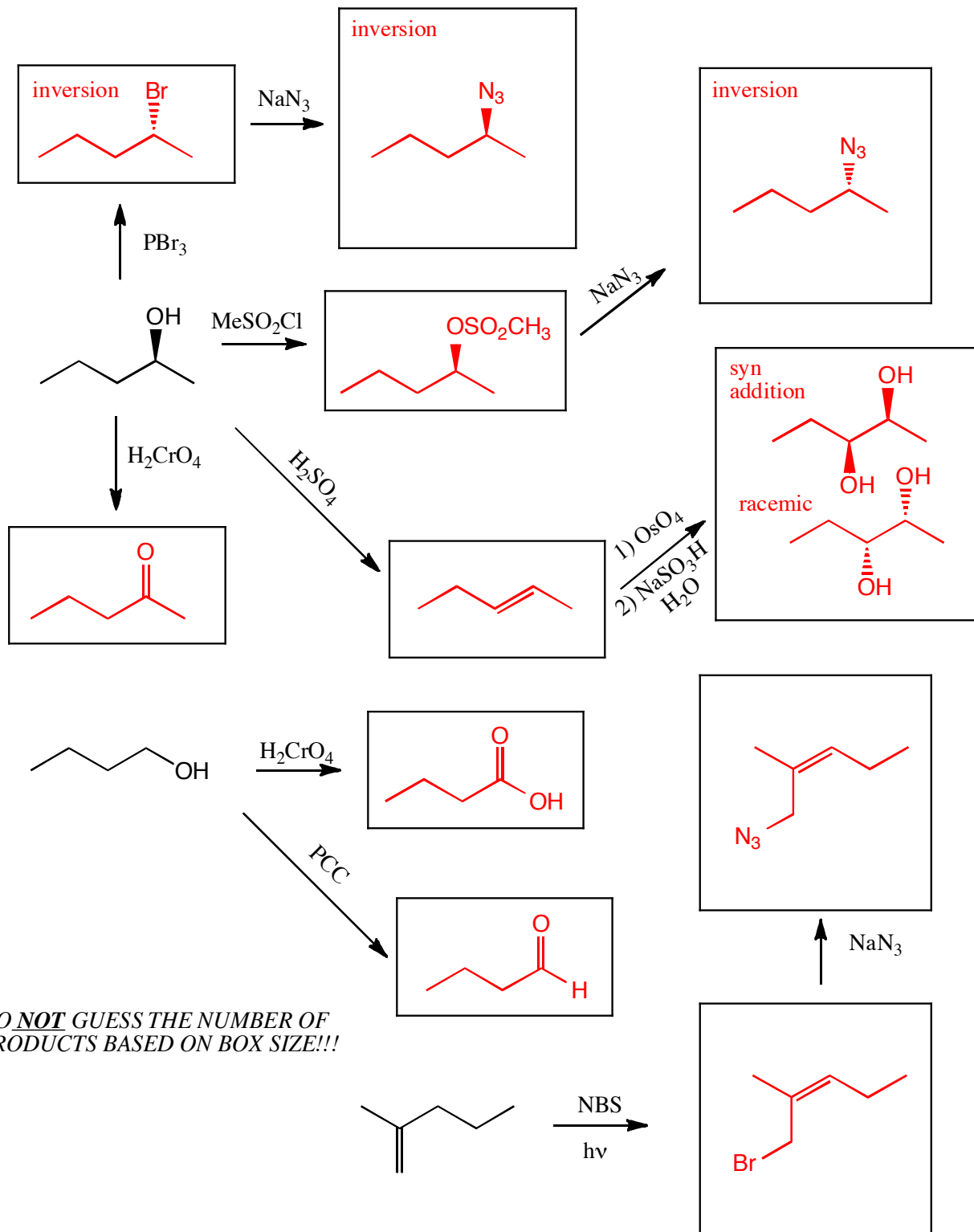
21. (3 or 5 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



Signature _____

Pg 15 _____(35)

