

Name: _____

LAST Name: _____

First Name: _____

UNI: _____

First letter of
your last name

Final Exam: Part A

Spring 2024

May 7

On my honor, I have not given or received help on this examination.

SIGNATURE

You are expected to work in accordance with the Honor Code. Please refer to the Columbia College website section on [Academic Integrity](http://www.cc-seas.columbia.edu/integrity) for more details (www.cc-seas.columbia.edu/integrity). This Exam is closed notes, closed book, and WiFi/internet off (you must be “disconnected” after you download this file). Find a quiet space to complete this exam by yourself. You have **3 hr** to complete both parts (A & B) between the hours of **9:00 AM to 6:00 PM EST**. Submit your final exam in PDF format by email to ltl2126@columbia.edu and lcamos@columbia.edu no later than 6:00 pm on Tuesday 5/7/24. You may use a smart pad to fill out the document. Should you decide to print this, you must use a PDF converter in order to submit your document. Sample PDF converter: [TurboScan for iOS Devices](#); [TurboScan on Google Play](#).

DO NOT UPLOAD PHOTOGRAPHS of your file!

- The NMR charts and Periodic Table are also provided as separate files.
- Write your name on every page.
- In addition to this document (printed or in editable format), all you need is a pencil, pen, or e-pen and an eraser.
- Write your answers **clearly** and **concisely** on the space provided.

Good Luck!!!

Think about a major obstacle that you have overcome. How did it make you stronger? You don't have to share the obstacle if you don't want to, but try to reflect and write about how you felt stronger.

