

NAME (Print): _____

Chemistry 310M/318M
Dr. Brent Iverson
3rd Midterm
November 18, 2010

SIGNATURE: _____

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

| | | |
|--|--|--|
| | | |
|--|--|--|

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 | | (14) |
| 3 | | (16) |
| 4 | | (19) |
| 5 | | (6) |
| 6 | | (29) |
| 7 | | (28) |
| 8 | | (27) |
| 9 | | (17) |
| 10 | | (20) |
| 11 | | (21) |
| 12 | | (14) |
| 13 | | (11) |
| 14 | | (13) |
| 15 | | (10) |
| 16 | | (15) |
| Total | | (289) |
| % | | |
| 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)

| Compound | | pK _a |
|--------------------|---|-----------------|
| Hydrochloric acid | $\text{H}-\text{Cl}$ | -7 |
| Protonated alcohol | $\text{RCH}_2\text{OH}_2^+$ | -2 |
| Hydronium ion | H_3O^+ | -1.7 |
| Acetic acid | $\text{CH}_3\text{C}(=\text{O})\text{OH}$ | 4.8 |
| Ammonium ion | H_4N^+ | 9.2 |
| 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 | HOH | 15.7 |
| Alcohols | RCH_2OH | 15-19 |
| Acid chlorides | $\text{RCH}_2\text{C}(=\text{O})\text{Cl}$ | 16 |
| Aldehydes | $\text{RCH}_2\text{C}(=\text{O})\text{H}$ | 18-20 |
| Ketones | $\text{RCH}_2\text{C}(=\text{O})\text{R}'$ | 18-20 |
| Esters | $\text{RCH}_2\text{C}(=\text{O})\text{OR}'$ | 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 |

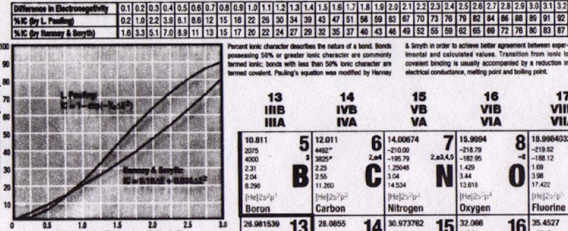
PERIODIC TABLE OF THE ELEMENTS

▼ Elementary Subatomic Particles

| | Electron | Proton | Neutron | Positron | Neutrino |
|---------------------------------------|-----------------------------------|----------------------------------|----------------------------------|-----------|-------------|
| Symbol | e | p | n | \bar{p} | $\bar{\nu}$ |
| Rest mass (kg) | 9.10938215 × 10 ⁻³¹ | 1.67262161 × 10 ⁻²⁷ | 1.67492716 × 10 ⁻²⁷ | 0 | ~ 0 |
| Relative mass (p/m) | 5.4857990943 × 10 ⁻⁴ | 1.007276472 × 10 ⁰ | 1.008664915 × 10 ⁰ | 0 | ~ 0 |
| Particle-electron mass ratio | 1 | 1836.152673(1) | 1838.68366(4) | 0 | ~ 0 |
| Particle-proton mass ratio | 5.44617013(1) × 10 ⁻⁴ | 1 | 1.00137461(9) | 0 | ~ 0 |
| Particle-neutron mass ratio | 5.438672(1) × 10 ⁻⁴ | 0.9990424 | 1 | 0 | ~ 0 |
| Specific charge (C/kg) | -1.75818632(3) × 10 ¹¹ | 9.57893329 × 10 ⁷ | 0 | 0 | 0 |
| Spin (h) | 1/2 | 1/2 | 1/2 | 1/2 | 1/2 |
| Spin quantum number | 1/2 | 1/2 | 1/2 | 1/2 | 1/2 |
| Compton wavelength (m) | 2.426310238 × 10 ⁻¹² | 1.32140987 × 10 ⁻¹⁵ | 1.319591023 × 10 ⁻¹⁵ | — | — |
| Magnetically moment (J/T) | 9.2847637(3) × 10 ⁻²⁴ | 1.4106076(1) × 10 ⁻²⁶ | 0.9862371(2) × 10 ⁻²⁶ | 0 | 0 |
| In Bohr magneton (μ _B) | 1.824846207(3) | 1.824846207(3) | 1.824846207(3) | 0 | 0 |
| In nuclear magneton (μ _N) | 1836.269832(7) | 1.824846207(3) | 1.824846207(3) | 0 | 0 |

Elementary particles are the fundamental constituents of energy and matter. The positron (\bar{p}) is a matter-antimatter pair which has the same mass as an ordinary electron. The antineutrino ($\bar{\nu}$) has the same mass as that of a neutrino. It is always emitted in the direction of motion, whereas the neutrino spin is always opposite to the direction of motion. Negative beta decay is the transformation of a neutron into a proton, a beta particle (electron) and an antineutrino ($\bar{\nu}$).

▼ % Ionic Character of a Single Chemical Bond



| Electronegativity (Pauling) | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 | 5.0 | 5.5 | 6.0 | 6.5 | 7.0 | 7.5 | 8.0 | 8.5 | 9.0 | 9.5 | 10.0 |
|-----------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|
| % Ionic Character | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

| | | | | | | | | | | | | | | | | | |
|----------|----------|-----------|----------|----------|----------|-----------|------------|------------|-------------|----------|-----------|------------|-----------|-----------|-----------|------------|-------------|
| 1 IA | 2 IIA | 3 IIIA | 4 IVA | 5 VA | 6 VIA | 7 VIIA | 8 VIIIA | 9 VIIIA | 10 VIIIA | 11 IB | 12 IIB | 13 IIIB | 14 IVB | 15 VB | 16 VIB | 17 VIIB | 18 VIIIB |
| 1 H | 2 He | 3 Li | 4 Be | 5 B | 6 C | 7 N | 8 O | 9 F | 10 Ne | 11 Na | 12 Mg | 13 Al | 14 Si | 15 P | 16 S | 17 Cl | 18 Ar |
| 19 K | 20 Ca | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | 31 Ga | 32 Ge | 33 As | 34 Se | 35 Br | 36 Kr |
| 37 Rb | 38 Sr | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd | 49 In | 50 Sn | 51 Sb | 52 Te | 53 I | 54 Xe |
| 55 Cs | 56 Ba | 57 La | 58 Ce | 59 Pr | 60 Nd | 61 Pm | 62 Sm | 63 Eu | 64 Gd | 65 Tb | 66 Dy | 67 Ho | 68 Er | 69 Tm | 70 Yb | 71 Lu | |
| 87 Fr | 88 Ra | 89 Ac | 90 Th | 91 Pa | 92 U | 93 Np | 94 Pu | 95 Am | 96 Cm | 97 Bk | 98 Cf | 99 Es | 100 Fm | 101 Md | 102 No | 103 Lr | |

