

NAME (Print): _____

Chemistry 320M/328M
Dr. Brent Iverson
3rd Midterm
November 15, 2012

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!!!

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)

Page	Points
1	(25)
2	(13)
3	(14)
4	(18)
5	(20)
6	(26)
7	(24)
8	(16)
9	(19)
10	(20)
11	(15)
12	(17)
13	(8)
14	(8)
Total	(243)

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
Acetic acid	$\text{CH}_3\overset{\text{O}}{\parallel}\text{C}-\text{H}$	4.8
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
Ethyl ammonium ion	$\text{H}_3\text{N}^+-\text{CH}_2\text{CH}_3$	10.8
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	$\text{RCH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{Cl}$	16
Aldehydes	$\text{RCH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{H}$	18-20
Ketones	$\text{RCH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{CR}'$	18-20
Esters	$\text{RCH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{OR}'$	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

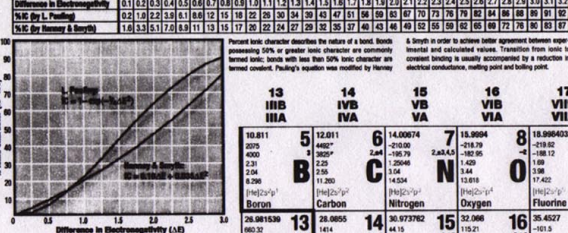
PERIODIC TABLE OF THE ELEMENTS

V Elementary Subatomic Particles

	Electron	Proton	Neutron	Photon	Neutrino
Symbol	e	p	n	γ	ν
Rest mass (kg)	9.10938971(5) × 10 ⁻³¹	1.6726231(1) × 10 ⁻²⁷	1.674928(1) × 10 ⁻²⁷	0	0
Rest mass (amu)	5.485799094(4) × 10 ⁻⁴	1.007276467(1) × 10 ⁻³	1.008664916(4) × 10 ⁻³	0	0
Particle-electron mass ratio	1	1836.152673(43)	1838.683601(49)	0	0
Particle-neutron mass ratio	5.485799094(4) × 10 ⁻⁴	1.001378404(9)	1	0	0
Particle-proton mass ratio	5.485799094(4) × 10 ⁻⁴	1	1.001378404(9)	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
Charge (elementary charge)	-1.602176634(4) × 10 ⁻¹⁹	1.602176634(4) × 10 ⁻¹⁹	0	0	0
Magnetic moment (μ _B)	-1.836119737(4) × 10 ⁻⁸	1.836119737(4) × 10 ⁻⁸	0	0	0
In nuclear magneton (μ _N)	1.00115865218(19) × 10 ⁻³	1.00115865218(19) × 10 ⁻³	0	0	0
In nuclear magneton (μ _N)	1.836119737(4) × 10 ⁻⁸	1.836119737(4) × 10 ⁻⁸	0	0	0

Elementary particles are the fundamental constituents of matter and energy. The proton (p) is a positively charged particle which has the same mass as the neutron (n). The electron (e) is a negatively charged particle which has the same mass as the positron (e⁺). The neutrino (ν) is a neutral particle which has a very small mass. The photon (γ) is a neutral particle which has no mass and travels at the speed of light. The spin quantum number (s) is a measure of the intrinsic angular momentum of a particle. The charge (q) is a measure of the electric charge of a particle. The magnetic moment (μ) is a measure of the magnetic dipole moment of a particle. The spin quantum number (s) is a measure of the intrinsic angular momentum of a particle. The charge (q) is a measure of the electric charge of a particle. The magnetic moment (μ) is a measure of the magnetic dipole moment of a particle.

V % Ionic Character of a Single Chemical Bond



13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIII
Aluminum	Germanium	Antimony	Tellurium	Iodine	Xenon
13.01	72.81	52.91	35.12	25.01	16.00
26.9815386	72.6305	121.757	127.603	126.90547	131.29
13.01	72.81	52.91	35.12	25.01	16.00
26.9815386	72.6305	121.757	127.603	126.90547	131.29

1 IA	2 IIA	3 IIIA	4 IVA	5 VA	6 VIA	7 VIIA	8 VIIIA	9 VIIIA	10 VIIIA	11 IB	12 IIB
Hydrogen	Lithium	Sodium	Potassium	Rubidium	Cesium	Francium					
1.00794	6.941	22.989769	39.0983	85.4678	132.90543	223.01848					
1.00794	6.941	22.989769	39.0983	85.4678	132.90543	223.01848					

13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIII
Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon
10.811	12.011	14.0074	15.9994	18.9984032	20.1797
10.811	12.011	14.0074	15.9994	18.9984032	20.1797

7 VIIA	8 VIIIA
Manganese	
54.938045	
54.938045	

9 VIIIA	10 VIIIA	11 IB	12 IIB
Cobalt	Nickel	Copper	Zinc
58.933200	58.933200	63.546	65.39
58.933200	58.933200	63.546	65.39

13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIII
Aluminum	Germanium	Antimony	Tellurium	Iodine	Xenon
26.9815386	72.6305	121.757	127.603	126.90547	131.29
26.9815386	72.6305	121.757	127.603	126.90547	131.29

Atomic Weight (A_r) indicates most stable or best known isotope. Melting Point (T_m) in °C. Density (ρ) in g/cm³ at 20°C. Electronegativity (χ) on Pauling scale. First Ionization Potential (I₁) in eV. Group Classification. Atomic Number (Z). Oxidation States. All values are most stable unless noted. Symbol. Name. Periodic Table of the Elements, 1991. Copyright © 1991 by Pergamon Press. Printed in Canada.

PAPERTECH

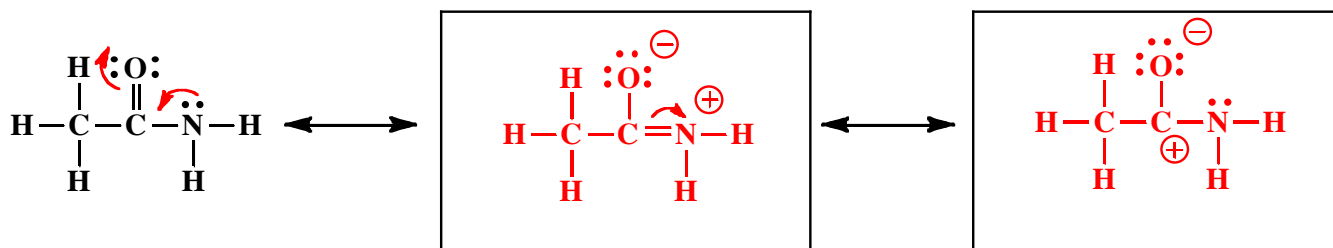
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1. (5 pts) What is the most important question in organic chemistry?

