

Chemistry 261: Organic Chemistry

Final Examination

December 18, 2013

Name: ANSWER KEY

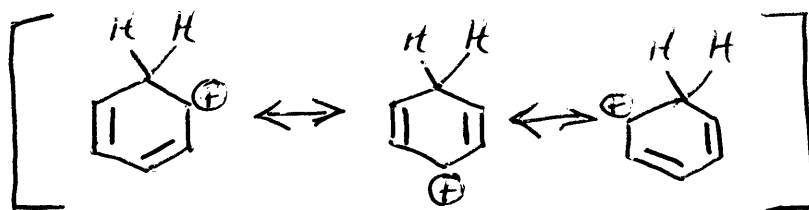
Student ID Number:

Exams will be returned via the Chem 261 wall-mount racks outside Lab Sci 300.

Please check the box if you would prefer to pick up your graded examination directly from Prof. Ponder during office hours.

Problem 1 (10 points; A & B = 3 points each, C = 4 points)

- (A) When benzene is protonated, the cyclohexadienyl cation is formed. This species is also known as the benzenium ion, and has the formula $C_6H_7^+$. Draw the structure of this cation, including all reasonable resonance forms.



(+1) EACH RESONANCE STRUCTURE

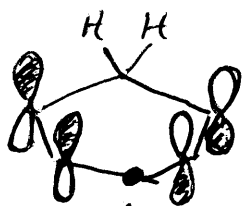
- (B) How many π -electrons does this cation contain? What is the hybridization state of the protonated carbon atom? Is this ion conjugated, or aromatic, or both?

(+1) TOTAL OF 4 π ELECTRONS

(+1) PROTONATED CARBON IS sp^3 HYBRIDIZED

(+1) CATION IS CONJUGATED (NOT AROMATIC)

- (C) Draw a picture of the HOMO for the benzenium cation? How many nodes does this orbital have?