**7
VIIA
VIB**

Atomic Weight¹
(1) indicates most stable or best known isotope

Melting Point², °C

Boiling Point², °C

Density³, g/cm³
(room temp. at 20°C, 1 atm)

Electronegativity⁴

First Ionization Potential⁵, eV

Group Classifications⁶

Atomic Number⁷

Oxidation States⁸
and indicates most stable state

Symbol⁹
and - gas, liquid, solid - normally prepared

Electronic Configuration¹⁰

Name¹¹

| | | | | | | | | | | | | | | | | | |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|-----------|-----------|-----------|----------|
| 19 K | 20 Ca | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | 31 Ga | 32 Ge | 33 As | 34 Se | 35 Br | 36 Kr |
| 37 Rb | 38 Sr | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd | 49 In | 50 Sn | 51 Sb | 52 Te | 53 I | 54 Xe |
| 55 Cs | 56 Ba | 57 La | 58 Ce | 59 Pr | 60 Nd | 61 Pm | 62 Sm | 63 Eu | 64 Gd | 65 Tb | 66 Dy | 67 Ho | 68 Er | 69 Tm | 70 Yb | 71 Lu | |
| 87 Fr | 88 Ra | 89 Ac | 90 Th | 91 Pa | 92 U | 93 Np | 94 Pu | 95 Am | 96 Cm | 97 Bk | 98 Cf | 99 Es | 100 Fm | 101 Md | 102 No | 103 Lr | |

| | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|----------|----------|------------|----------|-----------|----------|-----------|----------|----------|----------|----------|----------|-----------|----------|---------|----------|-----------|----------|-----------|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 140.115 | 58 Ce | 140.90765 | 59 Pr | 144.24 | 60 Nd | 150.36 | 61 Pm | 151.965 | 62 Sm | 157.25 | 63 Eu | 164.93032 | 64 Gd | 167.26 | 65 Tb | 168.93421 | 66 Dy | 171.9472 | 67 Ho | 174.967 | 68 Er | 176.93122 | 69 Tm | 178.94388 | 70 Yb | 180.94788 | 71 Lu |
| 232.0377 | 90 Th | 231.036888 | 91 Pa | 238.02891 | 92 U | 244.04042 | 93 Np | 247.0703 | 94 Pu | 247.0703 | 95 Am | 251.07958 | 96 Cm | 252.083 | 97 Bk | 257.0851 | 98 Cf | 258.10529 | 99 Es | 262.1088 | 100 Fm | 267.10372 | 101 Md | 268.1018 | 102 No | 271.10369 | 103 Lr |

PAPERTECH

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1. (11 pts) What is the most important question in organic chemistry?

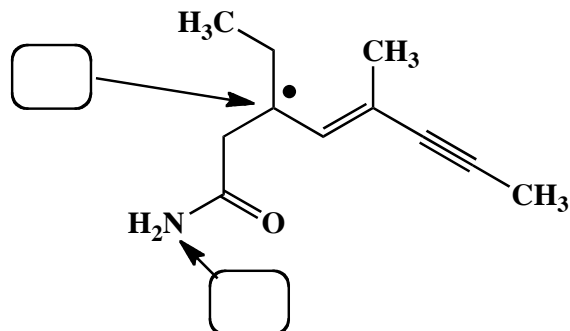
Now in no more than two sentences, explain why the above is the most important question in organic chemistry.

← NOTICE THIS!!

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. (4 pts. each) On the following structure, indicate the hybridization state of each atom indicated on the following radical



4. (14 pts) Consider the following statements. In the space provided write "a carbocation intermediate", "a radical intermediate" and/or "a single transition state with no intermediate" as appropriate.

Answer(s)

A. An S_N1 reaction involves

B. An S_N2 reaction involves

C. An E1 reaction involves

D. An E2 reaction involves

E. Stabilized by hyperconjugation

F. Reaction of an alkane with Br_2 , light involves

G. Reaction of an alkene with HBr, ROOR, light involves

H. Reaction of an alkene with NBS, light involves

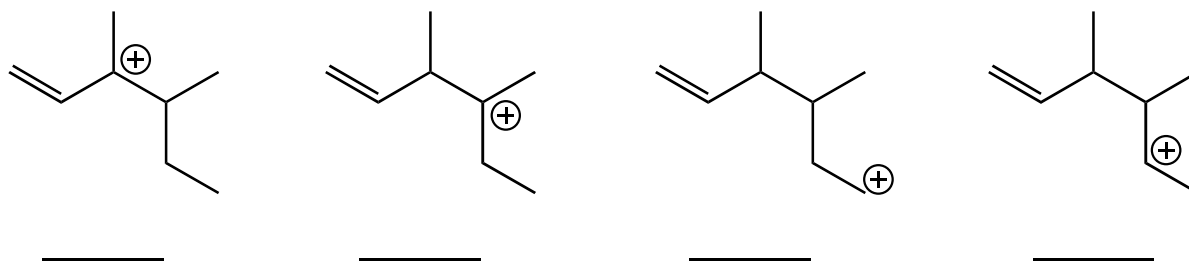
I. Reaction of an alkene with HBr but no ROOR involves

J. This is found in chain reaction mechanisms

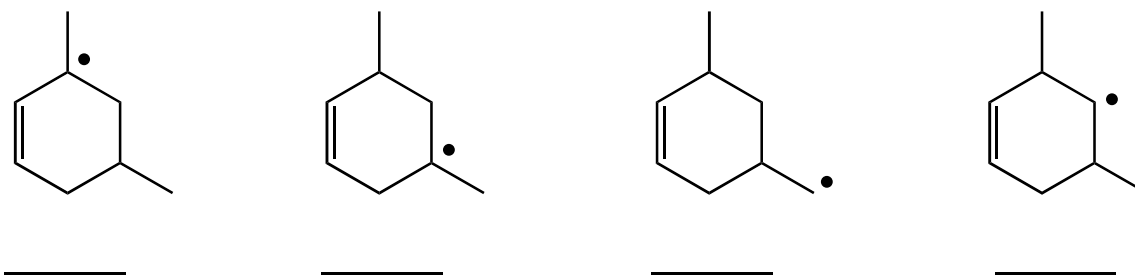
K. Intermediate most likely to rearrange

