

Last Name ANSWER	First Name KEY	MI
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Student ID Number:

Total Score 23φ / 200	Chem 30A Fall 2005 FINAL <i>(180 Min)</i> Weds Dec 14th	Course Grade A ⁺
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*****DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO*****

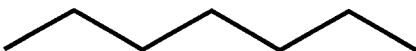
ONLY ANSWERS WRITTEN IN THE BOXES PROVIDED WILL BE GRADED

**INTERPRETATION OF THE QUESTIONS IS PART OF THE EXAM –
DO NOT ASK FOR THE QUESTIONS TO BE EXPLAINED TO YOU**

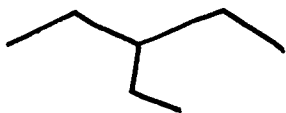
Q1	26 / 26	Q5	2φ / 20	Q9	15 / 15
Q2	21 / 21	Q6	31 / 31	Total 23φ / 200	
Q3	2φ / 20	Q7	32 / 32		
Q4	35 / 35	Q8	3φ / 30		

"Organic chemistry just now is enough to drive one mad. It gives me the impression of a primeval forest full of the most remarkable things, a monstrous and boundless thicket, with no way of escape, into which one may well dread to enter." - Friedrich Wöhler (1835)

Q1. (a) Using LINE FORMULAE draw the six other ACHIRAL CONSTITUTIONAL isomers (B-G) of heptane (A). (2 pt each) (b) Name each isomer using SYSTEMATIC naming rules. (1 pt each)

A  heptane

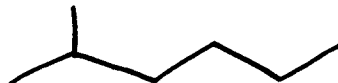
B



Name

3-ETHYLPENTANE

C



Name

2-METHYLHEXANE

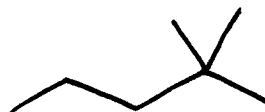
D



Name

3,3-DIMETHYLPENTANE

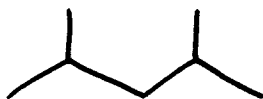
E



Name

2,2-DIMETHYLPENTANE

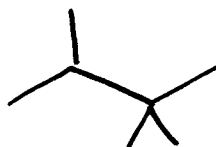
F



Name

2,4-DIMETHYLPENTANE

G

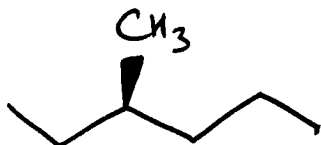


Name

2,2,3-TRIMETHYLBUTANE

(c) Using LINE FORMULAE (and wedges and dashes as necessary) draw the (R)-enantiomers of the two CHIRAL CONSTITUTIONAL isomers (H and I) of heptane (A) (3 points each). (d) Name each isomer using SYSTEMATIC naming rules. (1 pt each)

H

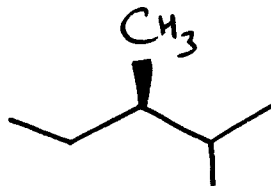


(R)-Enantiomer

Name

3-METHYLHEXANE

I



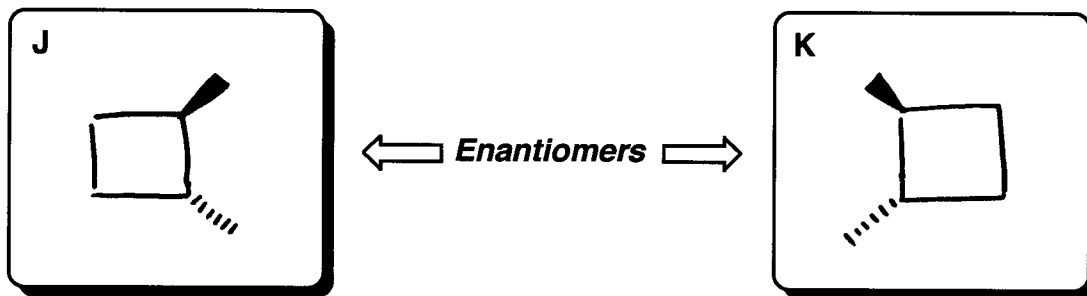
(R)-Enantiomer

Name

2,3-DIMETHYLPENTANE

Q2 There are **SEVEN** different isomers with the formula C_6H_{12} (**J-P**) that contain a 4-membered ring, i.e., a cyclobutane ring. Based upon the following statements, draw the appropriate structures (using line formulae with wedges and dashes as necessary) in the boxes below. (3 points each)

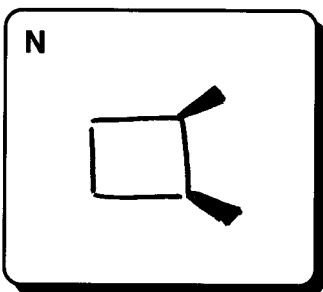
(i) **J** and **K** are enantiomers of one another



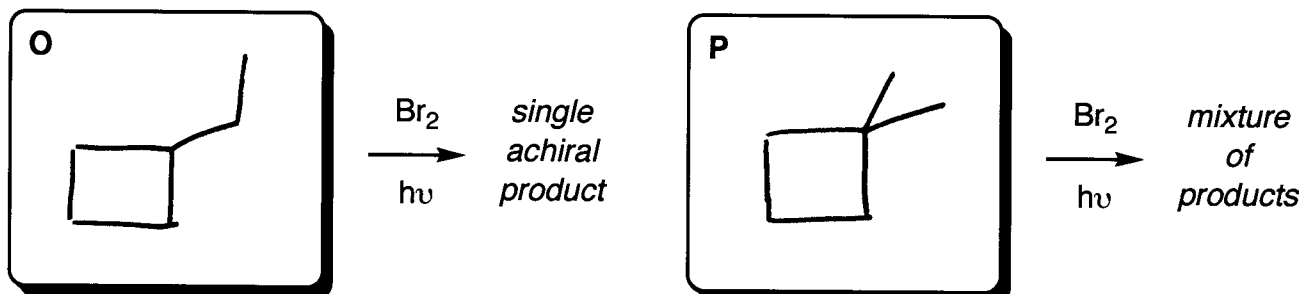
(ii) **L** and **M** are diastereoisomers of one another and both are **ACHIRAL**



