

NAME (Print): _____

Chemistry 320M/328M
Final Exam
December 10, 2022

EID _____

SIGNATURE: _____

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

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Please Note: Please take your time. You have three hours to take this exam. The final is comprehensive in nature and longer than the midterms. However, please do not rush. Making careless mistakes is not good for anyone! If you find yourself getting anxious because of a problem, skip it and come back. Please do not second guess yourself! Keep track of the questions worth a lot of points. (This does not mean they are hard, it just means we think they cover important material.)

One last thing: I recommend you close your eyes for a moment, then take some nice deep breaths before you begin. YOU GOT THIS!

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!!!

You have been a great class and I have very much enjoyed getting to know you. We all emerged from the strangeness of the pandemic and have had to readjust to in-person learning. You have done that and here we are, finishing our first semester meeting as a class. I wouldn't say we are back to a "normal" yet, but we are getting there together. You have proven that you are resilient and strong!

I put this on every final, but I think it has special meaning for all of you right now. Acknowledging what we have all been through, it is time for you to look forward to your futures with optimism and big dreams. As one of my favorite poets of the 20th century put it, here is my truly sincere wish for every one of you:

*"May your wishes all come true.
May you build a ladder to the stars
and climb on every rung.
May you stay forever young.*

*May you grow up to be righteous,
May you grow up to be true,
May you always know the truth
And see the lights surrounding you
May you always be courageous
Stand upright and be strong
May you stay forever young.*

*May your hands always be busy
May your feet always be swift
May you have a strong foundation
When the winds of changes shift
May your heart always be joyful
May your song always be sung.
And may you stay forever young."* BD

Remember, run every chance you get. Being fit for your entire life is truly the best gift you can give yourself and those you love. Staying fit will also allow you to stay forever young. Now, go crush this final!

Brent Iverson

Student Honor Code

"As a student of The University of Texas at Austin, I shall abide by the core values of the University and uphold academic integrity."

(Your signature)

PERIODIC TABLE OF THE ELEMENTS

Elementary Subatomic Particles

Particle	Electron	Proton	Neutron	Photon	Neutrino
Speed (m/s)	3.00×10^8	3.00×10^8	3.00×10^8	3.00×10^8	3.00×10^8
Rest mass (kg)	9.109×10^{-31}	1.673×10^{-27}	1.675×10^{-27}	0	0
Relative mass (1/1836)	1	1836	1839	0	0
Relative mass ratio	$1/1836$	1	1	0	0
Specific charge (C/kg)	-1.758×10^{11}	9.58×10^{17}	0	0	0
Spin quantum number	1/2	1/2	1/2	1	1/2
Compton wavelength (m)	2.426×10^{-12}	1.321×10^{-15}	1.319×10^{-15}	0	0
Magnetic moment (J/T)	9.274×10^{-24}	1.410×10^{-26}	6.908×10^{-27}	0	0
In Bohr magneton (μ _B)	1	1.836×10^{-3}	0.672×10^{-3}	0	0
In nuclear magneton (μ _N)	1.836×10^{-3}	1.836×10^{-3}	1.836×10^{-3}	0	0

% Ionic Character of a Single Chemical Bond

Percent ionic character describes the nature of a bond. Bonds containing 50% or greater ionic character are conventionally termed ionic; bonds with less than 50% ionic character are termed covalent. Pauling's equation was modified by Huggins.

Pauling's Equation: $\% \text{ Ionic Character} = 16 | \Delta \chi |$

Huggins' Equation: $\% \text{ Ionic Character} = 16 | \Delta \chi |^2$

Electronegativity (χ): A scale of relative ability of an atom to attract electrons towards itself. Values are given for Pauling's scale (χ_P) and Huggins' scale (χ_H).

Elementary Particles: Describes the fundamental constituents of energy and matter. The electron (e⁻) is a positive-energy particle which has the same mass as an ordinary electron. The positron (e⁺) has the same properties as that of a neutron (n) except it is electrically charged. The neutrino (ν) is a neutral particle which is always thought to be electrically neutral. Negative beta decay is the transformation of a neutron into a proton, a beta particle (negative electron) and a neutrino.

Periodic Table: Standard periodic table with element symbols, atomic numbers, and names. Includes groups IIA through VIIA and VIII through X.

Atomic Weight: (1) Indicates most stable or best known isotope. (2) Indicates average atomic weight.

Boiling Point: (1) °C, (2) °F.

Density: (1) g/cm³ at STP, (2) g/cm³ at 20°C.

Electronegativity: (1) Pauling's, (2) Huggins'.

Group Classifications: s-block, p-block, d-block, f-block.

Atomic Number: Z.

Block: s, p, d, f.

Configuration: Electron configuration notation.

Name: Element name.

PAPERTECH

Editors: T. K. Varga, M.A.Sc. & C. Bello, M.A.Sc.

Product No. L24-04F

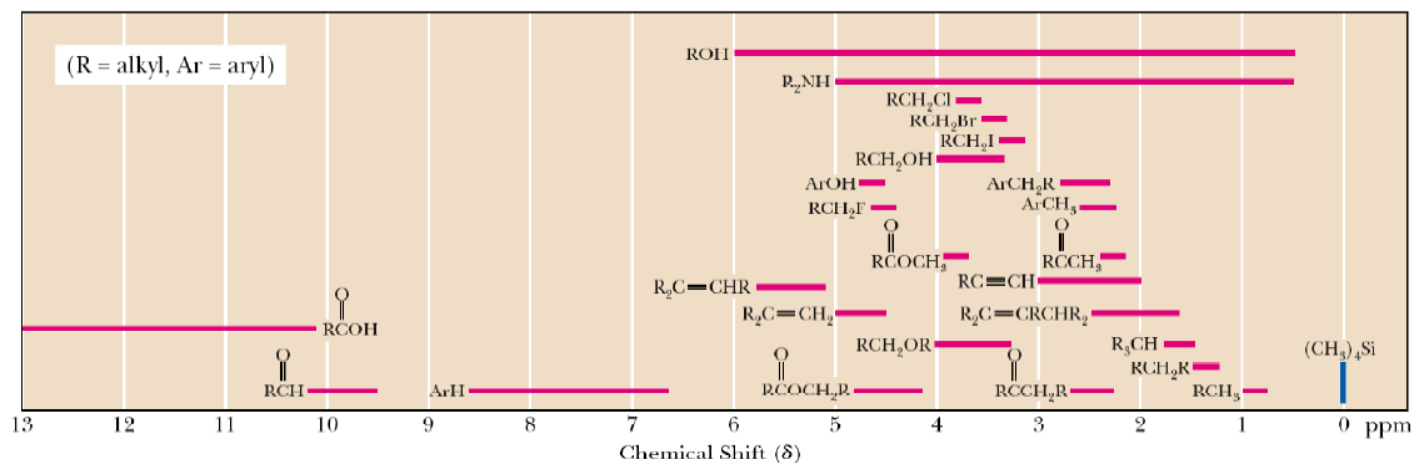
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Compound		pK _a
Hydrochloric acid	H-Cl	-7
Protonated alcohol	$\text{RCH}_2\text{O}^+\text{H}_2$	-2
Hydronium ion	H_3O^+	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-5
Thiols	RCH_2SH	8-9
Ammonium ion	H_4N^+	9.2
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CR}'$	10
Primary ammonium	$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_3$	10.5
β-Ketoesters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	11
β-Diesters	$\text{ROC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	16
Aldehydes	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	18-20
Ketones	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CR}'$	18-20
Esters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\text{H}$	25
LDA	$\text{H}-\text{N}(\text{i-C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{H}$	44
Alkanes	$\text{CH}_3\text{CH}_2-\text{H}$	51