L. Stabilized by resonance delocalization

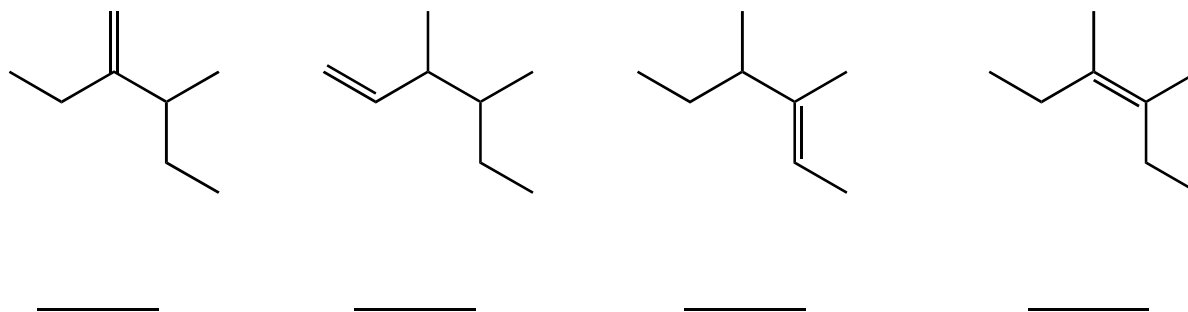
5. (4 pts) For the following molecules, rank them from 1-4 according to overall alkene stability, with a 1 under the LEAST STABLE CATION and a 4 under the MOST STABLE CATION.



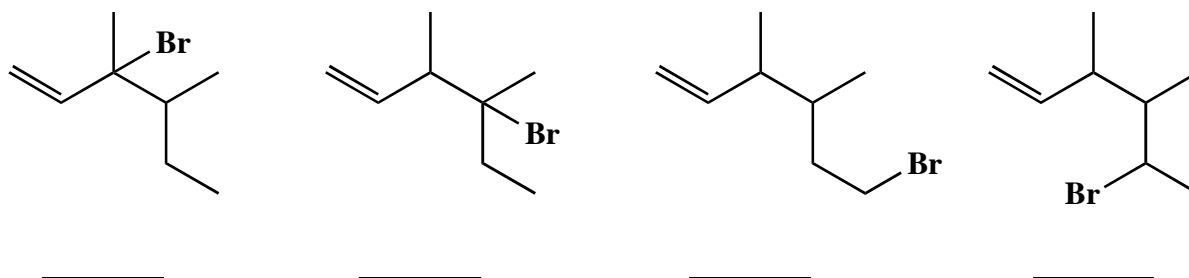
6. (4 pts) For the following molecules, rank them from 1-4 according to overall alkene stability, with a 1 under the LEAST STABLE RADICAL and a 4 under the MOST STABLE RADICAL.



7. (4 pts) For the following constitutional isomers, rank them from 1-4 according to overall alkene stability, with a 1 under the LEAST STABLE ALKENE and a 4 under the MOST STABLE ALKENE.

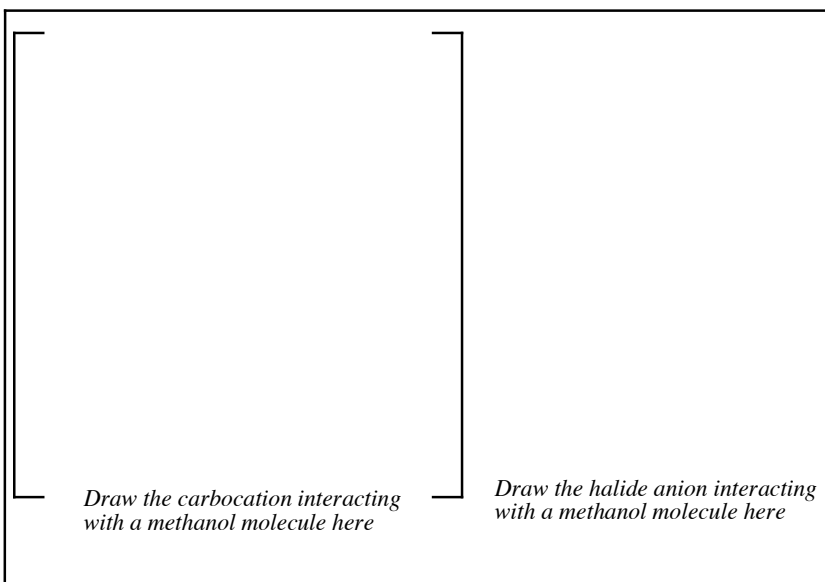
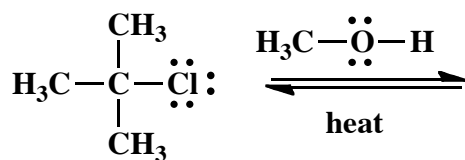


8. (4 pts) For the following alkyl halides, rank them from 1-4 with respect to reactivity in an $S_N1/E1$ reaction, with a 1 under the LEAST REACTIVE ALKYL HALIDE, and a 4 under the MOST REACTIVE ALKYL HALIDE.

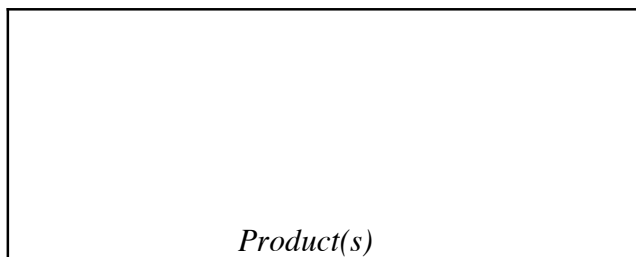
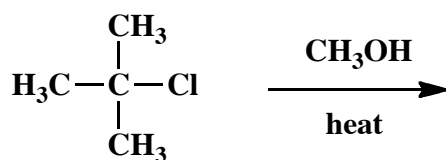


9. (5 pts) A hydrogen bond is the strongest interaction seen among neutral molecules. **In the space provided, draw two molecules of methanol (CH₃OH) and show a hydrogen bond between them. Use a dashed line (-----) to indicate the hydrogen bond. Show all lone pairs.**