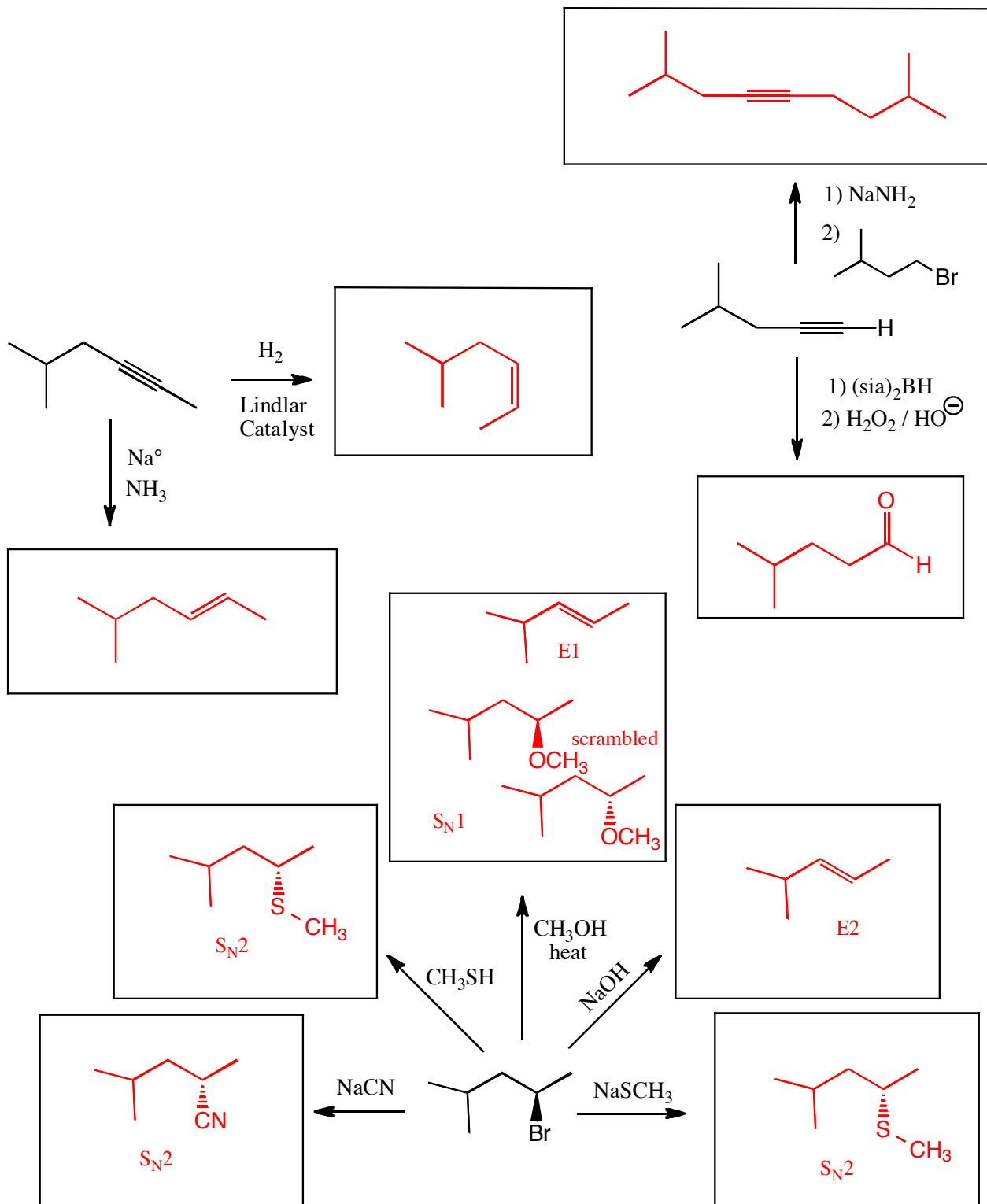
22. (3 or 5 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