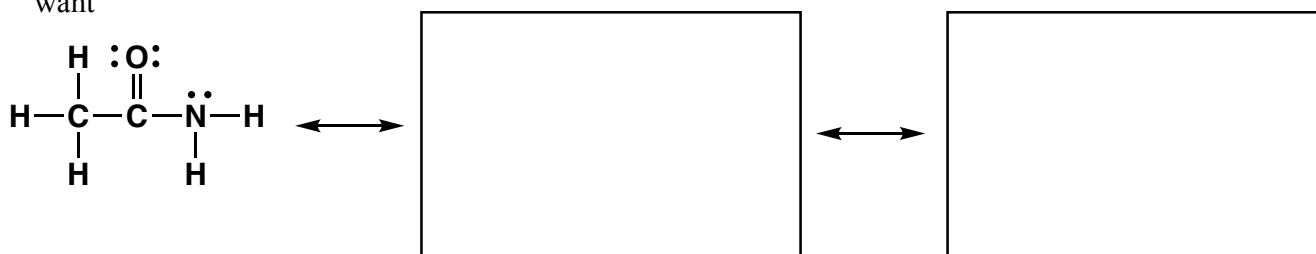
Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
R_2NH	0.5-5.0	RCH_2OH	3.4-4.0
ROH	0.5-6.0	RCH_2Br	3.4-3.6
RCH_3	0.8-1.0	RCH_2Cl	3.6-3.8
RCH_2R	1.2-1.4	$\begin{array}{c} O \\ \\ RCOCH_3 \end{array}$	3.7-3.9
R_3CH	1.4-1.7	$\begin{array}{c} O \\ \\ RCOCH_2R \end{array}$	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.



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

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. (1 pt each) Fill in each blank with the word that best completes the sentences. Yep, this is the MRI paragraph!

The popular medical diagnostic technique of 1. _____ 2. _____

3. _____ (_____) is based on the same principles as 4. _____,

namely the flipping (i.e. 5. _____) of nuclear spins of H atoms by

6. _____ frequency irradiation when a patient is placed in a strong

7. _____ 8. _____. 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

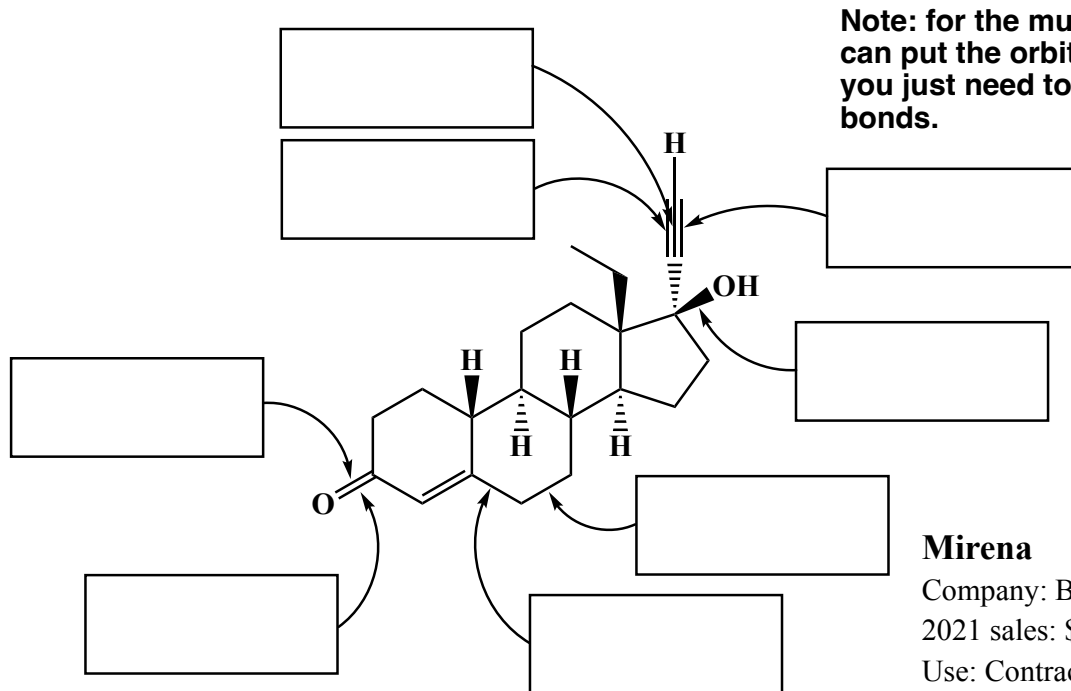
9. _____ that when 10. _____ make up the three-

dimensional image of 11. _____ amounts of H atoms, especially the H atoms

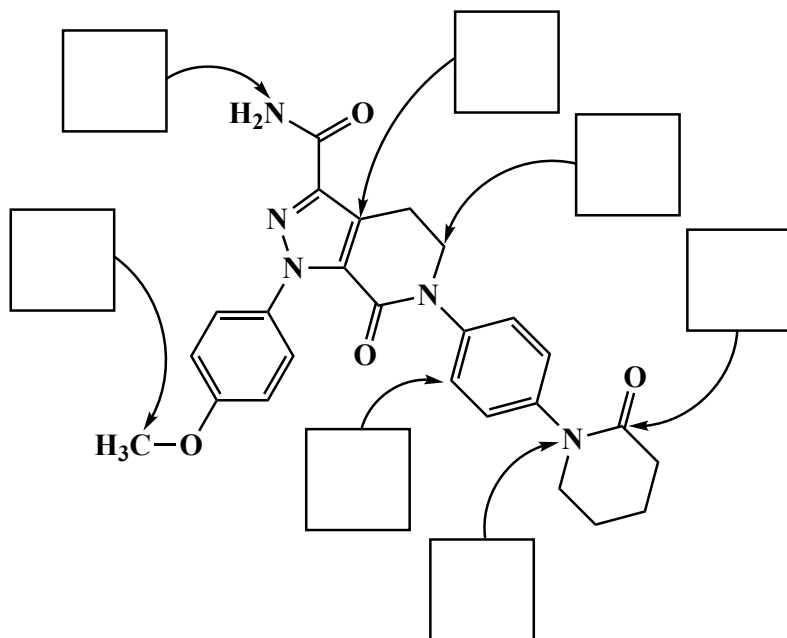
from 12. _____ and 13. _____, in the different

14. _____.

4. (2 pts each) In the spaces provided, indicate the type of bond, and the hybridized orbitals that overlap to form the bond. For example, one answer could be: σ Csp^3-H1s



5. (1 pt each) In the spaces provided, write the hybridization state of the atoms indicated by the arrow.



Signature _____

Pg 3 _____ (28)

6. (2 pts each) Fill in each blank with the word that best completes the sentences (you will recognize these as Rules of the Day!).

A. The best way to think of electrons in molecules is as _____, described mathematically by three-dimensional wave function equations.

B. When the 2s orbital is hybridized with all three 2p orbitals, you get _____ hybridization that has major lobes pointed in a tetrahedral geometry.

C. For _____ hybridization, the 2s and only two of the 2p orbitals combine to make three major lobes in a trigonal planar geometry.

D. The two extreme conformations in ethane are _____ (more stable) and _____ (less stable).

E. _____ isomers are molecules with the same molecular formula but different connectivities between atoms.

F. On cyclohexane rings, groups larger than H prefer to be _____ because when they are axial there is steric strain (also called non-bonded interaction strain or 1,3 diaxial interactions) with the other axial groups.

G. An _____ is any molecule that cannot be superimposed on its mirror image (it does not have a plane or center of symmetry).

H. _____ are molecules that are stereoisomers but not enantiomers; a situation that arises when there are more than one chiral center in the same molecule.

I. A _____ compound is a molecule with two or more chiral centers yet is not chiral because it contains a symmetry element, usually a plane of symmetry.