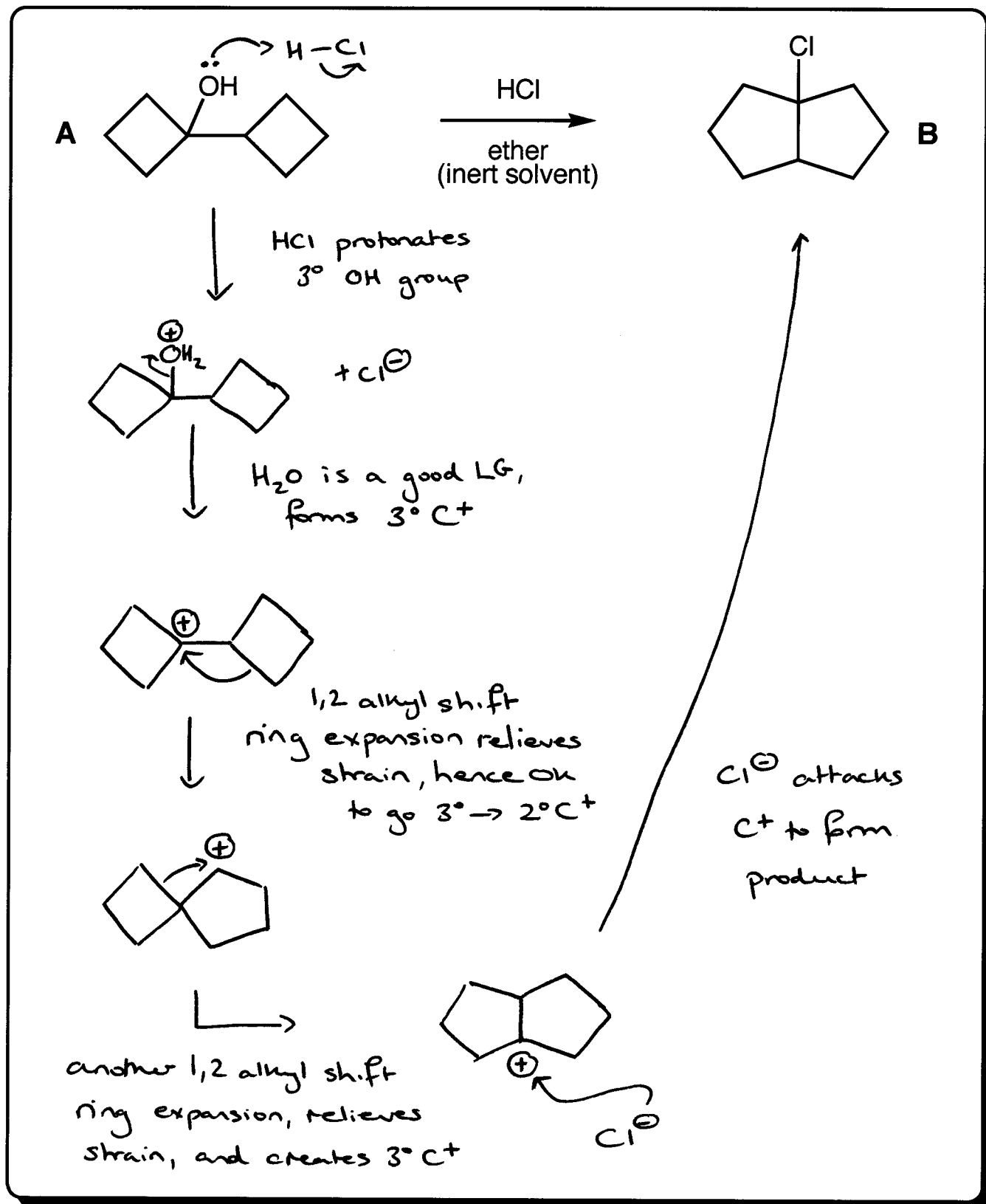
(iii) **N** contains two chiral centers, but is **ACHIRAL**; it is a diastereoisomer of both **J** and **K**



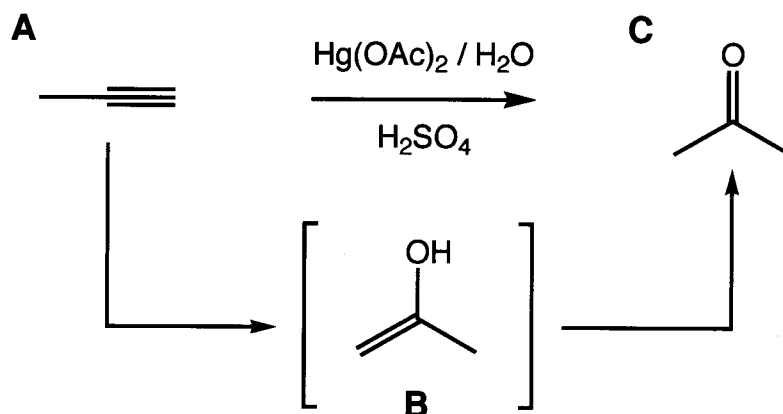
(iv) The monobromination ($Br_2/h\nu$) of **O** gives predominantly a single **ACHIRAL** compound whereas the monobromination ($Br_2/h\nu$) of **P** results in a mixture of three isomeric compounds, some of which are chiral



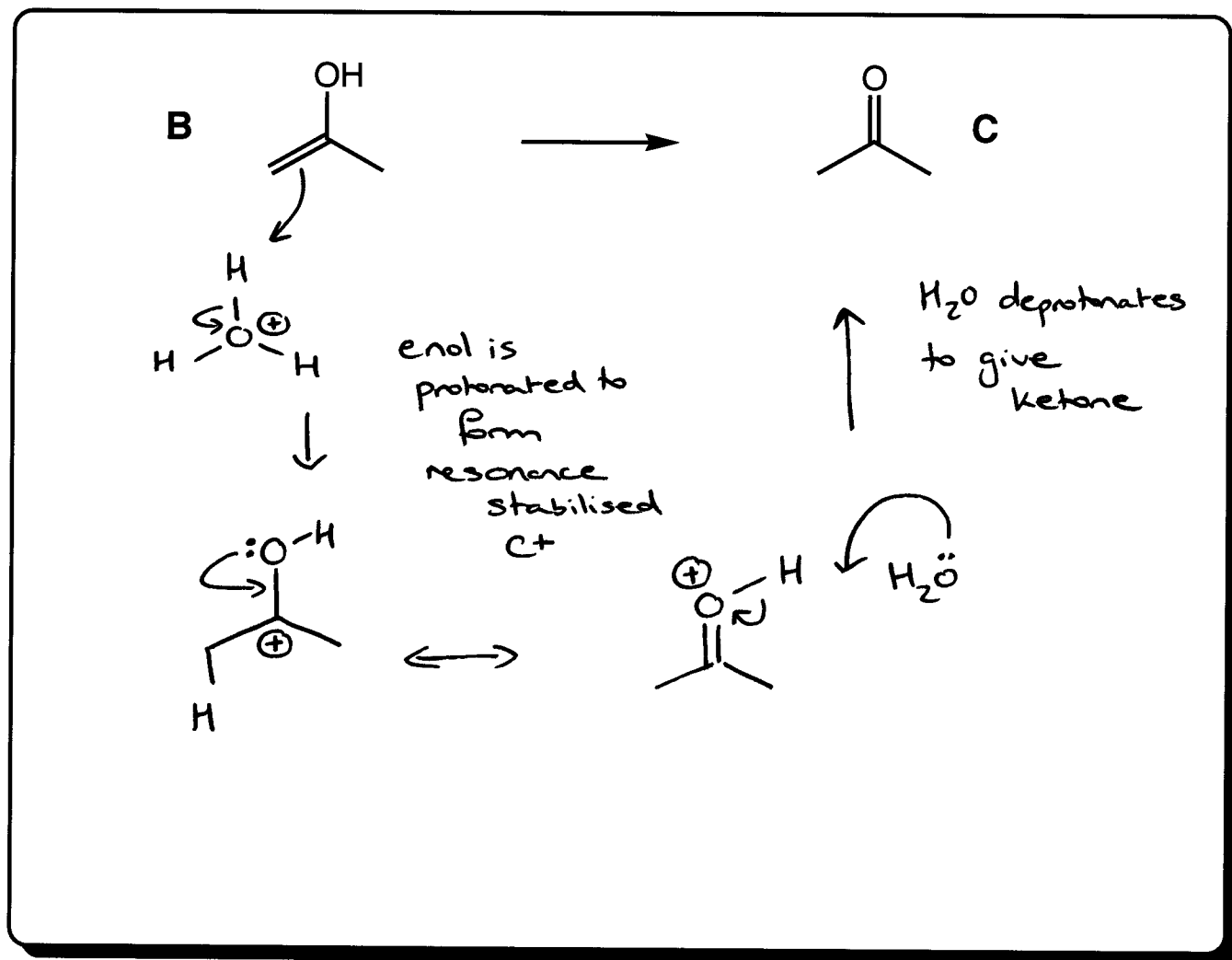
Q3. Propose a reasonable mechanism that accounts for the transformation of compound A into compound B shown below – (show all intermediates, all appropriate lone pairs, formal charges, significant resonance forms, and curly arrows). Explain each step with a few words. (20 points)