Signature _____

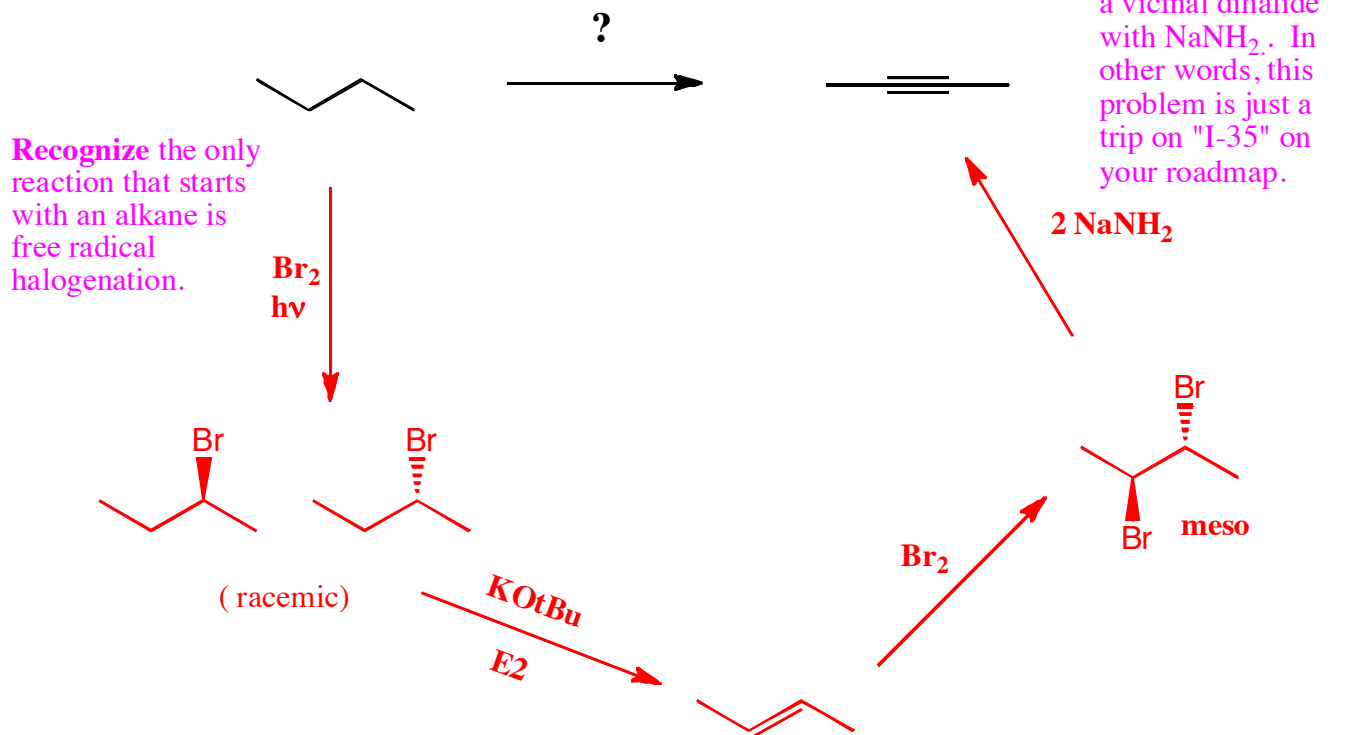
Pg 16 _____ (30)

23. (3, 5 or 6 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.

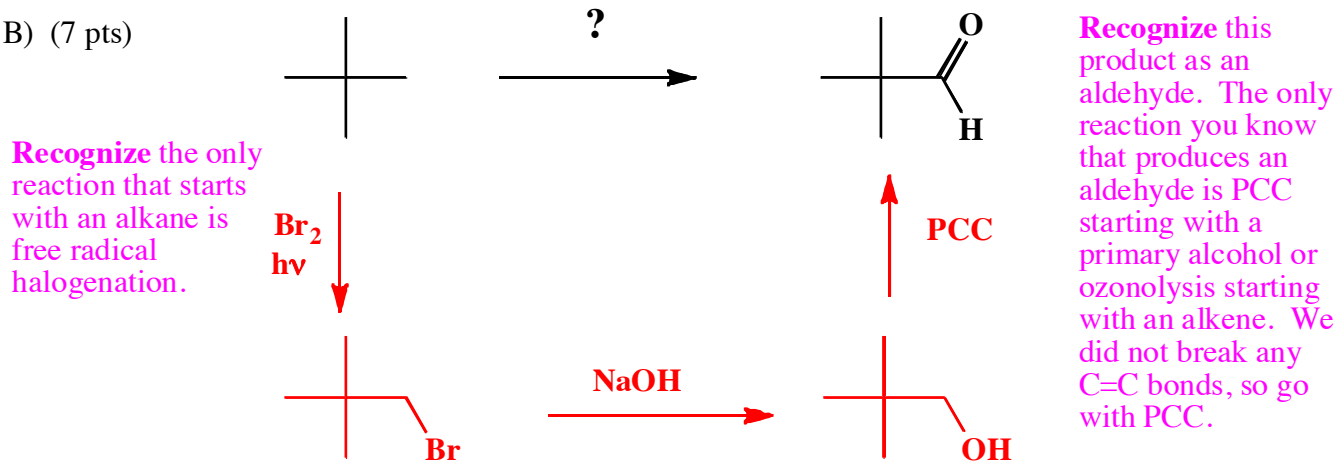


24. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate.