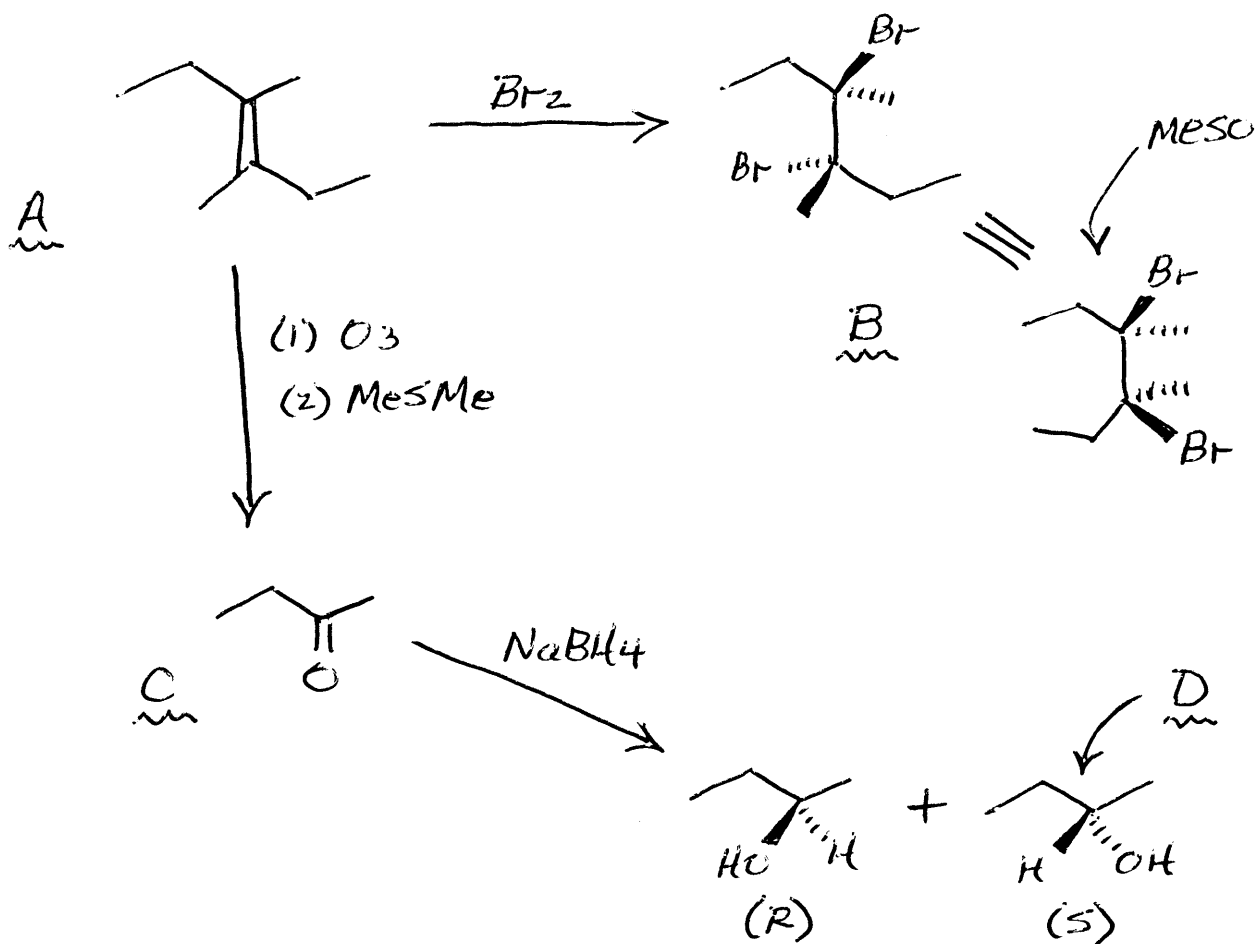
NODE AT MIDDLE CARBON ATOM

(+2) CORRECT ORBITAL DRAWING

(+2) HOMO HAS 1 NODE

Problem 2 (8 points)

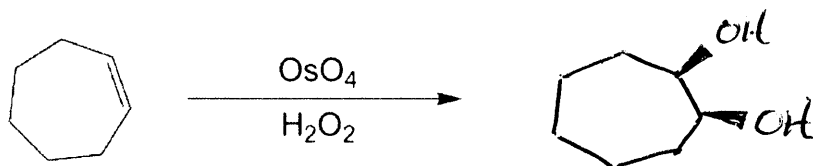
Molecule **A** (C_8H_{16}) reacts with Br_2 to give a *meso* product, **B** ($C_8H_{16}Br_2$). Ozonolysis of **A** followed by dimethyl sulfide workup yields only a single product, **C** (C_4H_8O). Reaction of **C** with sodium borohydride ($NaBH_4$) gives a racemic mixture of (*S*)-alcohol **D** and its enantiomer. Determine the structure of each species **A** through **D**.



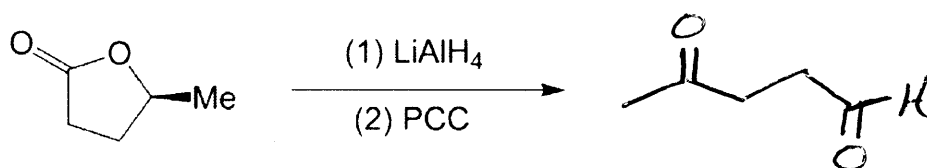
② EACH CORRECT
STRUCTURE, A-D

Problem 3 (12 points; A–D = 3 points each) Predict the major product resulting from each of the following reactions. Pay attention to stereochemistry when appropriate. You need not show mechanisms, intermediates or minor products.

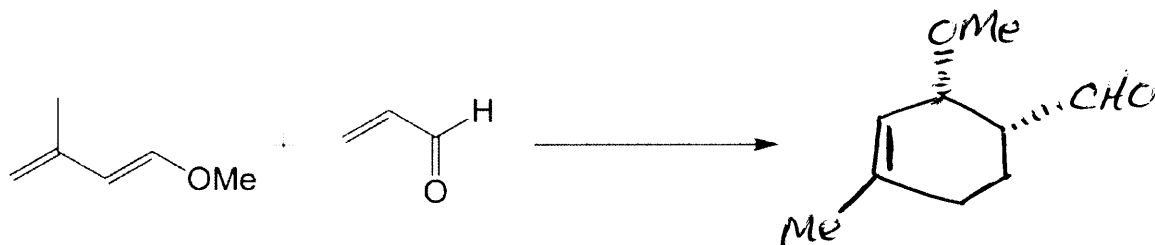
(A)



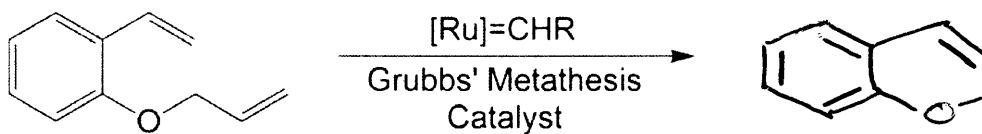
(B)



(C)



(D)

