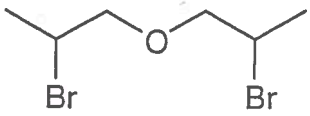
EXAM 1, Sp '02

-1 for incorrect # or alpha order

A. Nomenclature (3 points each; 9 total points)

Please provide an acceptable name for each of the following compounds, noting stereochemistry where appropriate.

1.



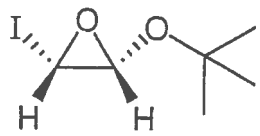
goes in front! yes, I lost 1 point!

1-(2-bromopropoxy)-2-bromopropane

OR

2-bromopropyl 2-bromopropyl ether

2.



(2S,3S)-

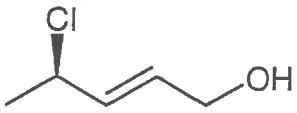
or

cis-2-t-butoxy-3-iodooxirane

OR

cis-1-t-butoxy-1,2-epoxy-2-iodo ethane

3.



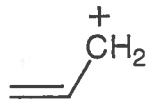
(2E,4R)

or

trans-(R)-4-chloro-2-penten-1-ol

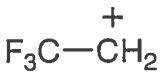
B. Facts (1 point for every blank; 19 total points)

1. Rank the stability of the following cations from lowest (**1**) to highest (**3**).



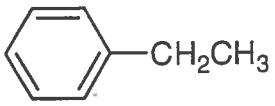
2

3

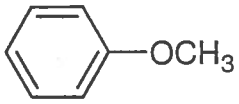


1

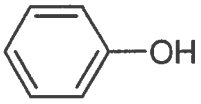
2. Rank the boiling points of the following molecules from lowest (**1**) to highest (**3**).



1



2

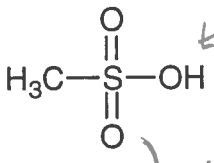


3

3. Rank the pK_a value of the following molecules from lowest (**1**) to highest (**3**).

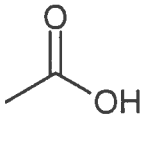
most acidic

least acidic

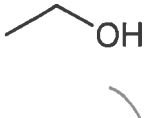


most acidic

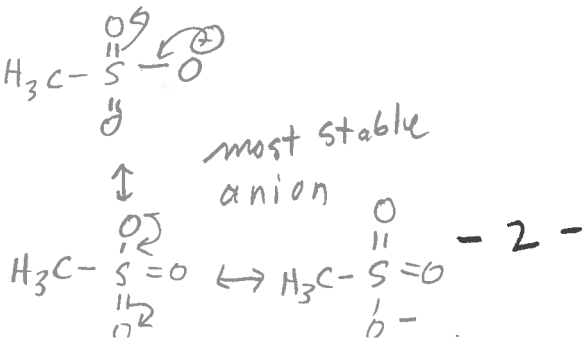
1



2



3



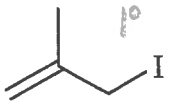
most stable anion

- 2 -

least stable anion from least acidic acid

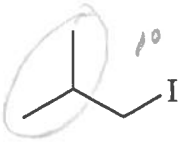
→ S_N2

4. Rank these molecules from slowest (**1**) to fastest (**3**) in their rate of reaction with $NaOCH_3$.



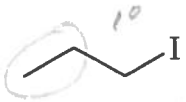
3

- allylic halide
- 40× faster than alkyl halide



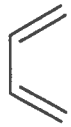
← slightly more crowded

1

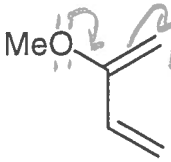


2

5. Rank the following molecules from slowest (**1**) to fastest (**3**) in their rate of Diels-Alder reactivity.

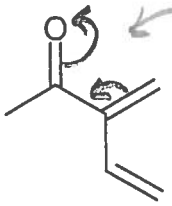


2



← e- donation increases reactivity

3

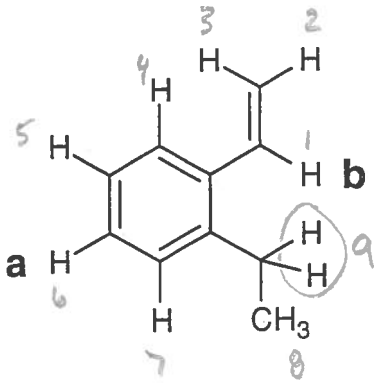


← e⁻ withdrawal decreases reactivity

1

These are dienes. The more e- rich the diene, the faster the Diels-Alder reaction rate.

