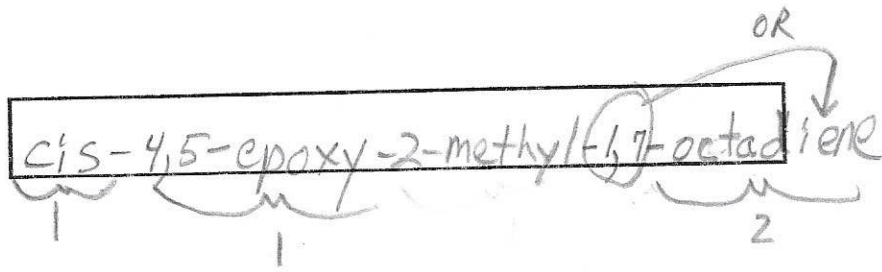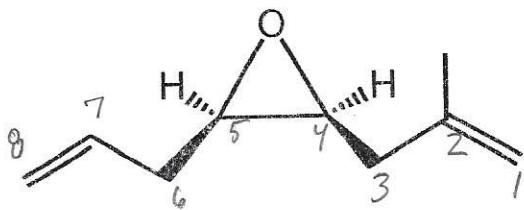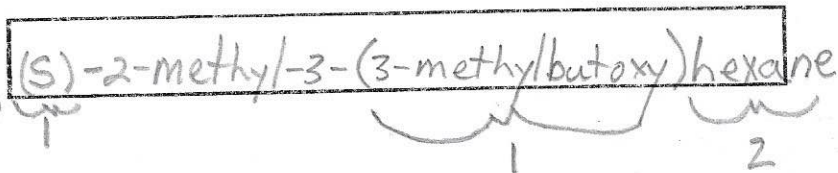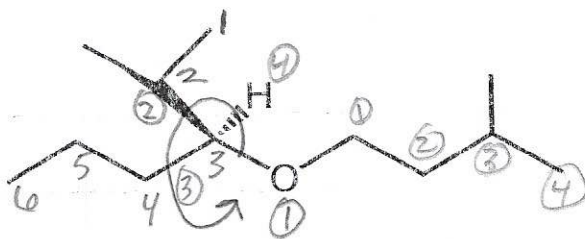Exam 1, Sp 24

A. Nomenclature: (12 points)
Give an acceptable name for each of the following compounds. Be sure to indicate the **stereochemistry** where appropriate.
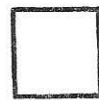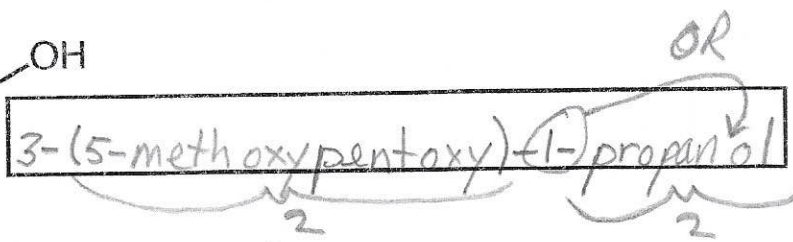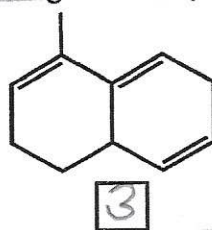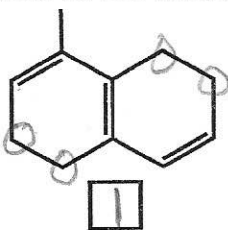
1.

cis-4,5-epoxy-2-methyl-1,7-octadiene

OR

cis-2-(2-methyl-2-propenyl)-3-(2-propenyl)oxirane

2.

(S)-2-methyl-3-(3-methylbutoxy)hexane

3.

OH

3-(5-methoxypentoxy)-1-propanol

OR

1-(3-hydroxypropoxy)-5-methoxypentane
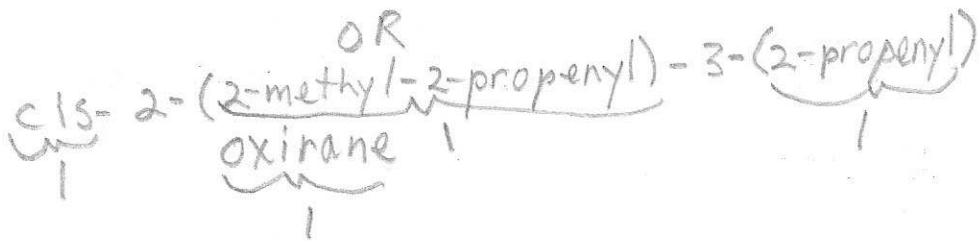
B. Facts: Total points = 20

most stable ↗ stable *least ↗ stable*
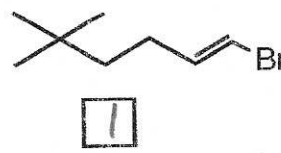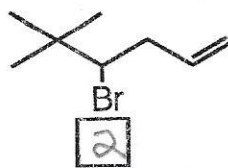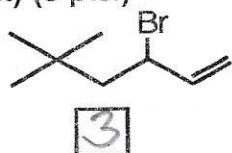
1. Rank the following alkenes in order of increasing heat of hydrogenation. (1=lowest, 3=highest) (3 pts.)