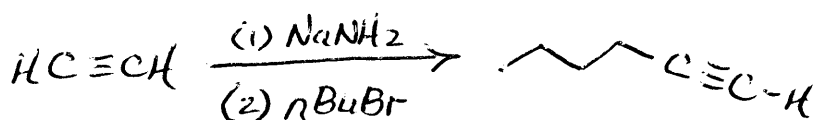
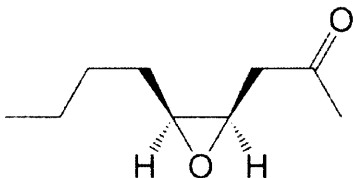


(+3) EACH CORRECT PRODUCT

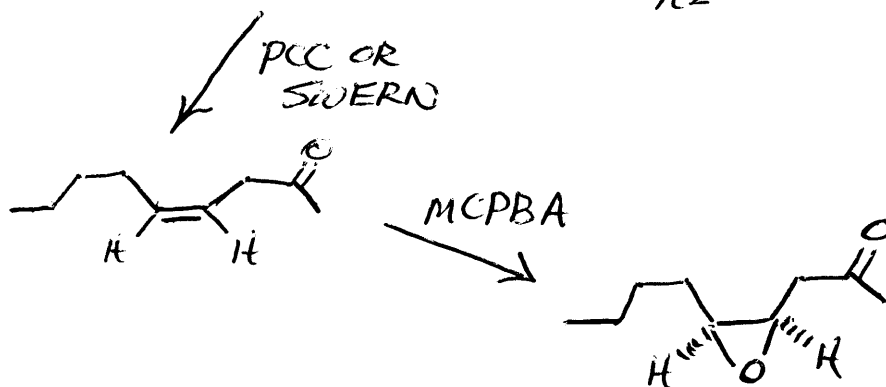
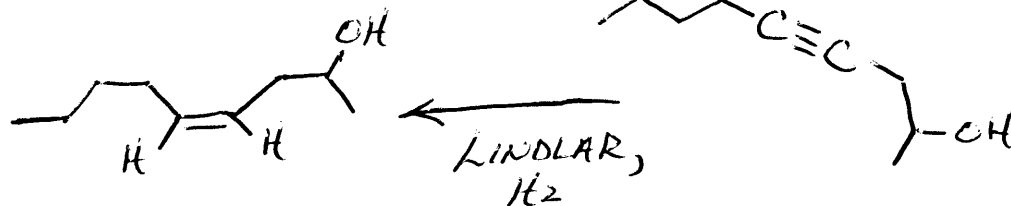
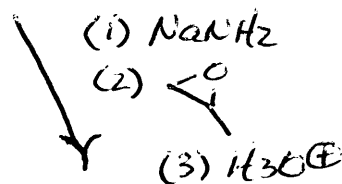
(-1) WRONG STEREOCHEMISTRY

Problem 4 (10 points)

Propose a synthesis of the compound shown below from organic starting materials of four carbons or less, and any needed reagents. Your synthesis will be evaluated on the total number of steps, the yield of the individual steps, and their selectivity.