Front page: _____ /1

Page 1: _____ /21

Page 2: _____ /18

Page 3: _____ /24

Page 4: _____ /15

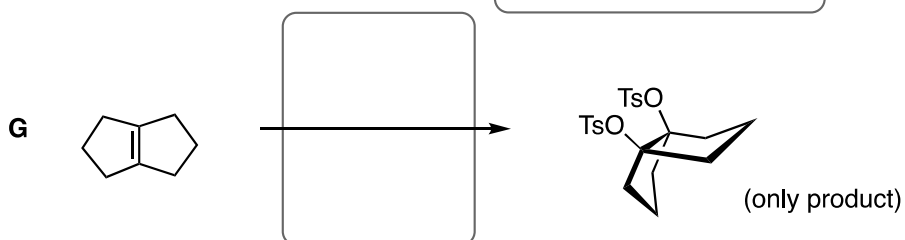
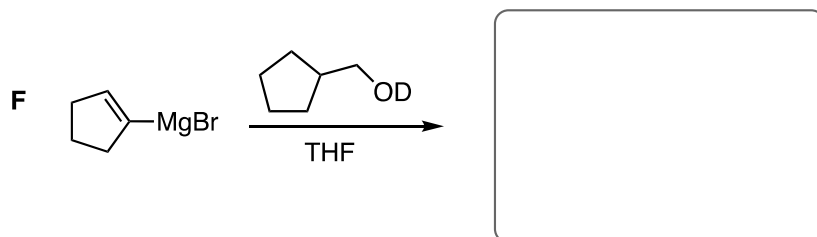
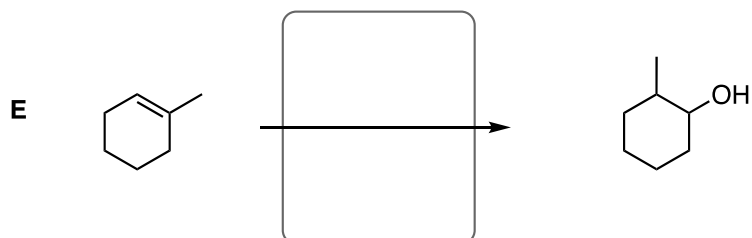
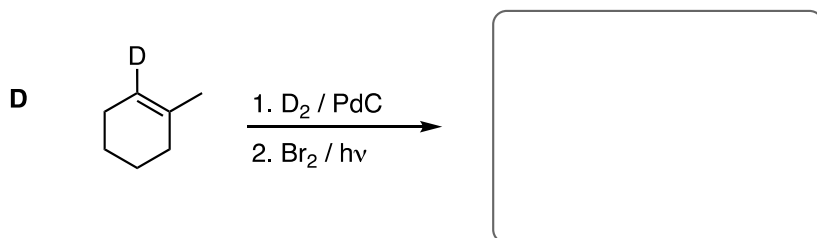
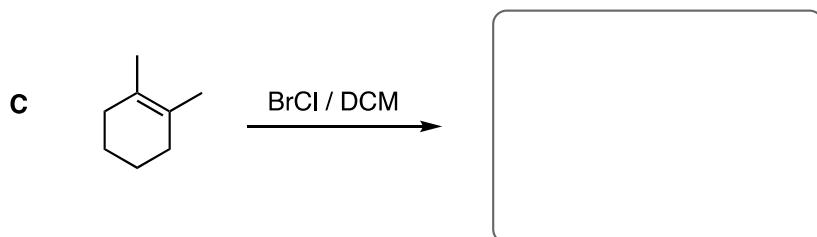
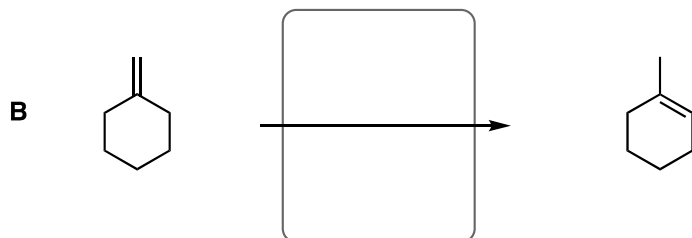
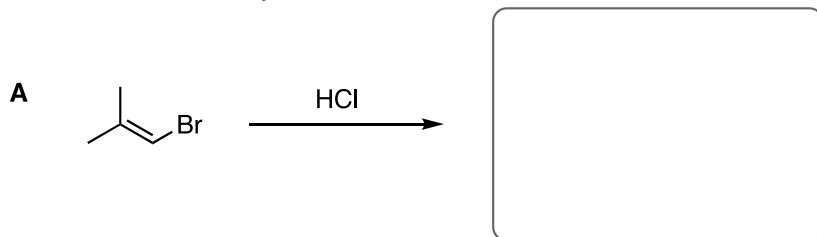
Page 5: _____ /12

Page 6: _____ /9

Total: _____ /100

Name: _____

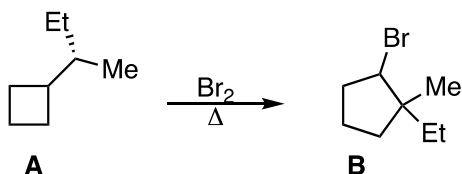
21 pts. 1. Draw the structure of the product(s) or reagents for the reactions below. Use dashes and wedges where necessary to show stereochemistry. In the case where a racemic mixture is obtained, **draw only one stereoisomer**.



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Name: _____

9 pts. **2a.** In the reaction below, product **B** was observed when compound **A** was heated in the presence of Br_2 . In the space provided, draw the **mechanism of the reaction**. You **do not have to include any termination steps**. Clearly label the *Rate Limiting Step (RLS)* and use dash/wedge formalism where necessary.



4 pts. **2b.** In the box below, draw the **Transition State Structure** of the rate limiting step (RLS).