[2]   [1]   [3] → SN^2
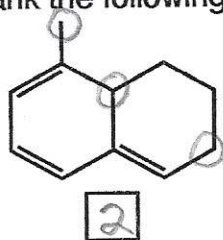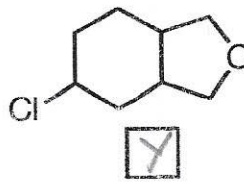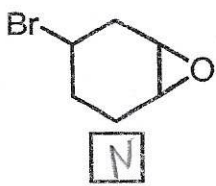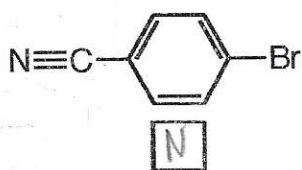
2. Rank the following compounds in order of increasing reactivity in NaI/acetone. (1=least reactive, 3=most) (3 pts.)

[3]   [2]   [1]
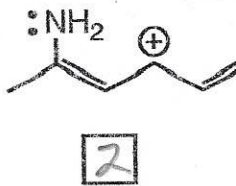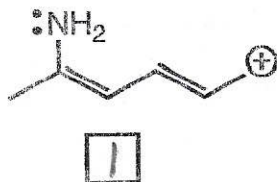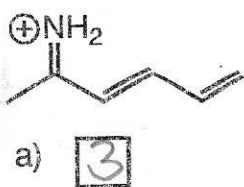
3. If a compound below will produce a Grignard reagent in good yield, place Y in the box. If it will not, place N in the box. (3 pts)
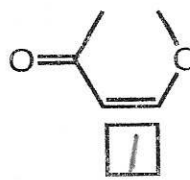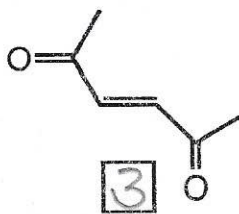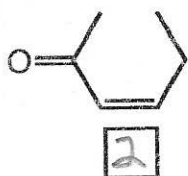
N≡C—〈 〉—Br   [N]   [N]   [Y]

4. Rank the following structures in order of increasing stability. (1=least, 3=most) (3 pts.) b) What is the hybridization of the nitrogen atom? (1 pt.)
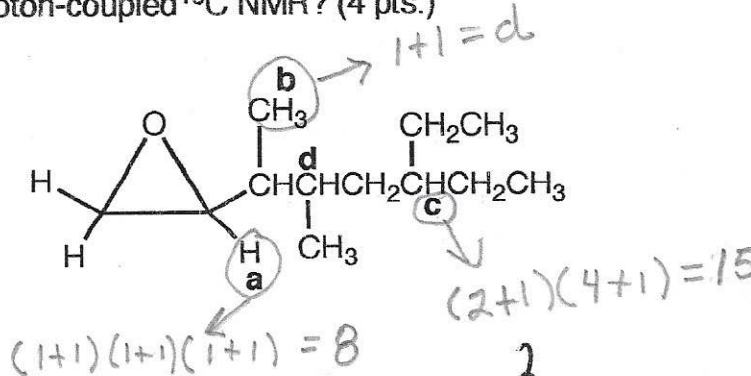
⊕NH₂   :NH₂   :NH₂ ⊕

a) [3]   [1]   [2]   b) [sp^2]

← these are resonance contributors * only the hybrid exists!

5. Rank the following compounds in order of increasing reactivity in a Diels-Alder reaction. (1=least reactive, 3=most) (3 pts)

[2]   [3]   [1]

6. Answer the following questions for the molecule below and place the answers in the appropriate boxes. (i) What is the theoretically predicited multiplicity of the signal for proton **a** in the ^1H NMR? (ii) What is the theoretically predicited multiplicity of the signal for proton **b**? (iii) What is the theoretically predicited multiplicity of the signal for proton **c**? (iv) What is the multiplicity of the signal for carbon **d** in the proton-coupled ^{13}C NMR? (4 pts.)