Q4. When propyne (A) undergoes an oxymercuration reaction ($\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}/\text{H}_2\text{SO}_4$) as shown below, the product of the reaction is acetone (C). An intermediate in the reaction is enol B.

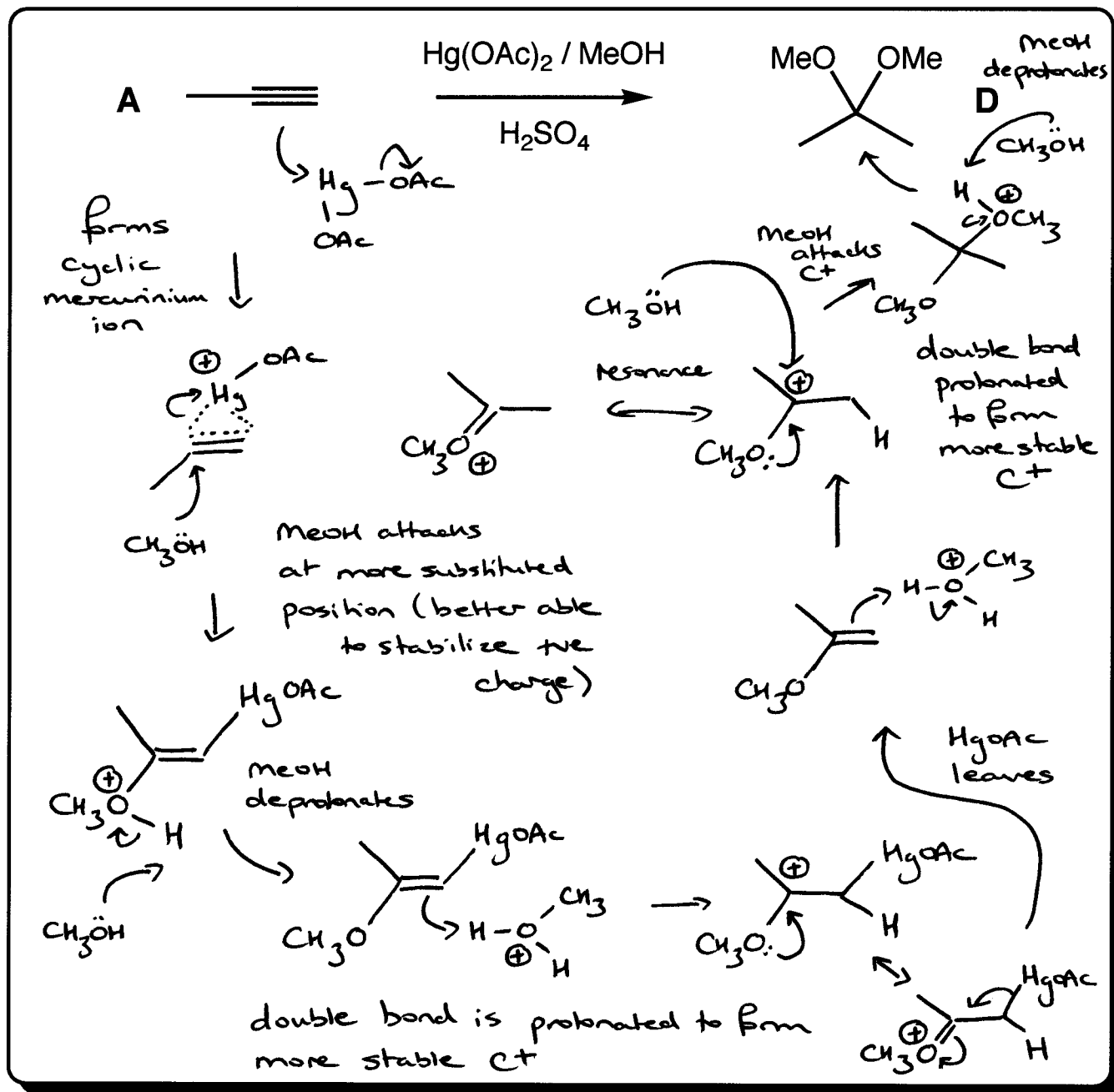


(a) Propose a reasonable mechanism that accounts for the acid-catalyzed transformation of enol B into ketone C (i.e., acetone) under the conditions of the oxymercuration reaction – show all intermediates, all appropriate lone pairs, formal charges, significant resonance forms, and curly arrows. Explain each step with a few words. (10 points)



Question 4 is continued on the next page...