Transition State Structure:

5 pts. **2c.** Explain the reason why chirality is lost in the product. *Use chemical structures to explain your answer!*

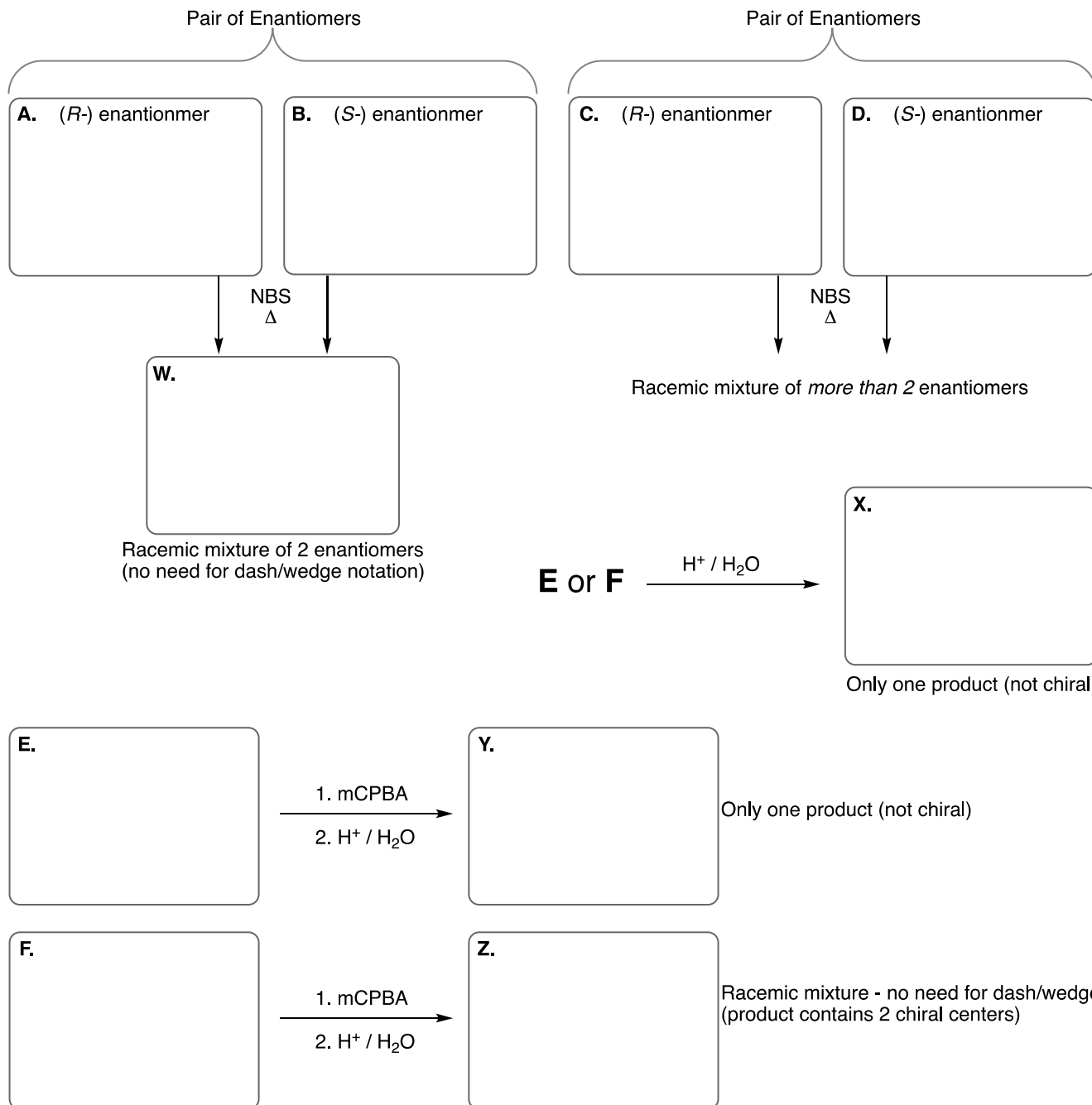


24 pts. 3. Compounds **A** – **F** are cyclic isomers of molecular formula C_7H_{12} . When **A** – **F** are reacted with H_2/PdC , all compounds yield only methylcyclohexane. In the boxes below, identify the structure of each C_7H_{12} isomer, in addition to their products (**W** – **Z**) when **A** – **F** reacted as described below.

Compounds **A** and **B** are enantiomers of each other. The allylic bromination of each of them yields the same product, but chirality is lost and a racemic mixture of two enantiomers is obtained (**W**).