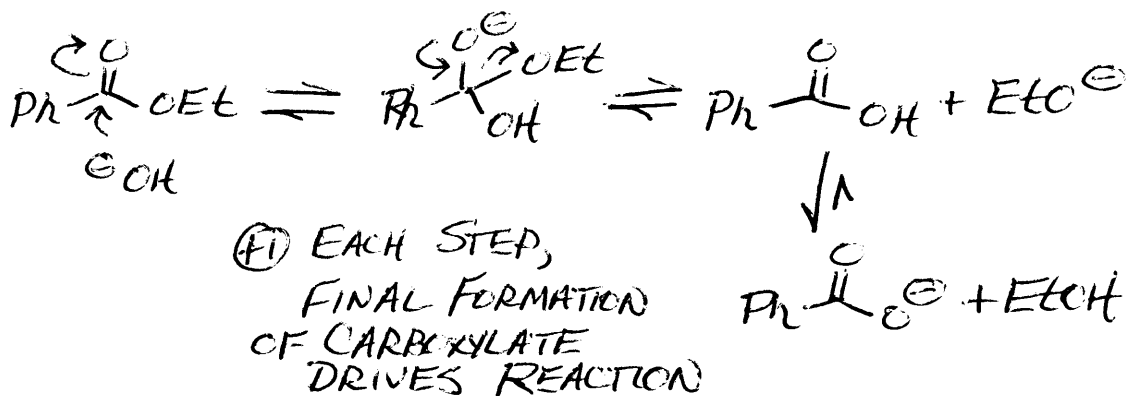


② PER STEP ON SYNTHETIC ROUTE

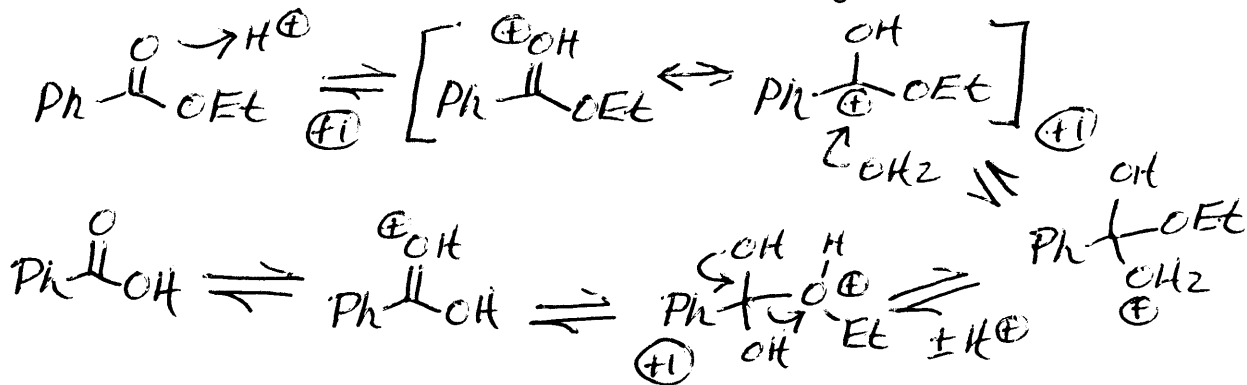


Problem 5 (10 points; A-B = 3 points each, C = 4 points)

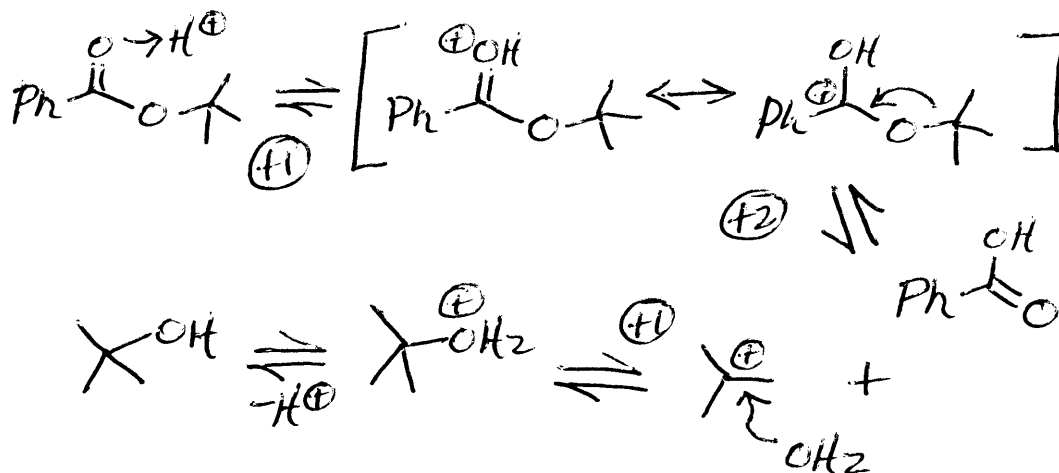
- (A) Base-catalyzed hydrolysis of esters is sometimes referred to as "saponification" after the traditional process used to produce soap from naturally occurring fats. Write the full mechanism for the hydrolysis of ethyl benzoate (PhCOOEt) in basic water. What feature of the products helps drive this reaction to completion?



- (B) Esters can also be hydrolyzed under acidic conditions. When ethyl benzoate is reacted with acid in ^{18}O -labelled water (i.e., $^{18}\text{OH}_2$ instead of the usual $^{16}\text{OH}_2$), ^{18}O is found only in the product carboxylic acid, and not in the alcohol. Write a detailed mechanism consistent with the observed labeling.