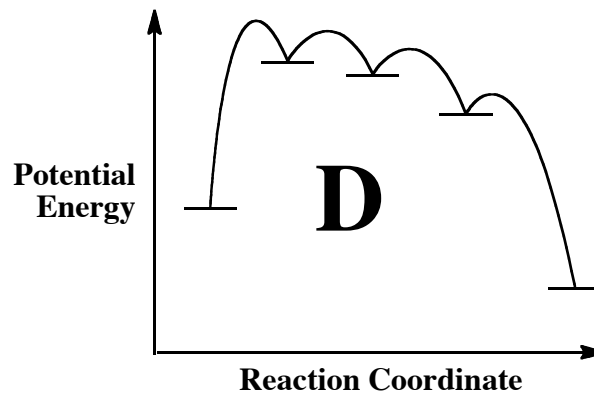
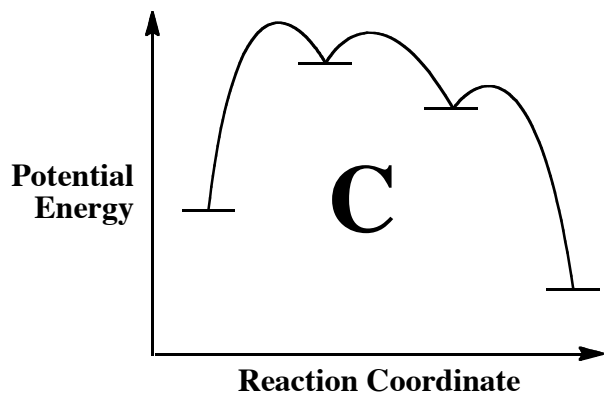
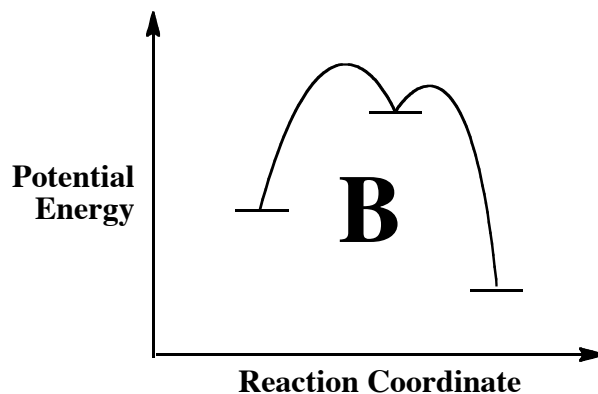
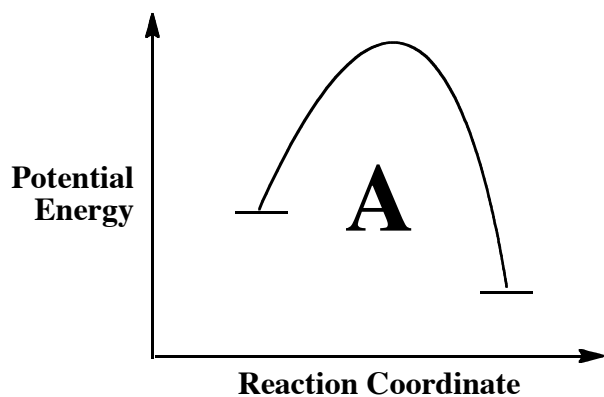
10. (14 pts) Alcohols are good solvents for S_N1 and E1 reactions of secondary and tertiary alkyl halides in part because they interact strongly with the carbocation intermediate and halide anion formed in the first mechanistic step. These strong interactions lower the energy of the carbocation intermediate. **For the following S_N1/E1 reaction, draw the carbocation intermediate and halide anion. Next draw a molecule of methanol interacting with the carbocation, and a different molecule of methanol hydrogen bonding to the halide anion. Use a dashed line (-----) to indicate a relatively strong interaction. Show all lone pairs and formal charges.**



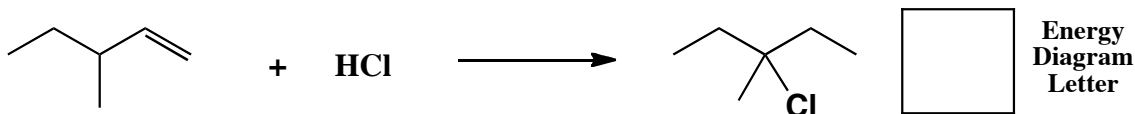
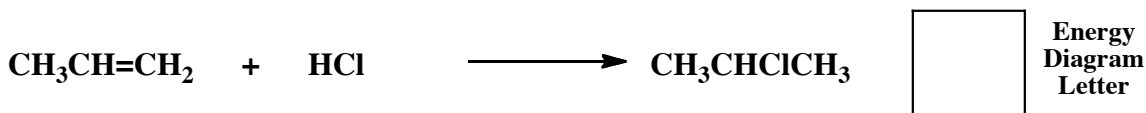
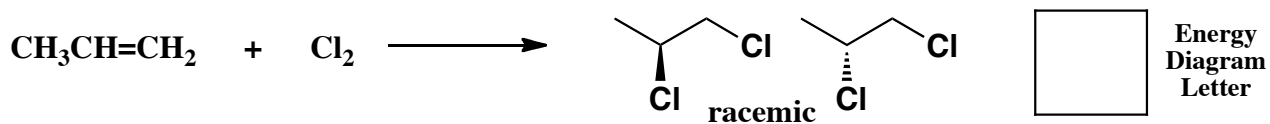
In the box provided draw the products of the above S_N1/E1 reaction.



