FINAL

Name_____ Student#_____

Course Code:	CHM 2120 B	Professor:	I. Dion
Course name:	Organic chemistry II	Room:	GYM D
Date:	December 6, 2013	Time:	9:30 - 12:30

- Documentation, **electronic devices** or programmable calculators are **NOT** allowed.
- Molecular models are allowed.
- Write directly on the exam. Indicate clearly if your answer continues on the other side of the page.
- **Attempt all questions**; part marks might be given for plausible answers.
- Remember: a picture is worth a thousand words: don't hesitate to draw molecules to support explanations.
- There are 7 questions + 1 bonus over 15 pages for a total of 112 points.

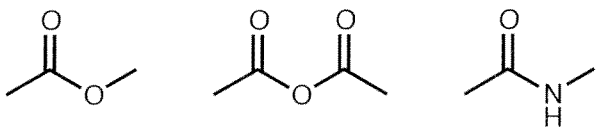
1a	2a	3b	4b	5b	6b	7b	8			1b	2b	3a	4a	5a	6a	7a	0
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106 106												

GOOD LUCK!

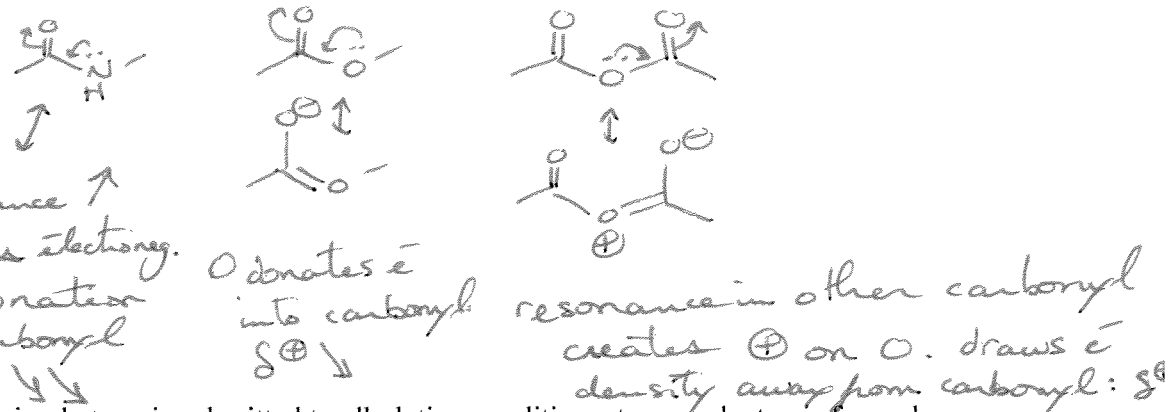
Q1) (12 points)

a) Put the following molecules in increasing order of electrophilicity (from least electrophilic to most electrophilic). **Justify your answer for each molecule.**

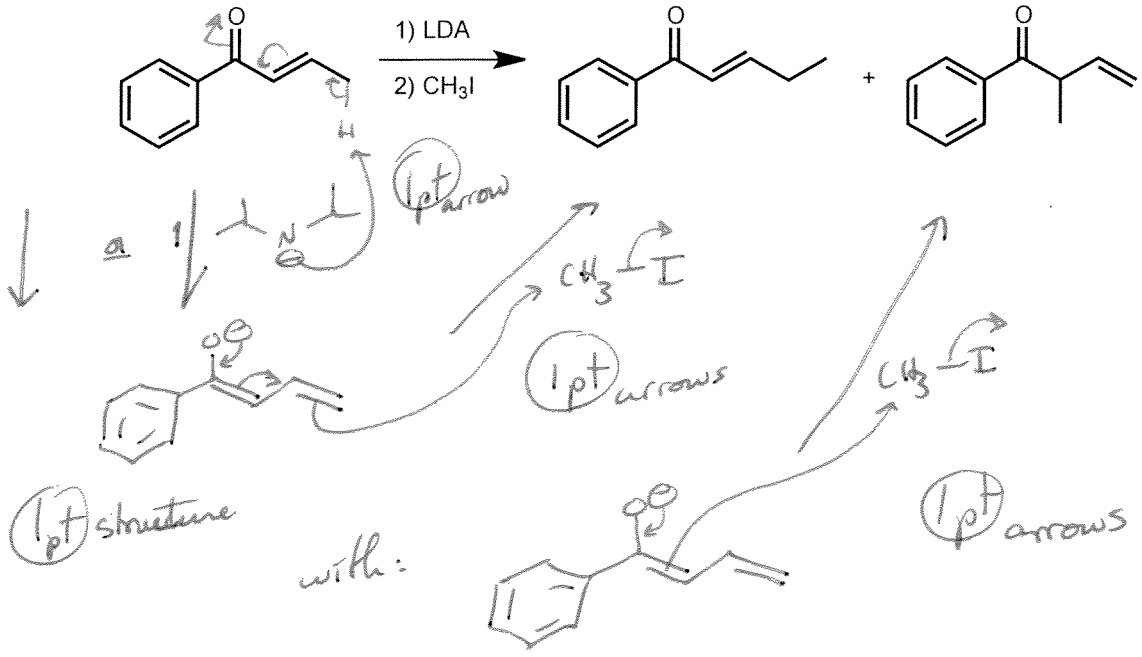
- 1pt order
- 3pts explain.



least E⁻ → most E⁻



b) When the following ketone is submitted to alkylating conditions, two products are formed. Explain the formation of both products.



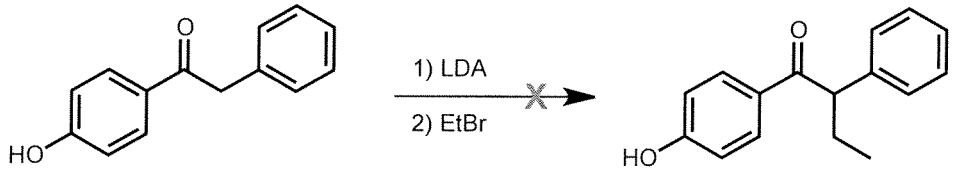
c) Explain why the alpha protons of a ketone are more acidic than the alpha protons of an amide.