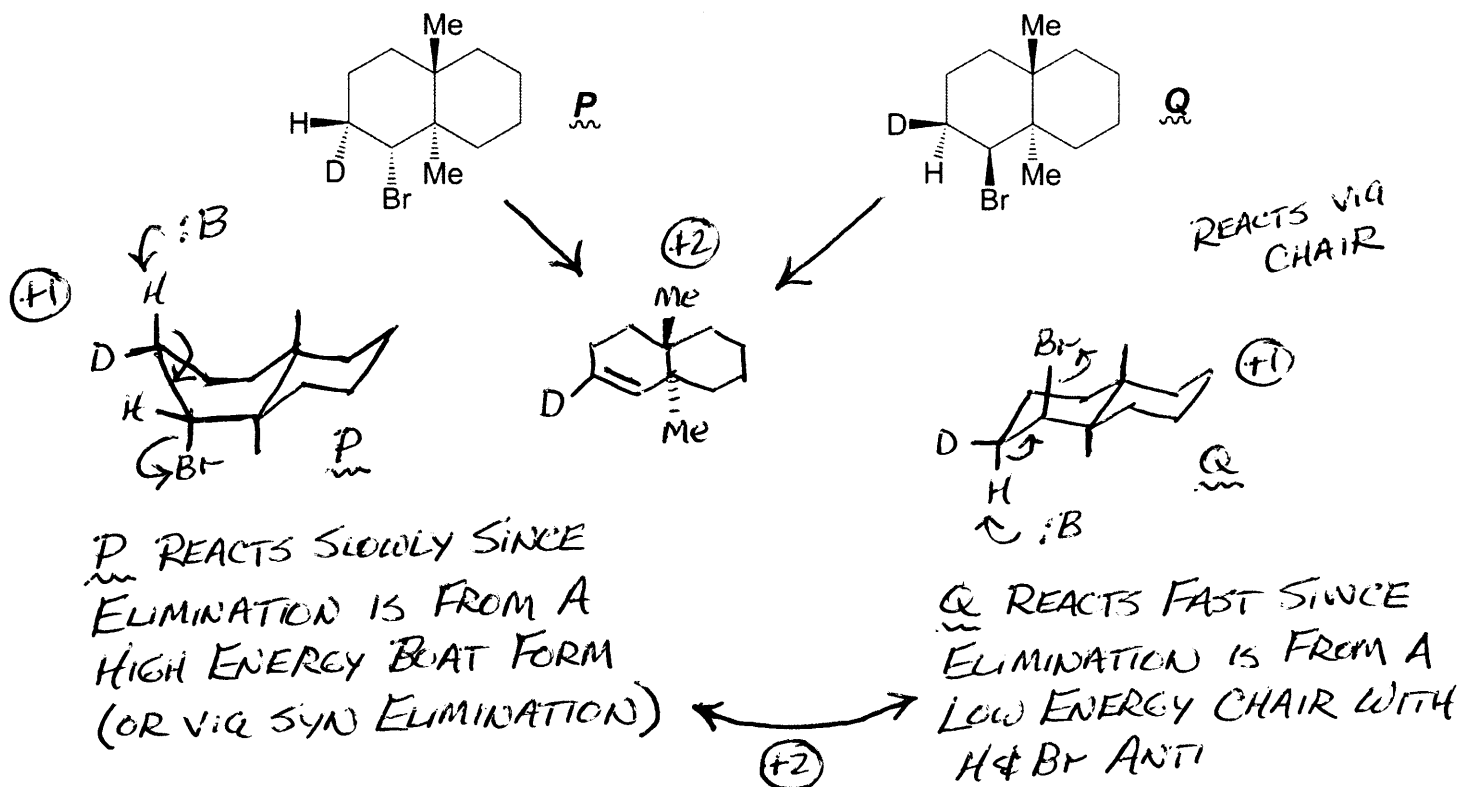


- (C) When a *t*-butyl ester, such as *t*-butyl benzoate, is hydrolyzed in ^{18}O -labelled acidic water, the label ends up in the alcohol, but not in the carboxylic acid. Propose a mechanism consistent with this result.



Problem 6 (10 points; A = 6 points, B = 4 points)

- (A) Upon treatment with excess sodium ethoxide in ethanol at 50°C, both molecules **P** and **Q** react to form the same major product. Under identical conditions, **P** and **Q** react at vastly different rates. What is the product? Which of the two starting molecules reacts faster? Explain the difference in rates. Illustrate your answer with clear drawings of the transition states for reaction of **P** and of **Q**. Note -D is a deuterium atom, a heavy isotope of hydrogen.



- (B) The reaction rates of the two molecules, performed at the same ethoxide concentration, are in the ratio 100,000 to 1. Estimate the difference in activation energy. Note the gas constant (R) is 1.987 cal/mol/K, and 0°C = 273.15K.