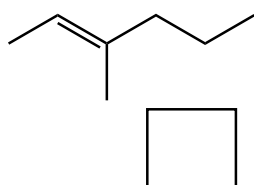
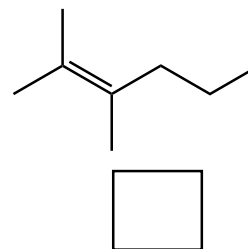
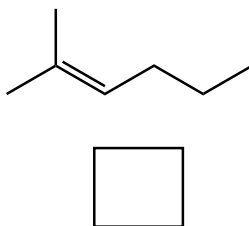
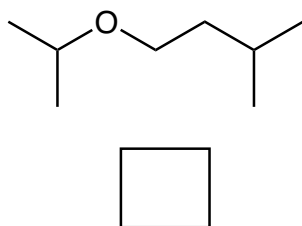
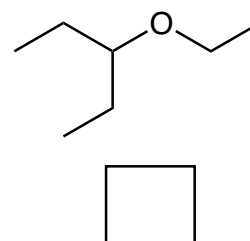
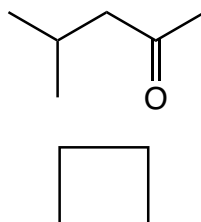
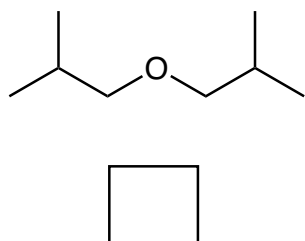
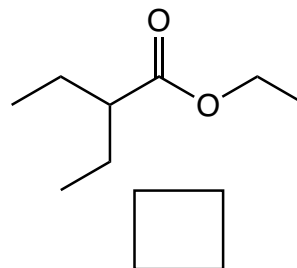
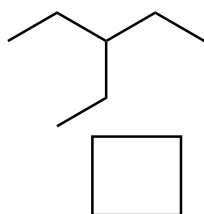
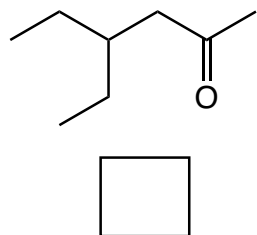
J. To understand NMR you need to know the following: Physics: Moving charge generates a _____ field, and a moving magnetic field causes charges to move in a conductor.

K. The difference in energy between the +1/2 and -1/2 nuclear spin states is proportional to the strength of the _____ field felt (experienced) by the nucleus.

L. The _____ under a given NMR signal is proportional to the number of equivalent hydrogen atoms that give rise to that signal.

M. The splitting of a -CH₂- group adjacent to a _____ center will be "messed up", that is split into many peaks.

7. (24 pts total) On the following four pages there are NMR spectra. The relative integrations are given above each signal. Each NMR spectrum has a letter on it. **In the spaces provided, write the appropriate letter underneath the molecules that would produce that spectrum.** Notice that not all of the molecules below will have letters underneath them, as there are only four spectra but nine molecules.

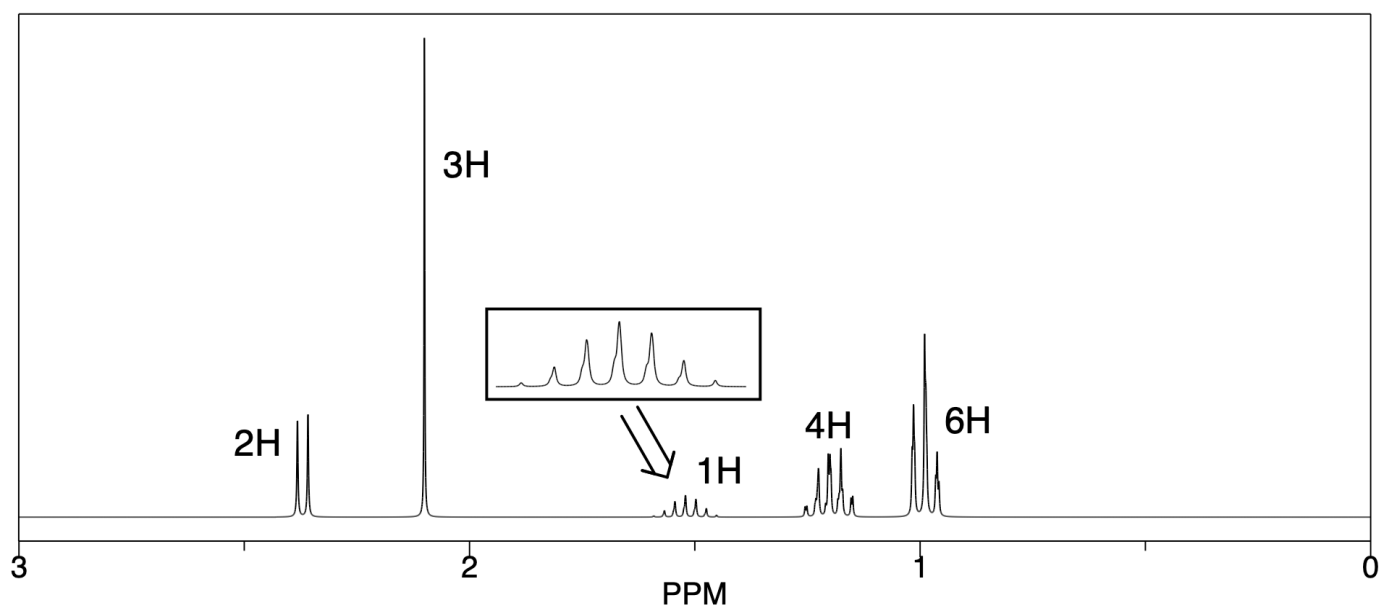


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Pg 5

Spectrum A

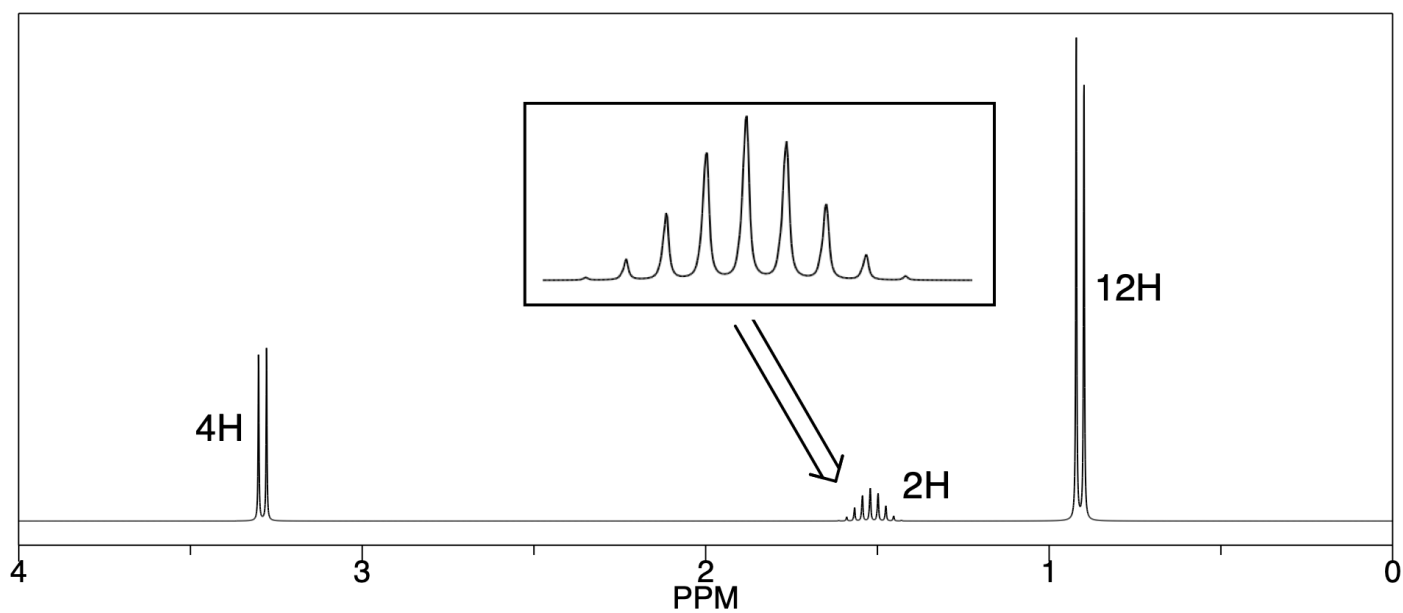
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Spectrum B