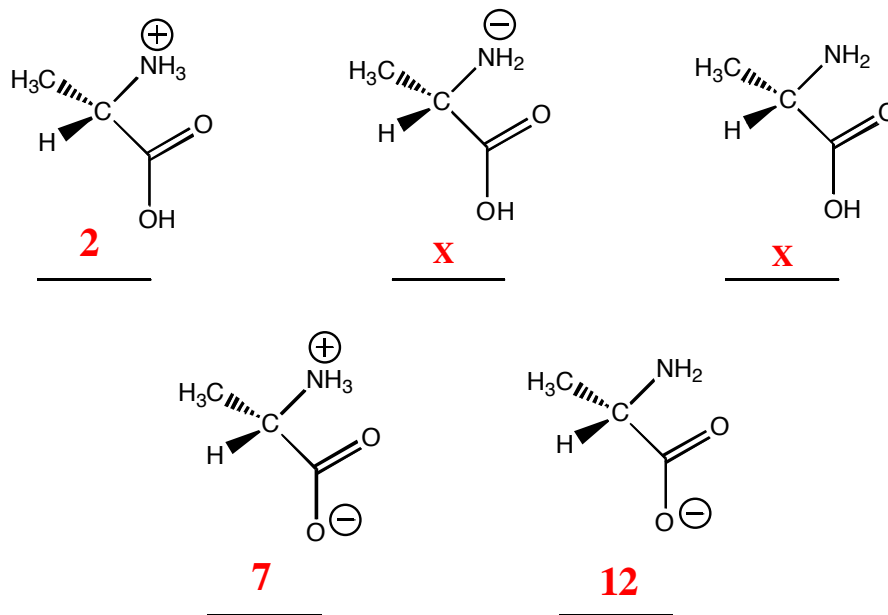
Where are the electrons?

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. (10 pts) Put a 7 under the species that will be present at pH 7.0, put a 2 under the species that will be present at 2.0, and put a 12 under the species that will be present at pH 12.0. **Put an "X" under the two species that cannot predominate at any pH.**

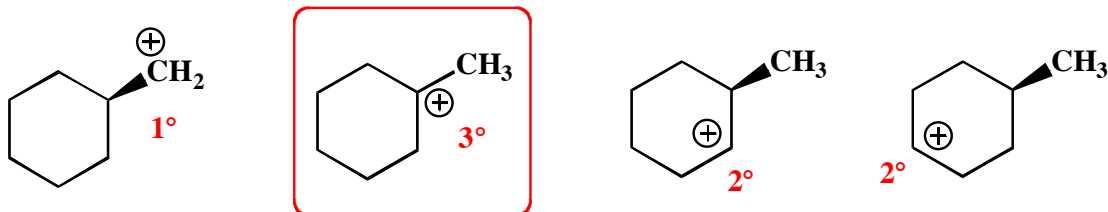
The pKa of a carboxylic acid (RCO₂H) is generally in the 4-5 range. The pKa of ammonium ions (RNH₃⁺) is in the 9-10 range.



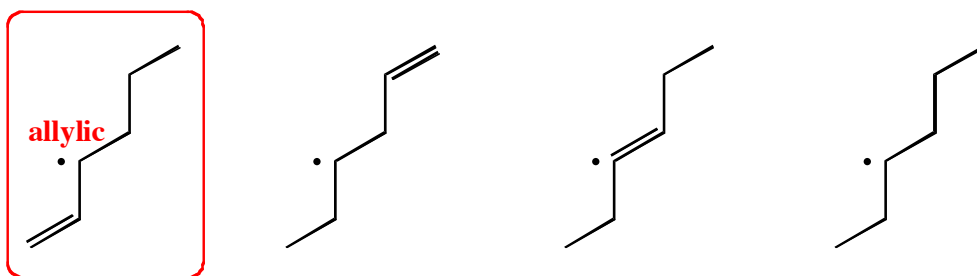
4. (13 pts) Consider the following statements that refer to S_N1 , S_N2 , $E1$, $E2$ or a radical chain reaction mechanism. To which mechanism(s), if any, does each statement apply?

- | | <i>Mechanisms</i> |
|---|---|
| A. Involves a carbocation intermediate | <u>$E1, S_N1$</u> |
| B. When reaction occurs at a chiral center on a pure sample of a single enantiomer, a single enantiomer product with inversion of configuration is created. | <u>S_N2</u> |
| C. When reaction occurs at a chiral center on a pure sample of a single enantiomer, a mixture of product enantiomers will be created | <u>$S_N1, \text{radical chain reaction}$</u> |
| D. Involves an antiperiplanar transition state geometry | <u>$E2$</u> |
| E. The order of reactivity is methyl halides > 1° haloalkanes > 2° haloalkanes and not 3° haloalkanes | <u>S_N2</u> |
| F. For alkane starting materials, the order of reactivity is 3° hydrogens > 2° hydrogens > 1° hydrogens | <u>radical chain reaction</u> |
| G. The reaction mechanism(s) that will occur when $KOtBu$ reacts with a 1° haloalkane | <u>$E2$</u> |
| H. The reaction mechanism(s) that will occur when Br_2 and light are used | <u>radical chain reaction</u> |
| I. The reaction mechanism(s) that will occur when HBr and peroxides with light are used | <u>radical chain reaction</u> |
| J. The reaction mechanism(s) that will occur when NBS and light are used | <u>radical chain reaction</u> |
| K. The reaction mechanism that occurs when the anion of a terminal alkyne reacts with a 1° haloalkane. | <u>S_N2</u> |

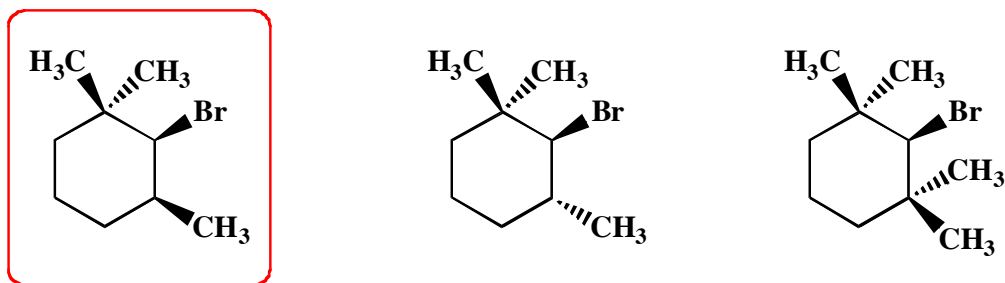
5. (4 pts) For the following series of cations, **circle the most stable cation.**



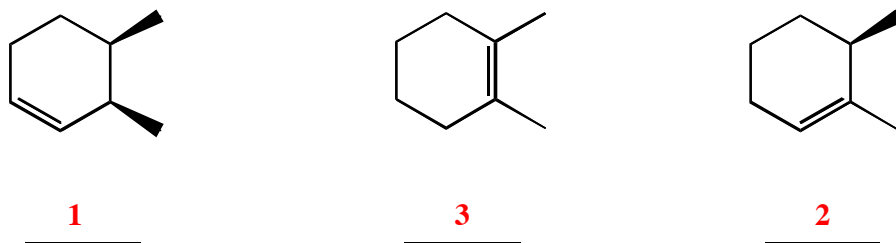
6. (4 pts) For the following series of radicals, **circle the most stable radical.**



