CHM 2120
Sample Final Exam – ANSWERS

DATE Professor: Alison Flynn

Time: 3 hours

Name: _____

Student Number: _____

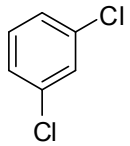
Notes:

- The final 2 pages contain a periodic table, a table of IR stretching frequencies, and a table of ^{1}H NMR chemical shifts. These pages may be detached.
- A calculator, ruler, and molecular models are permitted
- Total number of pages: 15
- Approximate number of points:
    - The marks are given as a guide and are subject to minor changes

GOOD LUCK!

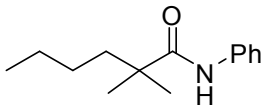
1. Name the following molecules using IUPAC nomenclature or accepted trivial names: **(2 points)**

a.



1,3-dichlorobenzene or
m-dichlorobenzene

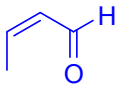
b.



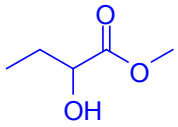
N-phenyl-2,2-dimethylhexanamide

2. Draw clear structures for the following molecules: **(2 points)**

a. (*Z*)-but-2-enal

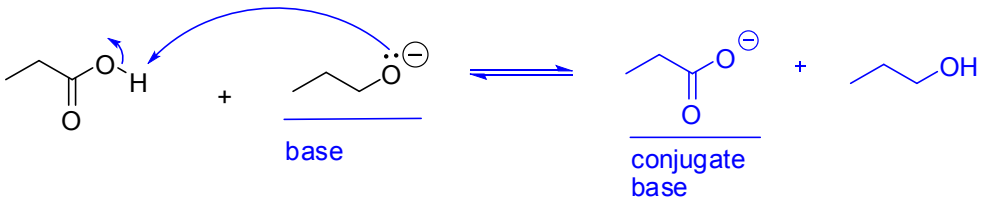


b. Methyl 2-hydroxybutanoate



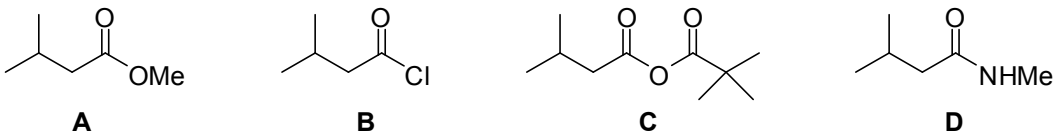
3.

a. Write equations for the following reaction using arrow notation. **(2 points)**
b. Will the reaction favour the starting materials or the products? **(1 point)**
c. Justify your choice. **(3 points)**



- Compare the base and the conjugate base
- Both have a negative charge on oxygen, but the conjugate base is resonance-stabilized, while the base is not.
- The conjugate base is therefore more stable than the base, and the equilibrium favours the weaker/more stable side, i.e. the products.

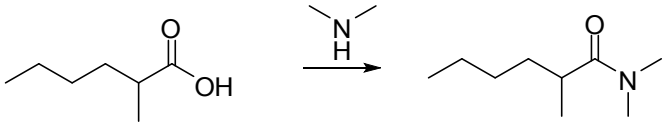
4. Rank the following molecules in *increasing* order of reactivity with H_2NEt. **(3 points)**



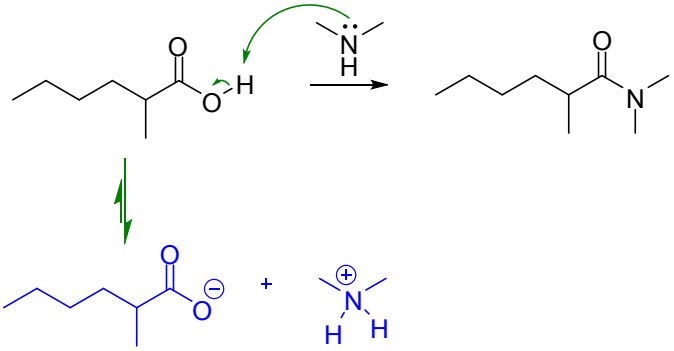
A **B** **C** **D**

____D____ < ___A_____ < ____C_____ < ____B_____

5. The following reaction won't work as shown:

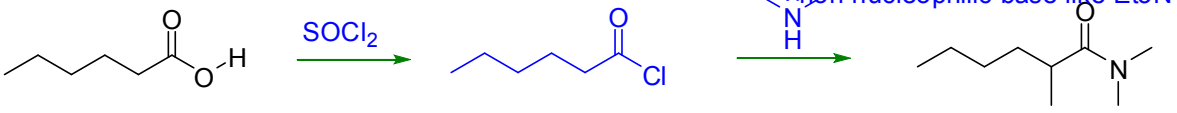


a. Show what would happen instead. **(2 points)**

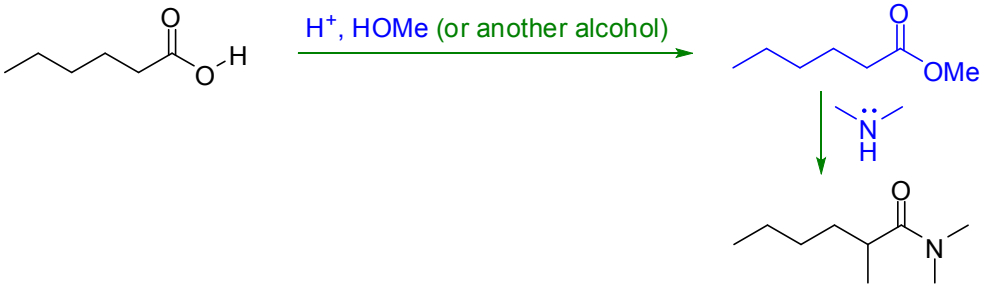


b. How could you obtain the desired product? Show the reagents to be used and the structures of any intermediates. **(3 points)**

This route works best:



An accepted answer:

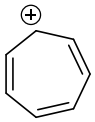


6.

a. What are the three criteria for aromaticity? **(3 points)**

- The ring(s) is planar
- All atoms are sp^2-hybridized
- There are $4n+2$ π electrons (n = 0, 1, 2...)