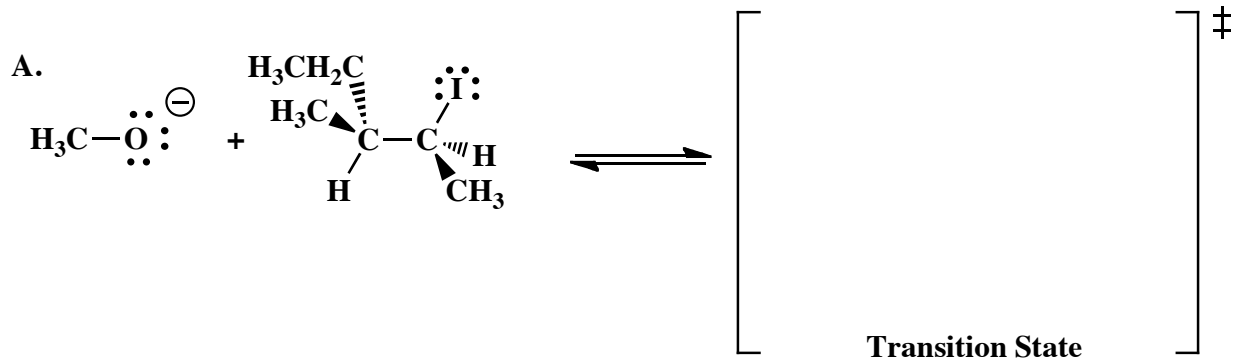
11. (8 pts.) Shown below are four different energy diagrams. Each is labeled with a letter. Use these letters to answer questions at the bottom of the page, and on the next TWO mechanism pages.



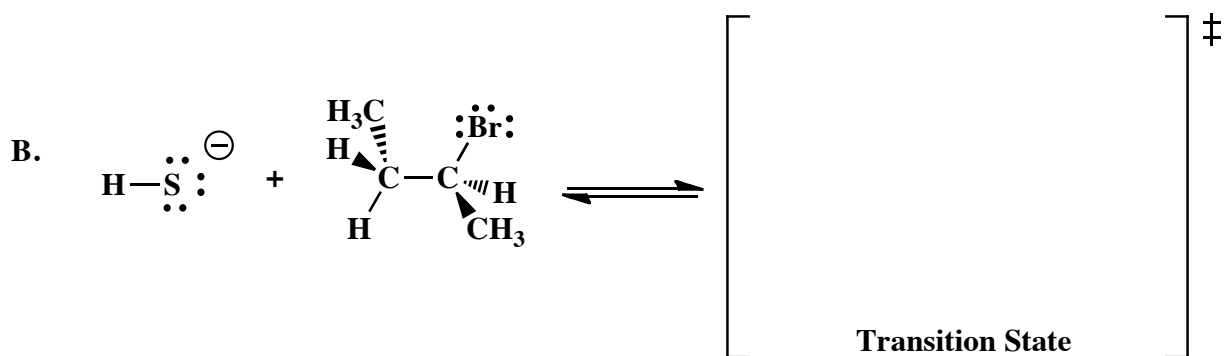
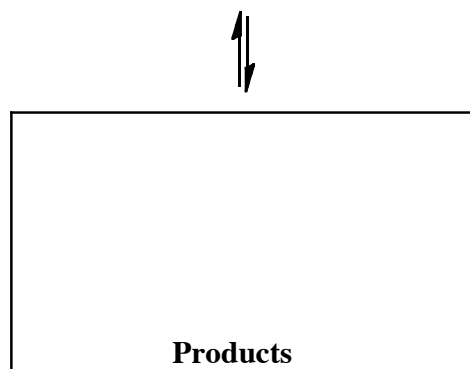
In the boxes provided, write the letter of the energy diagram that best describes the mechanism of the following reactions:



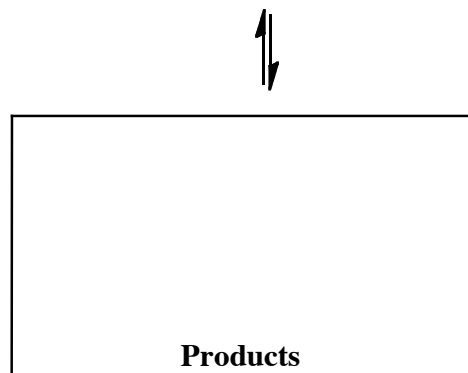
12. (29 pts total) For each set of reagents below, draw the **key transition state** that occurs during the indicated reactions and then the product. Use dotted lines to indicate bonds that are in the process of being broken or made. Write all lone pairs of electrons any formal charges that you think are important. On the starting structures, draw all appropriate arrows to indicate the flow of electrons. Make sure to draw all the products that are produced including stereochemistry where appropriate.



Of the energy diagrams on the previous page, which one looks the most appropriate to describe this reaction (write the letter in the box that corresponds to the correct energy diagram)



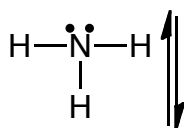
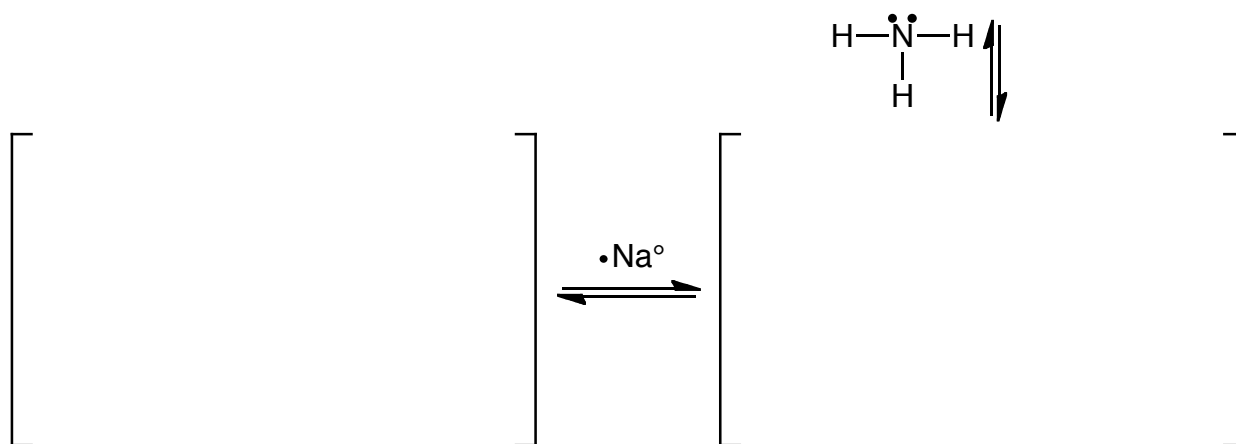
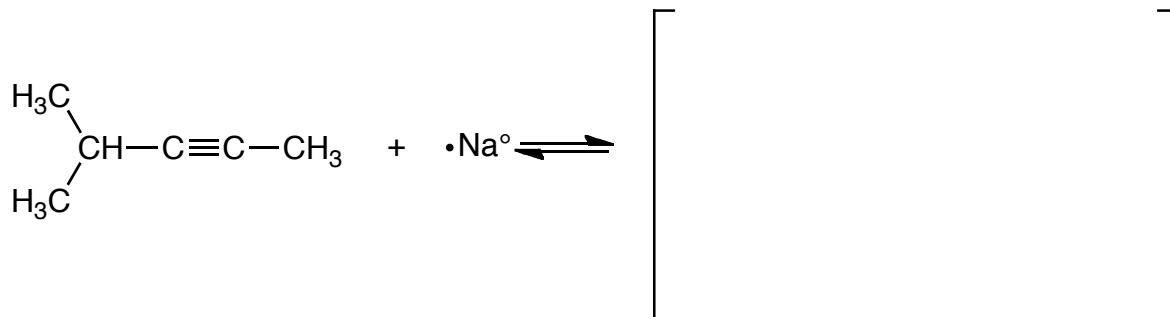
Of the energy diagrams on the previous page, which one looks the most appropriate to describe this reaction (write the letter in the box that corresponds to the correct energy diagram)