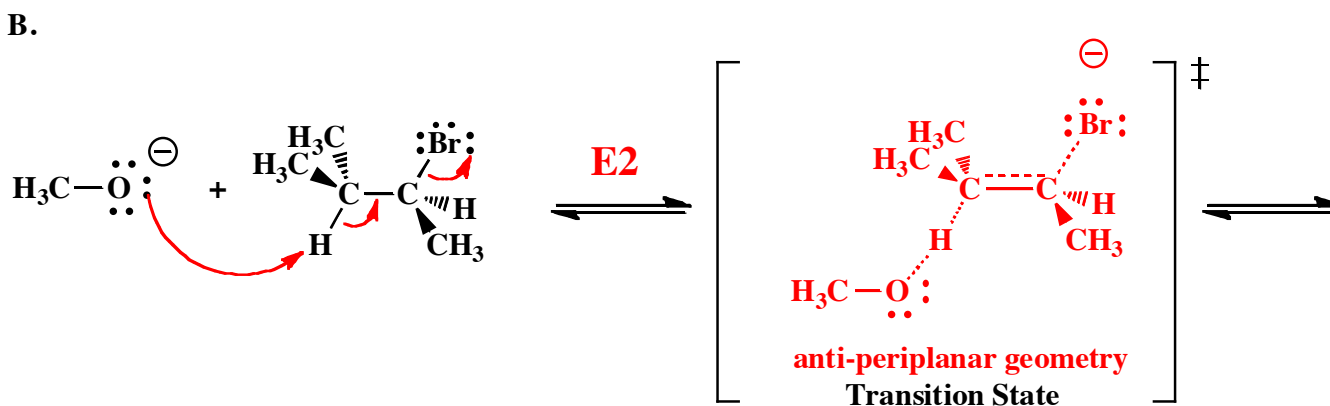
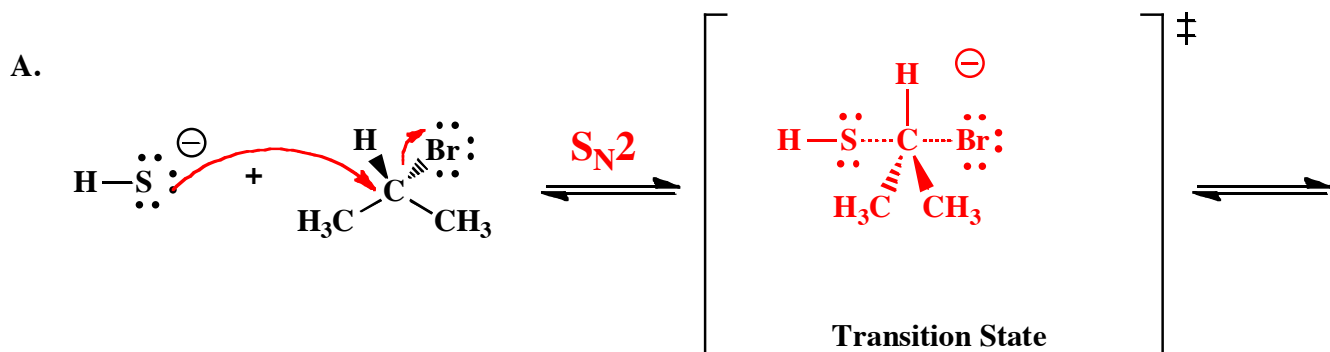
7. (3 pts) Circle the molecule that will react the fastest with strong base through an E2 mechanism.



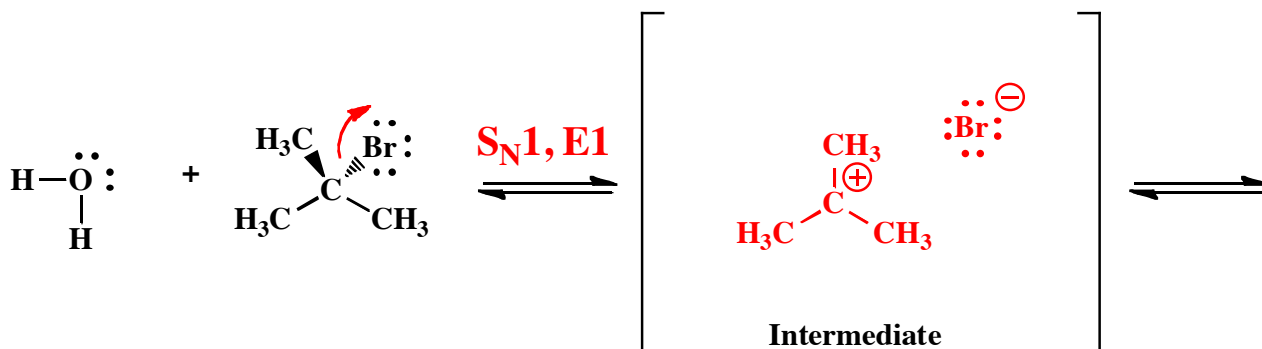
8. (3 pts) For the following constitutional isomers, rank them from 1-3 according to overall alkene stability, with a 1 under the LEAST STABLE ALKENE and a 3 under the MOST STABLE ALKENE.



9. (13 pts total) For each set of reagents below, draw the **key transition state** that occurs during the indicated reaction. We do not want the entire mechanism or products, just the first key transition state. Use dotted lines to indicate bonds that are in the process of being broken or made. Write any formal charges that you think are important. On the starting structures, draw all appropriate arrows to indicate the flow of electrons.



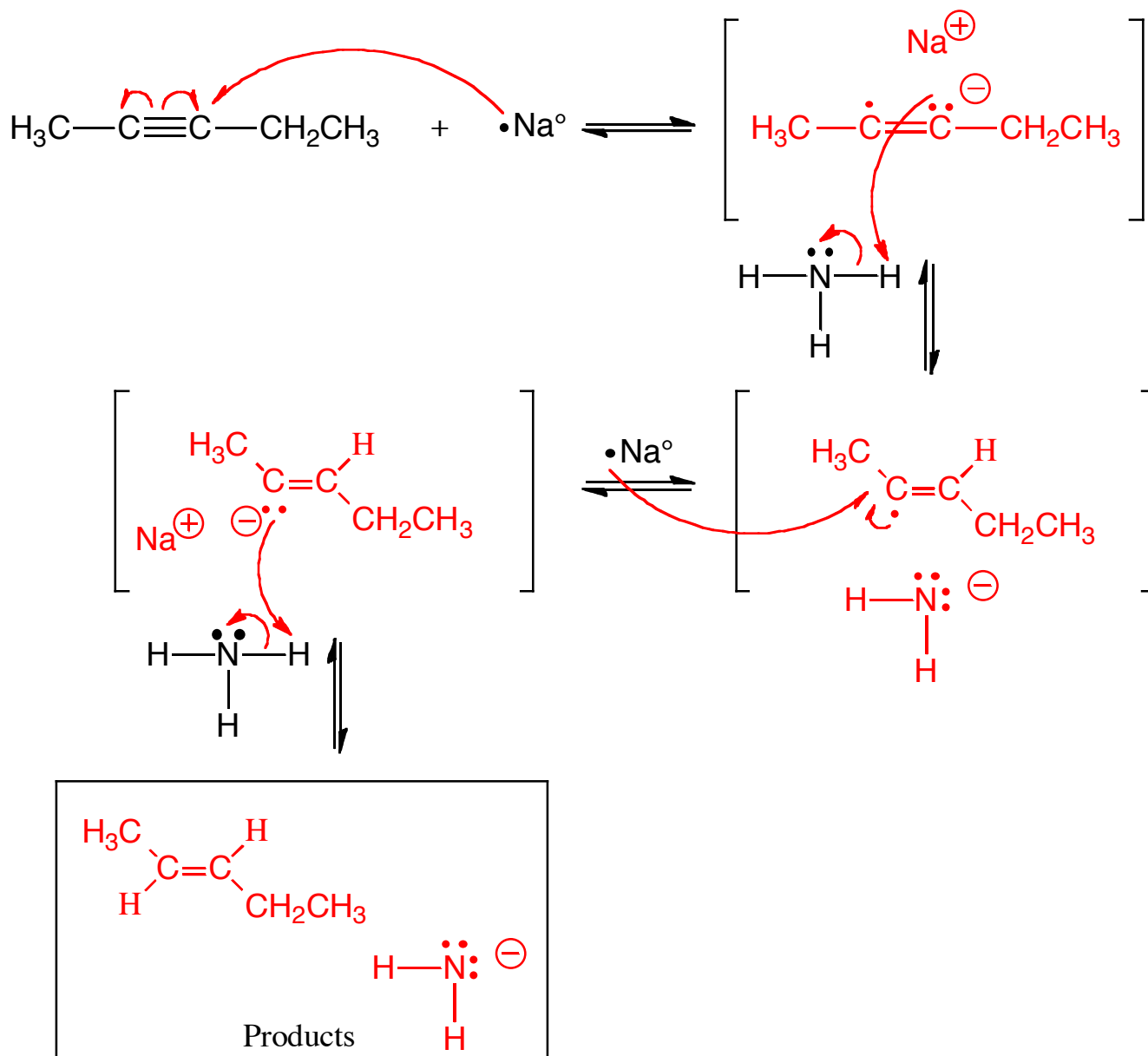
10. (5 pts total) For the set of reagents below, draw the **first key intermediate** that occurs during the indicated reaction. We do not want the entire mechanism or products, just the first key intermediate. Write any formal charges that you think are important. On the starting structures, draw all appropriate arrows to indicate the flow of electrons.