Compounds **C** and **D** are enantiomers of each other. However, the allylic bromination of each compound **C** and **D** yields a racemic mixture containing more than two enantiomers (no need to identify those products).

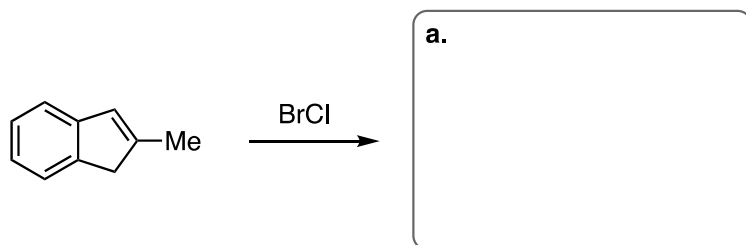
When either compound **E** or **F** are independently reacted with H^+/H_2O , the same product is obtained (**X**). To differentiate between **E** and **F**, compound **E** was reacted with mCPBA first, then H^+/H_2O , and only one product was obtained (no chiral centers). However, when **F** was treated the same way, a racemic mixture was obtained (the product was identified to have two chiral centers). For compound **Z**, draw only one structure.



Name: _____

The reaction below yields only one racemic product (a pair of enantiomers).

3 pts. **4a.** Draw the structure of the main product in the box below.

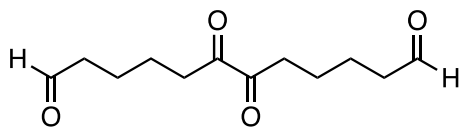


8 pts. **4b.** Draw the mechanism of the reaction above.

4 pts. **4c.** Explain the selectivity of the reaction above, which yields only one product. *Draw structures to aid your answer.*

Name: _____

6 pts. **5a.** Propose the synthesis of the compound below, starting from cyclohexane. *Hint: making a cyclohexene dimer can be helpful. Note that cyclohexyne is unstable – avoid making it.*

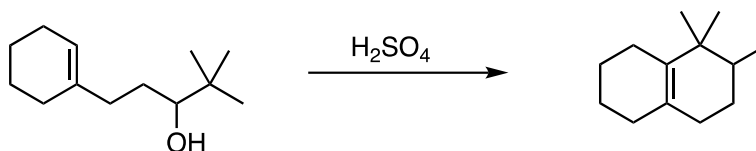


6 pts. **5b.** Draw the molecular orbital picture of the ketenimine: $\text{H}_2\text{C}=\text{C}=\text{NH}$. **Label** all molecular σ and π bonds and non-bonding orbitals.

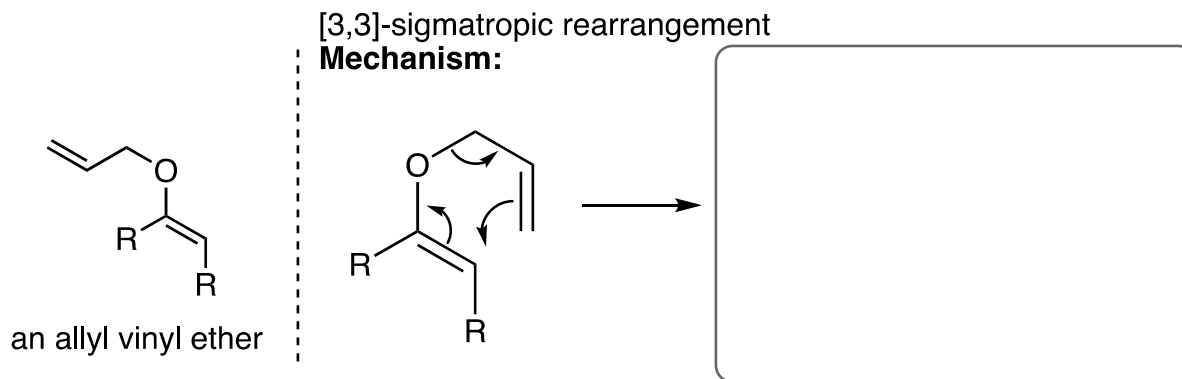


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6 pts. **6a.** Draw the mechanism that accounts for the reaction below.