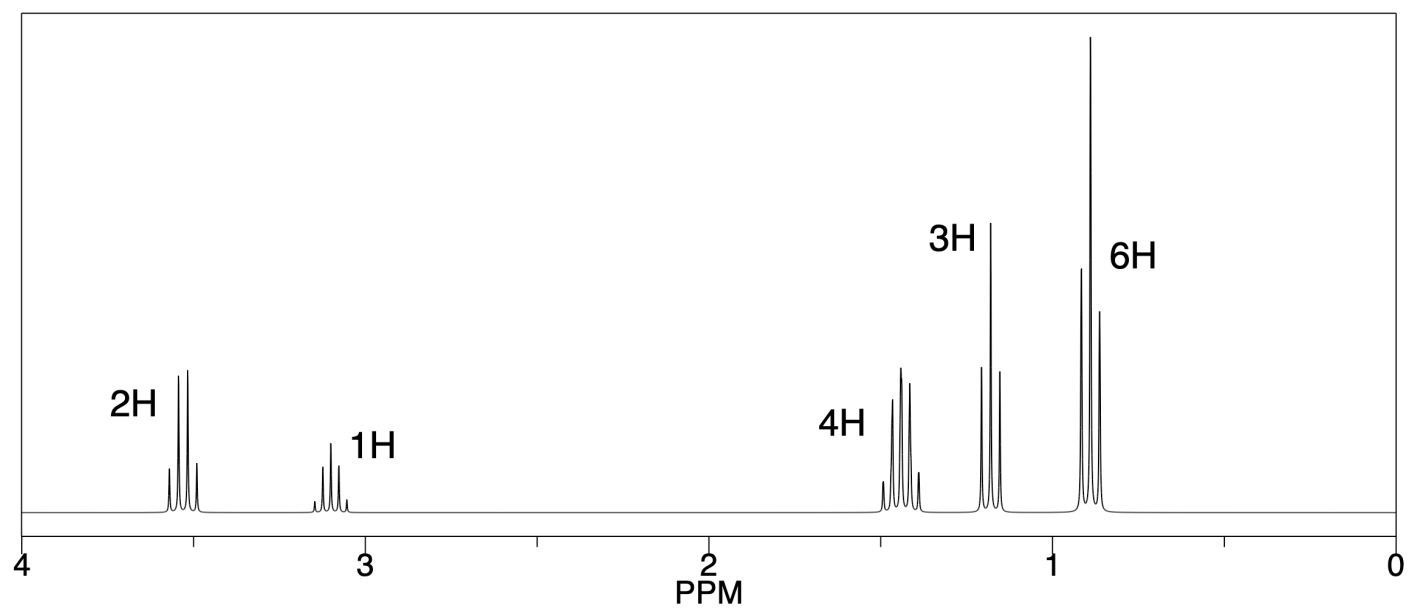
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Spectrum C

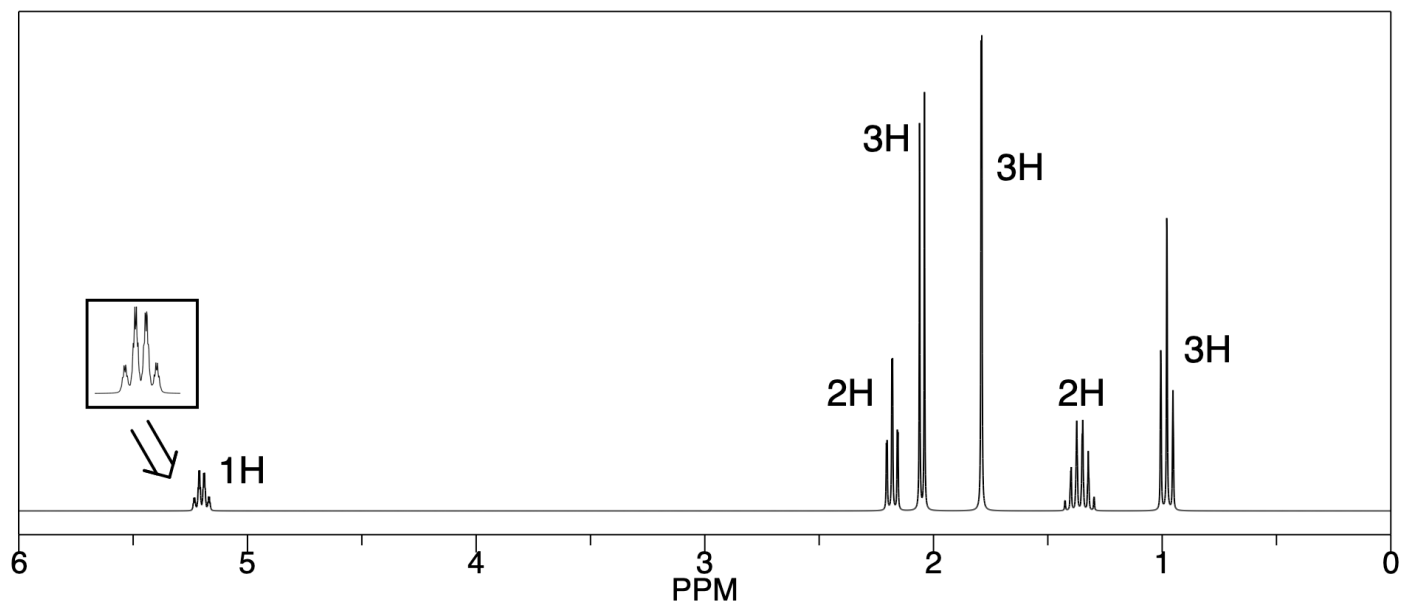
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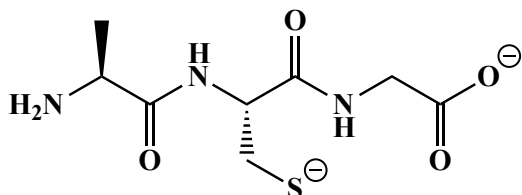
Spectrum D

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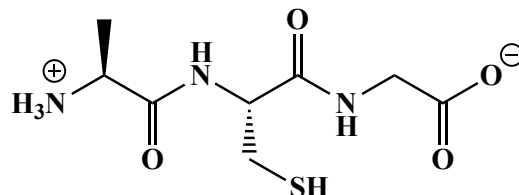
8. (8 pts.) Fill in the circle to indicate the pH at which the species shown will be the predominant one. Fill in the circle next to the "X" under a species that cannot be predominant at any pH.

The pKa of a carboxylic acid (RCO_2H) is generally in the 4-5 range. The pKa of ammonium ions (RNH_3^+) is in the 9-10 range and that of -SH groups is in the 8-9 range. PLEASE NOTE THAT LAST ONE: the pKa of -SH groups is in the 8-9 range!