(1pt) resonance of N e⁻ donating into carbonyl : ↘ δ⊕ (1pt)

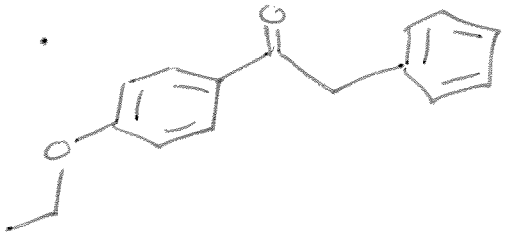
when deprotonating : less stabilization of conjugated base (1pt) neg. charge. in amide
= less basic & less electrophilic (1pt)

Q2) The following reactions are **not** taking place. Explain why and give the real product of the reaction. (12 points)

a)



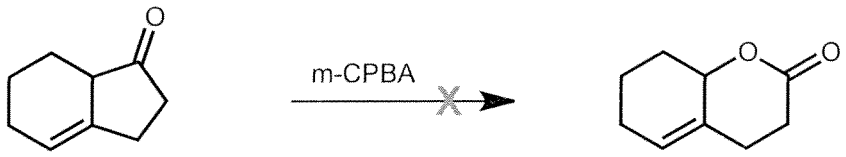
- OH gets deprotonated (2pts)



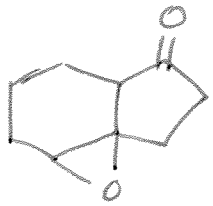
(2pts)

Q2 continued)

b)

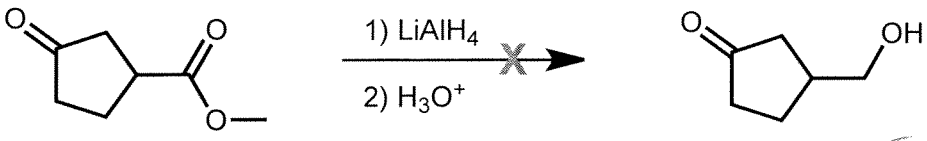


- Alkene is more reactive than carbonyl (2pts)



(2pts)

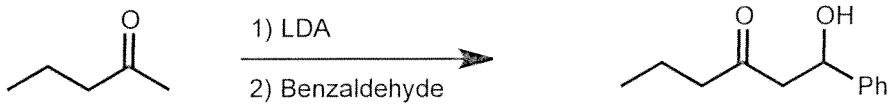
c)



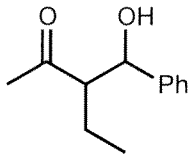
- LAH reduces everything (2pts)

(2 pts)

Q3) Reacting 2-pentanone in basic conditions, followed by addition of benzaldehyde, affords the following β-hydroxycarbonyl. (8 points)



a) What changes could you make to the reaction conditions to obtain this β-hydroxycarbonyl?



1) $RO^{\ominus}$ or $HO^{\ominus}$
2) Benzaldehyde

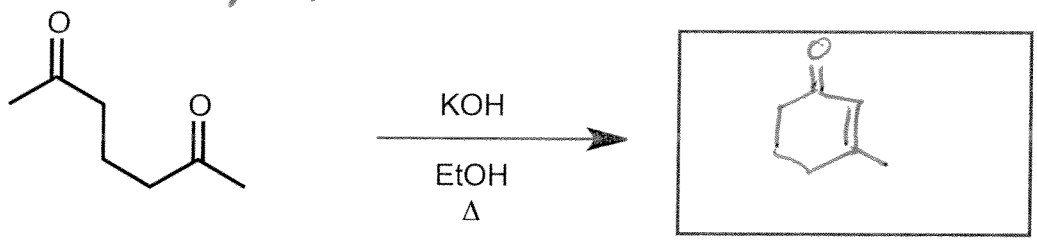
(2pts)

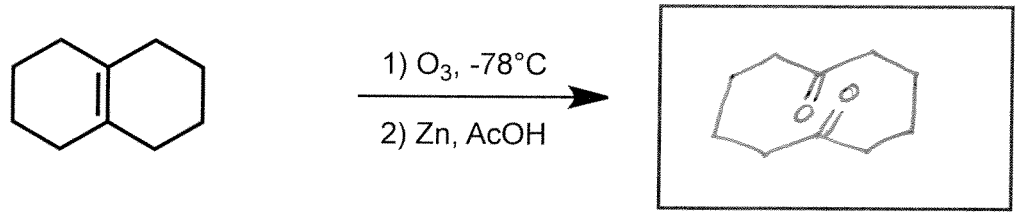
* must be in two steps!

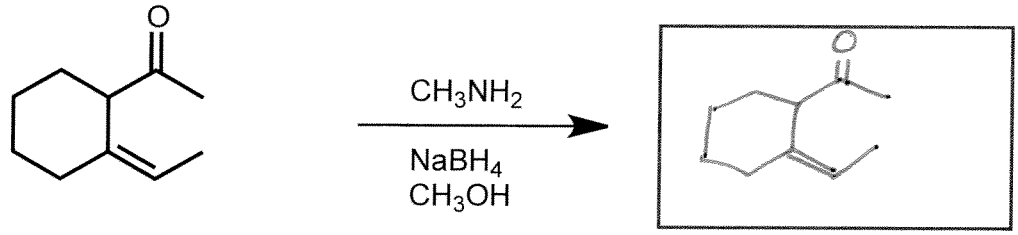
b) What is the main difference between the two sets of conditions? What important intermediate is formed in each set of conditions?

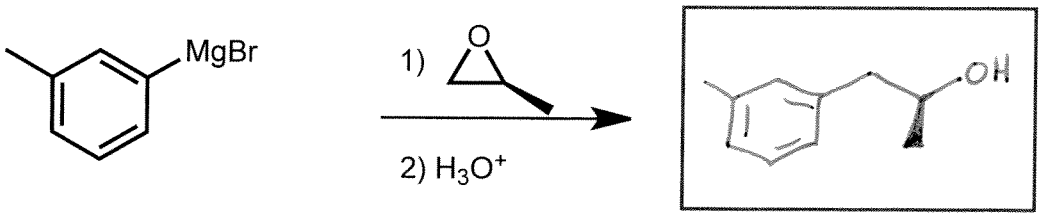
- LDA → stronger base (1pt) → kinetic enolate formed (2pts)
- $RO^{\ominus}$ or $HO^{\ominus}$ in 2 steps is a less strong base (1pt) → allows for equilibration = thermodynamic enolate is formed (2pts)

Q4 a) Provide the product or starting material for the following transformations. If more than one answer is possible, give the major product/starting material. Respect stereochemistry where needed. (12 points) 2pts / box.