3 pts. **6b.** Next semester you will learn another pericyclic reaction – the Claisen rearrangement. Heating an allyl vinyl ether leads to a (so called) [3,3]-sigmatropic rearrangement. The mechanism for the reaction occurs in **one step**. Considering the flow of electrons shown by the arrows, **draw the structure of the product** in the box.



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Final Exam: Part B

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Page 8: _____ /22

Page 9: _____ /25

Page 10: _____ /10

Page 11: _____ /8

Page 12: _____ /16

Page 13: _____ /12

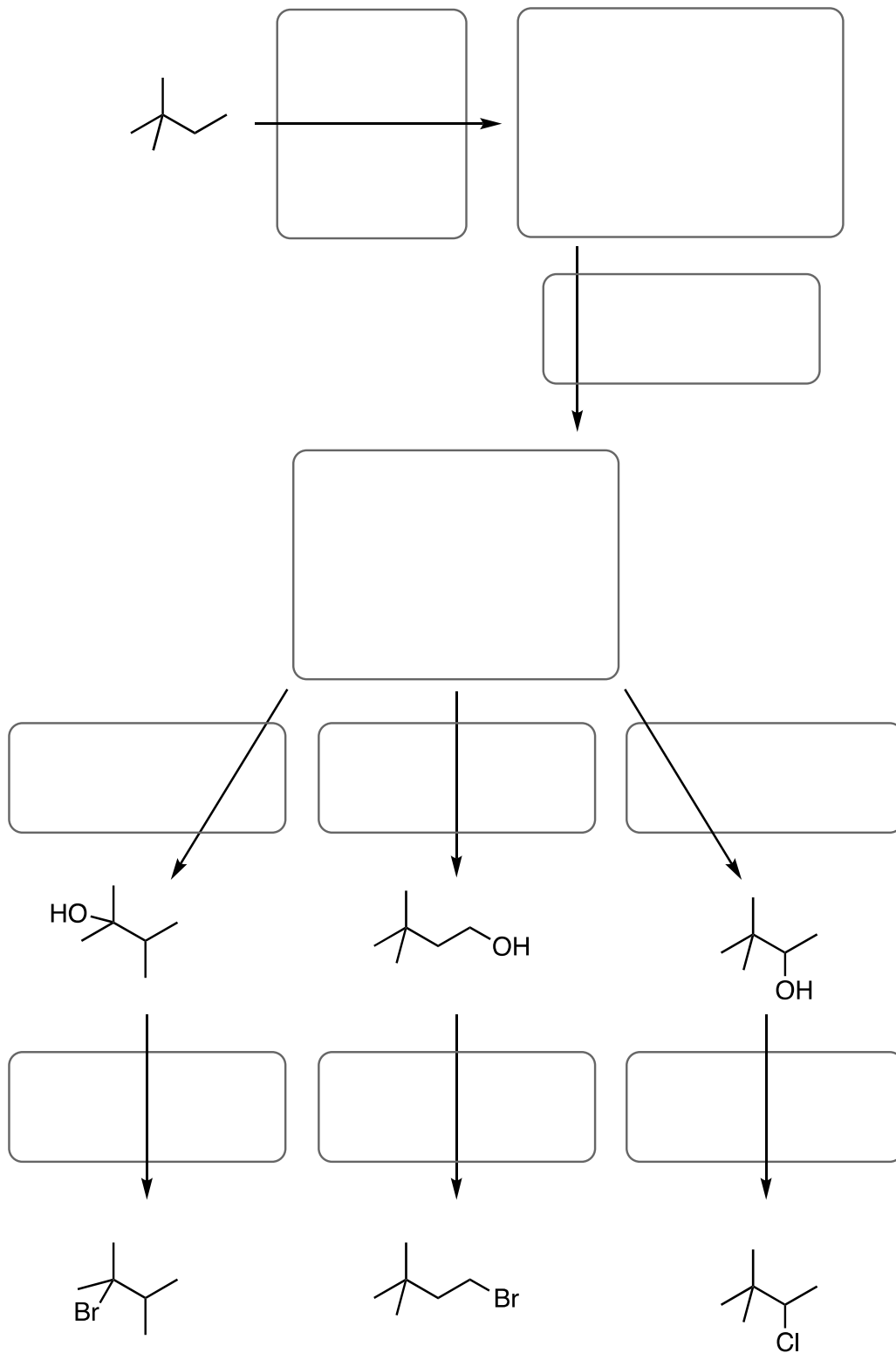
Page 14: _____ /7

Total: _____ /100

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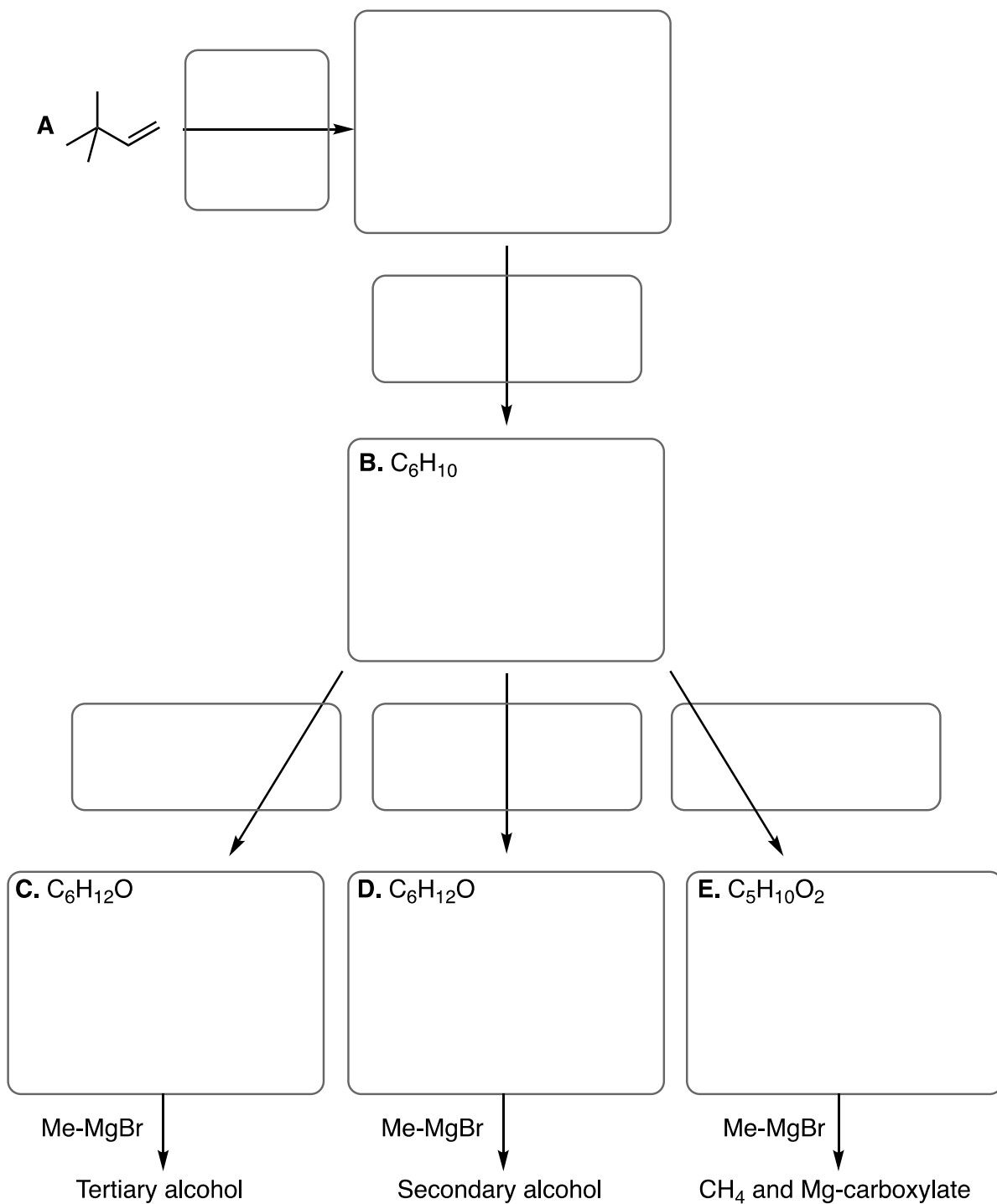
22 pts. 1. Fill in the missing compounds, reagents, and reaction conditions in the boxes below.