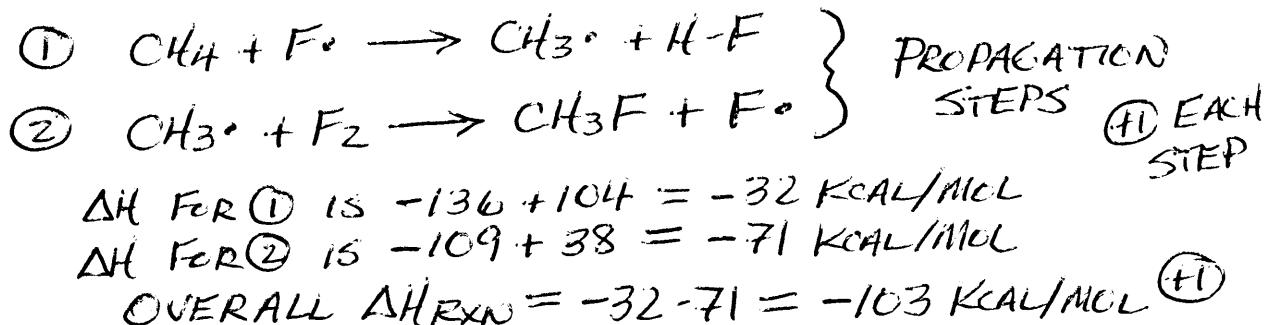
$$\begin{aligned} \text{RATIO} &= k_Q/k_P = 100000 = e^{-\Delta E_a/RT} \\ \text{SO, } \Delta E_a &= -RT \ln(100000) \\ &= -(1.987)(323.15) \cdot \ln(100000) \\ &= -7.39 \text{ KCAL/MOL} \end{aligned}$$

(+2) CORRECT EQUATION

(+2) CORRECT NUMERICAL VALUE (IGNORE SIGN)

Problem 7 (10 points; A & C = 3 points each, B & D = 2 points each)

- (A) Write the chain propagation steps for the free radical fluorination of methane to fluoromethane using F_2 as the fluorine source. Compute ΔH_{RXN} for the overall process.

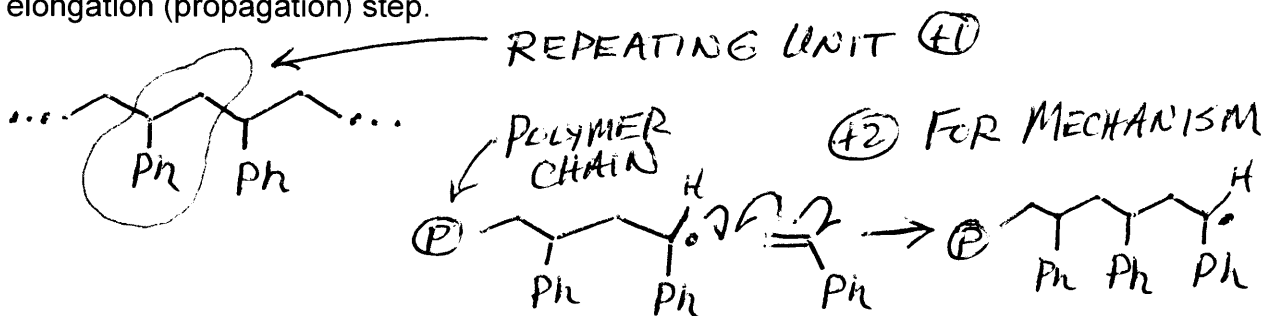


- (B) The F-F bond in F_2 is very weak at 38 kcal/mol with respect to homolytic cleavage. Why do you think this bond is so weak? What effect does this bond strength have on the thermodynamics of radical fluorination in part (A)?

$\textcircled{+1}$ BOND IS WEAK DUE TO ELECTROSTATIC REPELSION OF LONE PAIRS ON THE SMALL FLUORINE ATOMS

$\textcircled{+1}$ WEAK F-F BOND RESULT IN VERY EXOTHERMIC OVERALL REACTION

- (C) When heated in the presence of a peroxide initiator, styrene ("vinyl benzene", or $Ph-CH=CH_2$) polymerizes to form polystyrene. What is the structure of the "repeating unit" for this polymer? Write the curved arrow mechanism for a single elongation (propagation) step.