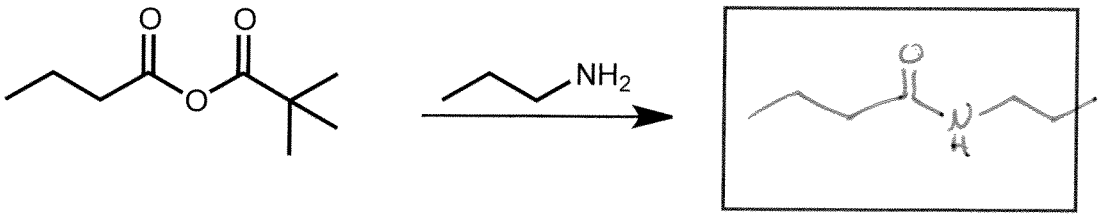


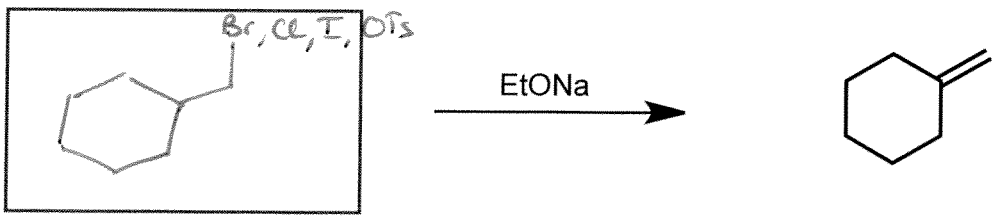




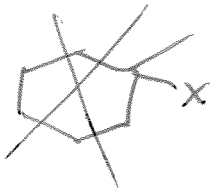


chirality (-1).