6. Answer the following questions for the molecule shown below and place the answers in the appropriate boxes. (i) How many distinct proton types are present in the molecule? (ii) How many signals would appear in the proton-decoupled ^{13}C NMR spectrum? (iii) & (iv) What are the theoretically predicted multiplicities (splitting patterns) of the signals for protons **a** and **b**?



(i) number of distinct proton types: [9]

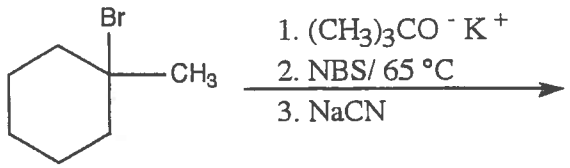
(ii) number of carbon signals: [10]

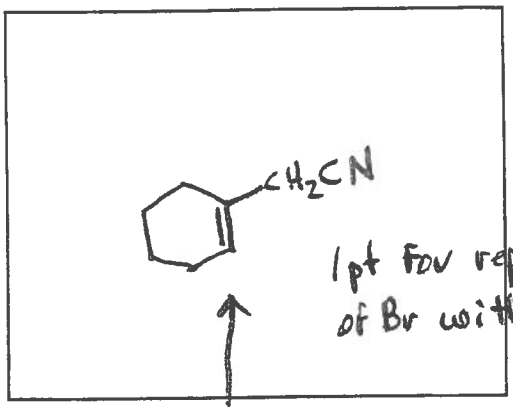
(iii) multiplicity of H_a: [dd] or 4 lines

(iv) multiplicity of H_b: [dd] or 4 lines

C. Reactions: Total = 30 points, 5 points each
Please provide the starting material or major product in the answer box. Be sure your drawing indicates stereochemistry if applicable. Partial credit is awarded only when intermediate products are shown below the reaction.

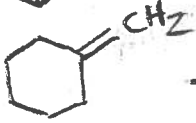
1.



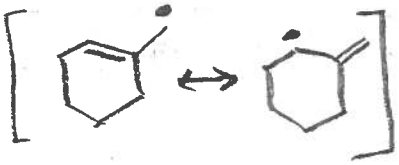


1pt for replacement of Br with CN

1)

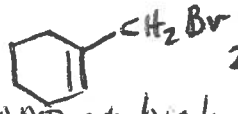


2)



2pts

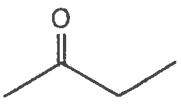
(1pt for internal)



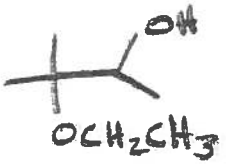
MAT at high T

2pts (1pt for Br on ring

2.



1. CH_3MgBr
2. H_2SO_4 / Heat
3. MCPBA
4. CH_3CH_2OH / H^+



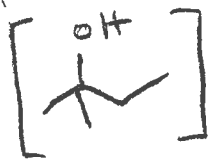
1.

2)

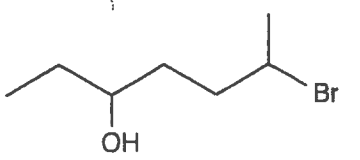
3)

4)

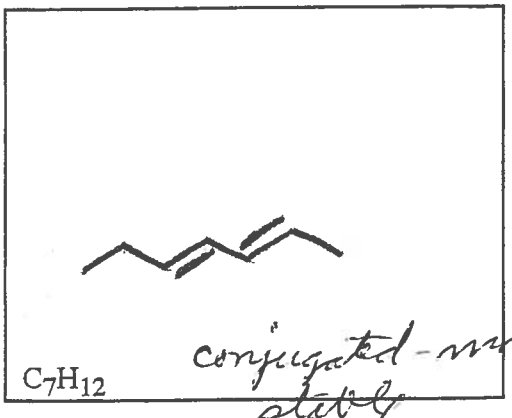
1pt 1pt 1pt



3.