Signature _____

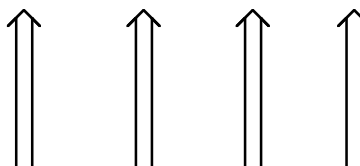
Pg 7 _____ (28)

13. (28 pts total) Complete the following mechanism for the reduction of an alkyne using sodium and 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"**



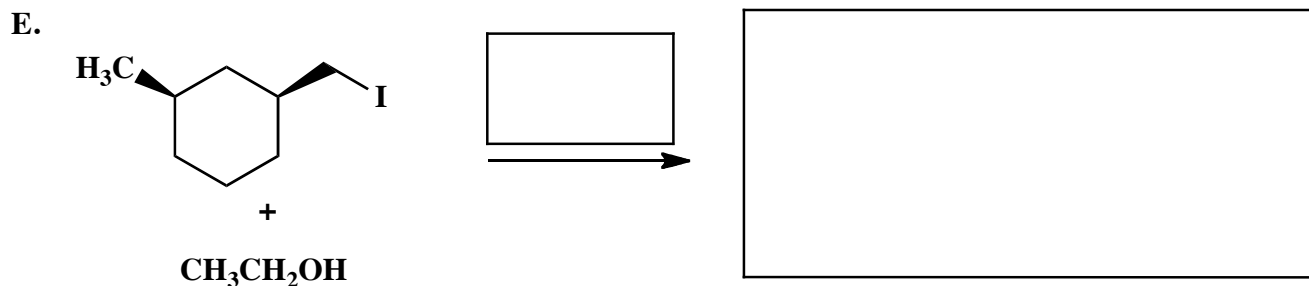
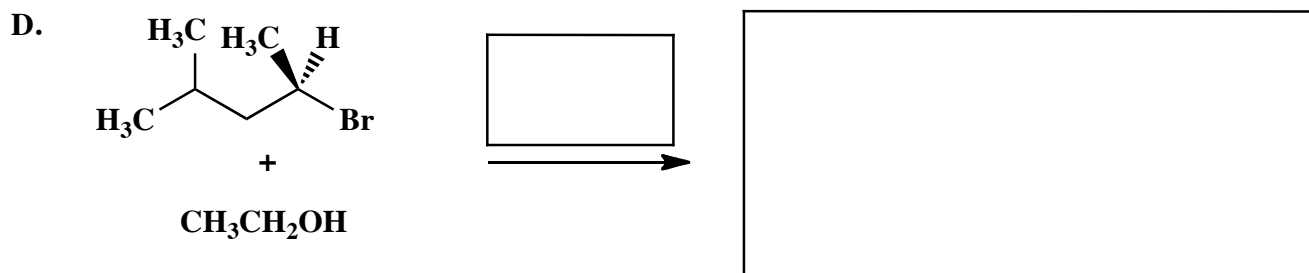
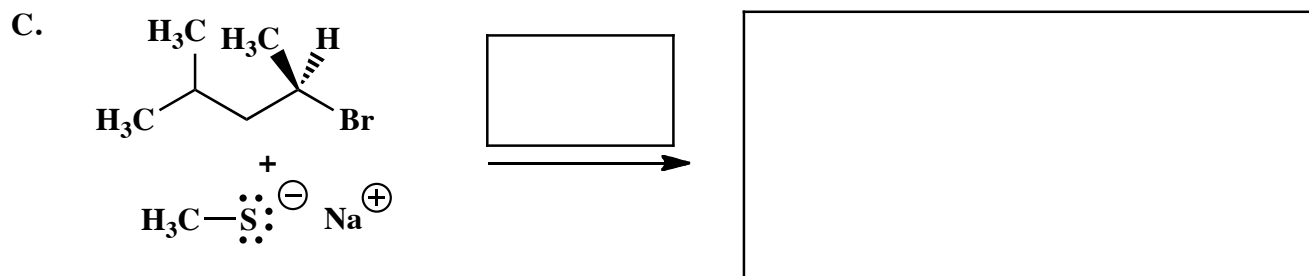
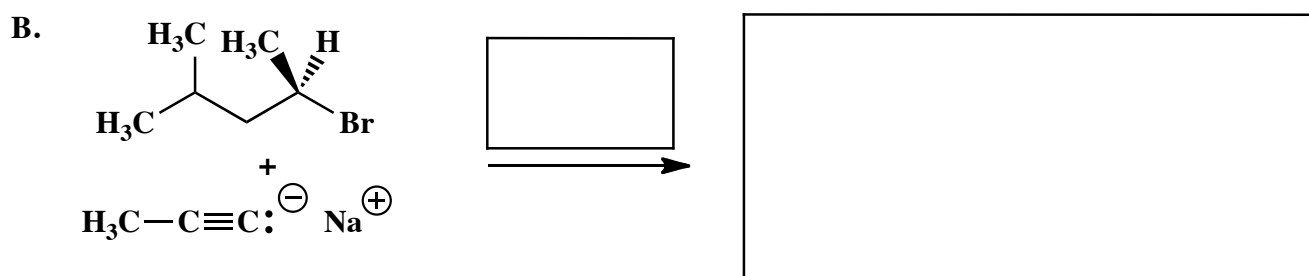
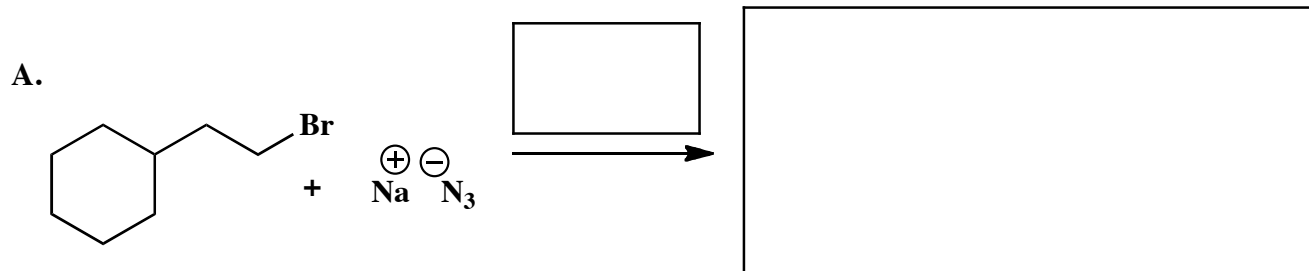
Products