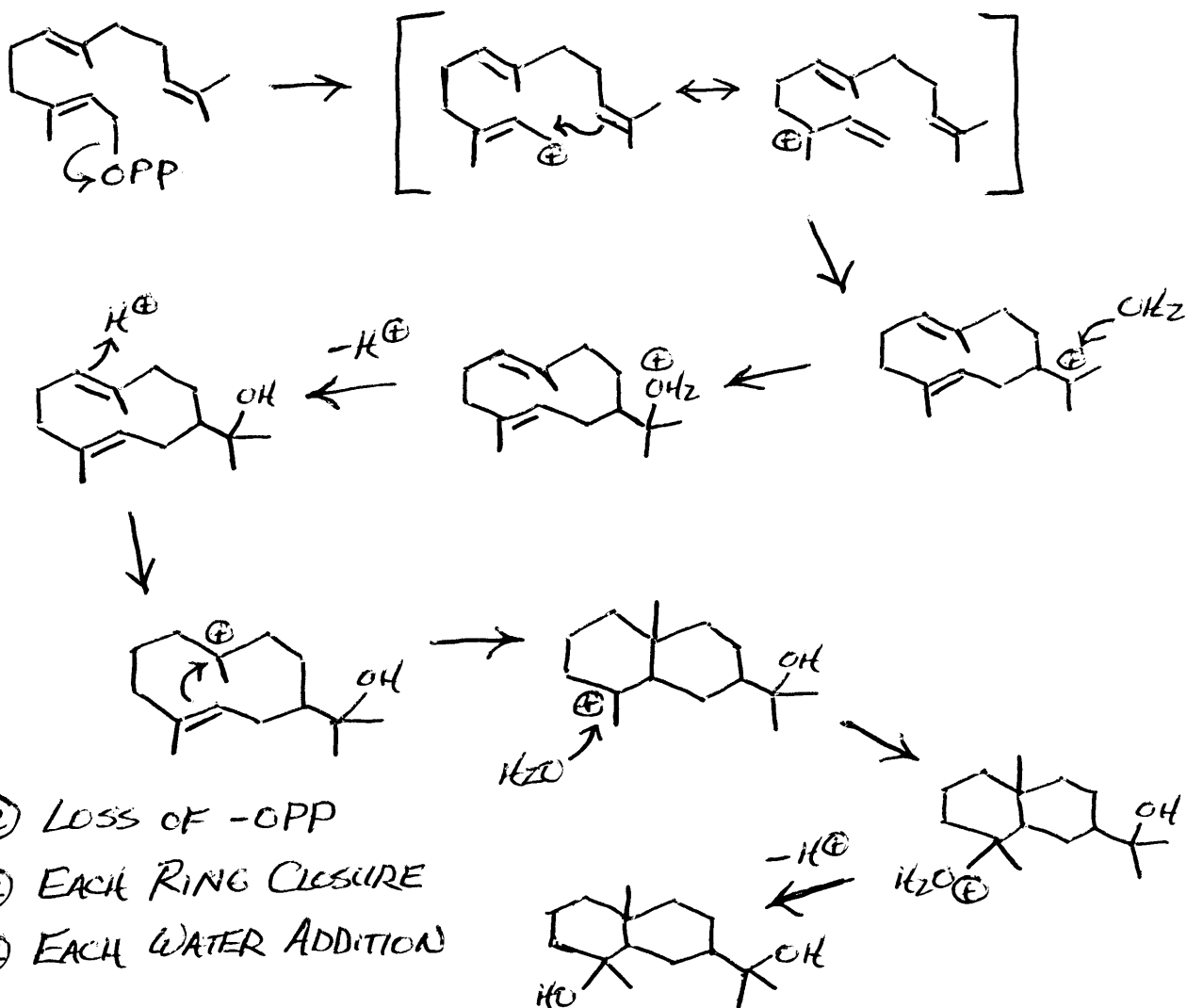
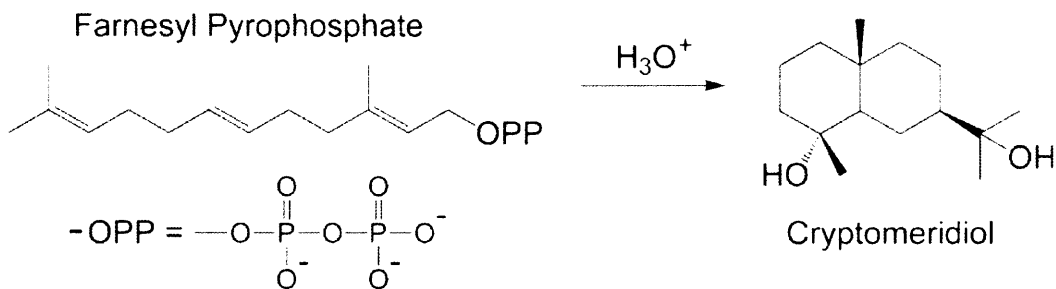
- (D) Polystyrene tends to form a "head-to-tail" polymer, with phenyl groups substituted on alternate carbon atoms along the polymer chain. Suggest two reasons why it is rare for the polymer to have phenyl groups on adjacent carbons of the chain.