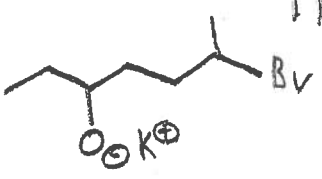
1. $(CH_3)_3CO^-$ K^+ / Heat
2. HI (xs)
3. $CH_3CH_2O^-$ Na^+



conjugated - more stable

1)

1pt

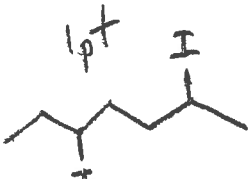


1pt

2)

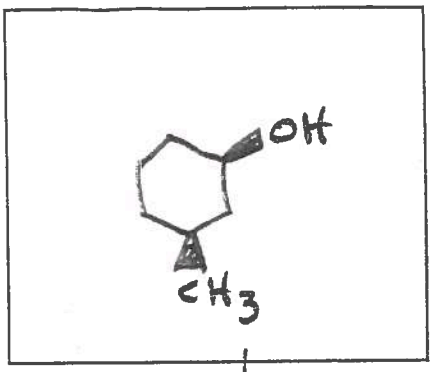
4

1pt

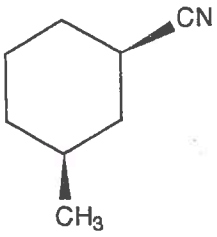


3)

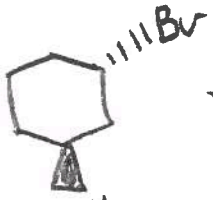
4.



1. PBr_3
2. NaCN



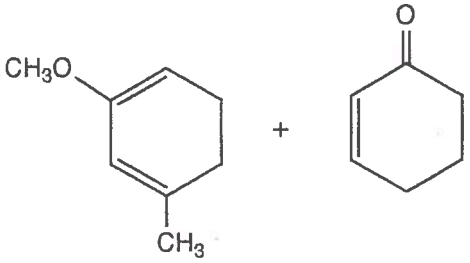
1)



2)

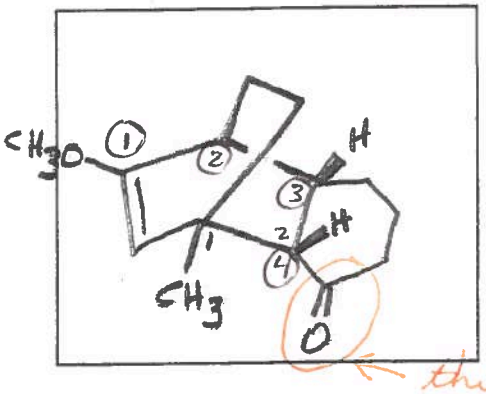
3pts

5.



+

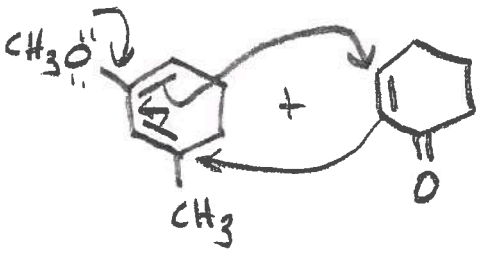
$\xrightarrow{\Delta}$



-2 wrong regiochemistry

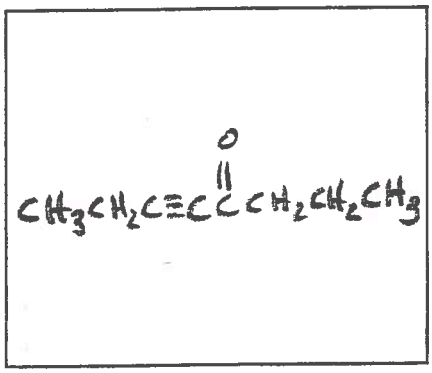
-1 for any wrong stereocenter

this is the e⁻ withdrawing group (W)

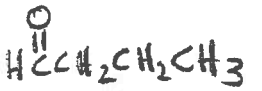


6. H-C≡C-CH_2CH_3

1. Sia_2BH
2. H_2O_2 / ^-OH
3. CH_3CH_2-C≡C $^-Na^+$
4. H_3O^+
5. PCC

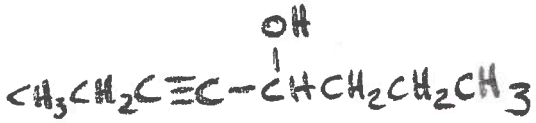


1)
2)