b → 1+1 = d
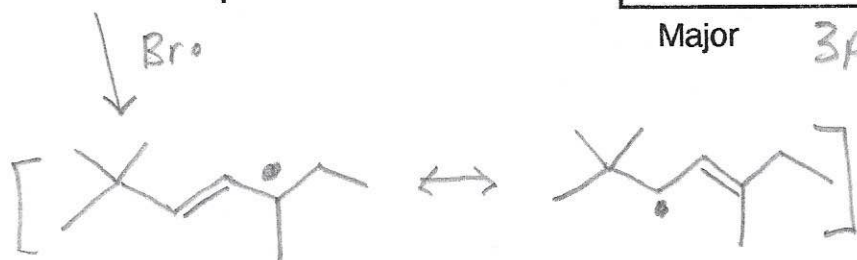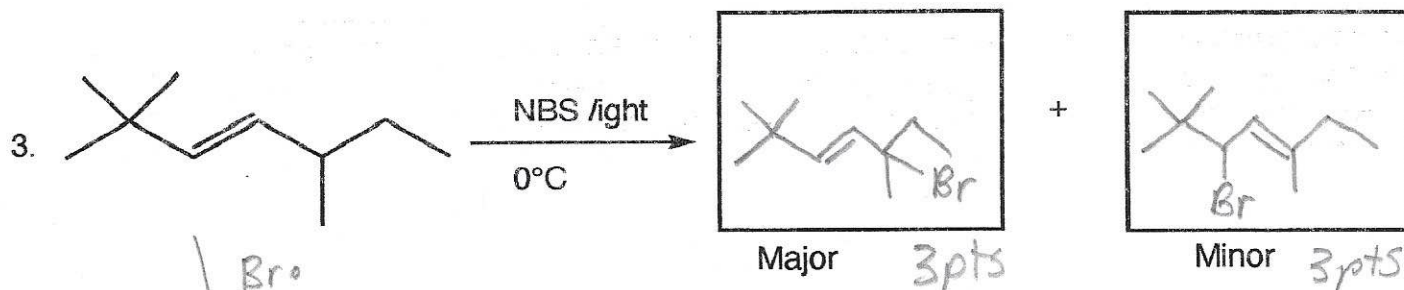CH₃ **d**
CH₂CH₃
H—〈epoxide〉—CHCHCH₂CHCH₂CH₃ **c**
H   H CH₃
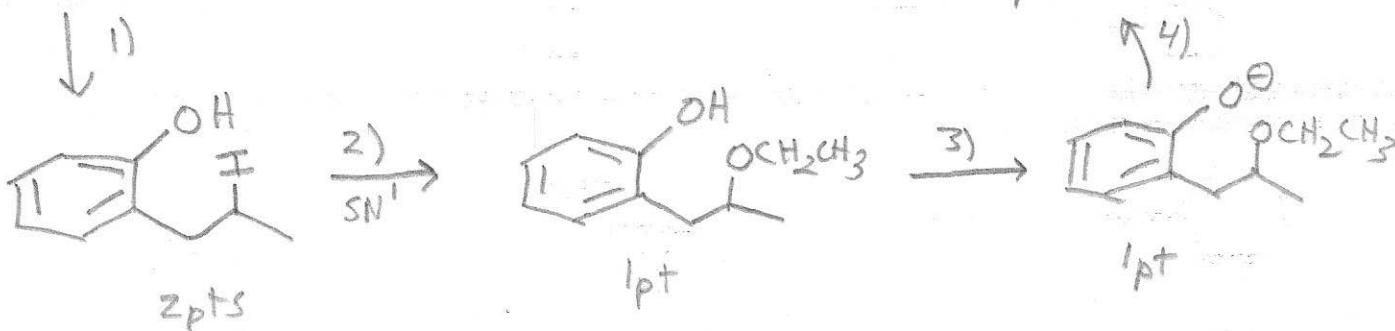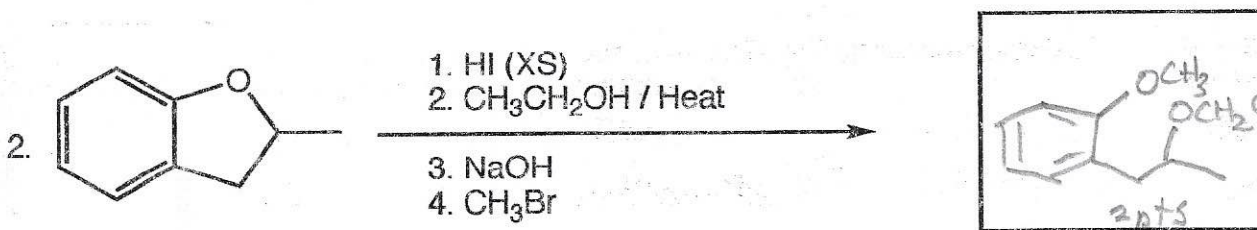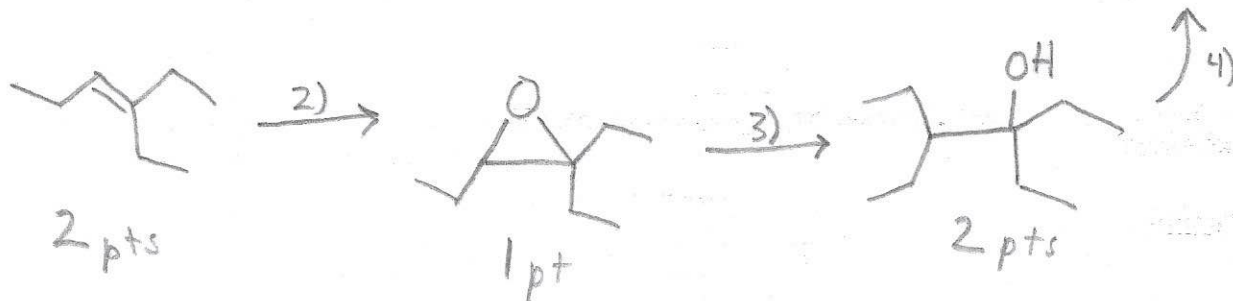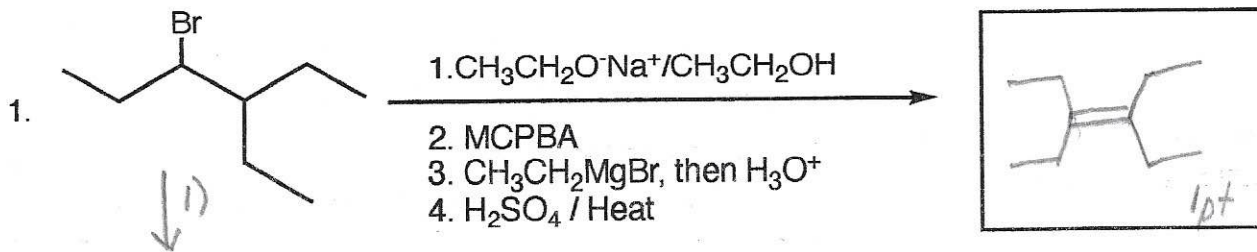**a**