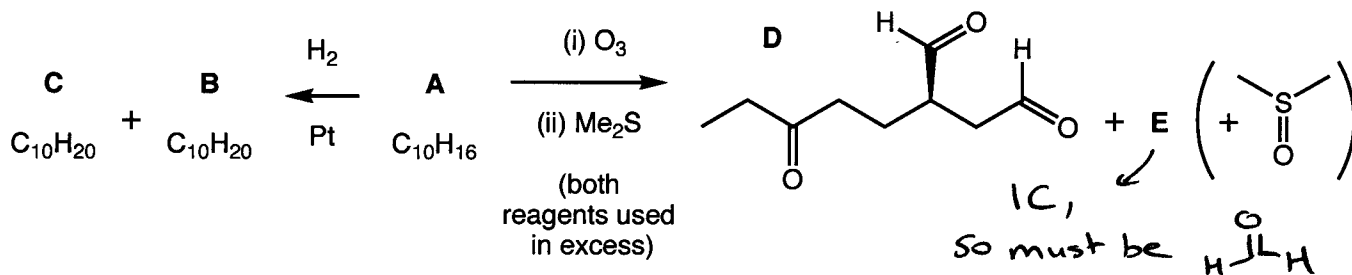
(b) If the oxymercuration reaction is performed using methanol (MeOH) rather than water, the product is NOT a ketone, but compound D as shown below. Propose a reasonable mechanism that accounts for the transformation of propyne (A) into compound D – show all intermediates, all appropriate lone pairs, formal charges, and curly arrows. Explain each step with a few words. (20 points)



(c) Suggest a reason why the reaction does not give a ketone as the product when it is performed in methanol rather than water. (5 points)

AS CAN BE SEEN FROM THE ABOVE MECHANISM, THE PRODUCT AFTER ONE ADDITION IS $\text{CH}_3\text{C}(\text{O}^+)\text{CH}_2\text{CH}_3$ RATHER THAN AN ENOL, AND SO TAUTOMERISATION TO A KETONE IS NOT POSSIBLE.

Q5. An optically active (chiral) compound **A** ($C_{10}H_{16}$) reacts with hydrogen in the presence of a platinum (Pt) catalyst to give two diastereoisomeric compounds **B** and **C**, each with the formula $C_{10}H_{20}$. Both **B** and **C** are optically inactive (achiral). When **A** undergoes an ozonolysis reaction (O_3/Me_2S), two compounds are formed; the ketodialdehyde (**D**) shown below, and compound **E** (in addition to the byproduct $Me_2S=O$). Draw the structures of compounds **A**, **B**, **C**, and **E**, in the boxes at the bottom of this page, including any relevant stereochemistry. (20 pt)



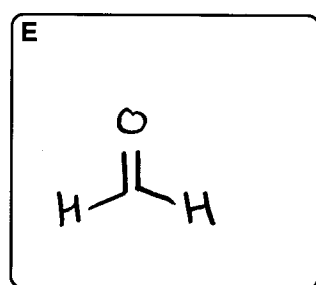
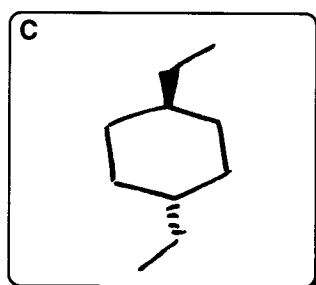
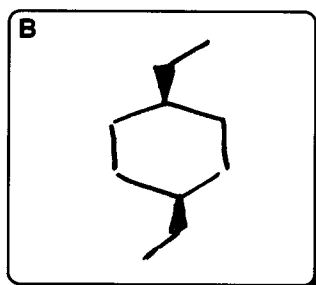
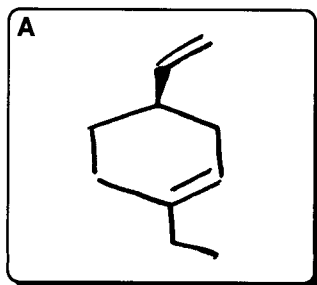
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3 POSSIBLE CONNECTIONS

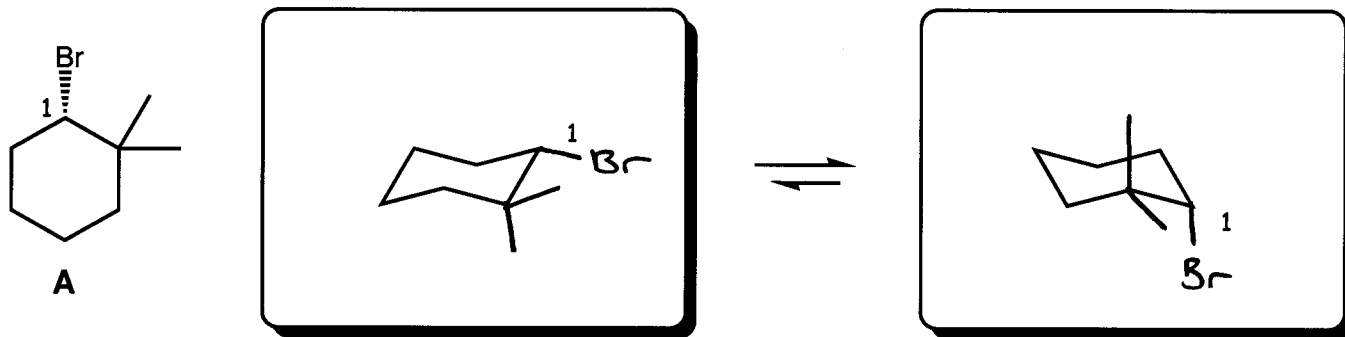
racemic mixture of chiral compounds

CHIRAL DIASTEREOMERS

ANSWER



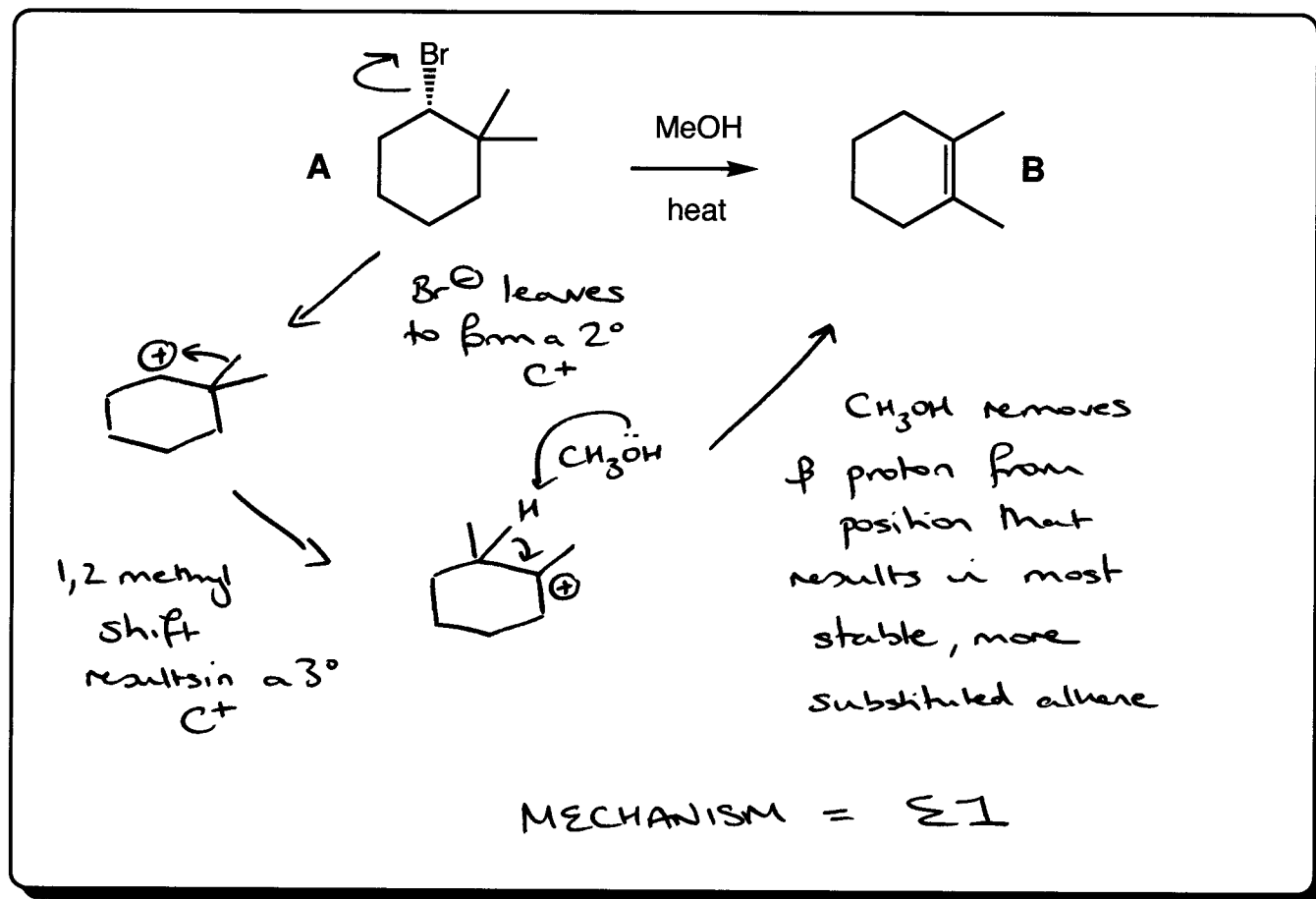
Q6. (a) The 1-bromo-2,2-dimethylcyclohexane derivative **A** shown below can exist in two different chair conformations. Complete the skeleton chairs as appropriate in the boxes below. (4 points)