A) (10 pts)

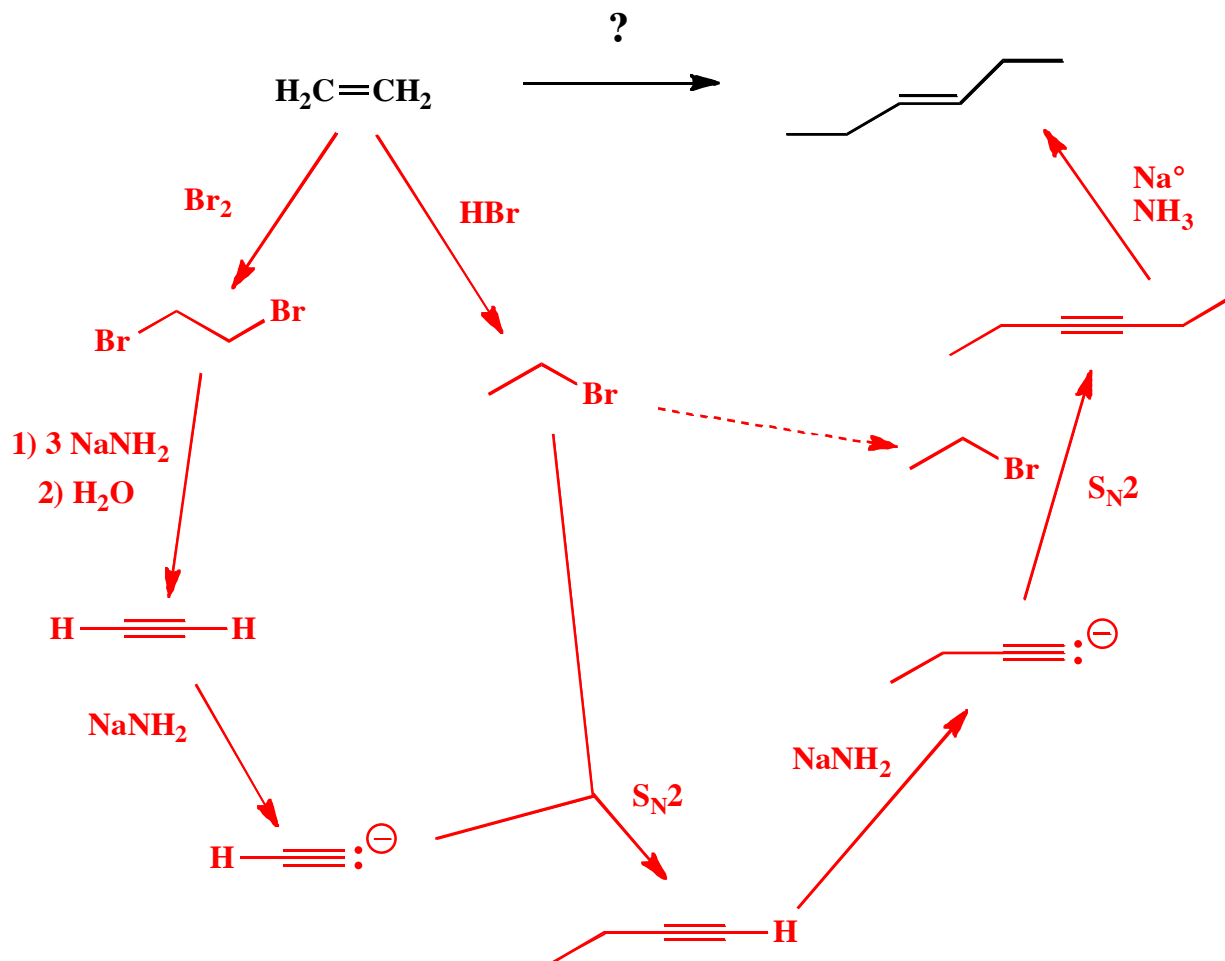


B) (7 pts)



