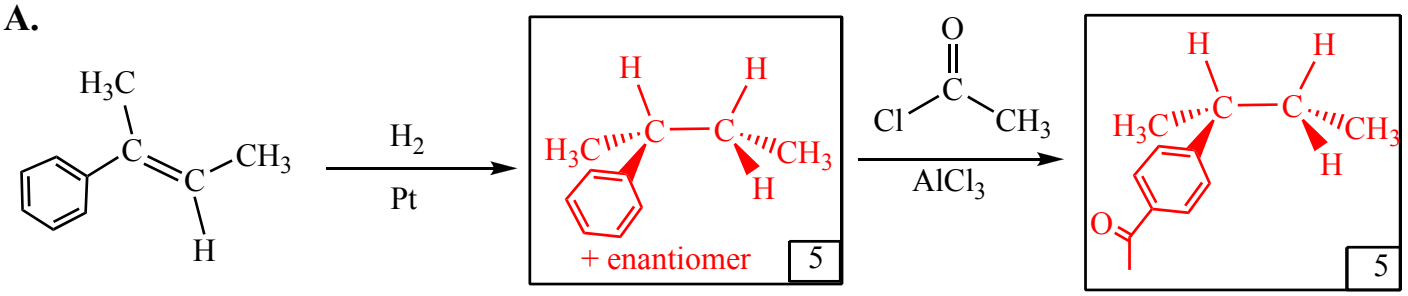
Name **KEY**

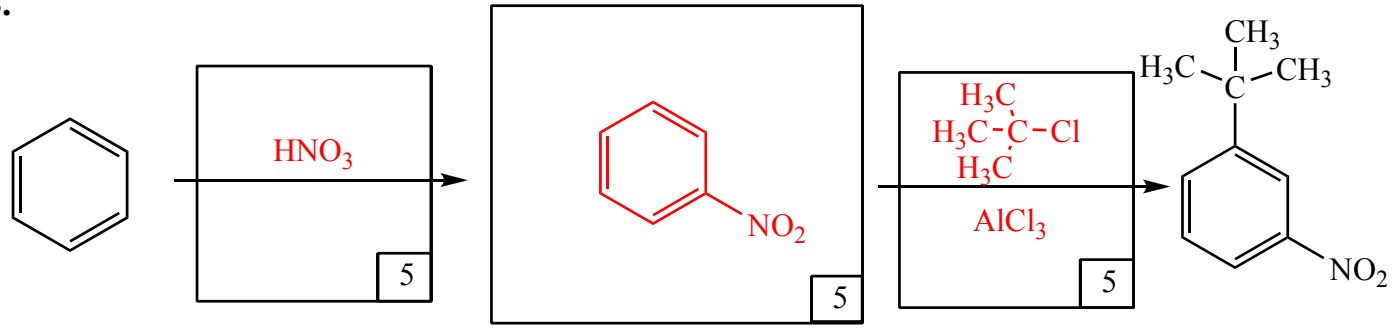
I. (38 points)

Complete the following reactions as directed. Transformations requiring sequential experimental steps should be numbered appropriately. Show the major organic product(s) unless otherwise specified. Abbreviations for reagents are **not** allowed. If a product forms as a stereoisomeric mixture, draw one and write "+enantiomer" or "+diastereomer" in the box.

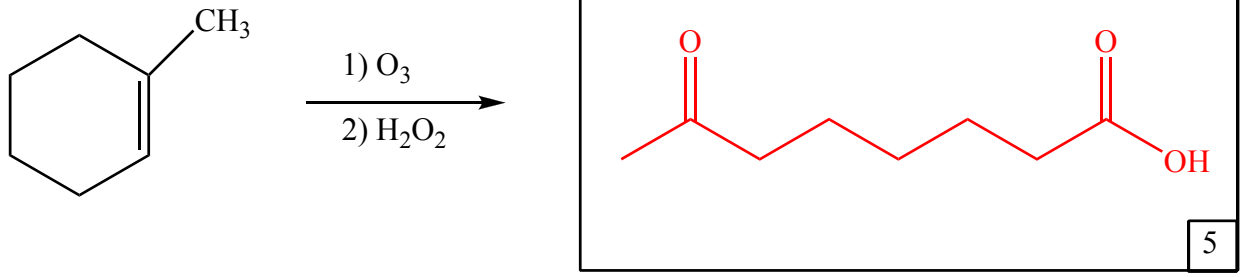
A.