(b) Assign the configuration of the chiral center present in the 1-bromo-2,2-dimethylcyclohexane derivative **A** shown above. (2 points)

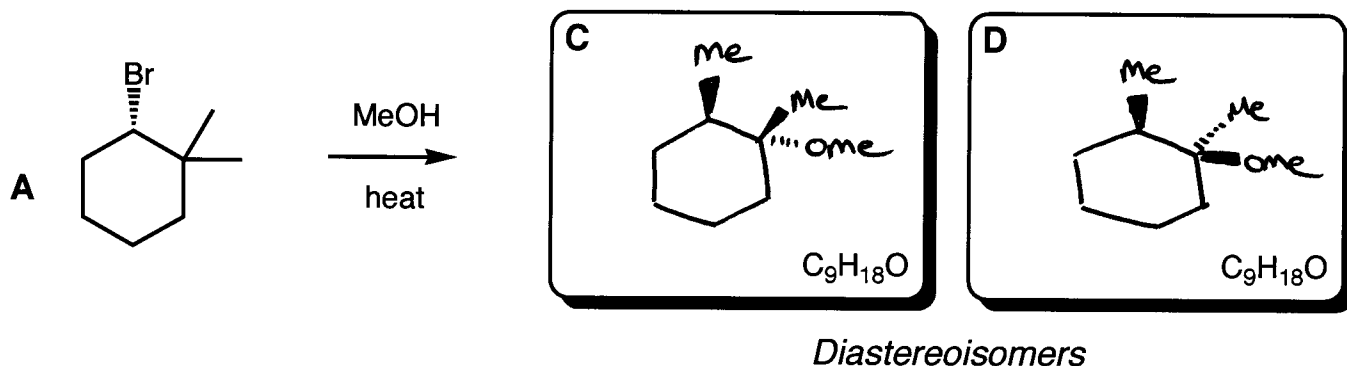
S

(c) When compound **A** is heated in methanol (MeOH), alkene **B** is formed. Propose a reasonable mechanism that accounts for the transformation of **A** into **B** – show all intermediates, all appropriate lone pairs, formal charges, significant resonance forms, and curly arrows. Explain each step with a few words and indicate the type of mechanism, i.e., E1, E2, S_N1, or S_N2. (10 points)

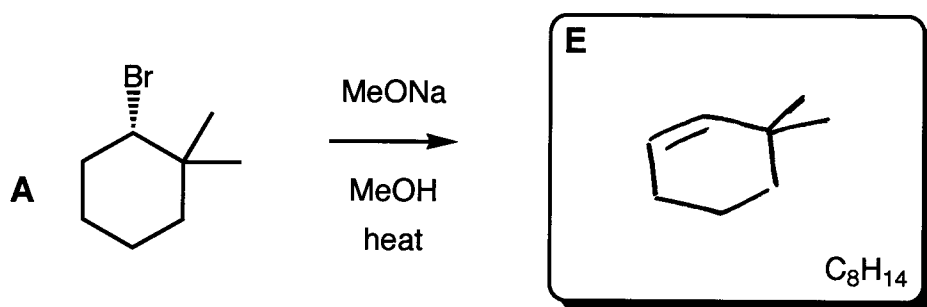


Question 6 is continued on the next page...

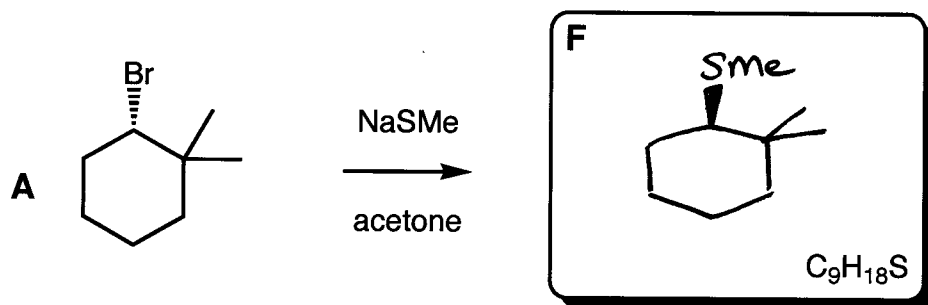
(d) When compound **A** is heated in methanol (MeOH), not only is alkene **B** formed, but two diastereoisomeric compounds (**C** and **D**) are also produced (each as a pair of enantiomers!) with the molecular formula $C_9H_{18}O$. Draw the structures of diastereoisomers **C** and **D** (using line formulae with wedges and dashes as necessary) in the boxes below. (6 points)



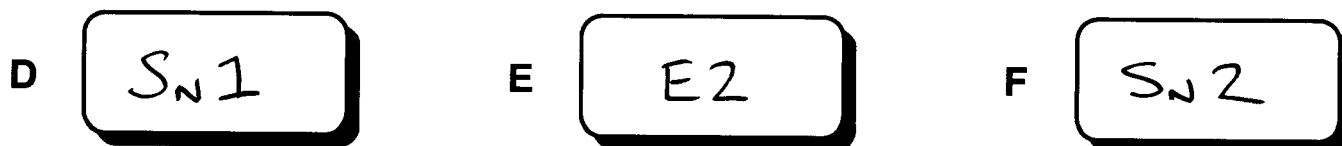
(e) When compound **A** is heated in methanol (MeOH) containing sodium methoxide (NaOMe), a single achiral alkene (**E**) with the molecular formula C_8H_{14} is formed. Draw the structure of alkene **E** in the box below. (3 points)