24 (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

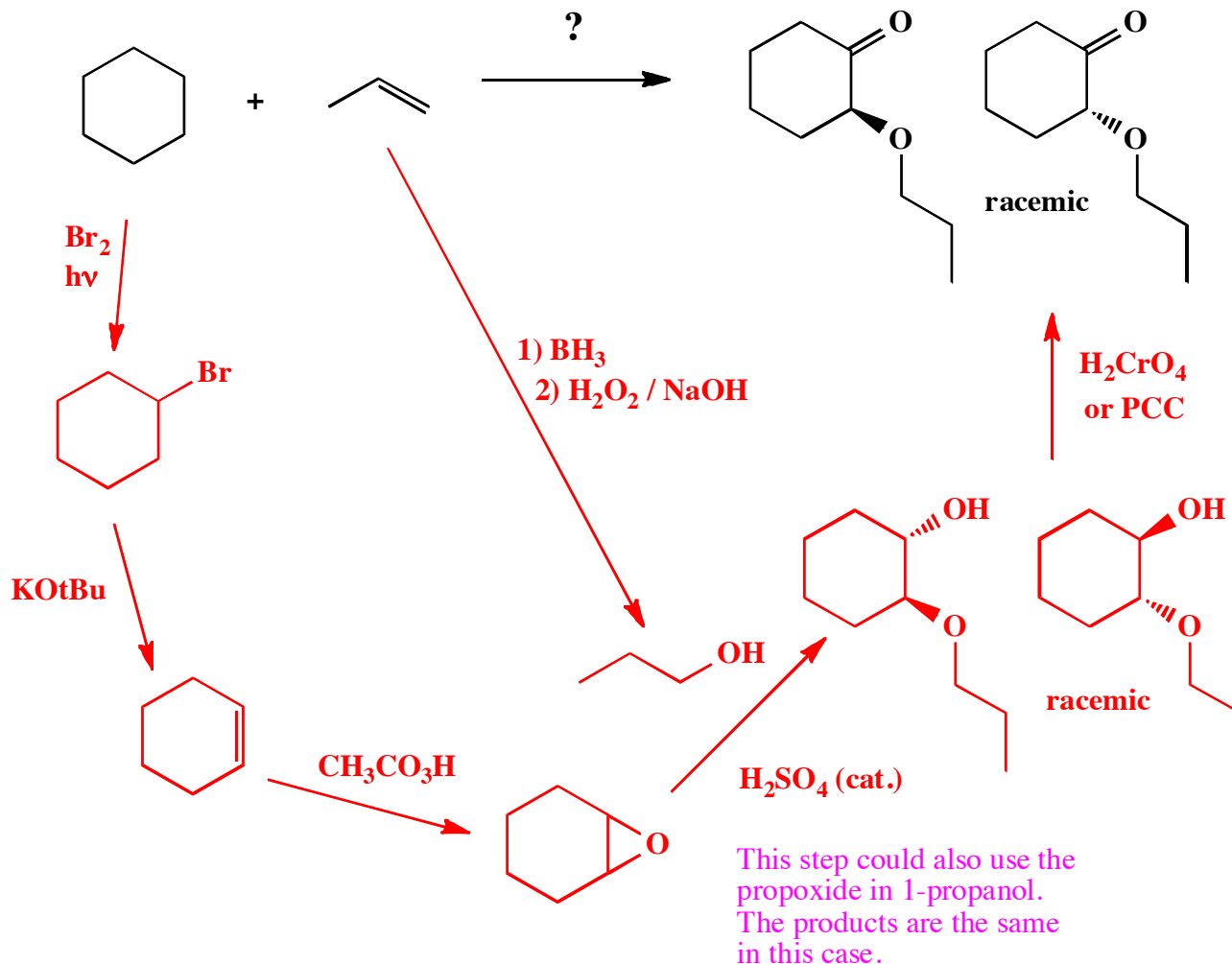
C) (21 pts)



Recognize that this molecule can be assembled from three different 2-carbon pieces, using the alkyne alkylation strategy each time. Therefore, an alkyne is required, so **recognize** that the last step must be the reduction of the alkyne group using Na^+ and NH_3 to give the *E*-alkene product. The rest is standard chemistry at this point.