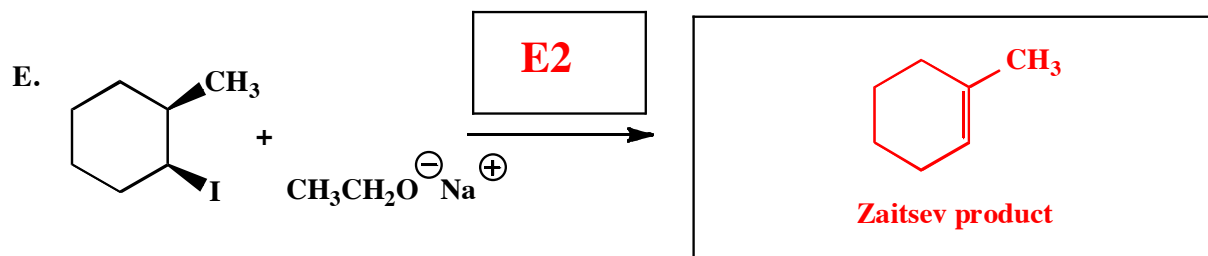
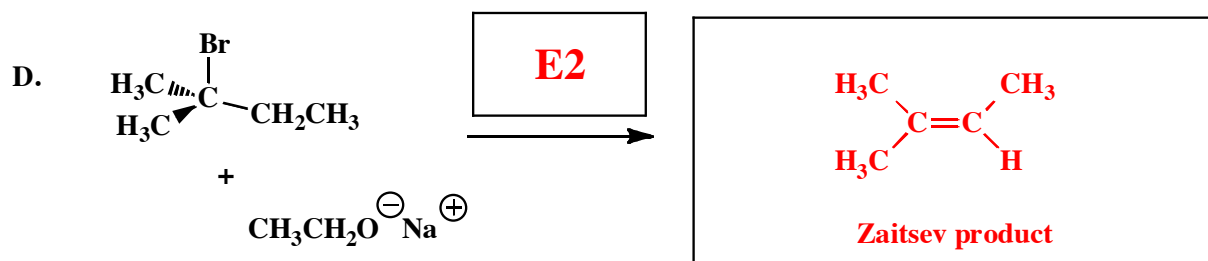
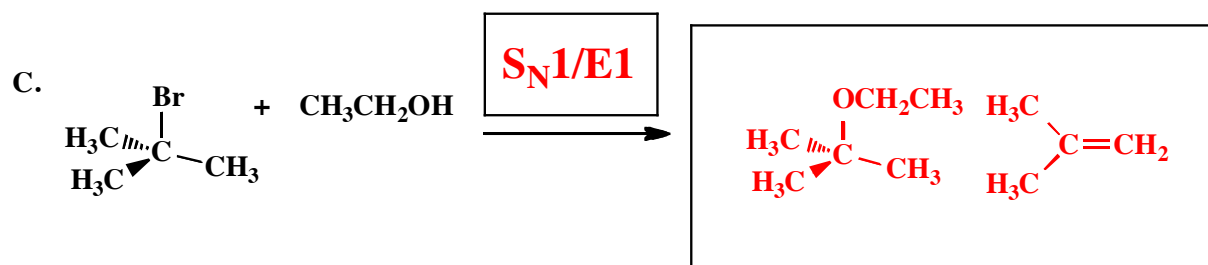
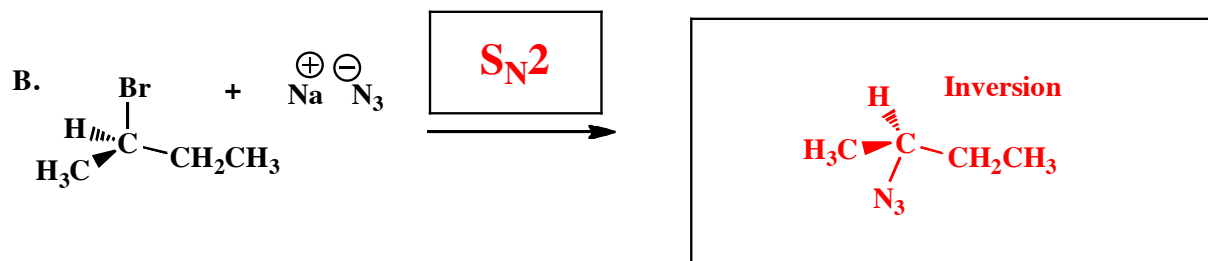
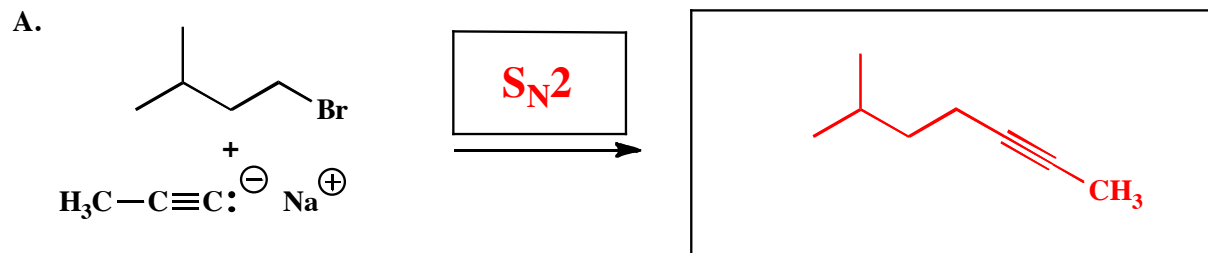
Signature _____