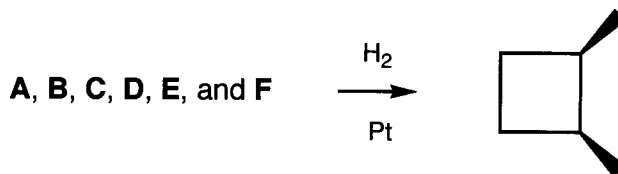
(f) When compound **A** is reacted with sodium methylthiolate (NaSMe) in acetone, a single chiral compound (**F**) with the molecular formula $C_9H_{18}S$ is formed. Draw the structure of compound **F** in the box below. (3 points)



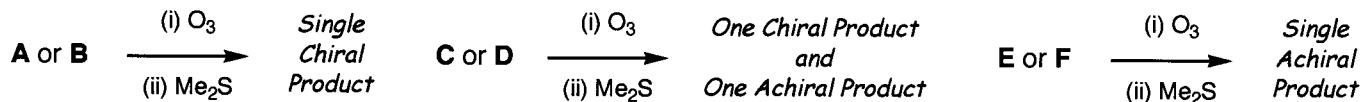
(g) For compounds **D**, **E**, and **F**, indicate what reaction mechanism is responsible for their formation, i.e., E1, E2, S_N1 , or S_N2 . (3 points).



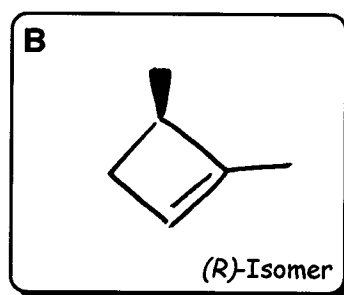
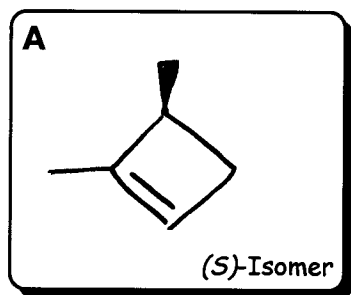
Q7. Six different cycloalkenes (A–F), each with the molecular formula C_6H_{10} , will yield *cis*-1,2-dimethylcyclobutane when subjected to catalytic hydrogenation (H_2 /Pt catalyst) – as shown below. (Note: in some cases it is the ONLY product, in some cases it is one of two of products).



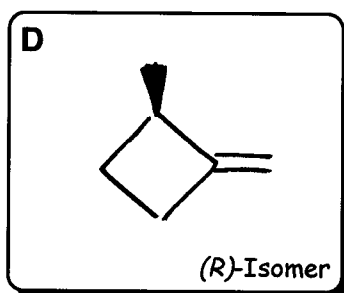
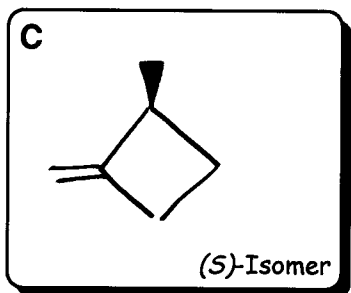
Furthermore, the results of the ozonolysis reactions (O_3 followed by Me_2S) of these cycloalkenes (A–F), are listed below (in each case the byproduct $Me_2S=O$ is also formed).



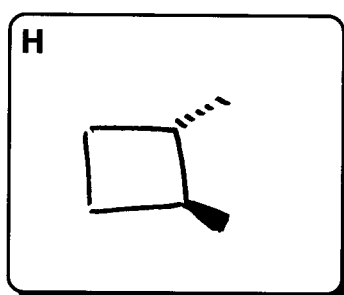
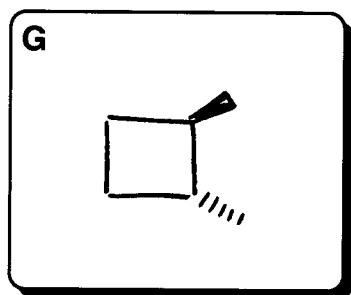
(a) Compounds A and B constitute a pair of enantiomers; the absolute configuration of the stereogenic center in compound A is (*S*) and in B it is (*R*). Draw these compounds below. (4 points)



(b) Compounds C and D also constitute a pair of enantiomers; the absolute configuration of the stereogenic center in compound C is (*S*) and in D it is (*R*). Draw these compounds below. (4 points)



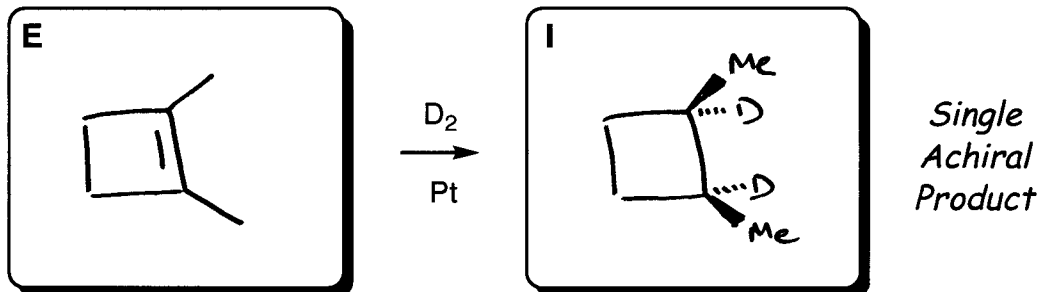
(c) When compounds A, B, C, and D are hydrogenated, *cis*-1,2-dimethylcyclobutane is not the only product formed, what two other compounds (G & H) with the formula C_6H_{12} are also formed (4 points)



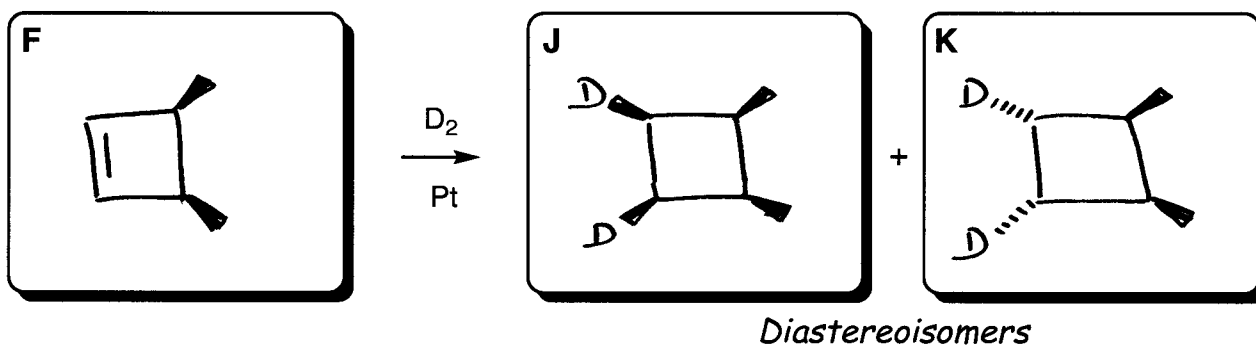
Question 7 is continued on the next page...