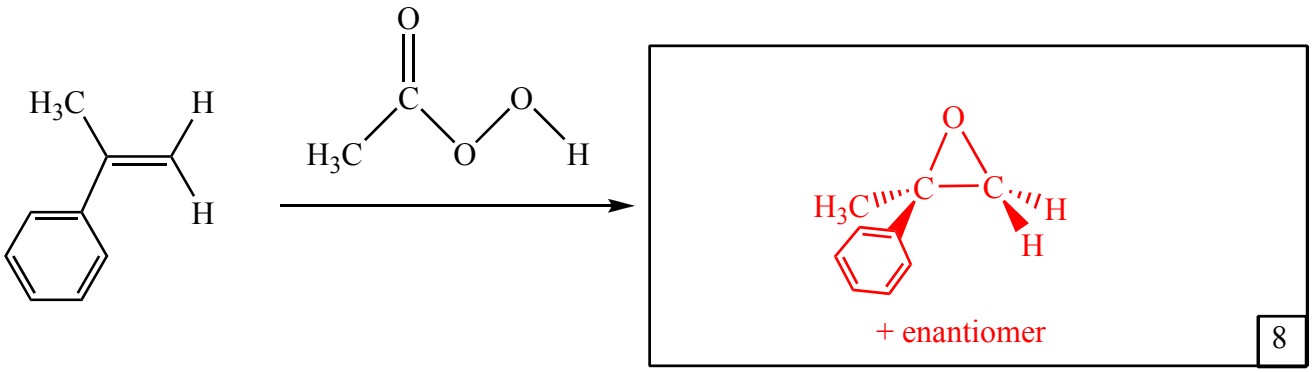
B.



C.