Of the energy diagrams on the previous page, which one looks the most appropriate to describe this reaction (write the letter in the box that corresponds to the correct energy diagram)

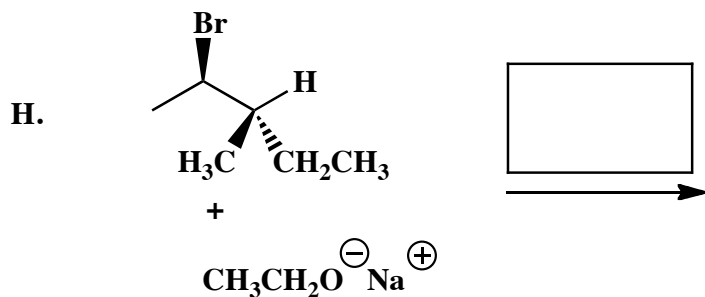
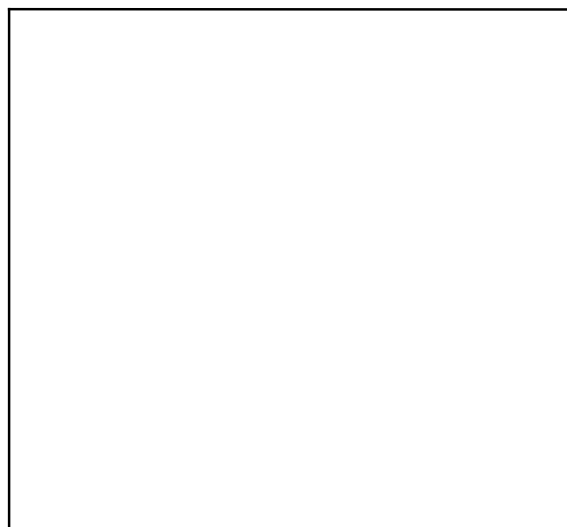
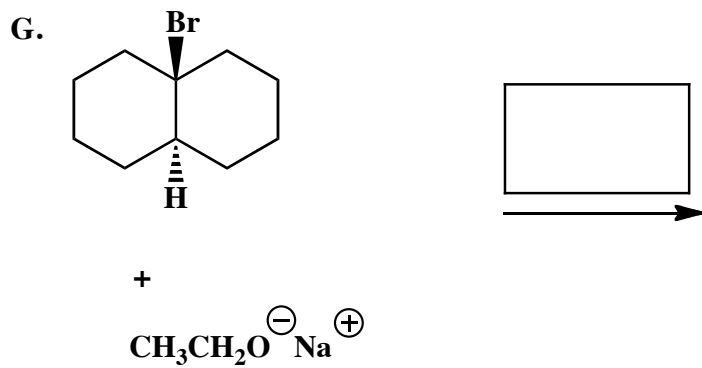
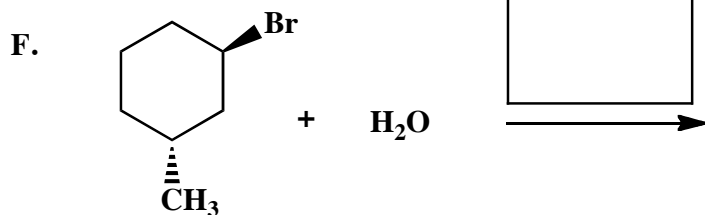


NOTICE THIS QUESTION AND THE TWO SIMILAR QUESTIONS ON THE PREVIOUS PAGE!!

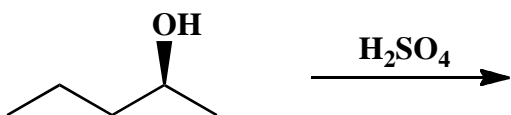
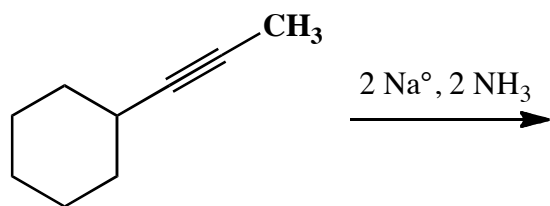
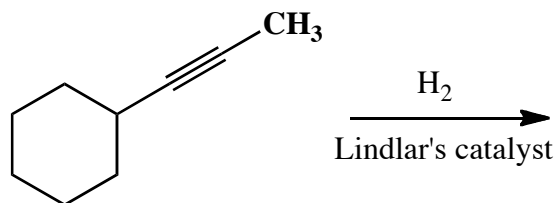
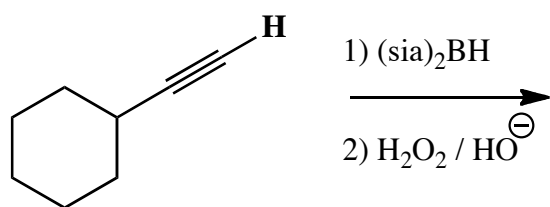
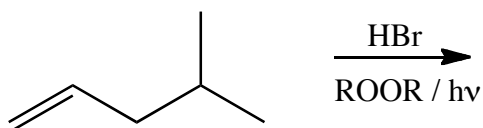
14. (5 or 7 pts each) The following reactions all involve chemistry of alkyl halides. **Fill in the box above the arrow with the mechanism that will be followed (S_N2 , E2, etc.). Then draw only the predominant product or products** and please remember that **you must draw the correct stereoisomers**. For $S_N1/E1$ reactions you must draw all significant products (including all stereoisomers).