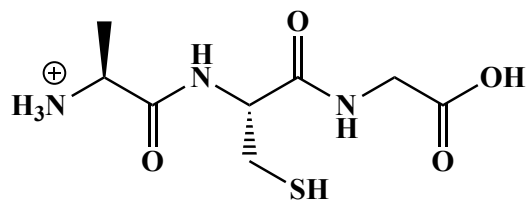
pH 2.0 pH 12.0

pH 7.0 X



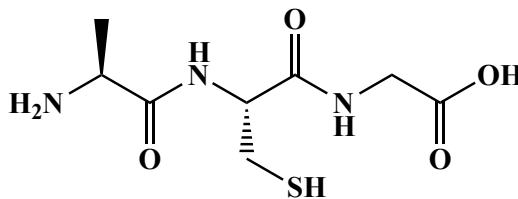
pH 2.0 pH 12.0

pH 7.0 X



pH 2.0 pH 12.0

pH 7.0 X



pH 2.0 pH 12.0

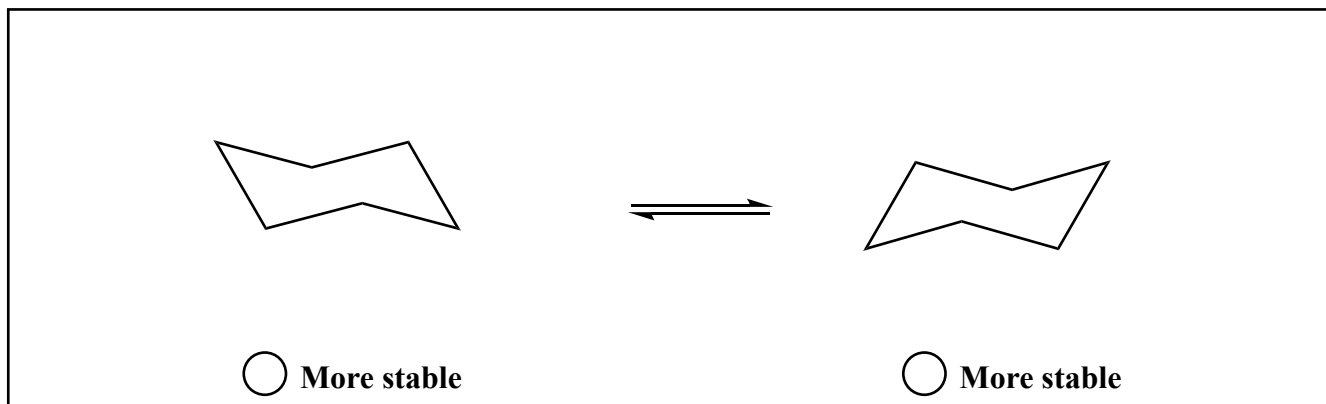
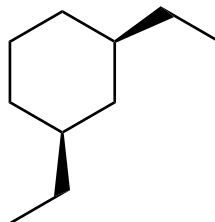
pH 7.0 X

9. (12 pts) For each pair of molecules, on the line provided state the relationship between the two structures. Possible answers could be **enantiomers**, **diastereomers**, **constitutional isomers**, or **same molecule**. Fill in the circle to indicate the correct relationship between the molecules shown. In the boxes provided next to each chiral center, write "R" or "S" to indicate the absolute stereochemistry present.

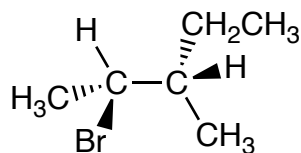
Relationship:

		<input type="radio"/> enantiomers <input type="radio"/> diastereomers <input type="radio"/> constitutional isomers <input type="radio"/> same molecule
		<input type="radio"/> enantiomers <input type="radio"/> diastereomers <input type="radio"/> constitutional isomers <input type="radio"/> same molecule

10. (10 pts) For the following cyclohexane derivative, draw the two alternative chair conformations. If there is a difference in stability, fill in the circle that says "More stable". If there is not any difference in stability, do not fill in any circle.

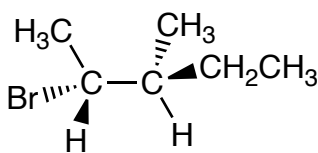


11. (8 pts) Drawn below are four conformations of the molecule (2*R*,3*S*)-2-bromo-3-methylpentane. Indicate any of the conformations that, **as drawn**, would be able to react through an E2 mechanism with a strong base.



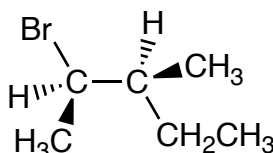
Reacts by E2

Cannot react by E2



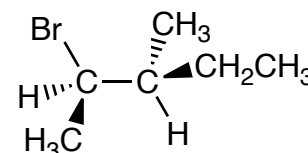
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Reacts by E2

Cannot react by E2



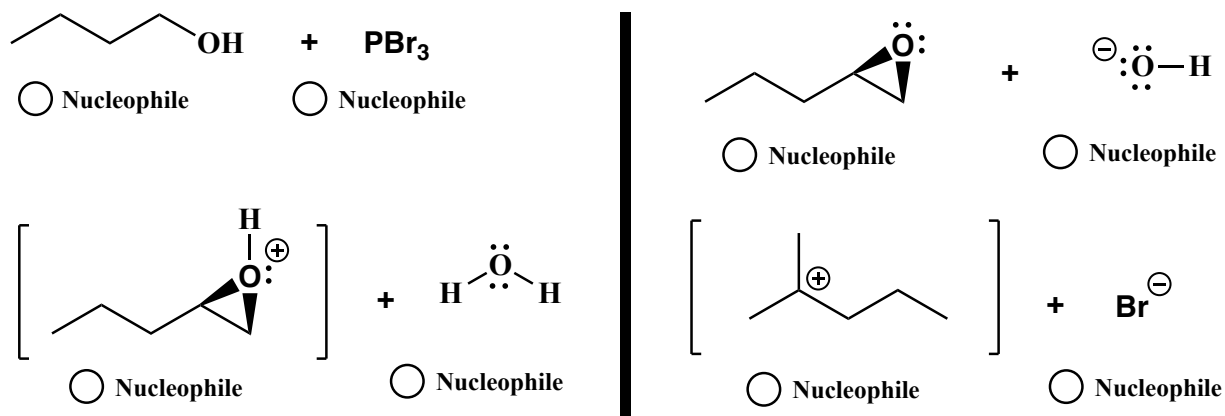
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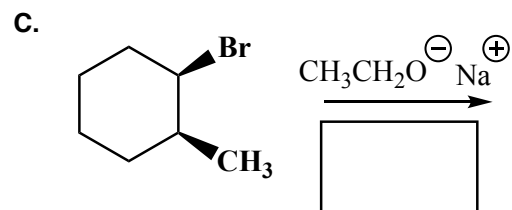
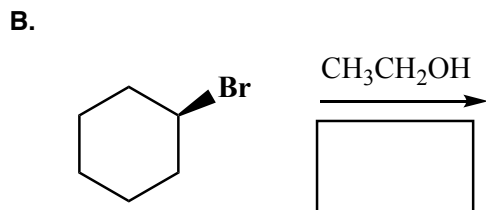
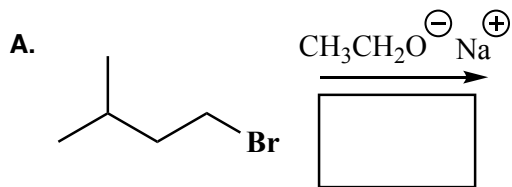
In the box, draw the product of the E2 reaction of (2*R*,3*S*)-2-bromo-3-methylpentane with strong base.