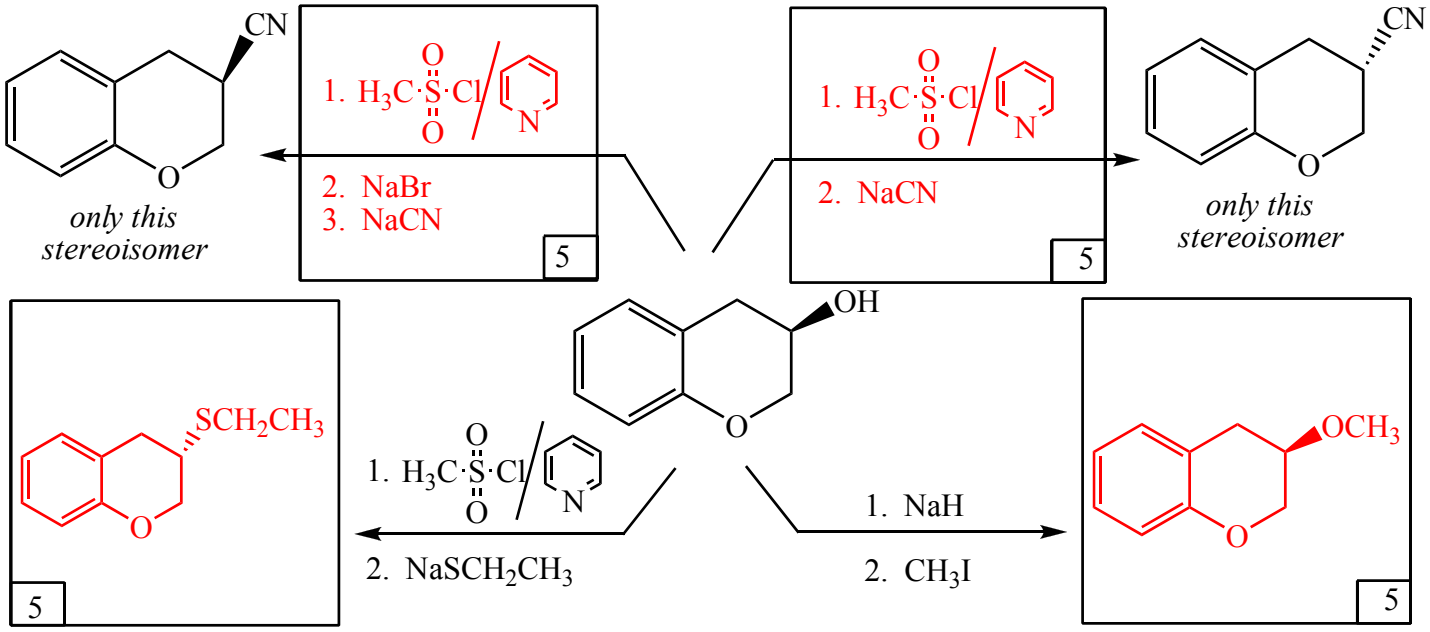


D.

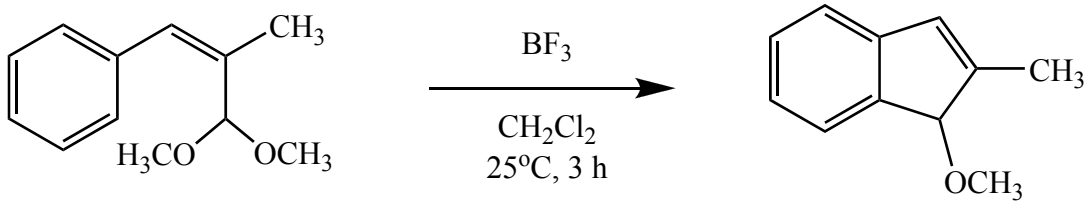


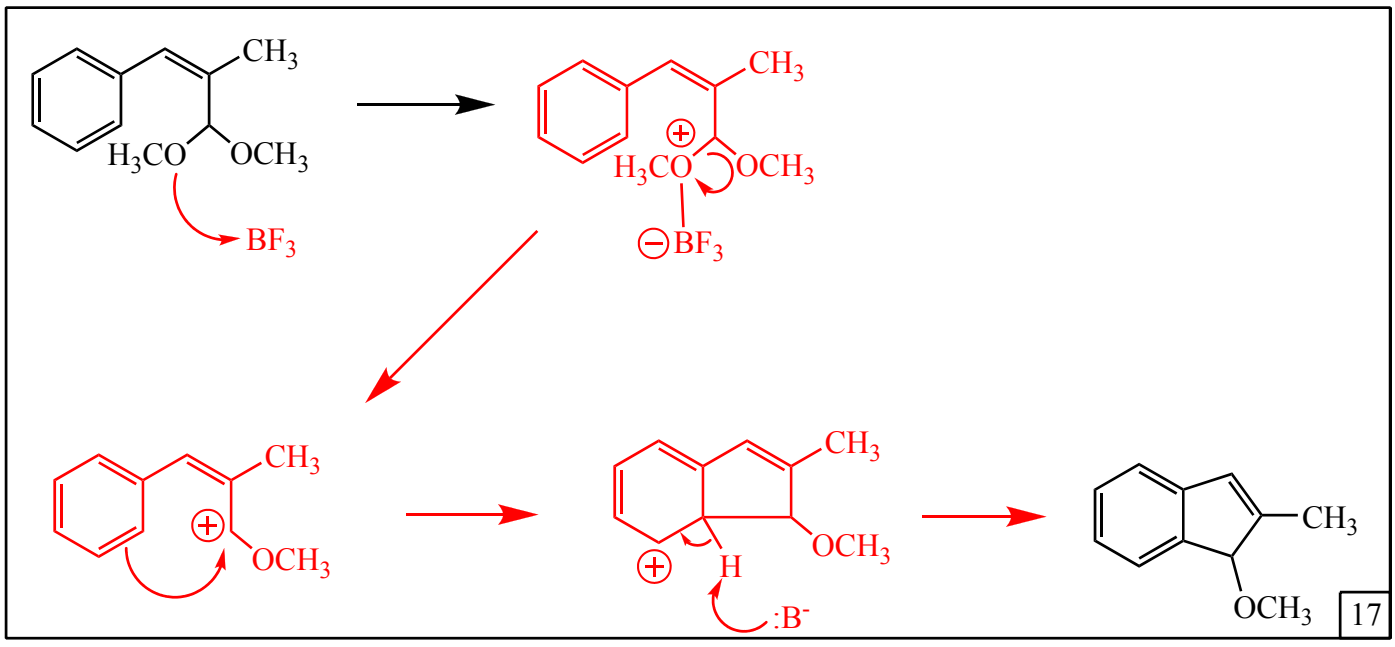
II. (37 points)