2pts

3)
4)



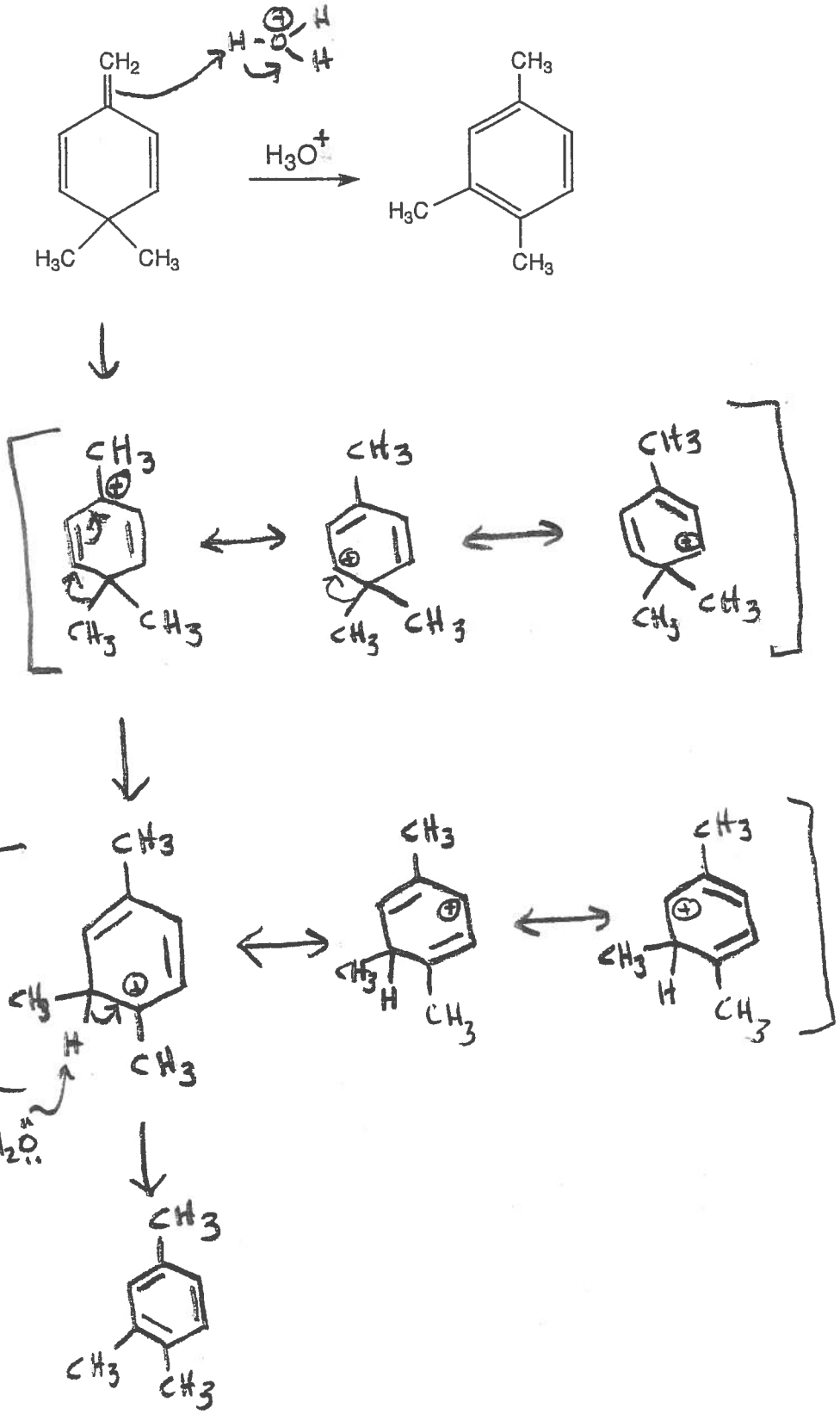
5)