Pg 5 _____ (20)

11. (20 pts total) Complete the following mechanism for reaction of the alkyne with sodium metal in ammonia. Use appropriate arrows to show movement of electron density, and show all non-bonding electrons as dots and show any formal charges. **If any of the species are really a racemic mixtures of enantiomers, you only need to draw one stereoisomer and write "racemic"**

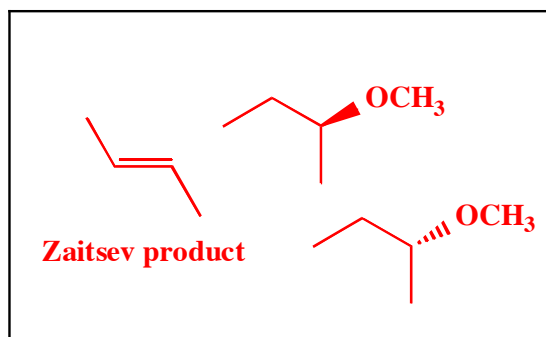
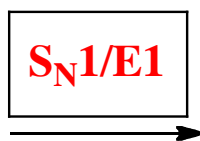
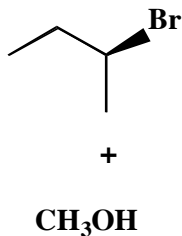


12. (5 or 6 pts each) The following reactions all involve chemistry of alkyl halides. **Fill in the box above the arrow with the mechanism that will be followed (S_N2 , E2, etc.). Then draw only the predominant product or products** and please remember that **you must draw the correct stereoisomers**. For $S_N1/E1$ reactions you must draw all significant products (including all stereoisomers).

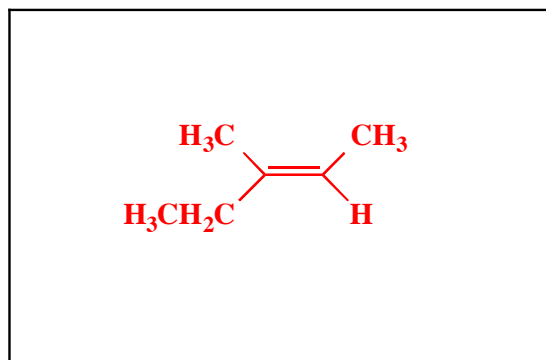
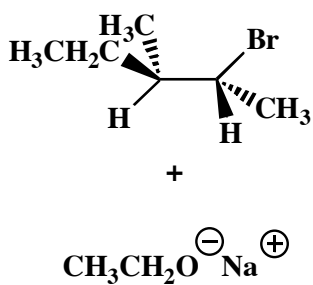


12. (5,7 or 9 pts each) The following reactions all involve chemistry of alkyl halides. **Fill in the box above the arrow with the mechanism that will be followed (S_N2 , E2, etc.). Then draw only the predominant product or products and please remember that you must draw the correct stereoisomers.** For $S_N1/E1$ reactions you must draw all significant products (including all stereoisomers).

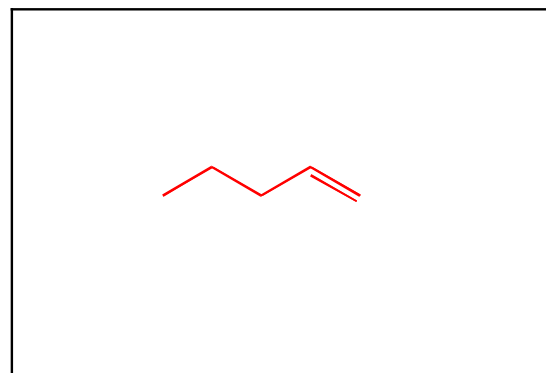
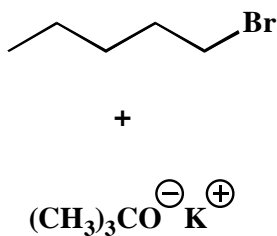
F.