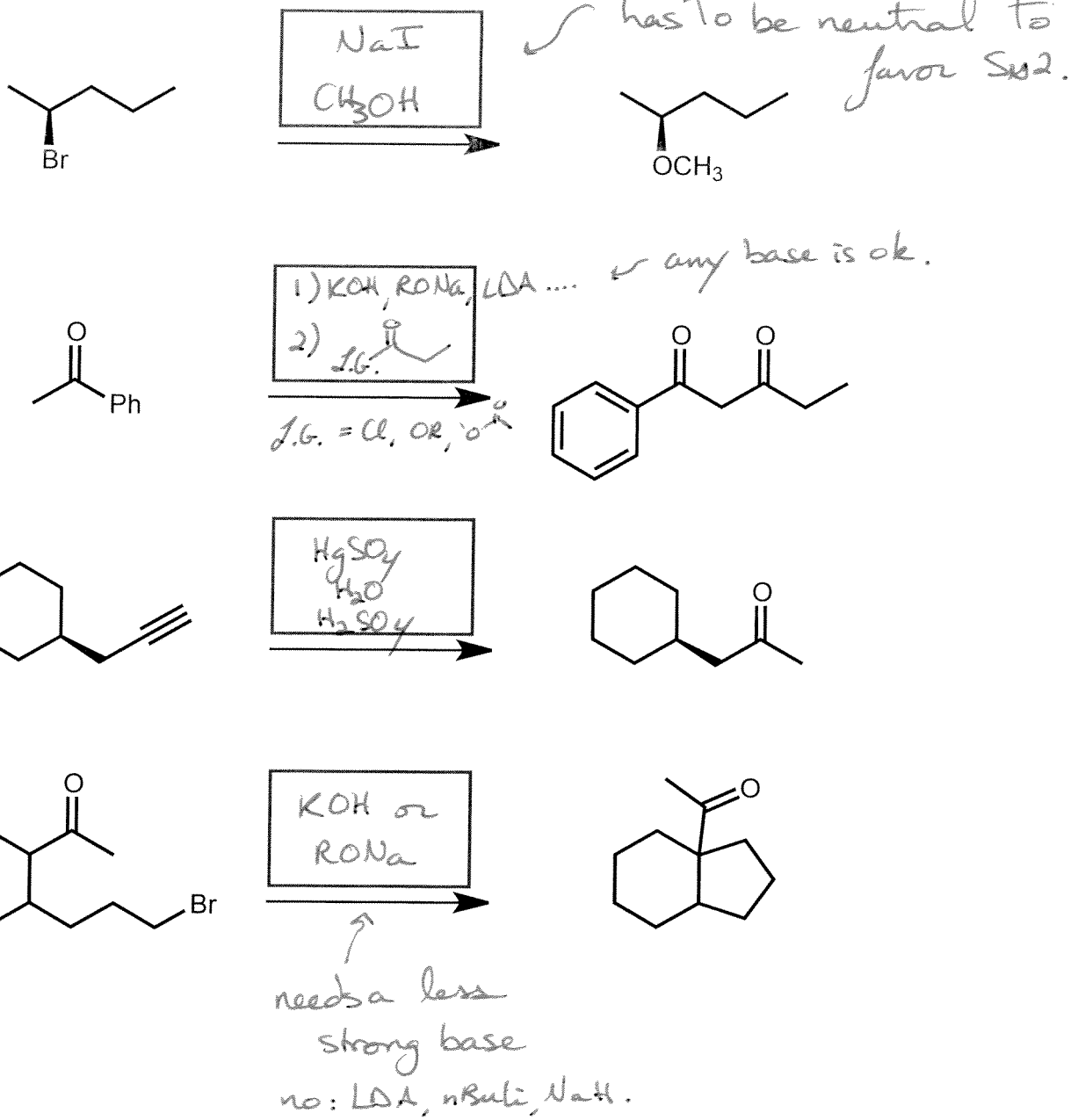




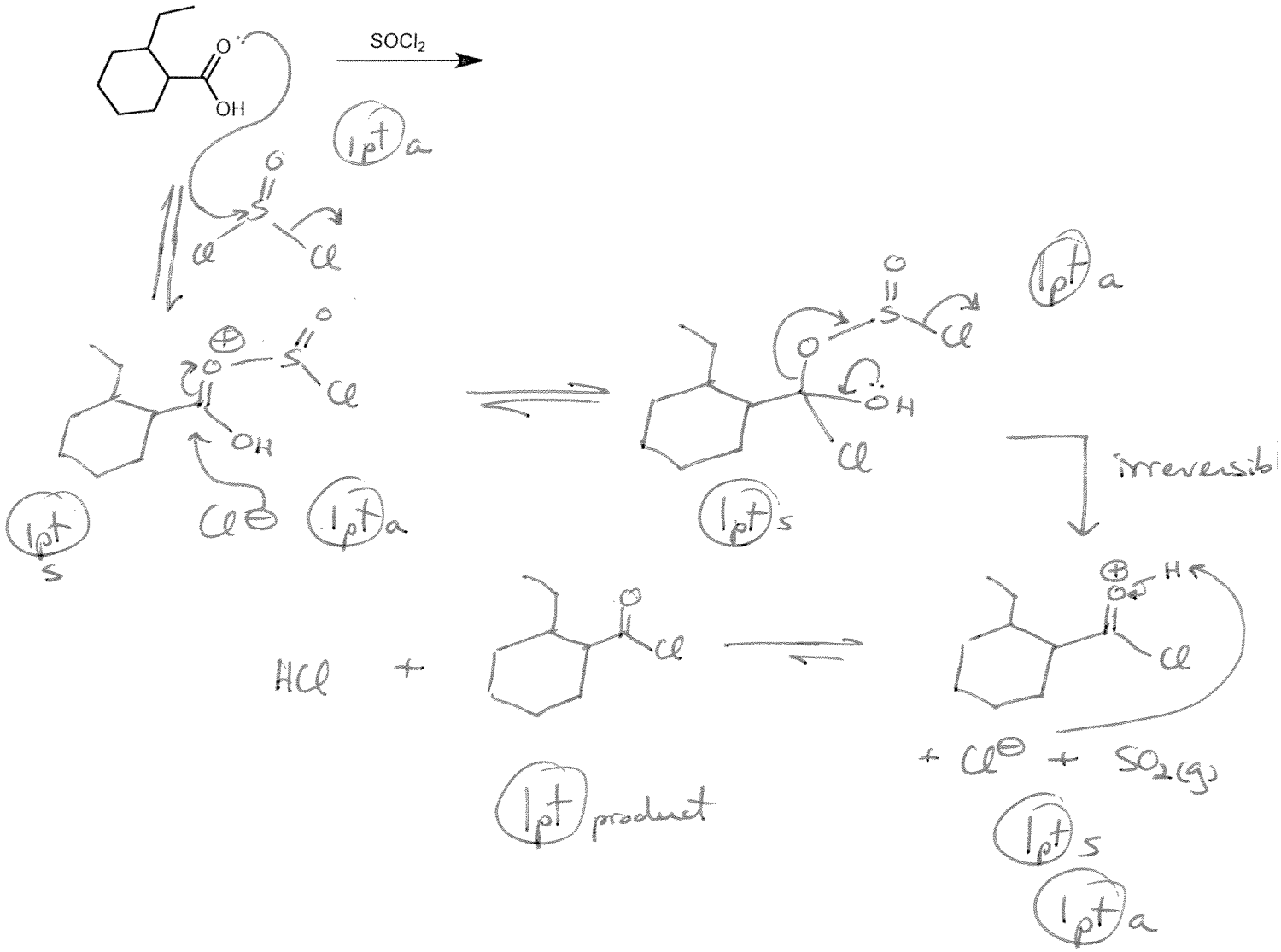
not



Q4 b) Provide the reaction conditions for the following transformations. More than one step might be needed per arrow. Respect stereochemistry where needed. (8 points) 2 pts/box