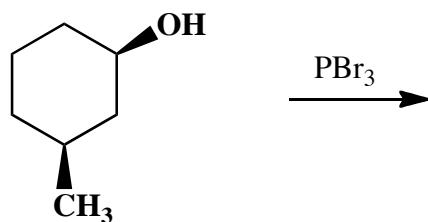
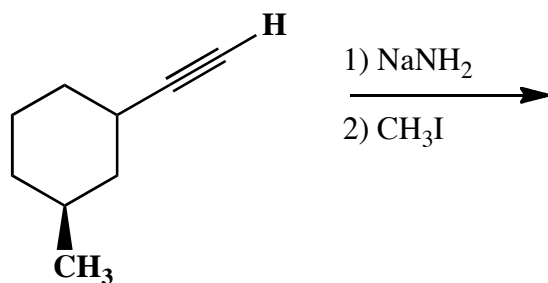
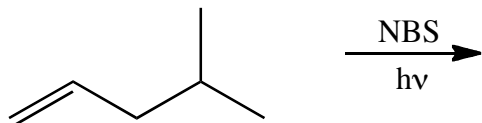
14 (cont.) (5 or 7 pts each) The following reactions all involve chemistry of alkyl halides. **Fill in the box above the arrow with the mechanism that will be followed (S_N2 , $E2$, etc.). Then draw only the predominant product or products** and please remember that **you must draw the correct stereoisomers**. For $S_N1/E1$ reactions you must draw all significant products (including all stereoisomers). These are a little harder so we gave you more room. **ASSUME THAT NO CARBOCATION INTERMEDIATES REARRANGE!!**



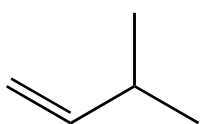
15. (3 or 5 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements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



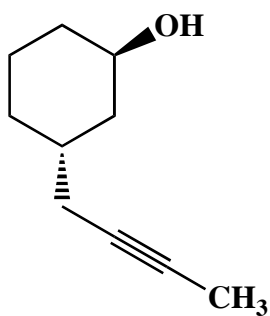
15. (3, 5 or 7 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



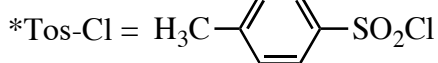
16. (7 pts each) For the following sequences of reactions, work through all the different steps and then write the final product(s). Assume only the predominant product is formed at each step. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



- 1) HBr, ROOR, hv
- 2) $\text{H}-\text{C}\equiv\text{C}:\ominus \text{Na}^{\oplus}$
- 3) $\text{H}_2\text{O}, \text{H}_2\text{SO}_4, \text{HgSO}_4$

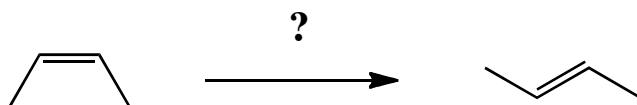


- 1) Tos-Cl*
- 2) $\text{CH}_3\text{S}^{\ominus} \text{Na}^{\oplus}$
- 3) H_2 , Lindlar's catalyst

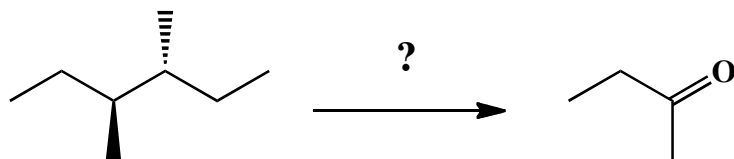


17. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized 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) (4 pts)



B) (7 pts)

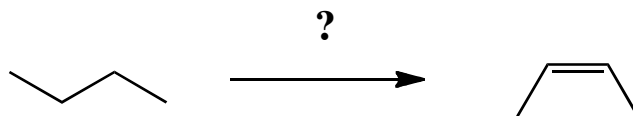


Signature _____

Pg 14 _____(13)

17. 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.

C) (13 pts)

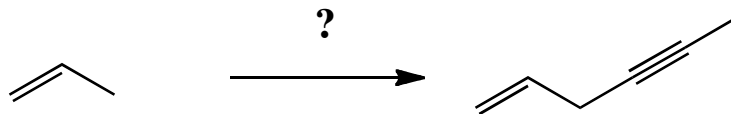


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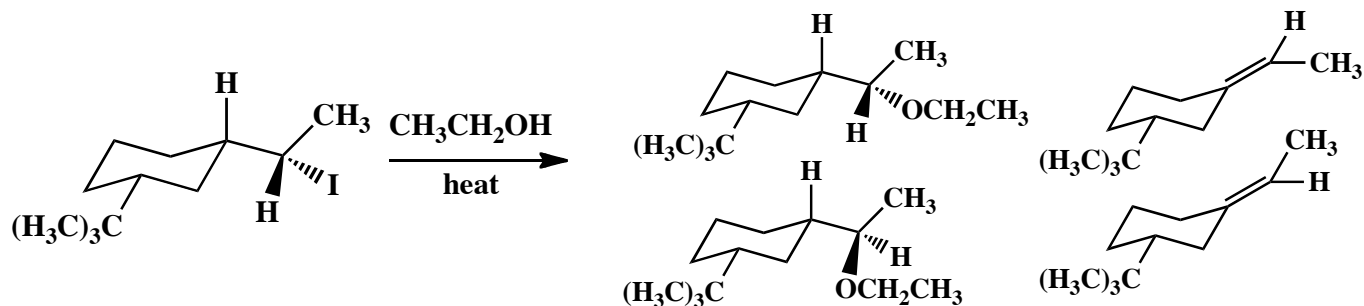
Pg 15 _____(10)

17. 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 of the carbon atoms of the product must come from the starting material shown!!**

D) (10 pts)



18. (15 pts) Here is an apply what you know question. Dr. Joe BagO'Doughnuts, a research chemist at the I.B. Dufus company, carried out the following reaction, and expected the four products shown.



Dr. BagO'Doughnuts was surprised to find that he actually had eight products, that is four in addition to the above four. Based on your understanding of the reaction mechanism, predict what these other four products are.

In no more than two sentences, explain how you came up with your answer. You can draw structures to help make your point, but you do not need to.