(1+1)(1+1)(1+1) = 8   (2+1)(4+1)=15   2

(i) multiplicity of Ha [8] lines
(ii) multiplicity of Hb [d] or 2 lines
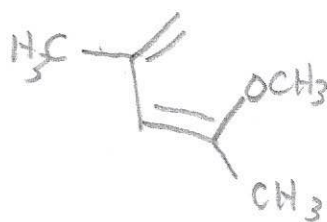(iii) multiplicity of Hc [15] lines
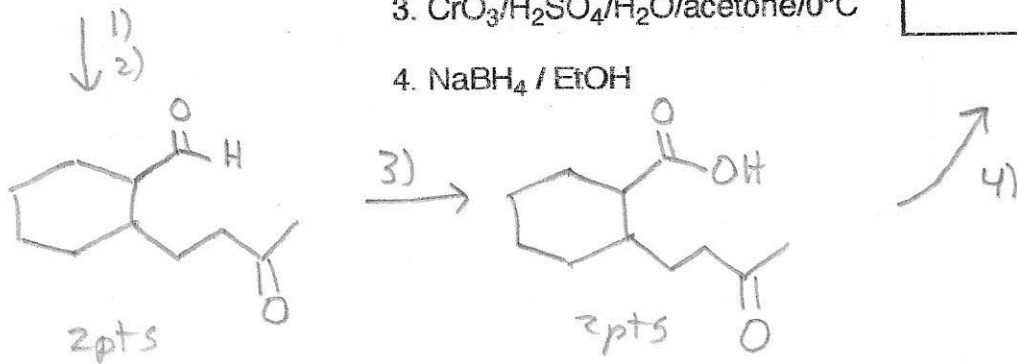(iv) multiplicity of Cd [d]

C. Reactions: Total = 36 points, 6 points each
Please provide the major product in the answer box unless otherwise indicated. Indicate
stereochemistry if applicable. **Full credit is awarded only when the product of each step in a multi-step reaction is shown below the reaction.**

1.

1. $CH_3CH_2O^-Na^+/CH_3CH_2OH$
2. MCPBA
3. CH_3CH_2MgBr, then H_3O^+
4. H_2SO_4 / Heat

2 pts   1 pt   2 pts

2.

1. HI (XS)
2. CH_3CH_2OH / Heat
3. NaOH
4. CH_3Br

2pts

2 pts   SN¹   1 pt   1 pt

3.

NBS /ight
0°C

Major   3pts   +   Minor   3pts

Bro

②if minor + major are switched

3

4.

1. Br_2 /CH_2Cl_2
2. $NaNH_2$ / 150°C, then H_3O^+
3. $HgSO_4$ / H_2SO_4 / H_2O

2pts

↓ 1)

2pts

2) →

2pts

3)

5.