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Name: _____

25 pts. 2. Fill in the missing compounds, reagents, and reaction conditions in the boxes below. The next page contains the ^{13}C -NMR spectra of compounds **A** – **E**. You may use that information to identify/confirm your answers on this page. In going from compound **A** to **B**, the first reaction is an “Addition” reaction and the second is an “Elimination” reaction.



Name: _____

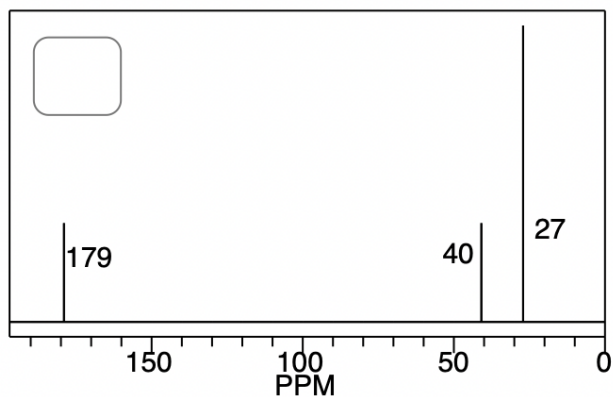
10 pts. 3. These are the ^{13}C -NMR spectra of compounds **A** – **E** from the previous page. In the corresponding boxes, add the label that matches compounds **A** – **E**.

Notes:

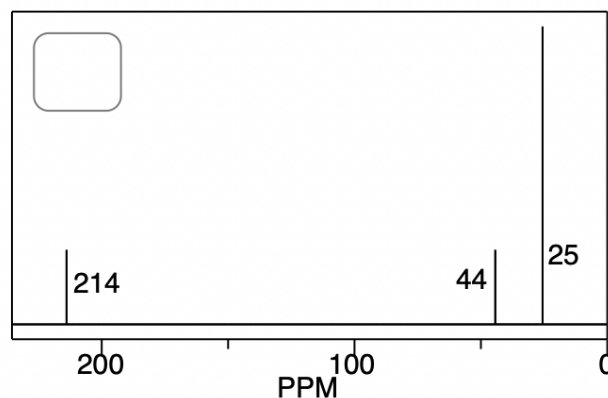
The spectrum of **b** has two overlapping signals at 25 ppm.

The ^1H -NMR (not shown) of **c** has a sharp peak at 9.7 ppm.

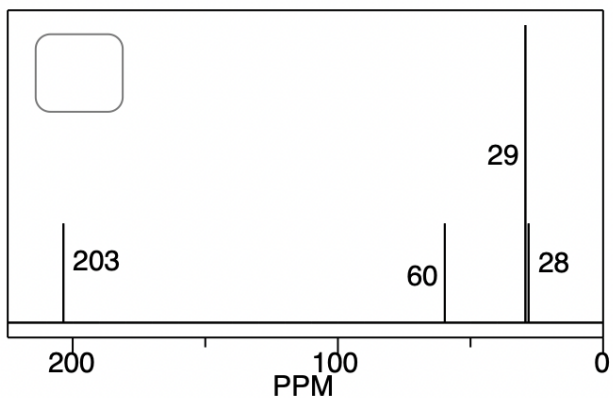
a.