A. Complete the following multi-step reactions starting from the starting material in the center below. Be sure to number steps where required. If a mixture of stereoisomers results, draw one and write "+enantiomer" or "+diastereomer" in the box. If a mixture of structural isomers results, draw the predicted major product.



B. The following reaction was recently reported (*Tetrahedron,* **2006**, *62*, 5717). In the box below, show the mechanism of this reaction. Use H-B and B^- for any Bronsted acids or bases, if needed. NOTE: Under certain conditions, alkoxy groups (like "OCH_3") can react with a Lewis acid to form a good leaving group.

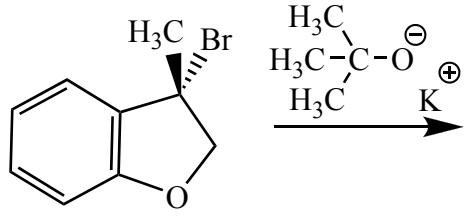




III. (33 points)

A. When **Compound A** is treated with a stong hindered base, a mixture of structurally isomeric products results. Draw these products.

i)



Compound A

Product B 4

Product C 4

ii) What mechanism is predicted to form these products?

(circle one)

S_N1 S_N2 E1 **E2** Electophilic addition EAS

3

iii) Due to relative stability, one of the two products above forms to a much greater extent then the other. Which is the more stable product and why?

More stable:
(circle one)

Product B

Product C

2

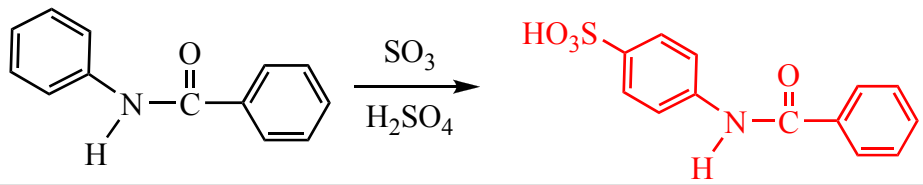
Why?

Elimination to form product B produces an aromatic ring.

4

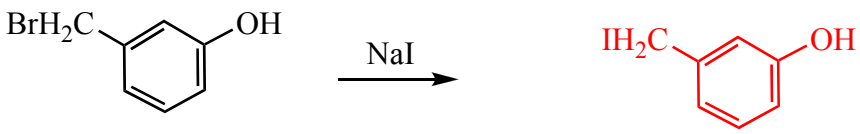
B. Each of the following reactions afford one predominant monosubstitution product. Draw the product.

i)



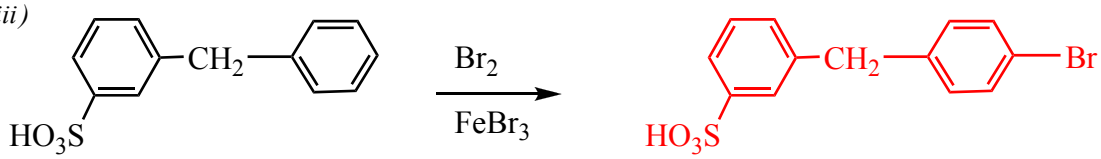
4

ii)