1. O_3
2. $(CH_3)_2S$
3. CrO_3/H_2SO_4/H_2O/acetone/0°C
4. $NaBH_4$ / EtOH

2pts

↓ 1) 2)

2pts
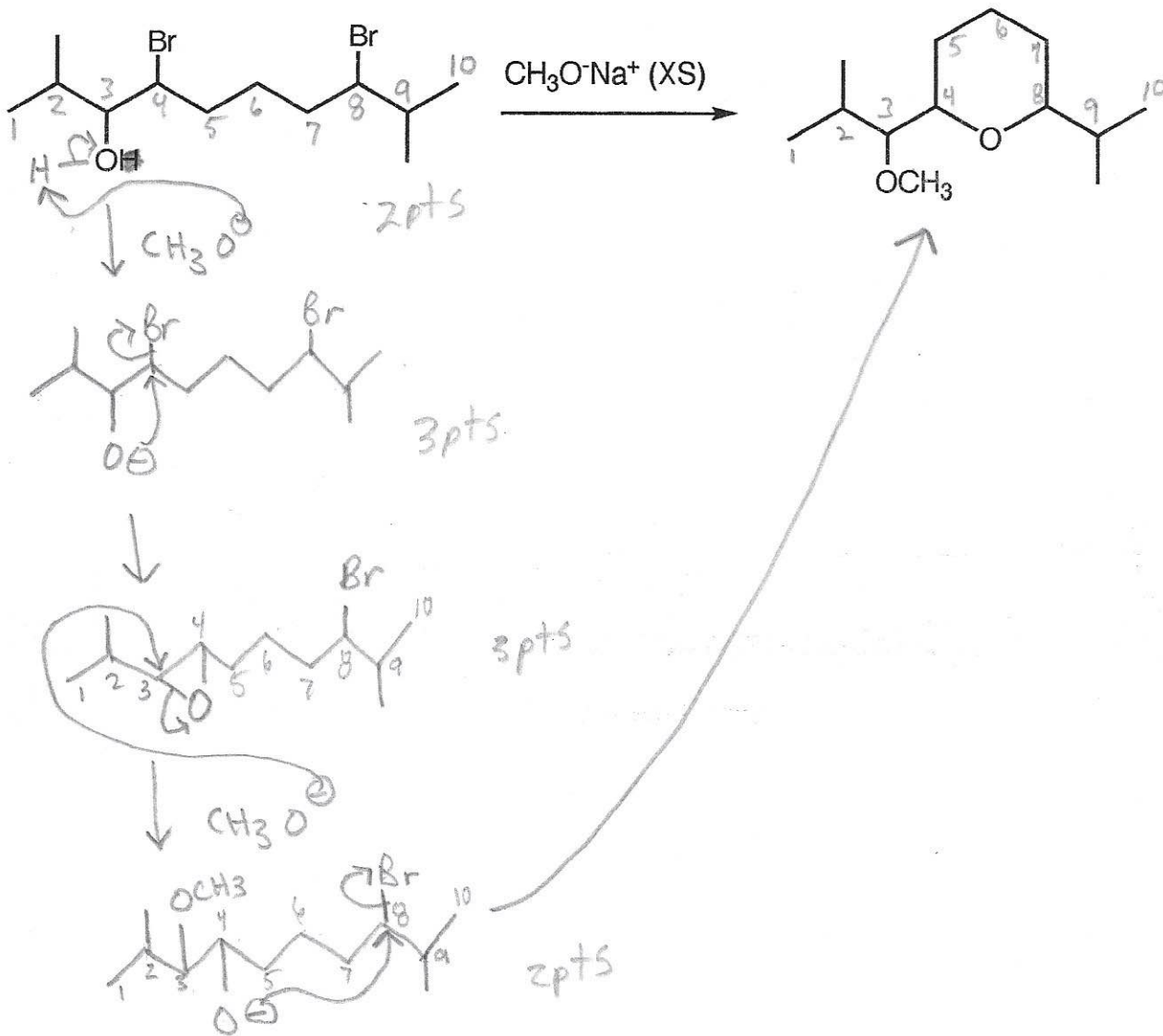
3) →

2pts

4)

6.