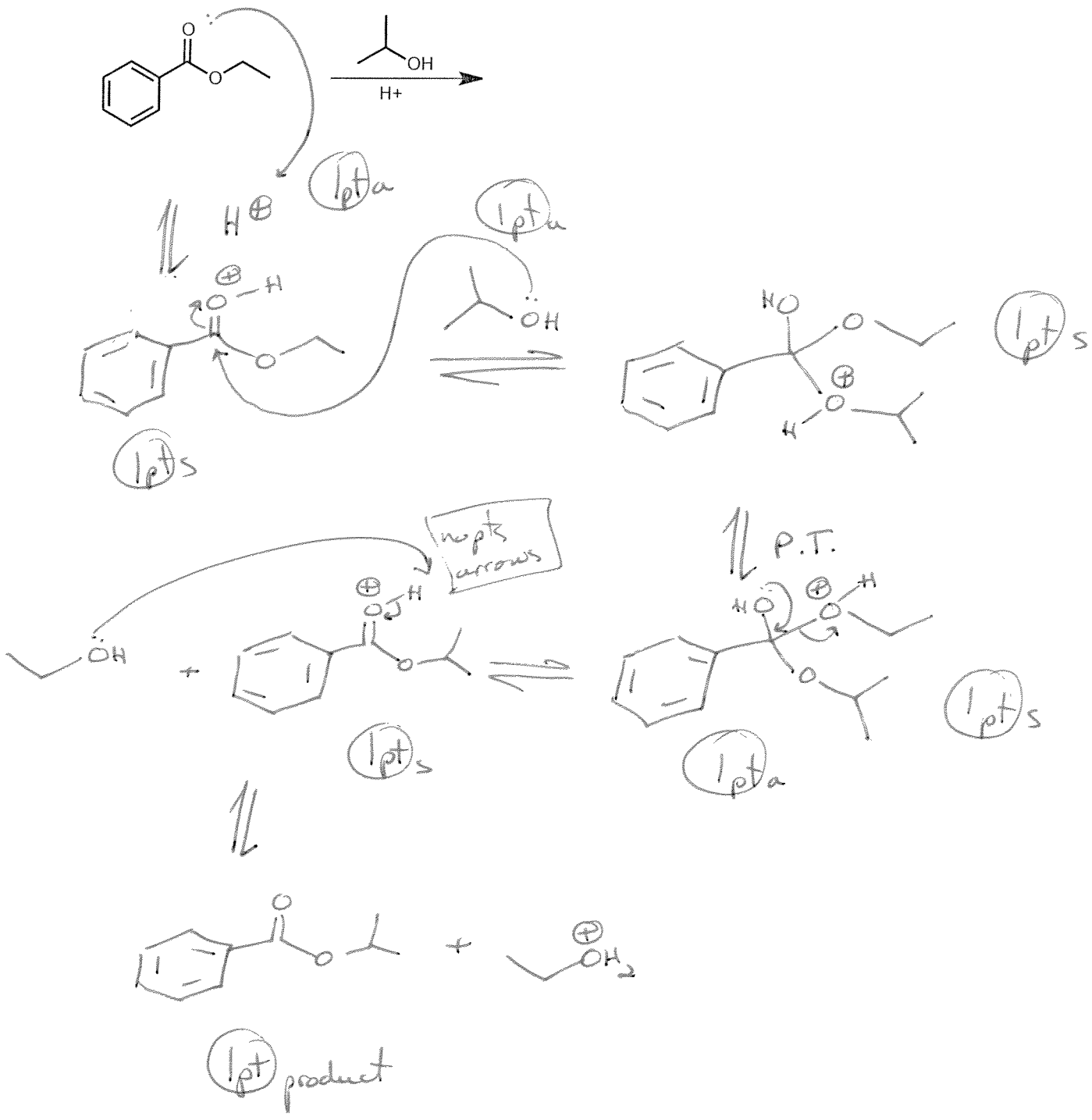


Q5 a) Provide the product of the following reaction and the mechanism of its formation. (8 points)



-1pt overall if bad rev-irrev. arrows.

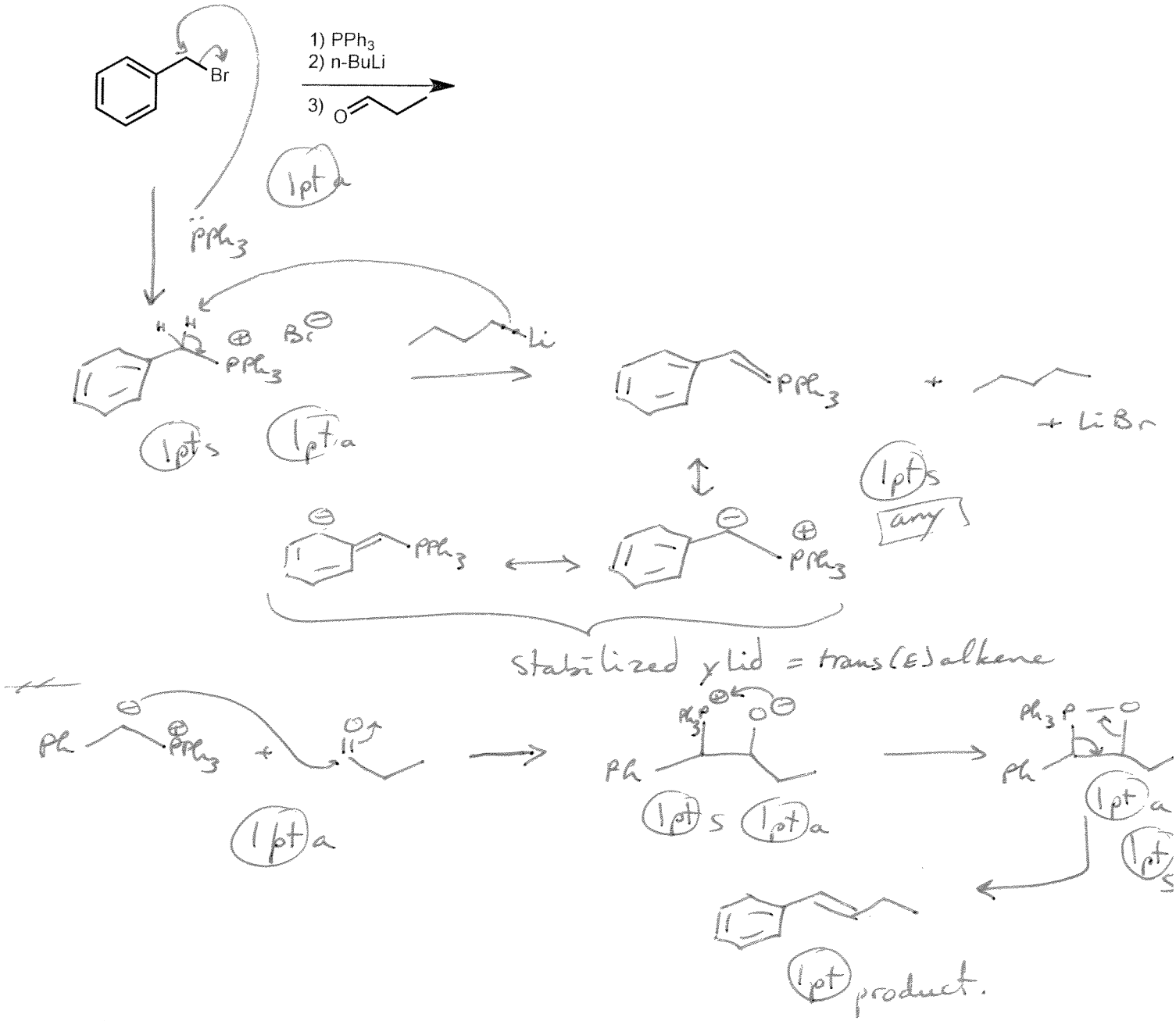
Q5 b) Provide the product of the following reaction and the mechanism of its formation. (8 points)



-1 if intramolecular proton transfer arrows shown

-1 overall for bad rev–irrev. arrows.