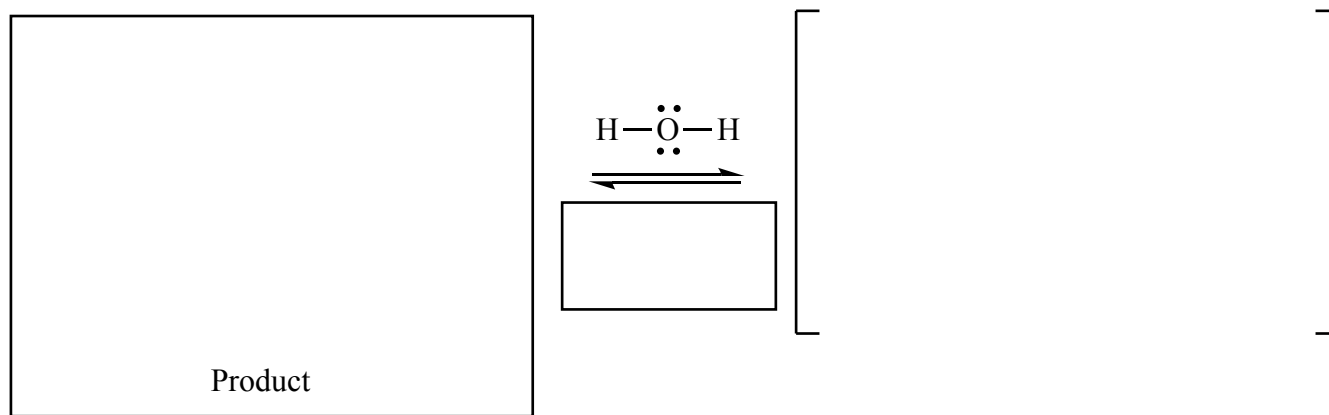
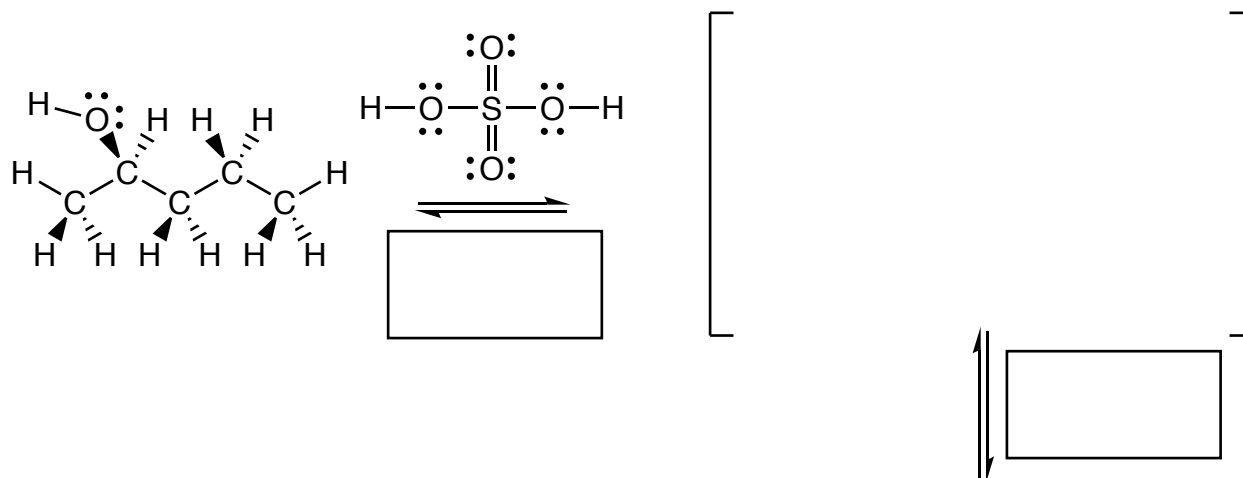
12. (8 pts) For the following four sets of reagents you have seen in various bond-making steps in mechanisms, **fill in the circle to indicate which of the two species is the nucleophile**. DO NOT WRITE THE PRODUCTS OF THESE STEPS, we only want to see circles filled-in here!!



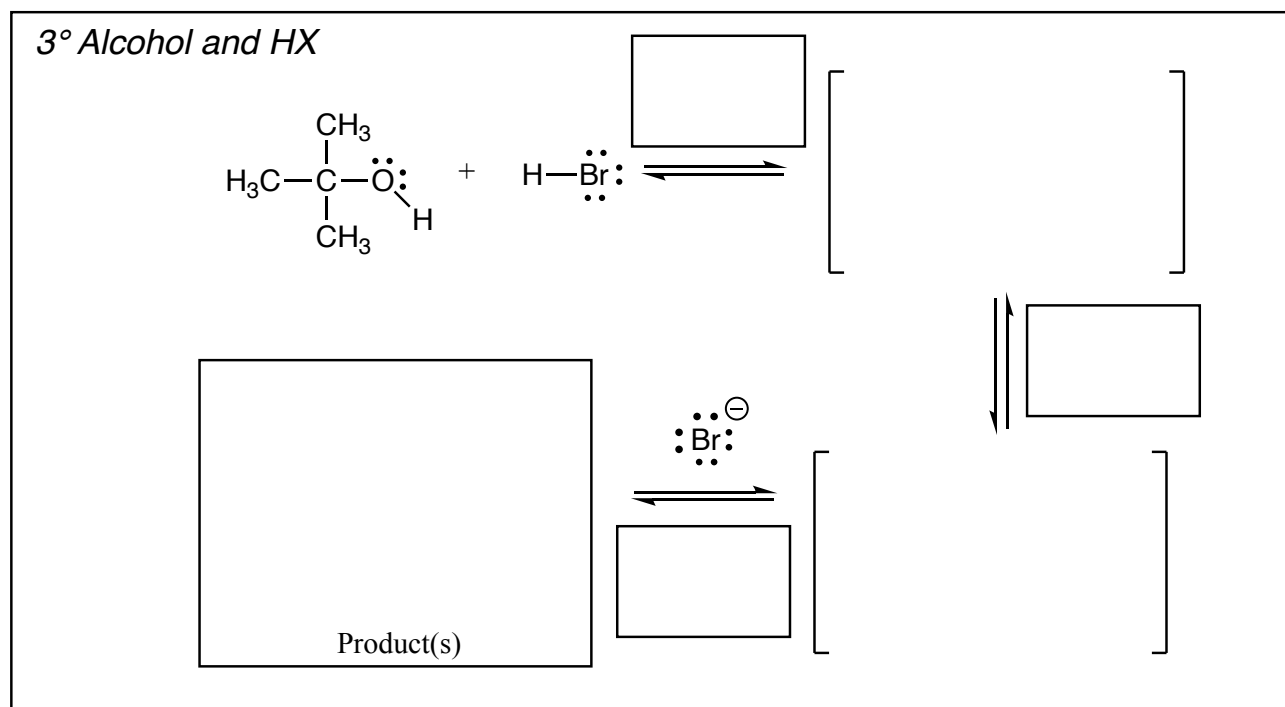
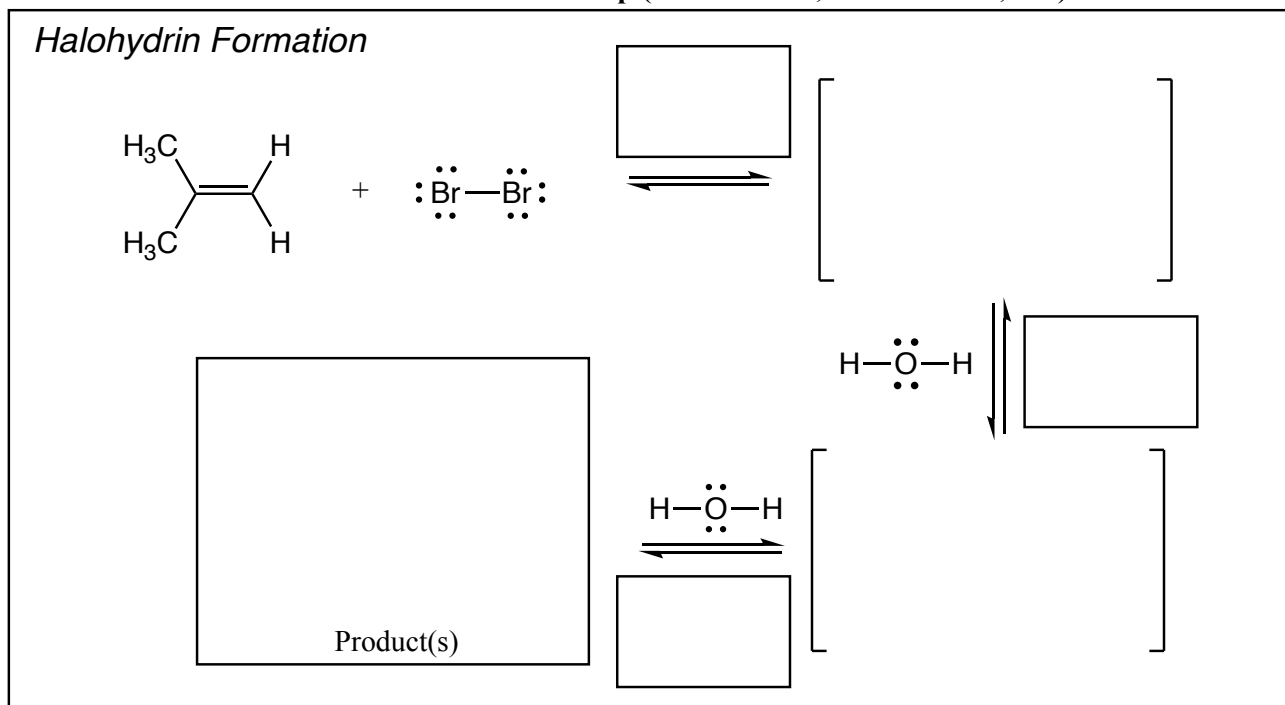
13. (18 pts) The following reactions all involve chemistry of haloalkanes. **Fill in the box below the arrow with the mechanism that will be followed ($\text{S}_{\text{N}}2$, $\text{E}2$, etc.). Then draw only the predominant product or products** and please remember that **you must draw the correct stereoisomers**. For $\text{S}_{\text{N}}1/\text{E}1$ reactions you must draw all significant products (including all stereoisomers).