24 (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

D) (16 pts)

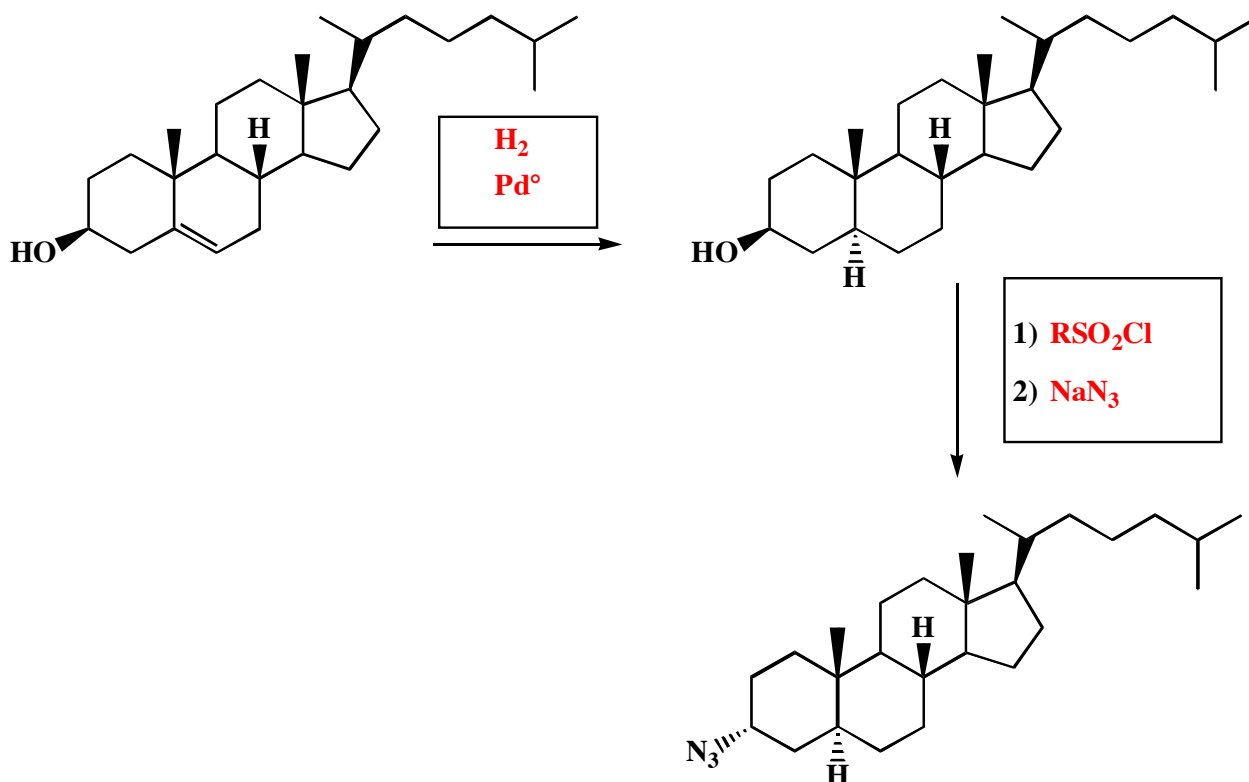
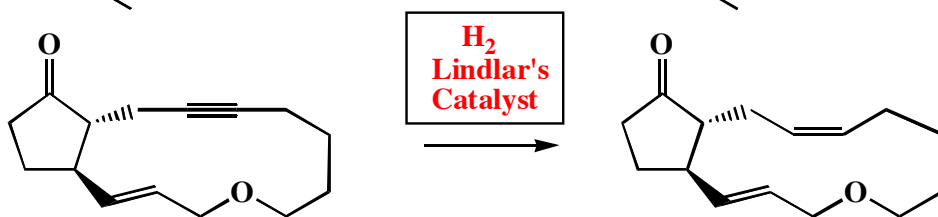
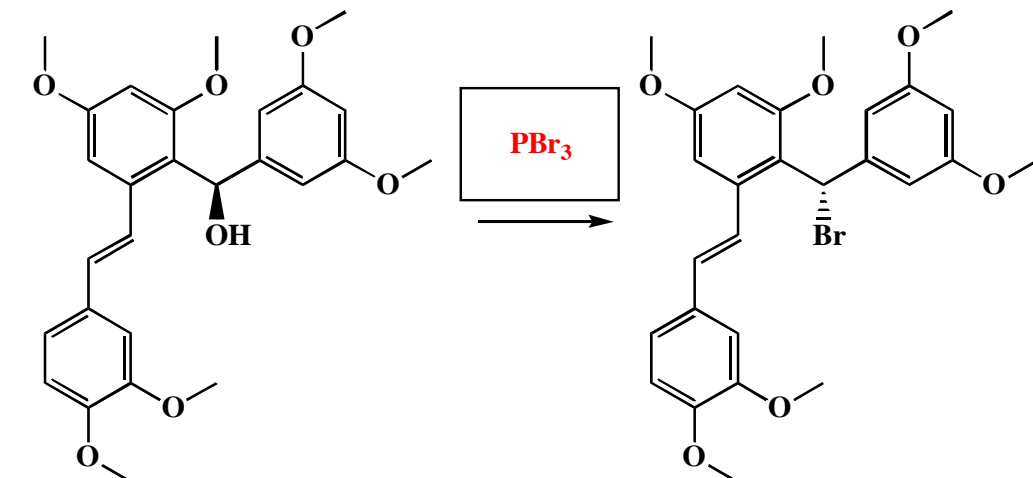