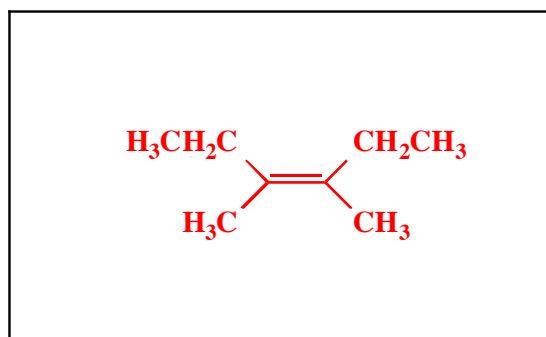
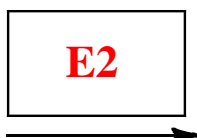
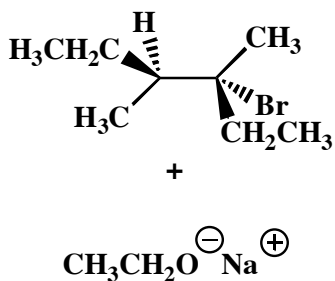
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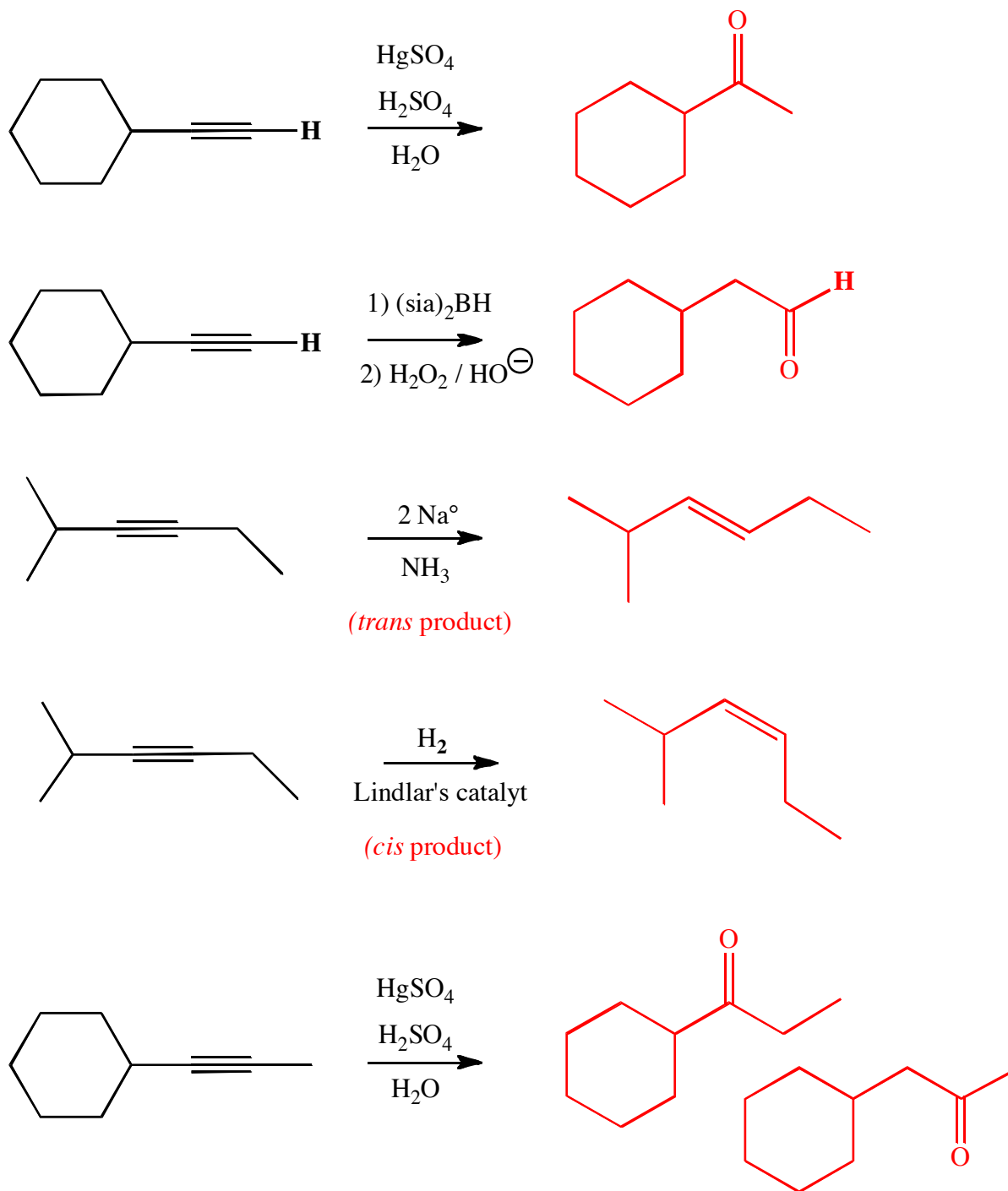
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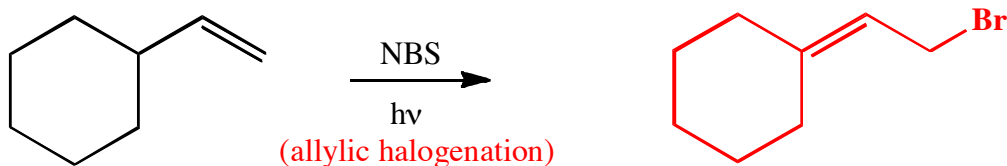
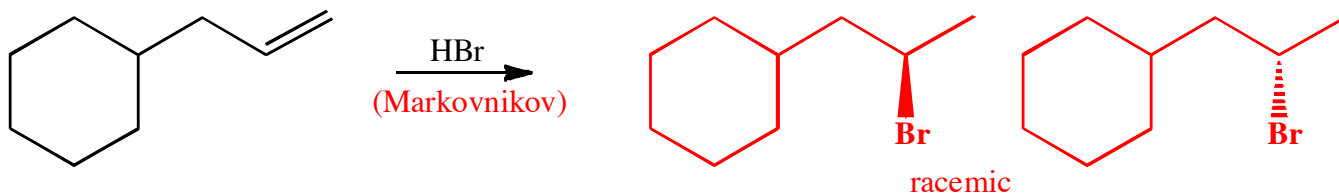
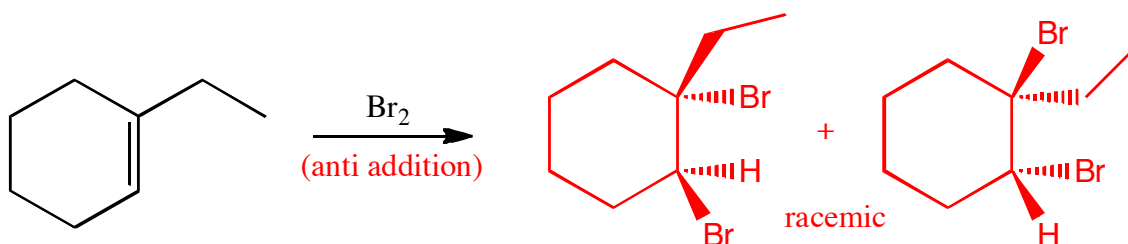
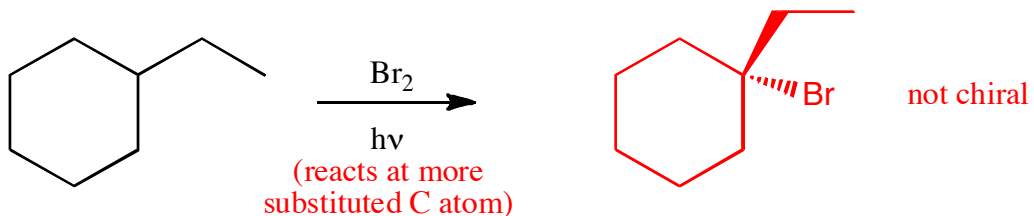
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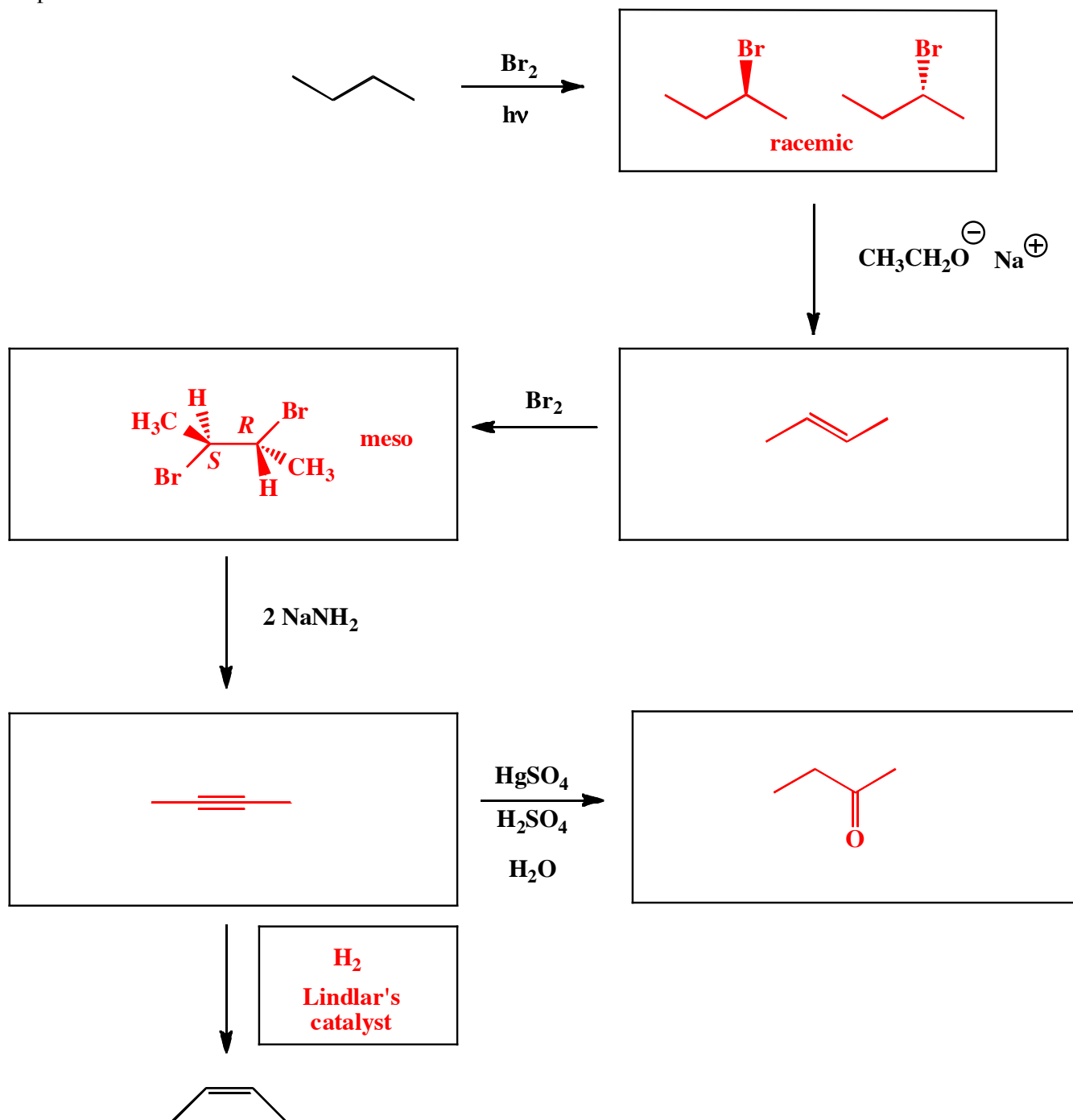
13. (3 or 4 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