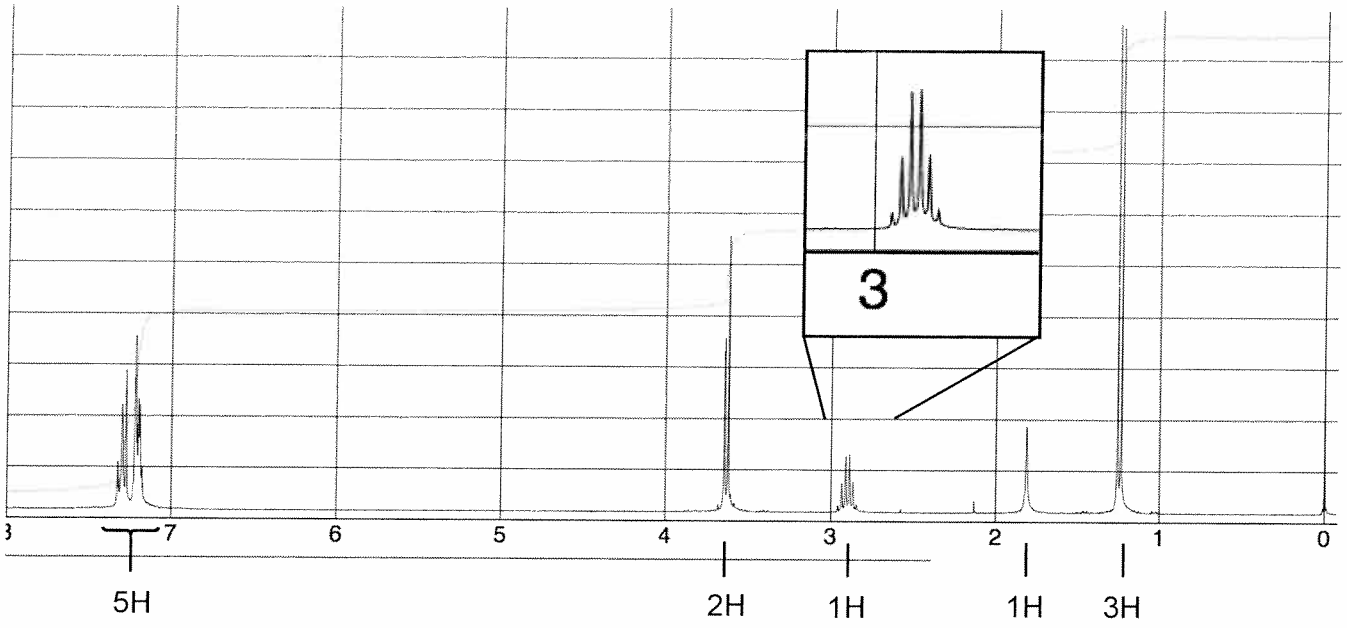
Q5 c) Provide the product of the following reaction and the mechanism of its formation. (10 points)

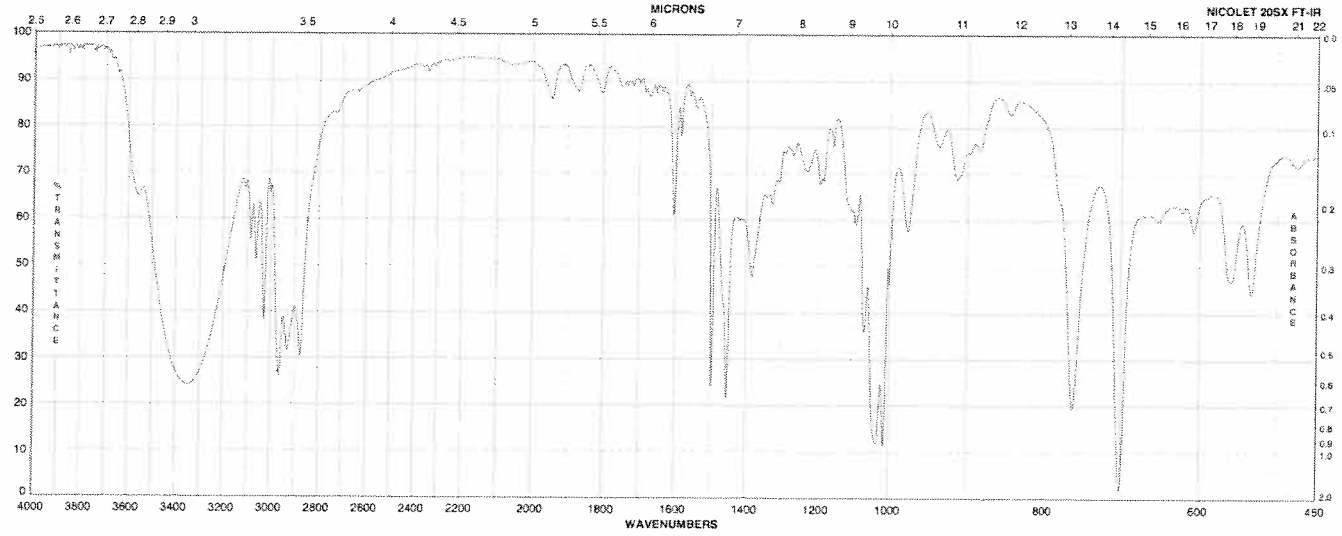


What is the name of the reagent formed after step 2 of Question 5c)? (1 point)

stabilized ylid

Q6) Find the structure of the following unknown molecule ($C_9H_{12}O$), given its IR and ^1H NMR spectra. Clearly explain each step of your reasoning on the following page. (Reference values can be found in the annex at the end of the exam). (21 points)





Q6 continued) Analyse the data of the spectra and provide your answer **on this page**. Every piece of information can be useful. Be detailed!

D.U.: $\frac{(2\times 9 + 2 - 12)}{2} = \frac{20-12}{2} = 8/2 = 4$ (1 pt) → · 1 arom. · 4 C=C · 4 rings ... (1 pt)

IR: (4 pts)

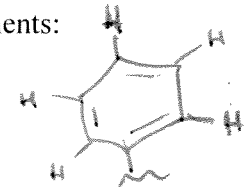
OH @ 3400 cm^{-1} CH sp^3 @ 2900 cm^{-1}

CH sp^2 @ 3100 cm^{-1} C=C @ 1600 cm^{-1}

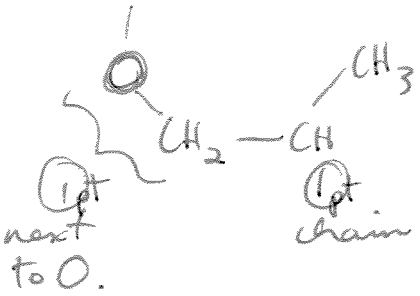
NMR:

signal	δ (ppm)	integration	multiplicity (3 pts)	comments (7 pts)
A	7.2-7.5	5H	m	aromatic (1)
B	3,6	2H	doublet n=1	deshielded (1) next to O? CH_2 next to CH (1)
C	2.8	1H	sextet n=5	slightly deshielded (1) CH next to 5H (1)
D	1.7	1H	singlet n=0	deshielded slightly. → OH (1) CH ?
E	1.4	3H	doublet n=1	CH_3 next to CH (1)

Fragments:

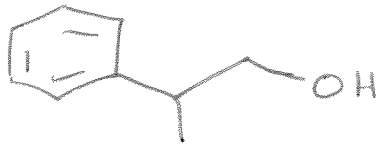


(1 pt)



12H, 9C, 1O.