Recognize the product as having a ketone, which in this class can only be made through ozonolysis of an alkene or oxidation of an alcohol. We can rule out ozonolysis because counting carbons makes it clear there are no C-C bonds broken, thus propose the last step as an oxidation of the alcohol. The hard part of this synthesis is to **recognize** that to make the vicinal ether-alcohol in high yield you must use 1-propanol to open an epoxide in either acid (shown) or basic conditions. Alkylating a vicinal diol would not work for this because the yield would be seriously compromised by creating a statistical mixture of products. The rest of the required chemistry is fairly straightforward.

Signature _____

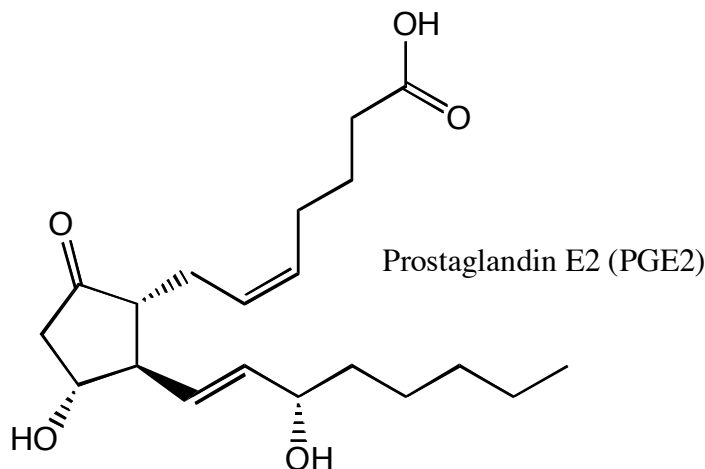
Pg 20 _____(12)

25. (12 pts) As we emphasized at the end of the semester, a key paradigm in organic chemistry is that reactions of functional groups work the same in complex molecules as they do in the simpler molecules we usually examine in first semester courses. The following complex molecules and reactions were used in actual syntheses. In the space provided, write the reagents that will produce the transformation shown.



26. In reflecting over the semester, it occurs to me that I have not given you ample opportunity to identify functional groups in complex molecules. This is important because, as emphasized on the previous page, the key paradigm in organic chemistry is that a functional group will react the same in complex molecules as it does in simpler ones. For this reason, most textbooks, including ours, is organized around the different functional groups. This semester we have covered the properties and reactions of alkenes, alkynes, haloalkanes, alcohols, thiols, and ethers. We also talked about other functional groups such as aldehydes, ketones, amides and carboxylic acids. It is important that you can recognize these functional groups whenever you encounter them. Below is an important biological molecules and you will be asked to identify functional groups. I have seen similar types of questions on real MCAT exams.