$\textcircled{+1}$ LESS STERIC CROWDING IN HEAD-TO-TAIL

$\textcircled{+1}$ HEAD-TO-TAIL RESULTS IN RESONANCE STABILIZED BENZYL RADICAL

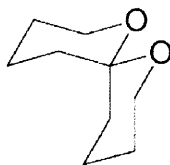
Problem 8 (10 points)

Farnesyl pyrophosphate is produced from isoprene in both plants and animals, and is the biosynthetic precursor of a large family of interesting organic molecules. Provide a detailed curved arrow mechanism for the transformation of farnesyl pyrophosphate into cryptomeridiol. *Hint: The overall process can be viewed as loss of pyrophosphate ion via "solvolysis", followed by reaction of the resulting carbocation.*

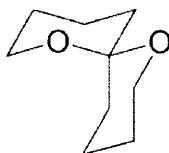


Problem 9 (8 points; A & B = 4 points each)

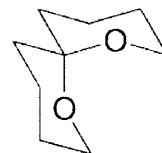
- (A) Shown below are three similar structures, all of formula $C_9H_{16}O_2$. At room temperature, where relatively low energy conformational barriers are freely crossed, what kind of isomerism is represented by structures **F** and **G**? Similarly, what is the relationship between structures **G** and **H**? *Hint: Build models!*



F



G



H

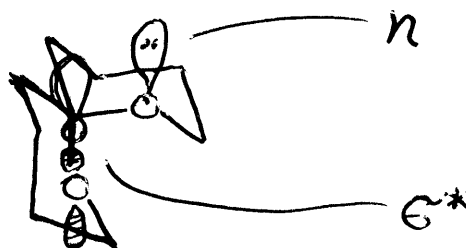
(+2) **F** & **G** ARE ENANTIOMERS

(+2) **G** & **H** ARE CONFORMATIONAL ISOMERS
(ALSO ACCEPT **G** & **H** ARE "THE SAME")

- (B) Based on hyperconjugation arguments, which of the three specific structures from part (A) is expected to be the most stable? Using one of the structures to illustrate your answer, draw and label the orbitals involved in a hyperconjugative interaction.

(+2) **H** IS THE MOST STABLE

(+2)

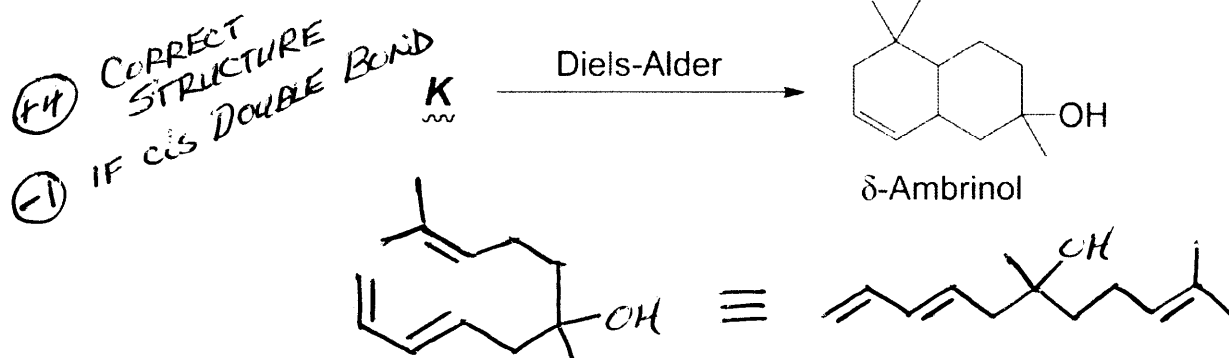


OXYGEN "AXIAL" LONE PAIR IS PARALLEL TO & OVERLAPS WITH THE C-O σ^* ORBITAL

Problem 10 (12 points; A = 4 points, B = 8 points)

(A) Sperm whales eject intestinal slurry into the ocean, where it hardens and collects along the shoreline as waxy, flammable "rocks" called ambergris. Ambergris is highly prized in the perfume industry, and can be worth up to \$4000 per ounce.

One component of ambergris is δ -ambrinol, which has been synthesized via an intramolecular Diels-Alder reaction. Draw the structure of the precursor molecule, **K**, that undergoes a Diels-Alder reaction to form δ -ambrinol.



(B) Complete a synthesis of δ -ambrinol by showing how the Diels-Alder precursor **K** can be prepared from starting materials containing four carbon atoms or less.