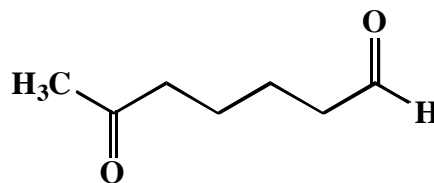
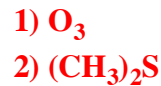
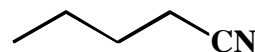
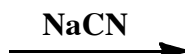
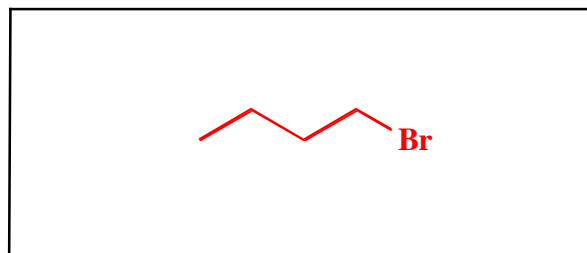
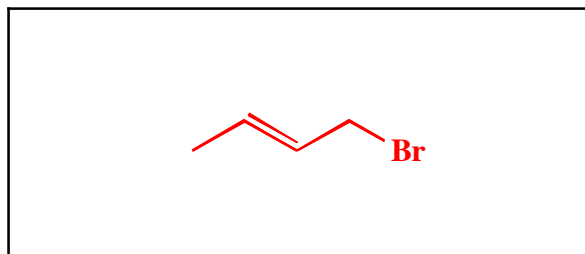
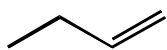
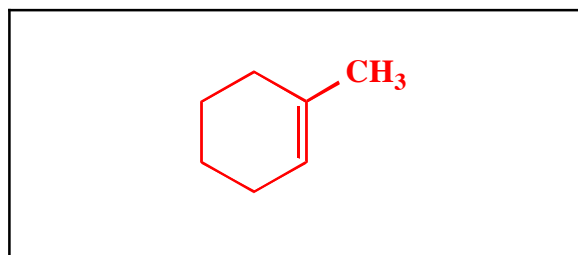
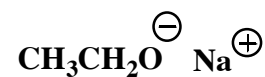
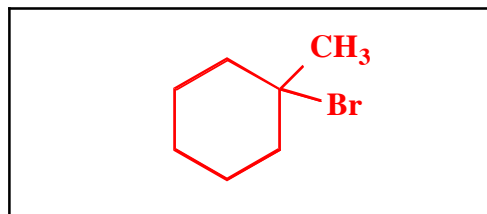
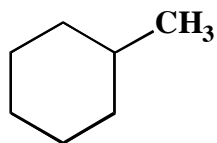
14. (3 or 5 pts each) For the following reactions, all of which involve reagents containing bromine atoms, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



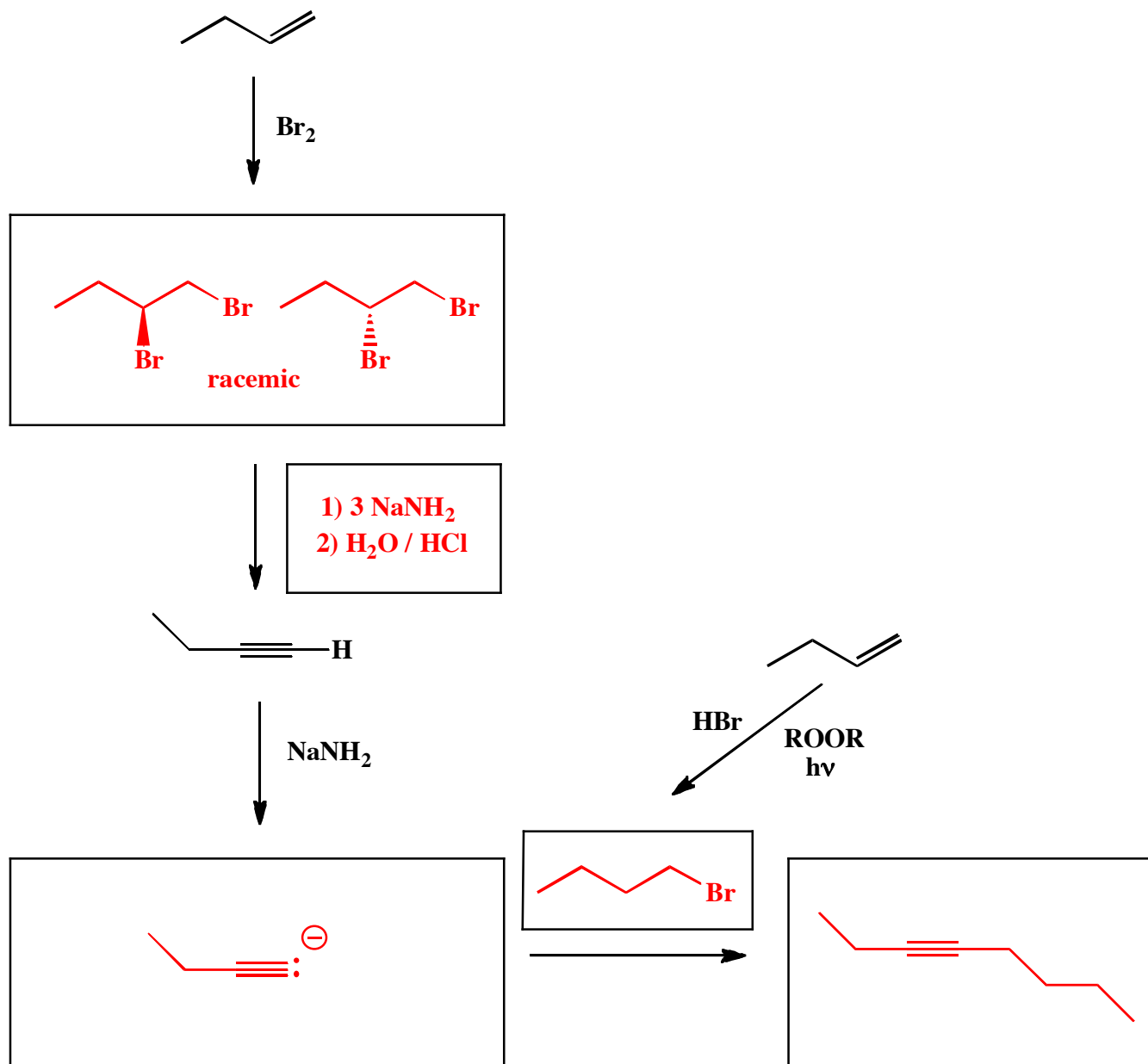
15. (3 or 5 pts each) For the following reactions, fill in the box with the predominant products or reagents necessary to complete the following syntheses. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



16. (3 or 5 pts each) For the following reactions, fill in the box with the predominant products or reagents necessary to complete the following syntheses. 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.