Prostaglandins are molecules found in low concentration in the bloodstream, but they regulate important complex functions such as smooth muscle contraction and blood pressure. Following is the structure of a prostaglandin named prostaglandin E2 (PGE2)



For the following multiple choice questions, circle the correct answer.

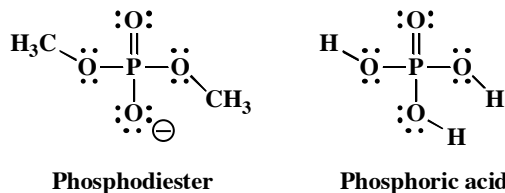
Circle the answer that best describes the functional groups in prostaglandin E2

- A) Three alcohol groups, two ketones and two alkenes
- B) Two alcohol groups, a ketone, a carboxylic acid and two alkenes**
- C) Three alcohols, an aldehyde, a ketone and two alkenes
- D) Three alcohols, a ketone and a partridge in a pear tree.

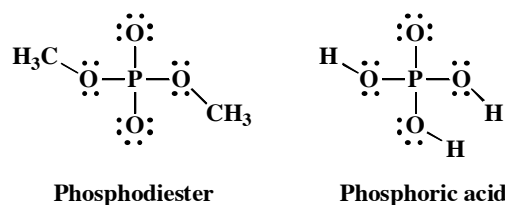
How many total stereoisomers are possible for the prostaglandin E2 molecule?

- A) 2^4
- B) 2^5
- C) 2^6 (There are 4 chiral centers and 2 alkenes that can be either E or Z).**
- D) 2^7

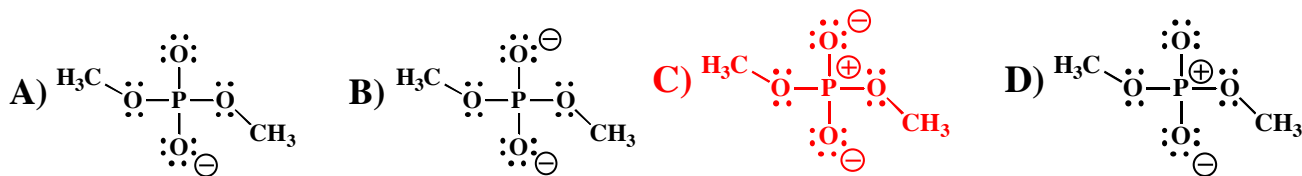
27. Every once in a great while a discovery comes along that changes how chemists think about chemical structure. Such an event occurred over the past decade in which it was determined that our understanding of hybridization in many compounds containing sulfur and phosphorus was previously inaccurate. As a result, most of the chemical literature and textbooks have misleading structures. Phosphorus and sulfur are second row elements, so their bonding was thought to involve d orbitals. For that reason, it is common to see more than four bonds to phosphorus in functional groups such as phosphodiester (found in the DNA backbone) and even in phosphoric acid.



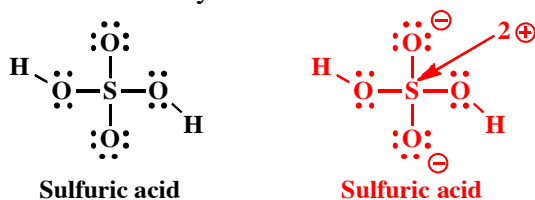
Recent calculations have convincingly shown this representation to be incorrect. The d orbitals are not significantly involved in bonding of the phosphorus atom in these molecules. Instead, the phosphorus atom in these molecules is actually sp^3 hybridized and only has four single bonds, no double bonds. For the following multiple choice questions, circle the correct answer.



Above are drawn structures of a phosphodiester and phosphoric acid with the appropriate hybridization at phosphorus. I intentionally left off the formal charges on the atoms. Which of the following four possibilities best describes the formal charges present on the O and P atoms of the phosphodiester assuming sp^3 hybridization?



It turns out that the same applies to sulfur atom hybridization in molecules such as sulfuric acid.



Assuming that the sulfur atom in sulfuric acid is sp^3 hybridized as shown above, what is the formal charge on sulfur?

- A) -1 B) neutral (no formal charge) C) +1 **D) +2**