2pts

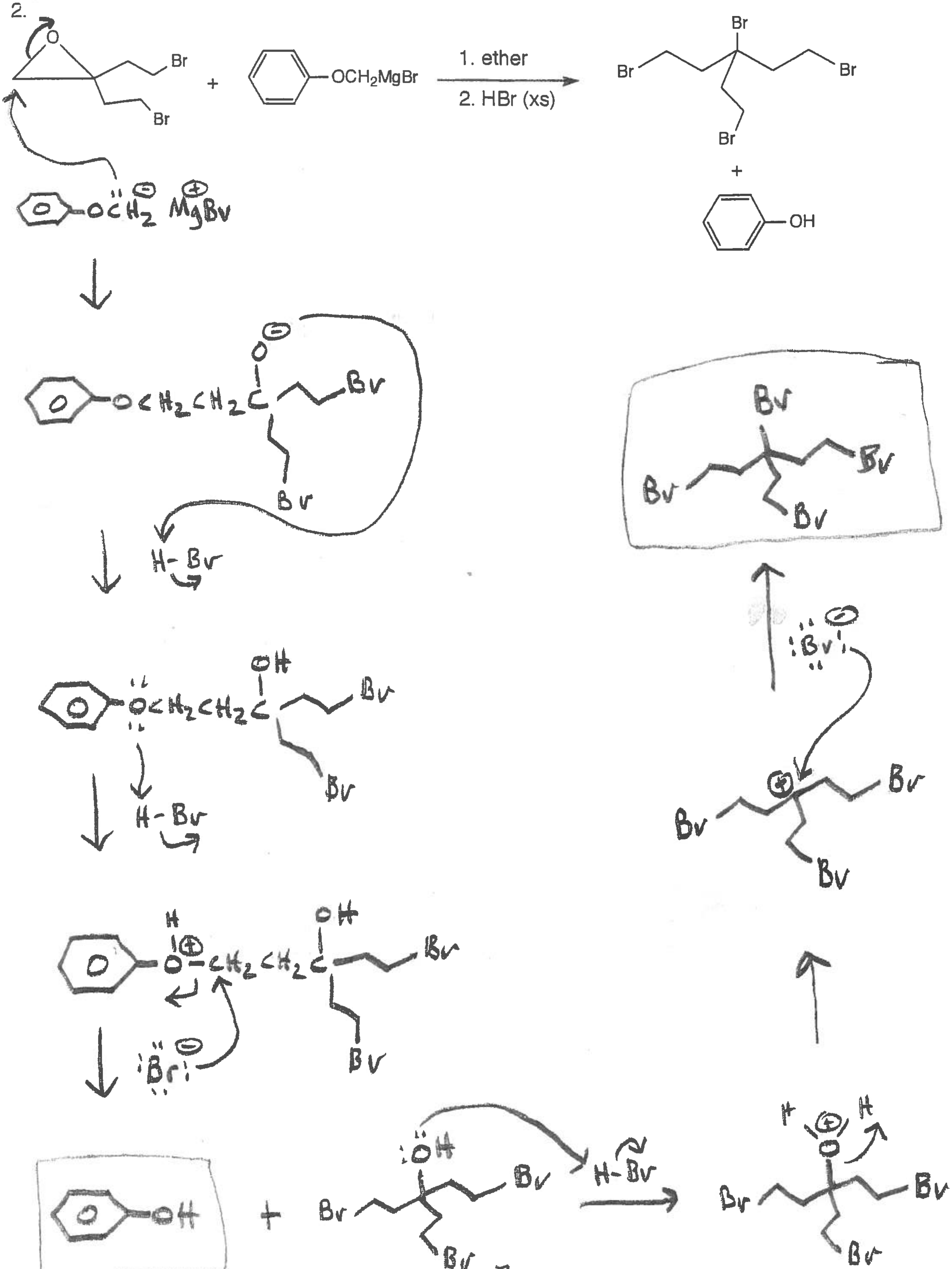
D. Mechanisms: (9 points each)

Provide clear mechanisms for reactions 1 and 2. Use curved arrows to indicate "electron flow". Remember to show only one step at a time. **Show all intermediates and all formal charges**. If there is more than one resonance structure, you must show the "best" (i.e. lowest energy) structure.

1.