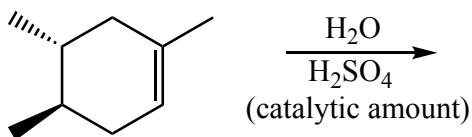
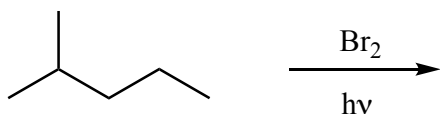
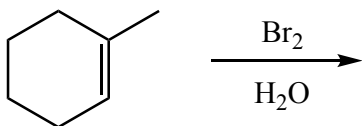
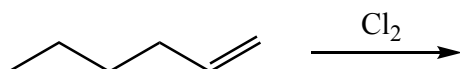
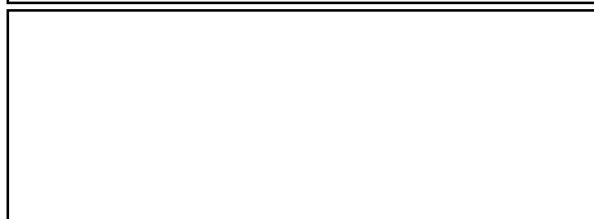
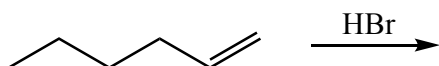
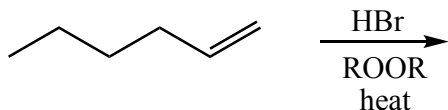
14. (20 pts) You have seen this one before! Complete the mechanism for the following acid-catalyzed alcohol dehydration reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. YOU ONLY NEED TO DRAW ONE STEREOISOMER OF A CHIRAL INTERMEDIATE OR PRODUCT (using wedges and dashes as appropriate) IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. In the three boxes provided, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).



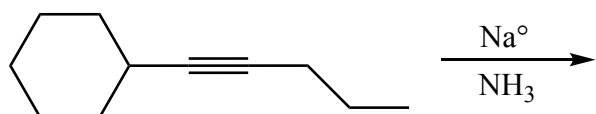
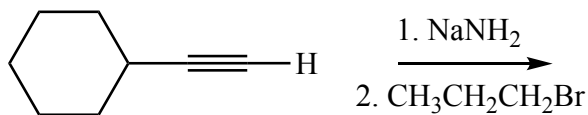
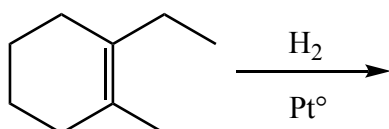
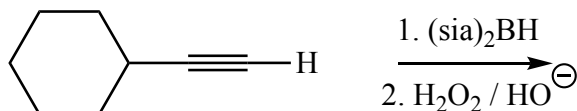
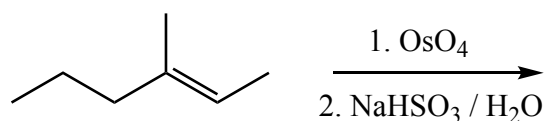
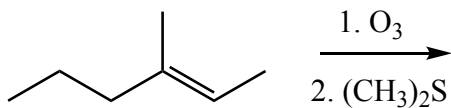
15. (33 pts) For these two mechanisms, use **arrows to indicate movement of all electrons**, write **all lone pairs**, **all formal charges**, and **all the products for each step**. Remember, I said **all** the products for each step. **YOU ONLY NEED TO DRAW ONE STEREOISOMER OF A CHIRAL INTERMEDIATE OR PRODUCT (using wedges and dashes as appropriate) IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE.** In the boxes provided, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).



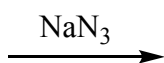
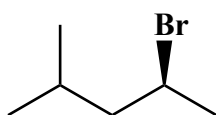
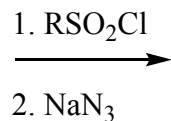
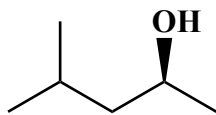
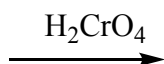
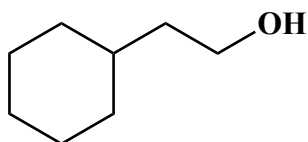
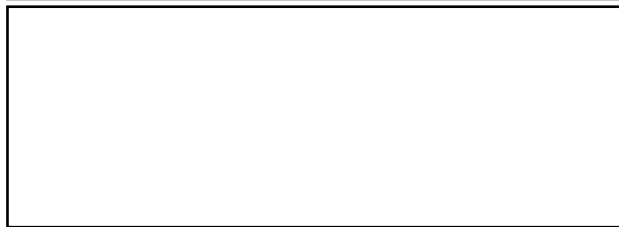
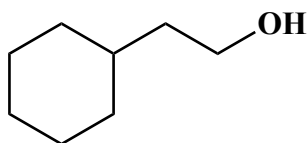
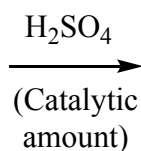
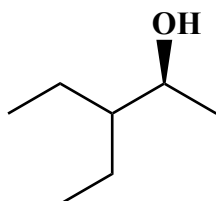
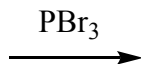
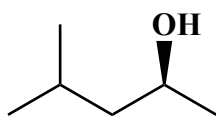
16. (25 pts) Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov, etc.) and please remember that you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry. When a racemic mixture is formed, you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES.



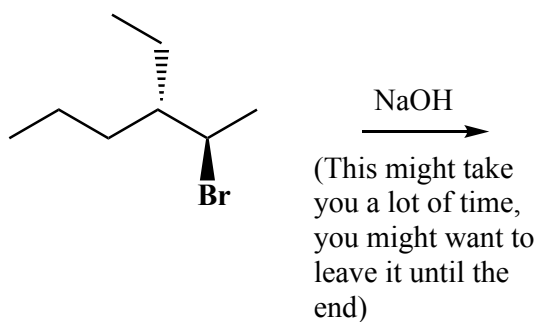
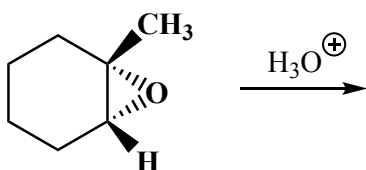
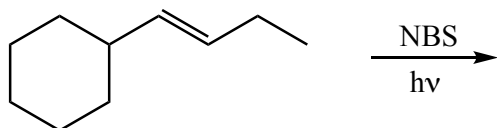
16. (23 pts) Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov, etc.) and please remember that you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry. When a racemic mixture is formed, you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES.



16. (18 pts) Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov, etc.) and please remember that you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry. When a racemic mixture is formed, you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES.