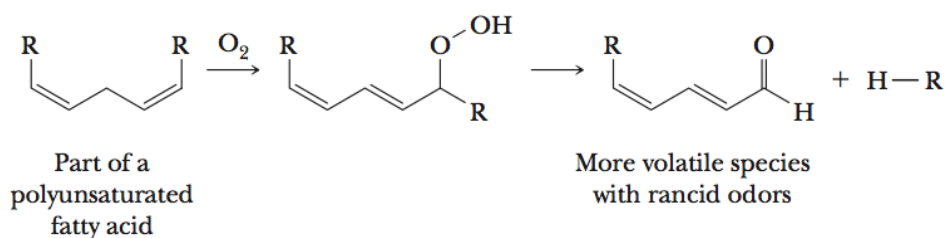
17. (3 or 5 pts each) For the following reactions, fill in the box with the predominant products or reagents necessary to complete the following syntheses. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



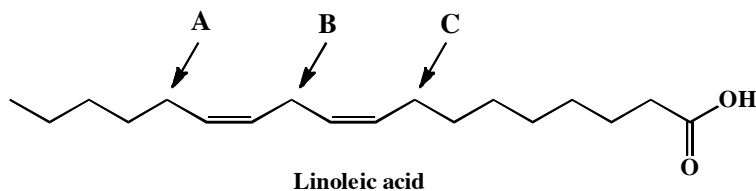
18. Here is an "apply what you know" problem in the format of an MCAT style passage. Circle the correct answers.

Antioxidants

Many plants contain polyunsaturated fatty acid esters in their leaves or seeds, as do the foods derived from these plants. Such structures are prone to autoxidation that gives hydroperoxides leading to lower molecular weight oxidized products, such as volatile aldehydes, ketones, and hydrocarbons. These products are indicative of the rotting of the food, and result in the unpleasant "rancid" odors familiar to anyone who has smelled old cooking oil.



1. Linoleic acid is shown below. This common fatty acid is particularly susceptible to autoxidation because the hydrogens at certain position(s) on the chain are very reactive in a radical process. Which ones?



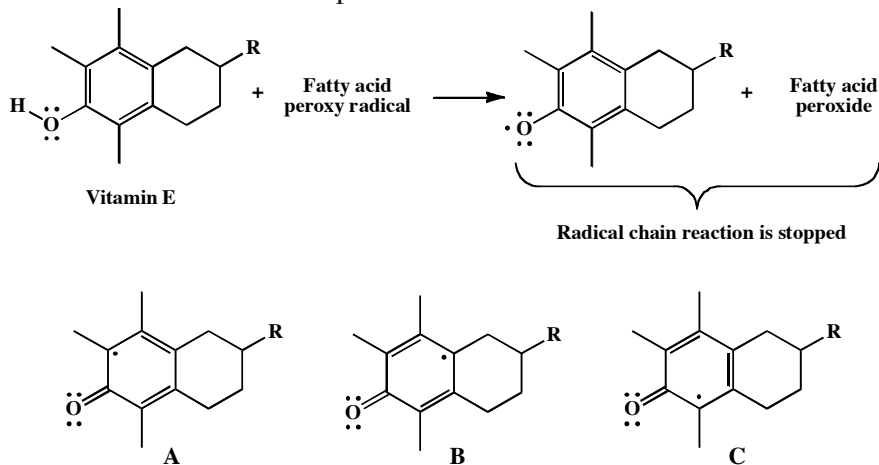
- A. A hydrogen on the carbon labeled as "A" will be the most likely to be abstracted to create a radical.
B. A hydrogen on the carbon labeled as "B" will be the most likely to be abstracted to create a radical.
 C. A hydrogen on the carbon labeled as "C" will be the most likely to be abstracted to create a radical.
 D. Hydrogens on both carbons labeled as "A" and "C" will be tied for the most likely to be abstracted to create a radical.

2. Your answer to part 1 above is due to the fact that:

- A. The radical created on the carbon labeled as "A" will be doubly allylic, and therefore highly stabilized by resonance delocalization (a pi-way).
B. The radical created on the carbon labeled as "B" will be doubly allylic, and therefore highly stabilized by resonance delocalization (a pi-way).
 C. The radical created on the carbon labeled as "C" will be doubly allylic, and therefore highly stabilized by resonance delocalization (a pi-way).
 D. The radicals created on the two carbons labeled as "A" and "C" will be equally doubly allylic, and therefore equally highly stabilized by resonance delocalization (a pi-way).

18. (cont.).

Nature protects against autoxidation by a variety of agents, one of the most important of which is α -tocopherol (vitamin E). This compound is a phenol, which is defined as an OH group on a benzene ring as shown in the diagram. The characteristic of phenols that makes them protective agents against autoxidation is their O-H bond, which is even better at forming radicals than the C-H bond from which hydrogen is abstracted by O_2 in the polyunsaturated fatty acid. This means that Vitamin E reacts quickly with the peroxy radical formed during fatty acid autoxidation to give a highly stabilized radical, resulting in termination of the radical chain process.

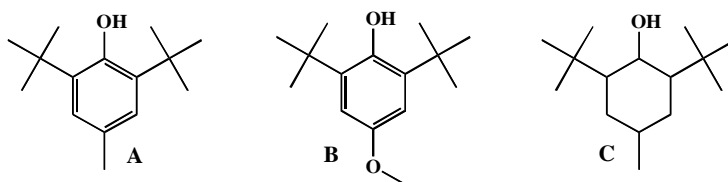


3. The radical formed from vitamin E is highly stable because of resonance delocalization of the radical. Which of the following statements best describes why this radical is so stable.

- A. The structure labeled as "A" is a significant resonance contributor of the radical.
- B. The structure labeled as "B" is a significant resonance contributor of the radical.
- C. The structure labeled as "C" is a significant resonance contributor of the radical.
- D. All three structures, "A", "B", and "C", are significant resonance contributors of the radical.**

Vitamin E is often referred to as a natural preservative because it prevents autoxidation and therefore food spoilage. Processing of foods can remove the natural vitamin E, so artificial preservatives are added to these foods in order to retard their spoilage.

4. Based on your answer to 3 above, consider the following structures. Select the statement that best describes which of the structures could serve as a preservative in place of vitamin E?



- A. The structure labeled as "A" could be a preservative.
- B. The structure labeled as "B" could be a preservative.
- C. The structure labeled as "C" could be a preservative.
- D. Both structures "A" and "B" could be preservatives.**