+

Heat →
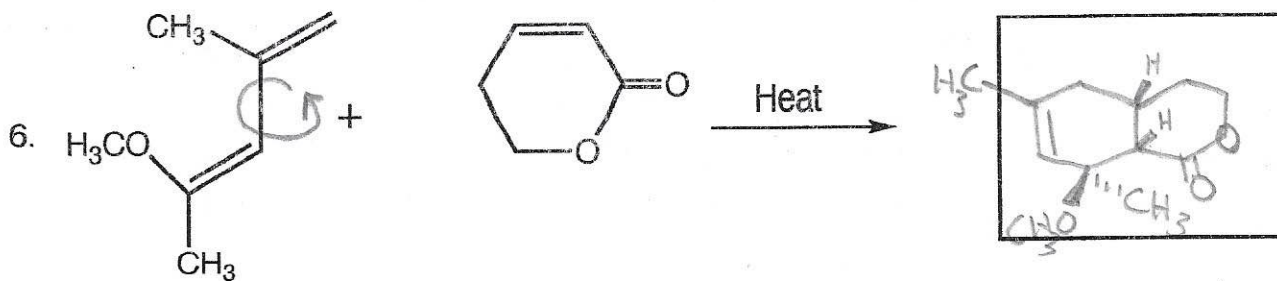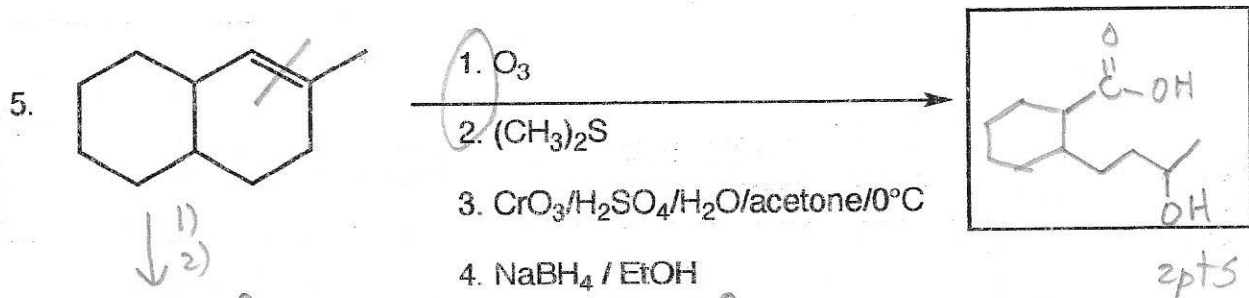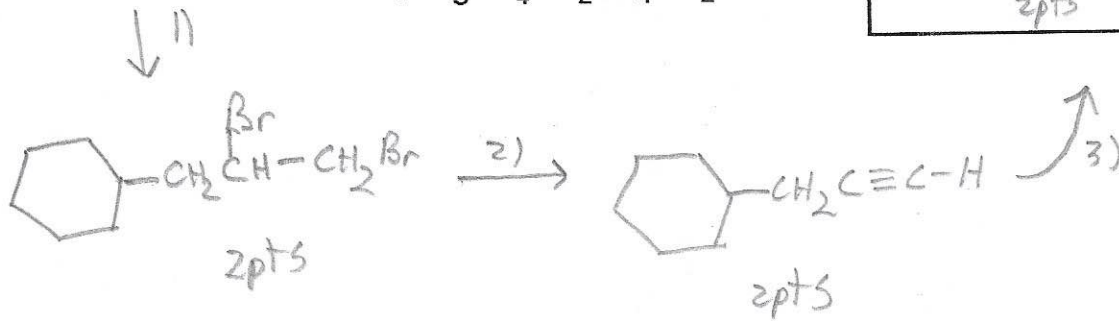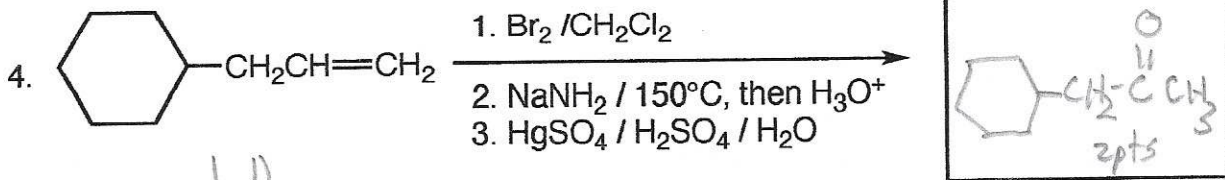
2 pts → correct rings
2pts → stereo
2pts → regio
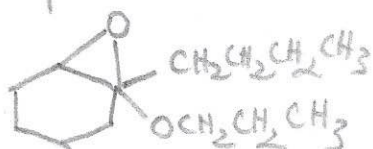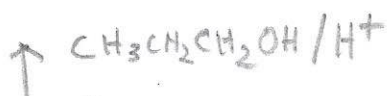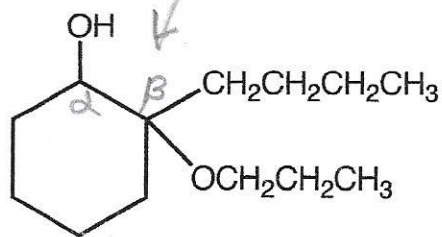
4