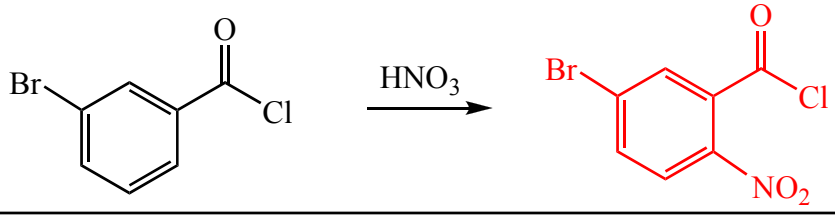
4

iii)



4

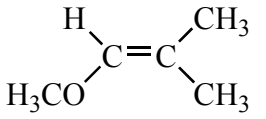
iv)



4

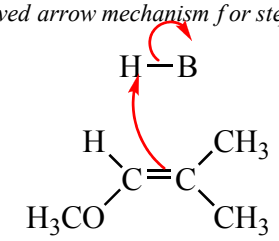
IV. (49 points)

The following three-step reaction can create two different regioisomeric products. Complete the reaction mechanism with curved arrows and structures as needed and as indicated. Use H-B and B^- for any Bronsted acids or bases needed.

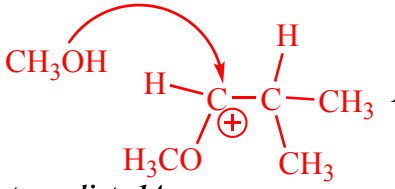


CH_3OH, H_2SO_4 (cat) → Two regioisomeric products

i) curved arrow mechanism for step 1 — 3

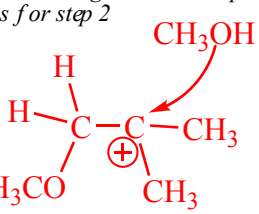


ii) intermediate leading to the major product & curved arrows for step 2



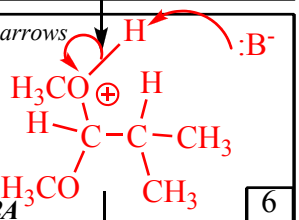
Intermediate 1A — 6

iii) intermediate leading to the minor product & curved arrows for step 2



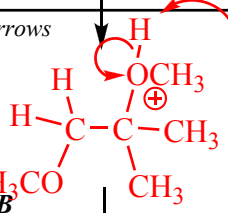
Intermediate 1B — 6

iv) structure and arrows



Intermediate 2A — 6

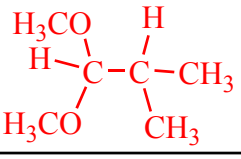
v) structure and arrows



Intermediate 2B — 6

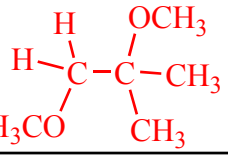
Include the intermediate structure and the curved arrows for the next step in these boxes!