(d) When cycloalkenes E & F are reacted with deuterium gas (D_2) instead of hydrogen gas (H_2), different results are observed.

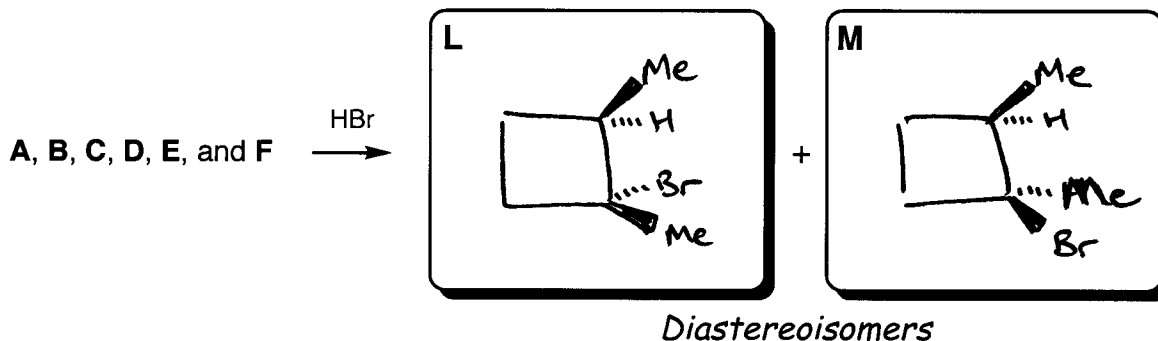
(i) Cycloalkene E reacts to form a single achiral product (I) – draw these compounds in the appropriate boxes below. (4 points)



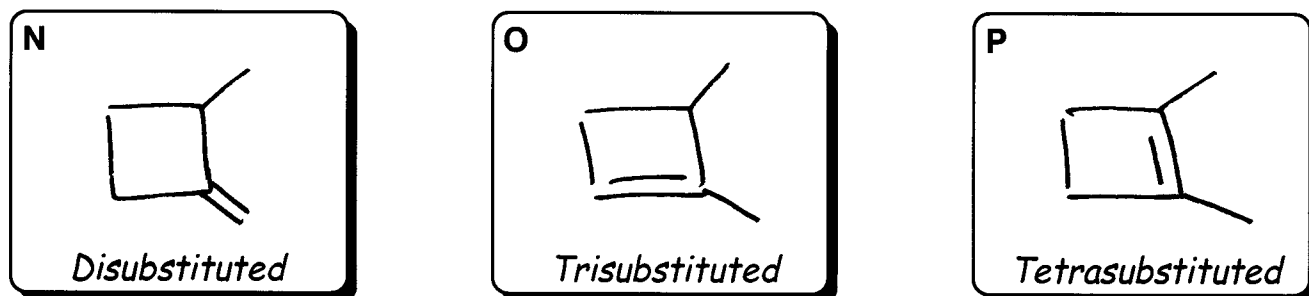
(ii) Cycloalkene F reacts to form a two diastereomeric compounds (J & K), each of which is achiral – draw these compounds in the appropriate boxes below (note – the labels J & K are arbitrary). (6 points)



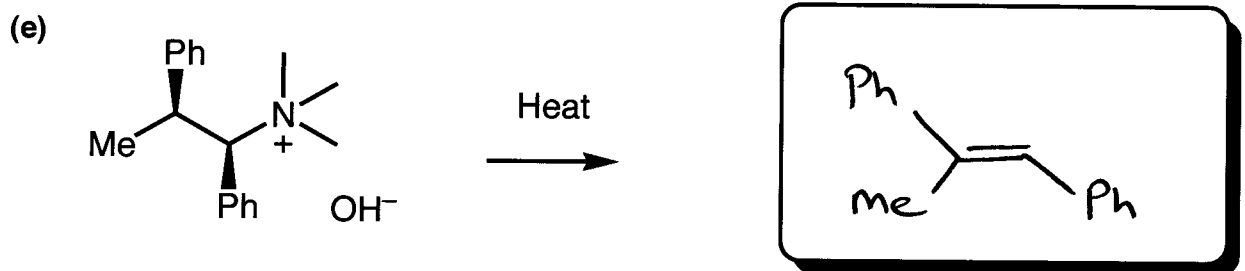
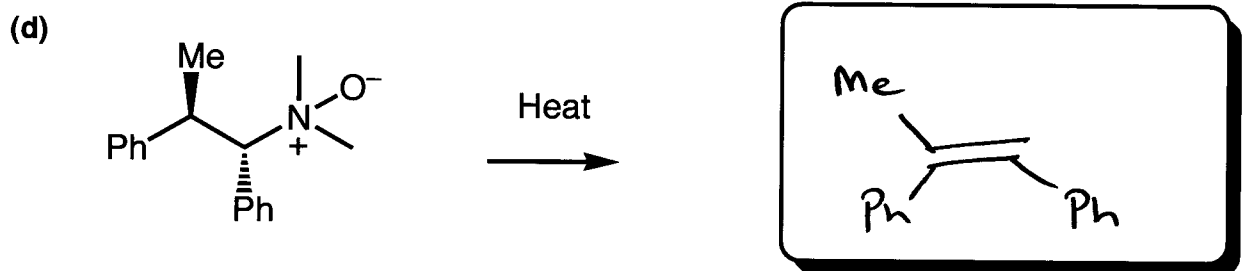
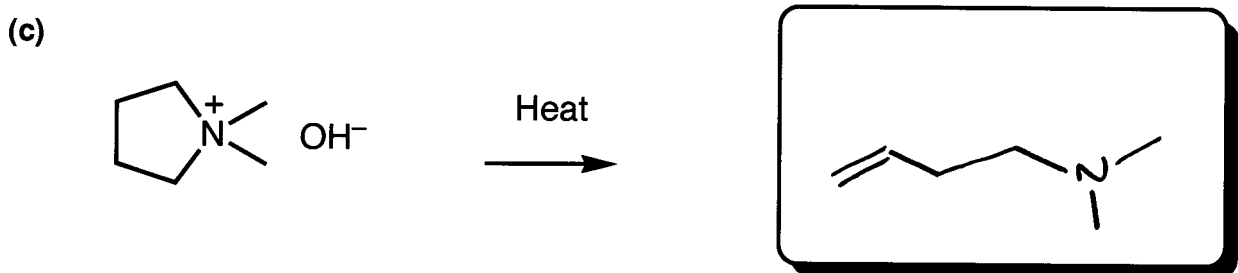
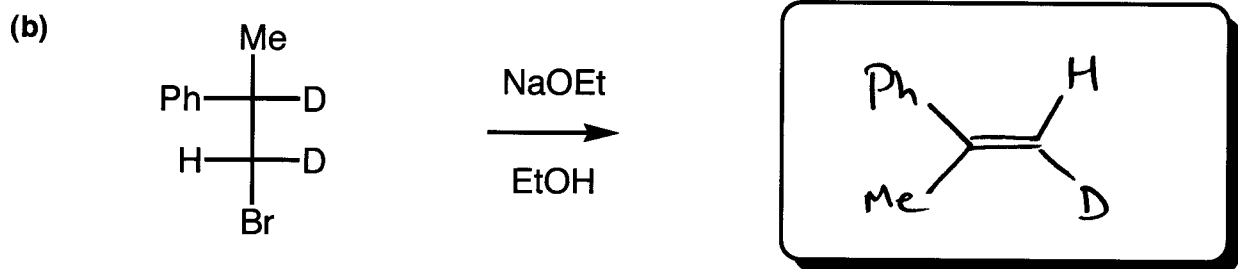
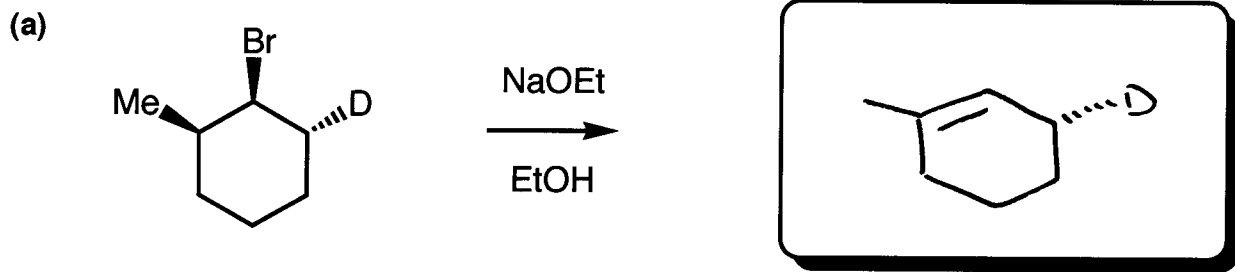
(e) No matter which of the six cycloalkenes (A–F) are reacted with hydrogen bromide (HBr), the same two diastereomeric compounds (L and M) are formed (each as a pair of enantiomers!) with the molecular formula $C_6H_{11}Br$. (4 points)