D. Mechanism: (10 points)
Provide a clear mechanism to explain the formation of the product shown. Use curved arrows to indicate "electron flow". <u>Remember to show only one step at a time.</u> **Show all intermediates and all formal charges**. Please do not show transition states.
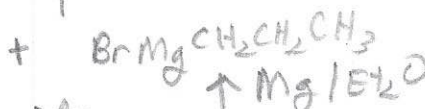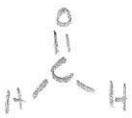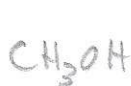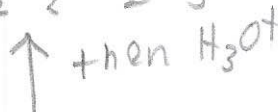
E. Synthesis: 12 Points

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

OH

α β $CH_2CH_2CH_2CH_3$

$OCH_2CH_2CH_3$

↑ $CH_3CH_2CH_2OH / H^+$ ← cannot use

$CH_2CH_2CH_2CH_3$
$OCH_2CH_2CH_3$

$CH_3CH_2CH_2O^{\ominus}$ ← attacks wrong side

↑ MCPBA

$CH_2CH_2CH_2CH_3$

↑ $H_2SO_4 / heat$

OH
$CH_2CH_2CH_2CH_3$

↑ then H_3O^+

=O   + $BrMgCH_2CH_2CH_2CH_3$

↑ Mg / Et_2O

$BrCH_2CH_2CH_2CH_3$

↑ PBr_3

$HOCH_2CH_2CH_2CH_3$

↑ then H_3O^+

OH → Jones' ox

CH_3OH →PCC→ $H\overset{O}{\underset{}{C}}H$ + $BrMg CH_2CH_2CH_3$

↑ Mg / Et_2O

$CH_3CH_2CH_2OH$ →PBr₃→ $BrCH_2CH_2CH_3$
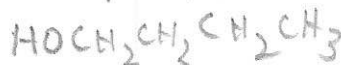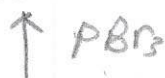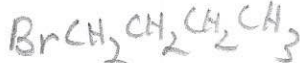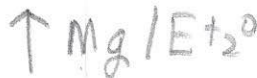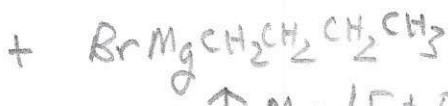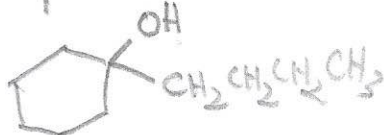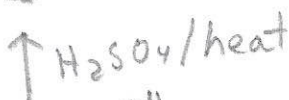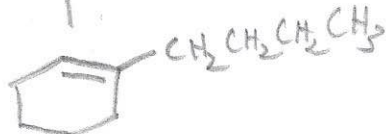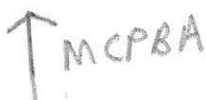
F. Spectroscopy: 10 Points

A compound with the formula $C_{11}H_{14}O_2$ exhibits the IR, ^{1}H NMR, and proton-spin decoupled ^{13}C NMR spectra shown below. Please identify this compound and draw the structure in the box provided below.

IR spectrum (% TRANSMITTANCE vs WAVENUMBERS), with labeled peaks: 2981.04, 2936.03, 2874.30, 1693.72, 1603.05, 1510.45, 1488.02, 1394.71, 1313.69, 1259.68, 1215.31, 1181.29, 1024.32, 833.35