Product A — 6



vi) Major regioisomeric product

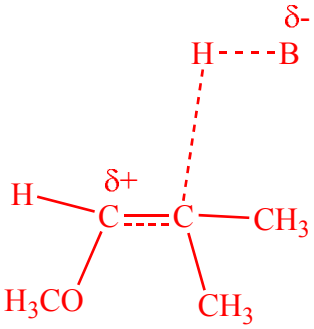
Product B — 6



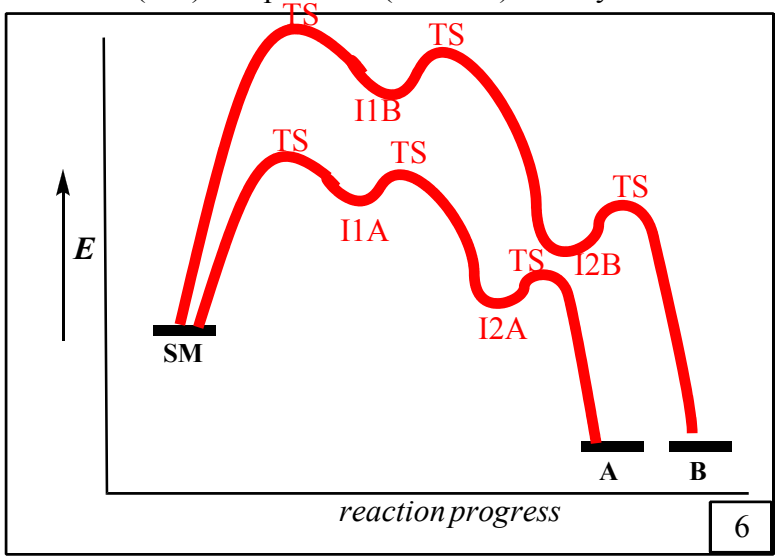
vii) Minor regioisomeric product

viii) Draw the structure of the transition state from the step between the starting material and Intermediate 1A.

vi) transition state drawing — 4



ix) Draw an energy diagram of the above reaction. Indicate the locations of all intermediates (I1A, I1B, I2A, I2B), and all transition states (TS). Use the locations of the starting materials (SM) and products (A and B) already drawn.



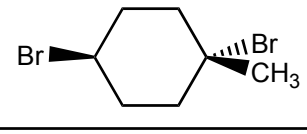
6

V. (53 points)

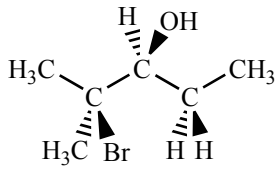
Name **KEY**

A. There are seven molecules shown. For each question, you should circle the letter corresponding to the molecule for which the statement is true. You will be graded by the molecule, not the question,

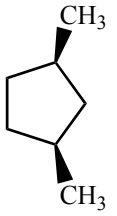
A



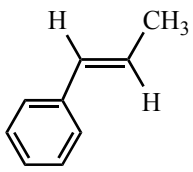
B



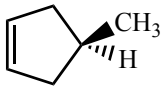
C



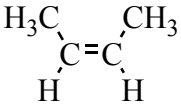
D



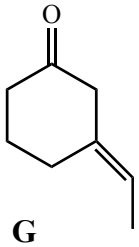
E



F



G



i. Circle the letters for those molecules (A-G) that...

	A	B	C	D	E	F	G
		S	SR	E		Z	E
a) ... has an enantiomer	A	**B**	C	D	E	F	G
b) ... has at least one (R)-stereocenter	A	B	**C**	D	E	F	G
c) ... is optically active	A	**B**	C	D	E	F	G
d) ... is unique and has no stereoisomers	A	B	C	D	**E**	F	G
e) ... has at least one optically inactive diastereomer	**A**	B	C	**D**	E	**F**	**G**
f) ... has at least one optically active diastereomer	A	B	**C**	D	E	F	G
g) ... is a meso compound	A	B	**C**	D	E	F	G
h) ... forms a racemic mixture upon addition by OsO_4	A	B	C	**D**	E	F	**G**
	3	3	3	3	3	3	3

ii. Give the full name of compounds B and F in the appropriate box below.

Compound B

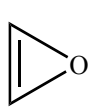
(*S*)-2-bromo-2-methylpentan-3-ol [6]

Compound F

(*Z*)-but-2-ene [6]

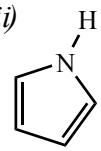
C. For each of the following compounds, count the number of electrons contained in the cyclic π system - is it aromatic?

i)



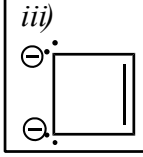
π electrons: 4 — *aromatic?* **Yes** / **No** [4]

ii)



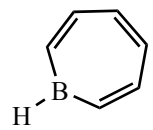
π electrons: 6 — *aromatic?* **Yes** / **No** [4]

iii)