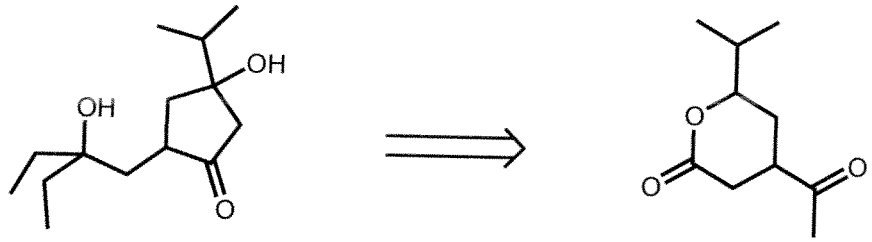
Molecule:



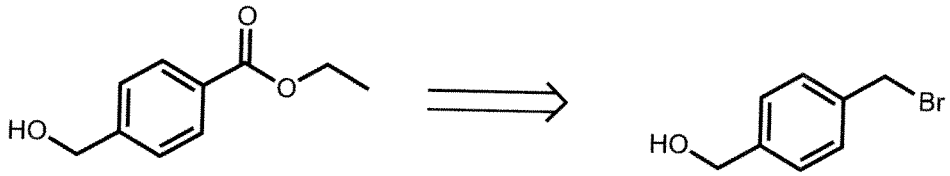
(2 pts)

Q7) Suggest a synthesis for **one of the three** following transformations. Clearly indicate which synthesis you want corrected. If none is selected, synthesis a) will be corrected. Partial marks will be given for reasonable answers. Try something! (12 pts)
Note: You can use any reagent and reaction seen in class since the beginning of the semester.

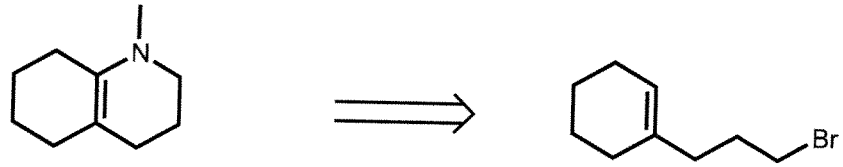
a)



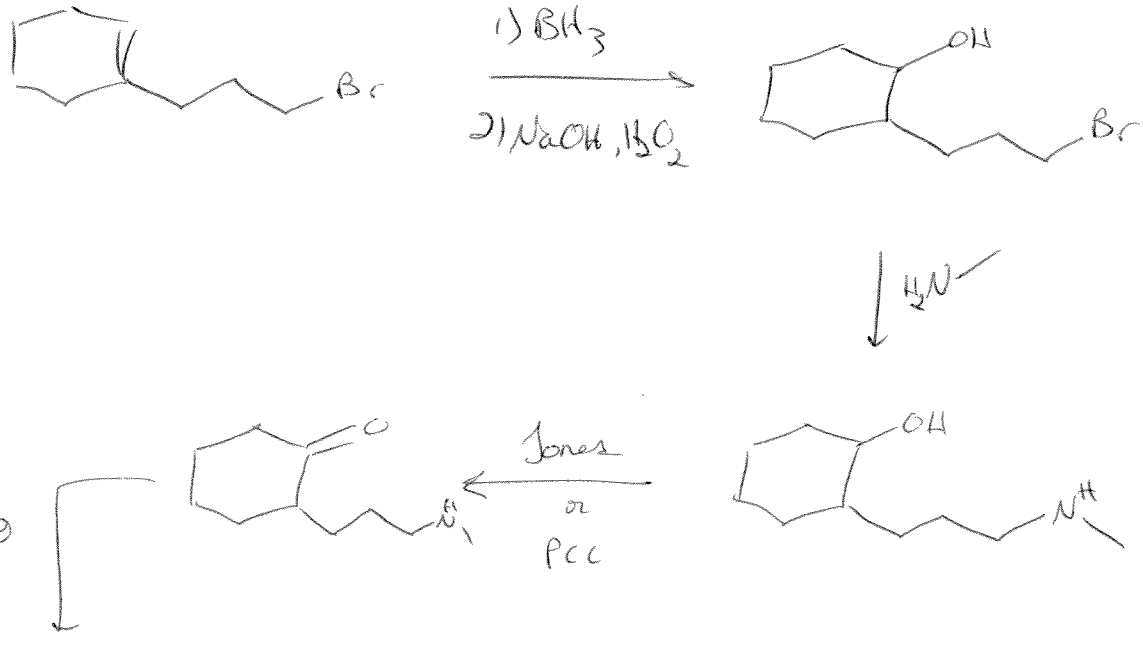
b)



c)