Proton NMR: peaks labeled 1H, 2H, 2H, 2H (at ~4.0), 2H, 2H, 3H

Carbon 13 NMR

Handwritten notes (left side):
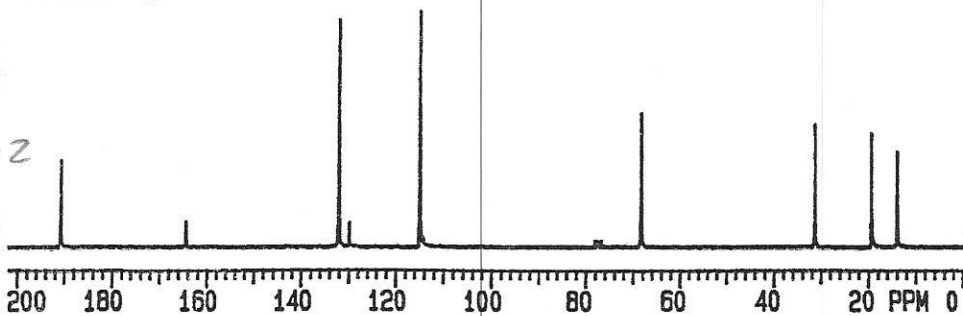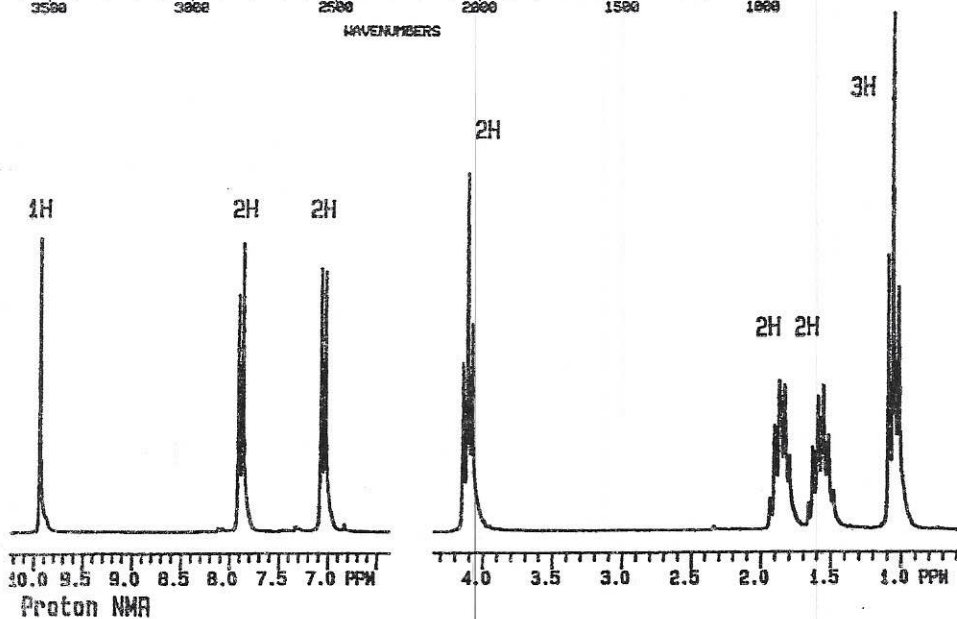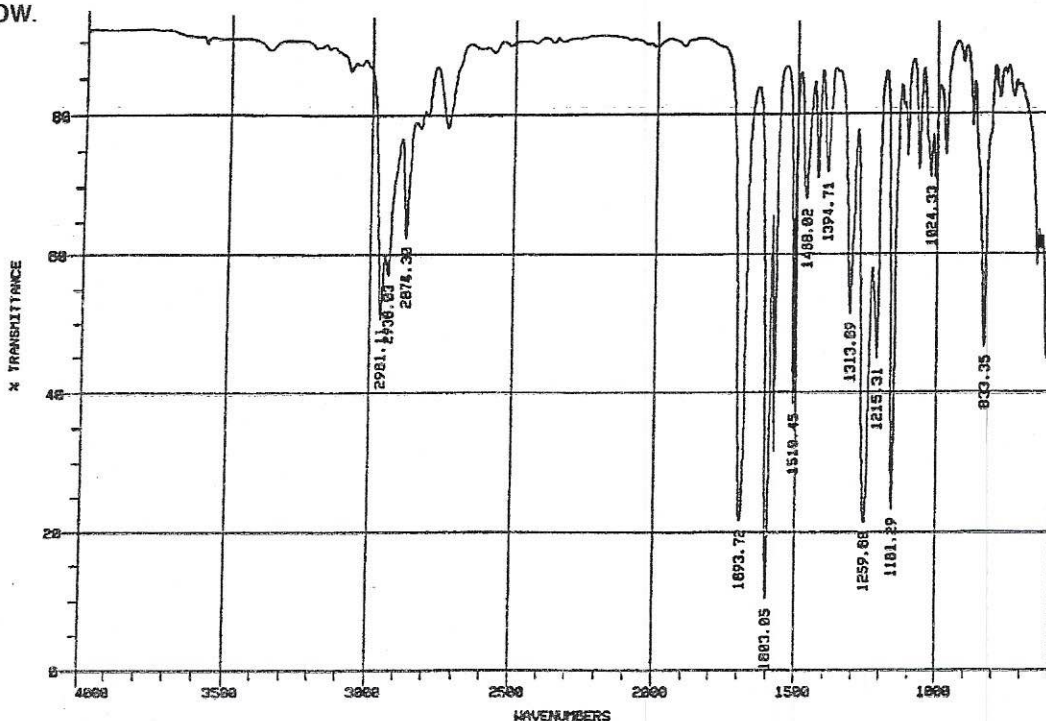
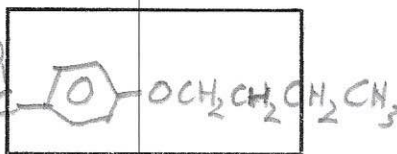any aldehyde +1
any ether +1
any ⬡O +1
para ⬡O× +2
any / OCH₂|CH₂ +2
any CH₂|CH₃ +1
—CH₂— +1
↑
multiplet because

diff it's on each side
but chem shift must be reasonable

Handwritten (box in center):

O=C(H)—⬡O—OCH₂CH₂CH₂CH₃

Handwritten (right side):

if not para
(−1)