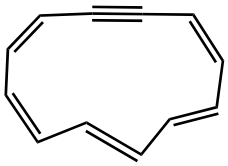
π electrons: 6 — *aromatic?* **Yes** / **No** [4]

iv)



π electrons: 6 — *aromatic?* **Yes** / **No** [4]

v)

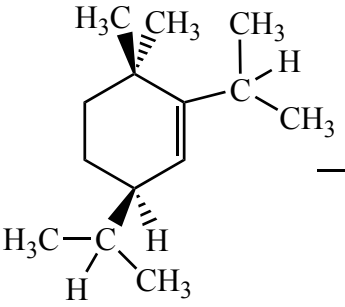


π electrons: 12 — *aromatic?* **Yes** / **No** [4]

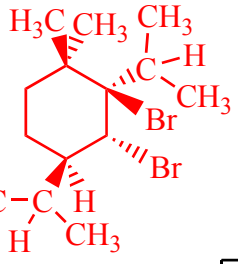
VI. (30 points)

Name **KEY**

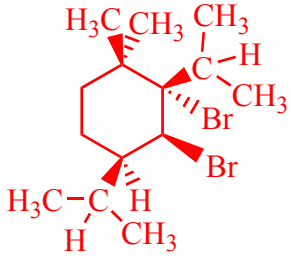
A. i. The following bromination reaction results in the formation of two stereoisomeric products. Draw them in the spaces below.



Br_2



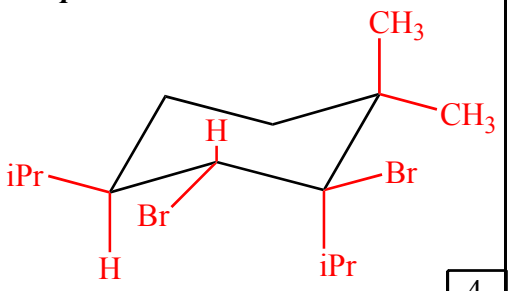
Compound D 4



Compound E 4

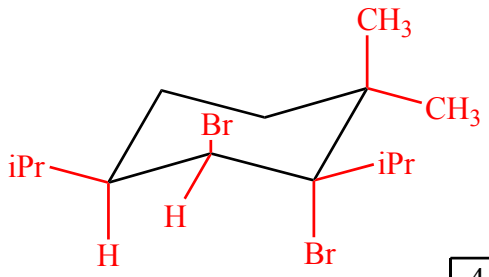
ii. Draw in the substituents for the **most stable** chair form of compounds D and E on the chairs below. You may use the abbreviation iPr for the isopropyl groups. Be sure to put the right compound in each box. The information in the table on the right may be useful.

Compound D



4

Compound E



4

equitorial $\rightleftharpoons$ axial

ΔG^{o}_{eq}

-X	ΔG^{o}_{eq}(kcal/mol)
$-CH_3$	1.7
$-CH_2CH_3$	1.8
$-CH(CH_3)_2$	2.1
$-C(CH_3)_3$	5.4
-OH	1.0
-Cl	0.5
-Br	0.6

iii. When the mixture of compounds D and E was reacted with sodium ethoxide in ethanol for a short period of time, only one of the two compounds reacted. Which compound reacted, why, and what is the product of that reaction?

Compound D or *Compound E* $\xrightarrow[CH_3CH_2OH]{NaOCH_2CH_3}$ Product F

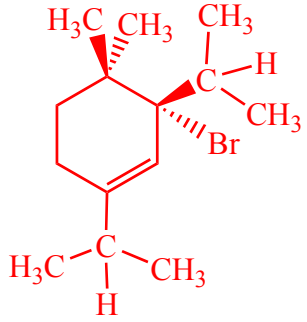
Which reacts with ethoxide? (*circle one*) *Compound D* *Compound E* 3

Why that one and not the other?
One or two sentences will suffice.

In compound E, one of the bromines is ANTI to a β-H.
That is not true in compound D.

6

Draw Product F here



5