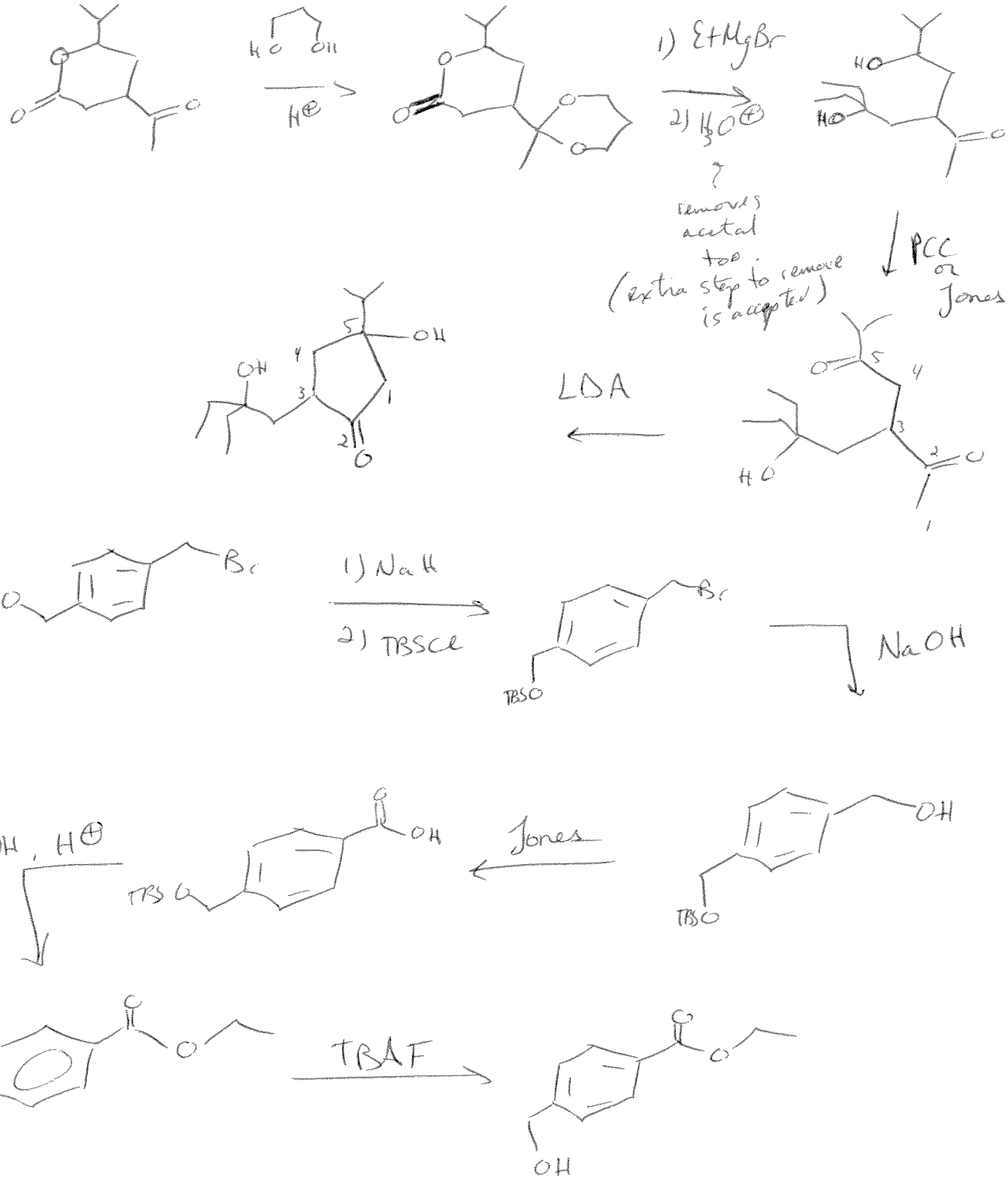


c)



Q7 continued (extra space for your synthesis) Please indicate CLEARLY the one you want corrected.

a)

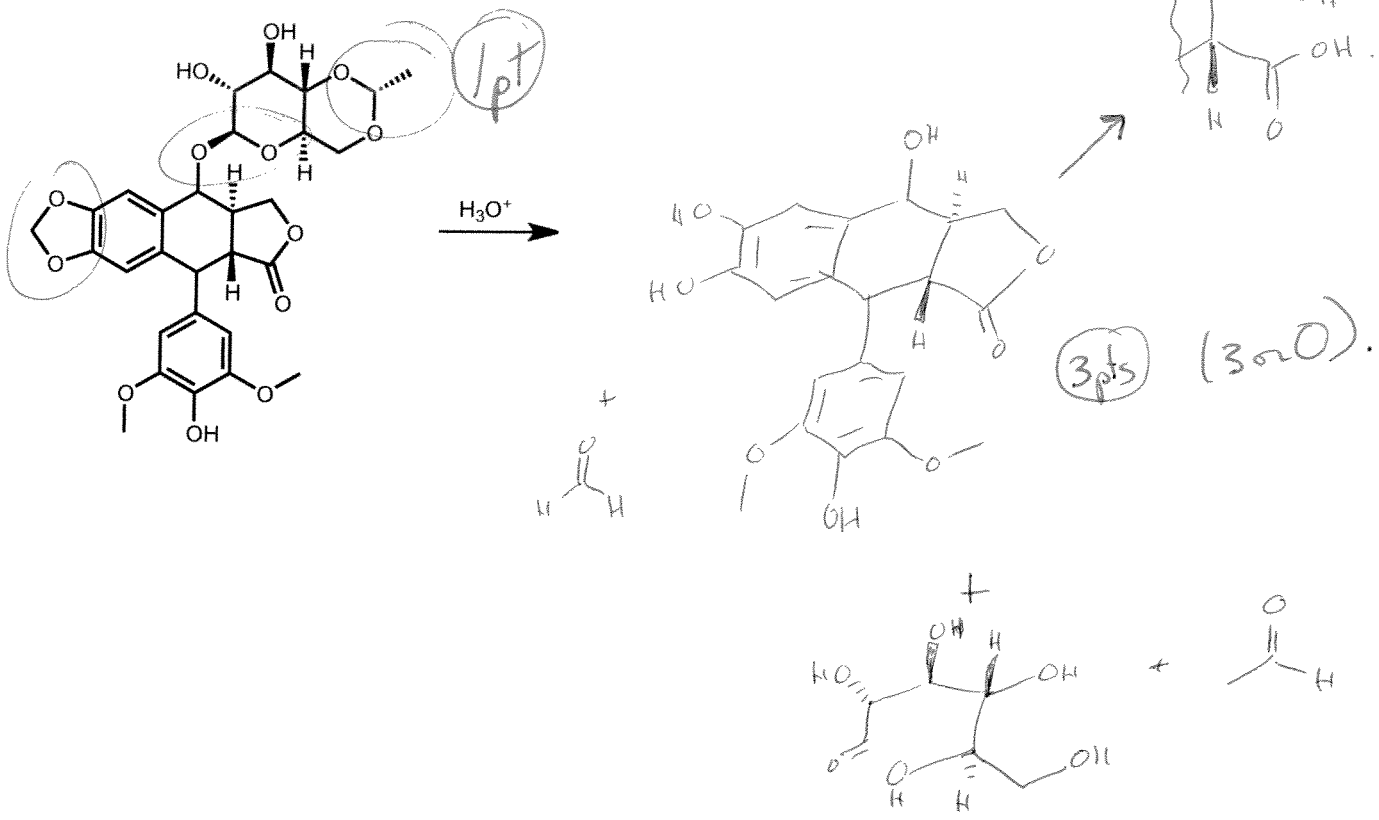


Bonus Question: (5 pts)

The anticancer drug Etopophos is made of the active ingredient Etoposide.

a) Locate all the acetals in the molecule

b) Provide the products formed when the molecule is reacted with H_3O^+.



Happy holidays and good luck on the rest of your exams!

Unofficial final marks will be posted on Virtual Campus as soon as available.