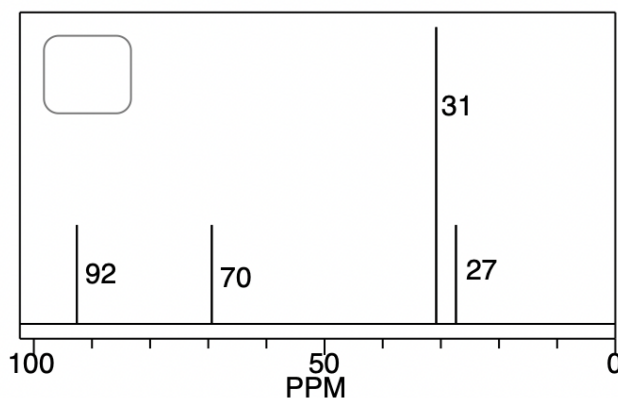
b.



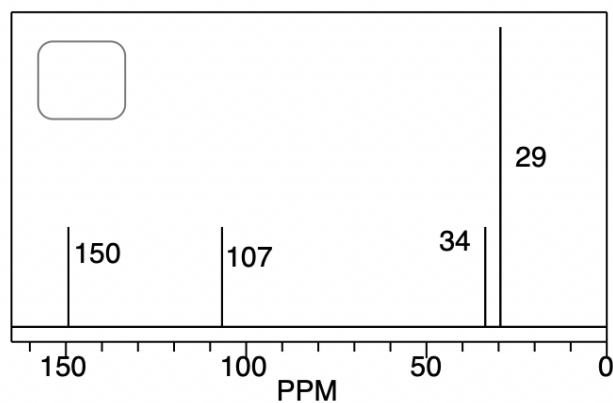
c.



d.



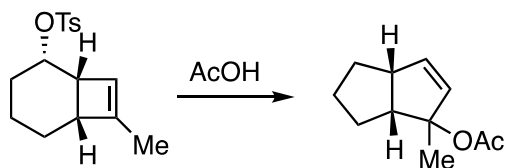
e.



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8 pts. 4. In the reaction below, the tosylate surprisingly solvolyzes in acetic acid (AcOH) to yield the bicyclic product in the scheme. Propose the mechanism that accounts for the formation of the product below.



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8 pts. 5. What is the major product when the following alkyl chlorides are reacted with AlCl_3 and benzene?

1-chloropentane



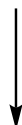
3-chloropentane



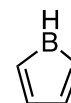
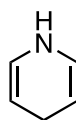
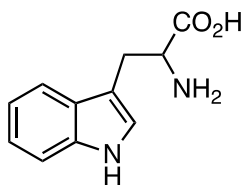
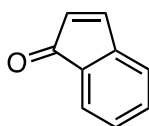
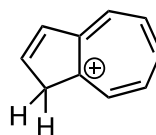
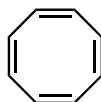
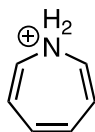
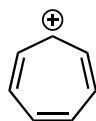
1-chloro-3-methylcyclopentane



1-chloro-2-methylcyclopentane



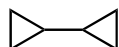
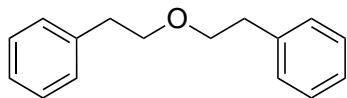
8 pts. 6. Circle the aromatic compounds.



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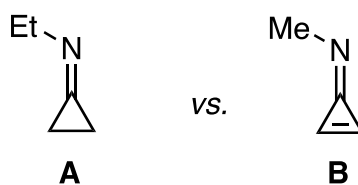
Name: _____

12 pts. 7. Propose the synthesis of the compounds below, using **benzene**, **acetylene**, and any **organic compound that contains only one carbon** (e.g. methane, chloromethane, etc) as your only sources of carbon. You may use any other reagents to carry out the necessary transformations.



Name: _____

7 pts. 8. Consider the two imines below. Which one do you expect to be the stronger base? Explain your answer below. Use structures to aid your answer.



pts. this pg.