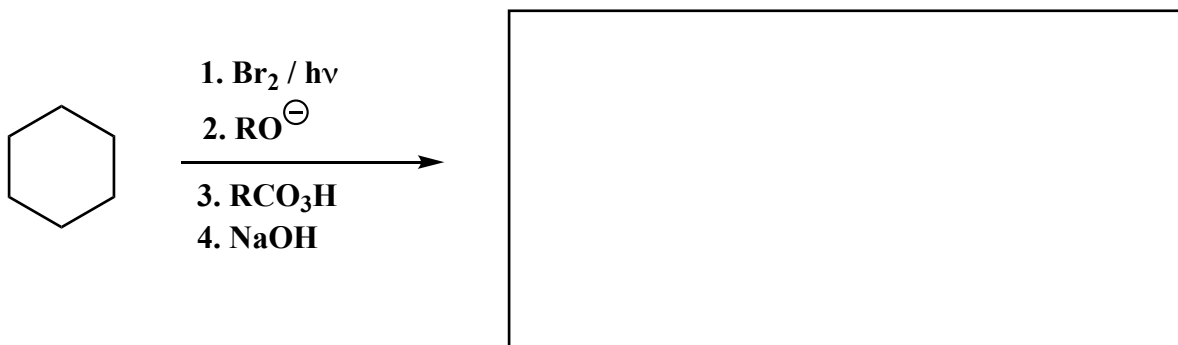
16. (18 pts) **These are more complicated so please take your time!** Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov, etc.) and please remember that you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry. When a racemic mixture is formed, you must write "racemic" under both structures **EVEN THOUGH YOU DREW BOTH STRUCTURES.**



Signature _____

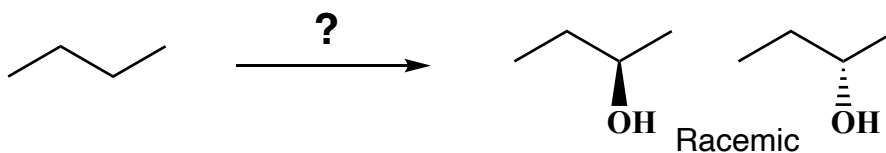
Pg 18 _____ (8)

17. (8 pts) Here is a warm-up for the synthesis problems. For the following series of reactions, write the **final** product(s) that you will see. Make sure draw all stereoisomers produced and to use wedges and dashes to indicate all stereochemistry, and you must write racemic if appropriate.

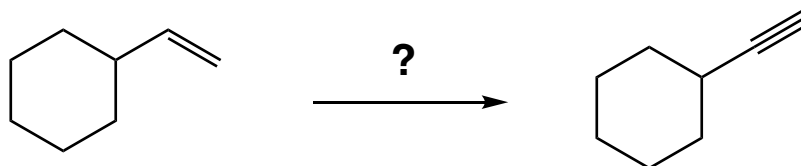


18. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized 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.**

A) (7 pts)

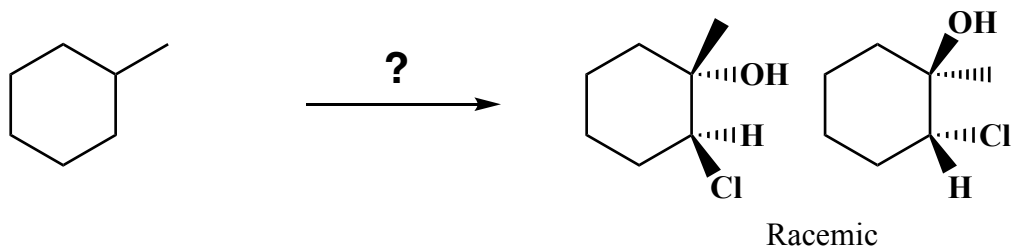


B) (4 pts)

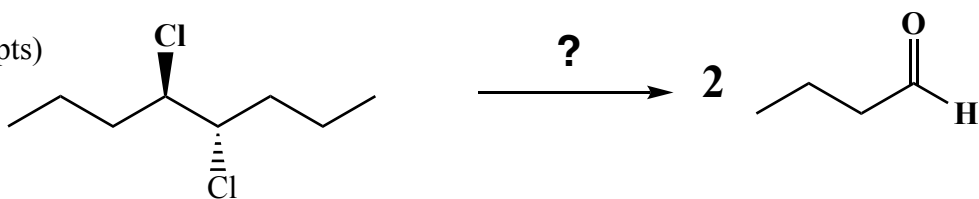


18. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized 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) (7 pts)



D) (7 pts)

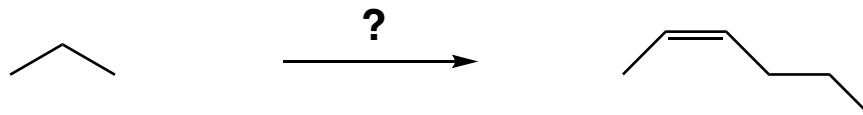


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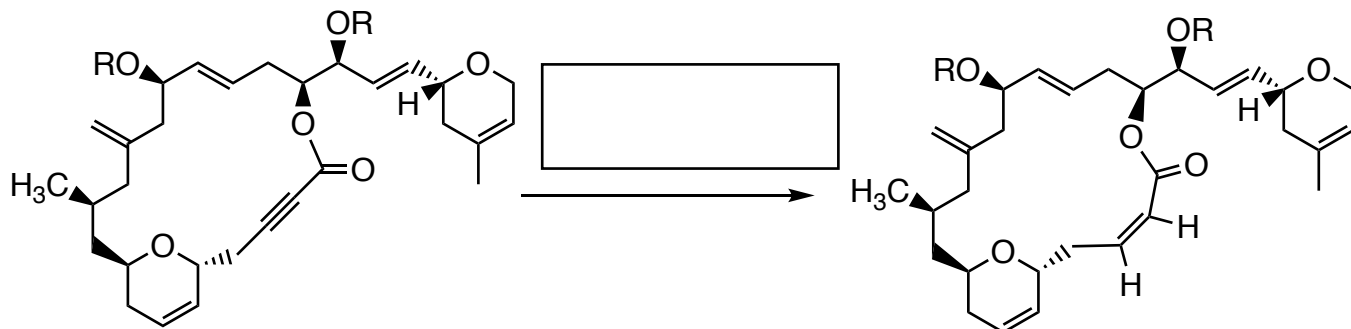
Pg 21 _____ (22)

18. 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.** OK, this is a long one. Work hard to Recognize that product and work backwards. You can do this!

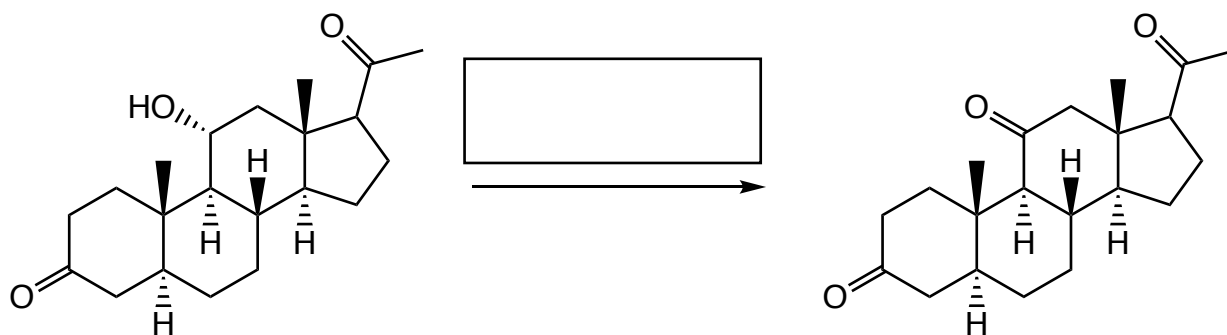
E) (22 pts)



19. (8 pts) The chemistry you have learned this semester is used in the synthesis of important pharmaceuticals. Here are two examples. Fill in the boxes with the reagent(s) required to carry out the transformation indicated.



Swamy, *et al.*, Tetrahedron Letters, 2018, 59, 419-429



Have a great holiday break!!

...And remember to run every chance you get!

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:

A. Predicting Structure and Bonding 1. In most stable molecules, all the atoms will have filled valence shells. 2. Five- and six-membered rings are the most stable. 3. There are two possible arrangements of four different groups around a tetrahedral atom.

B. Predicting Stability and Properties 4. The most important question in organic chemistry is "Where are the electrons?" 5. Delocalization of charge over a larger area is stabilizing. 6. Delocalization of unpaired electron density over a larger area is stabilizing. 7. Delocalization of pi electron density over a larger area is stabilizing.

C. Predicting Reactions 8. Reactions will occur if the products are more stable than the reactants and the energy barrier is low enough. 9. Functional groups react the same in different molecules. 10. A reaction mechanism describes the sequence of steps occurring during a reaction. 11. Most bond-making steps in reaction mechanisms involve nucleophiles reacting with electrophiles.