(f) When L undergoes an E1 elimination reaction, three isomeric alkenes can, in theory, be formed. The tetrasubstituted alkene P is the major product, a minor amount of the trisubstituted alkene O is formed, and only trace amounts of the disubstituted alkene N is observed (6 points)

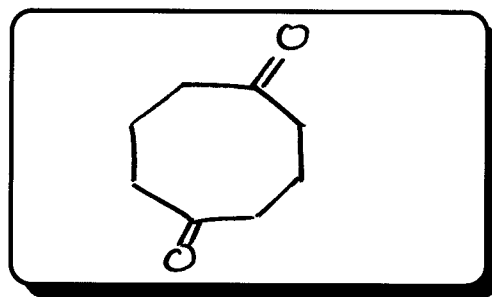
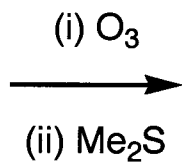
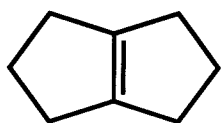


Q8. For each of the reactions shown below draw the MAJOR PRODUCT (paying particular attention to any appropriate stereochemical relationships) in the boxes provided. Note: for two-step reactions, just give the final product, DO NOT draw intermediates. (30 points)

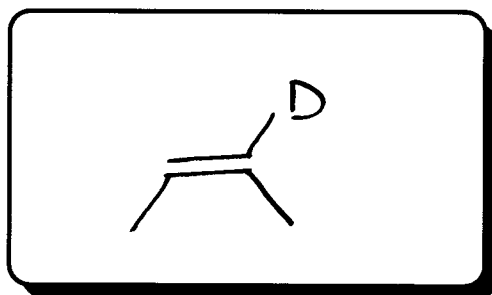
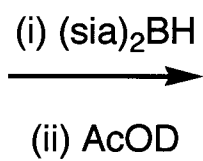


Question 8 is continued on the next page...

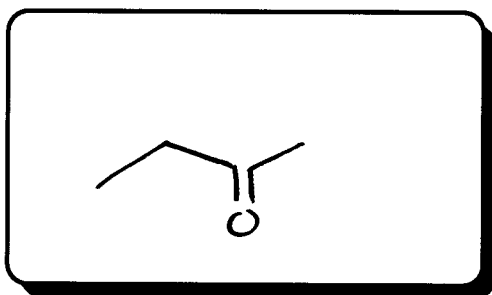
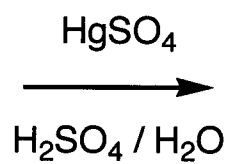
(f)



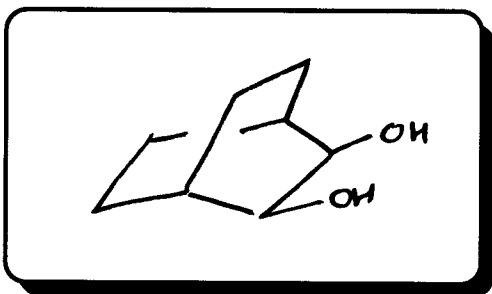
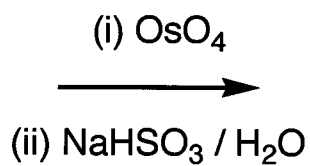
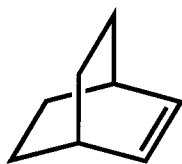
(g)



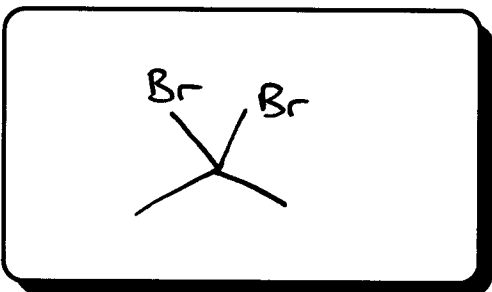
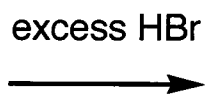
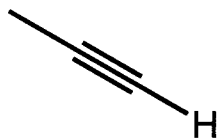
(h)



(i)



(j)



Q9. Propose a short sequence of reactions (you can't do it in one-step!) that converts 2,3-dimethyl-but-2-ene (**A**) into 2,3-butanedione (**B**) as depicted below. Show all intermediate compounds, and the reagents necessary for each transformation. **DO NOT SHOW MECHANISMS!** (15 points)