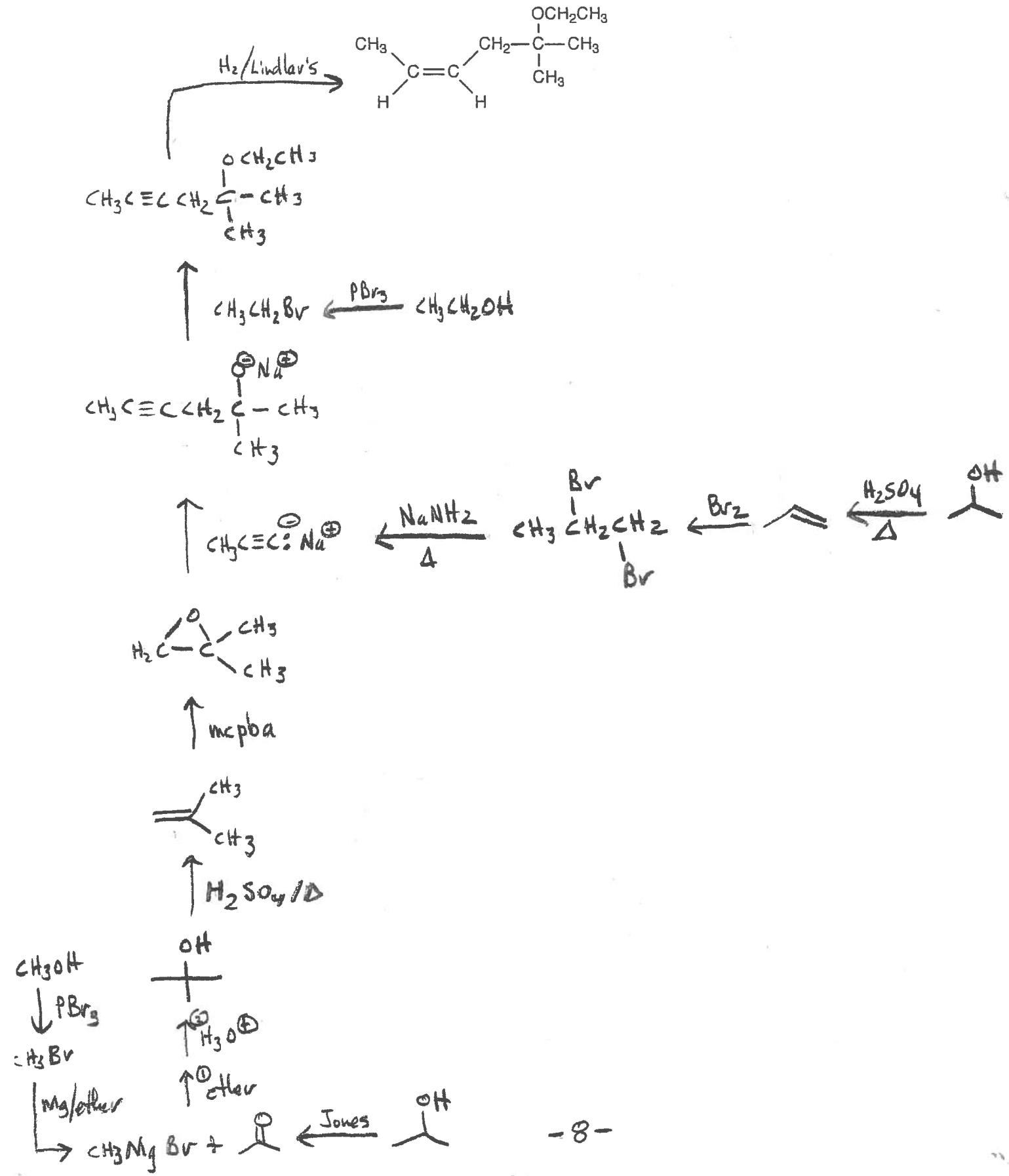


2.



E. Synthesis: (14 points)

Synthesize the molecule below using any of the following reagents: alkanes, alkenes or alcohols of **three carbons or less**, any inorganic reagents, any oxidizing or reducing agents, and any peroxyacids.



F. Spectroscopy: 10 Points

A compound with the formula $C_7H_{16}O_2$ exhibits the IR, ^1H NMR, and proton-decoupled ^{13}C NMR spectra shown on the following page. Please identify this compound and draw the structure in the box provided below.