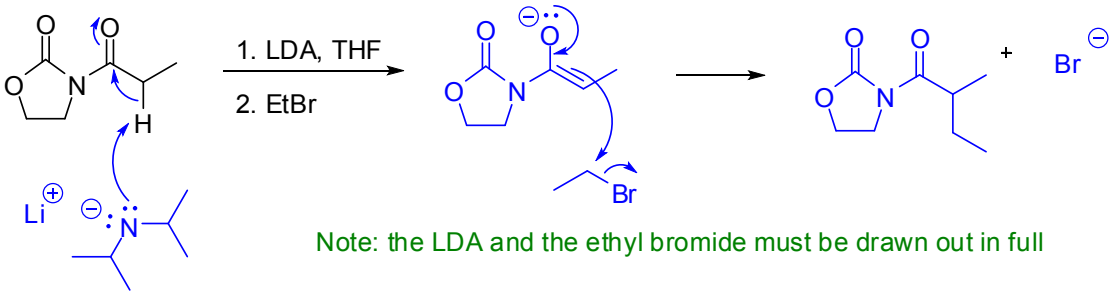
b. Is the following ion aromatic? Explain clearly how you came to this conclusion. **(2 points)**



- Ring is planar
- All the ring atoms are sp^2-hybridized, including the carbocation (contains an empty p-orbital)
- There are 6 π electrons, so n = 1

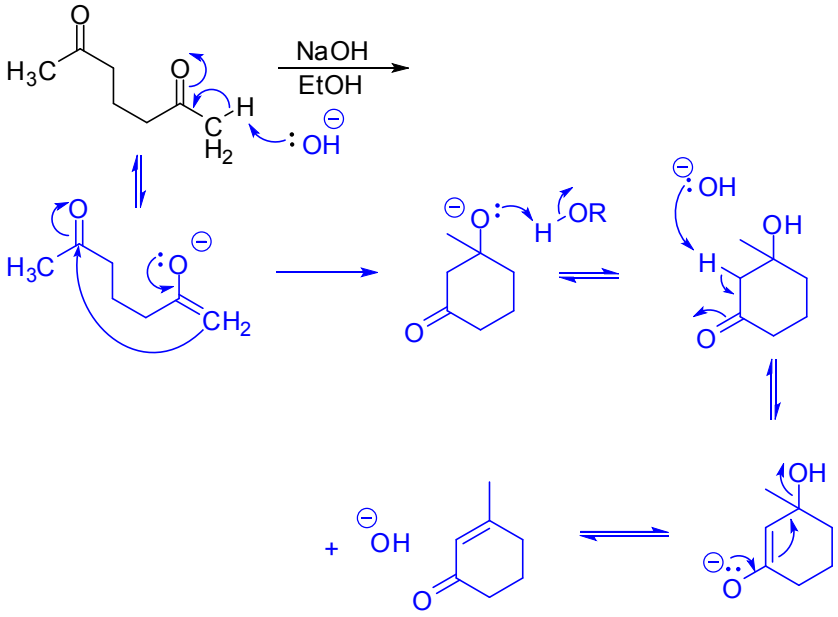
Yes, this molecule is aromatic

7. Give a mechanism for each step in the following reaction sequence: **(5 points)**



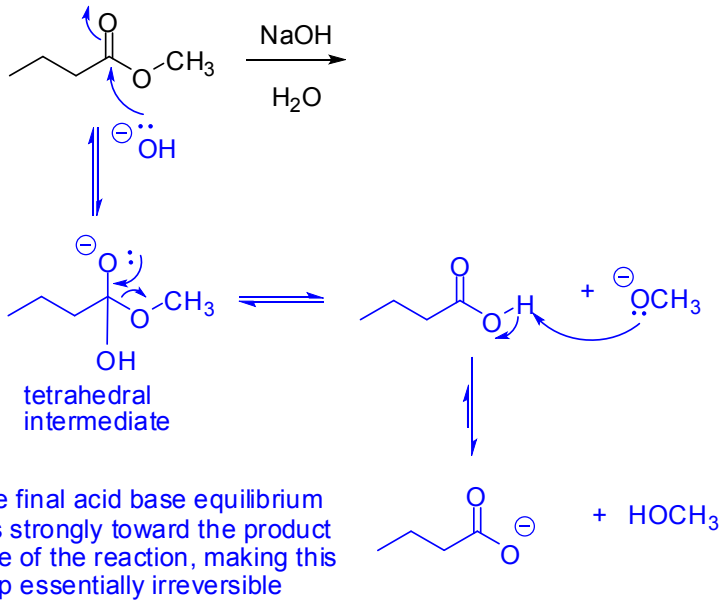
Note: the LDA and the ethyl bromide must be drawn out in full

8. Provide a mechanism for the following reaction: **(6 points)**



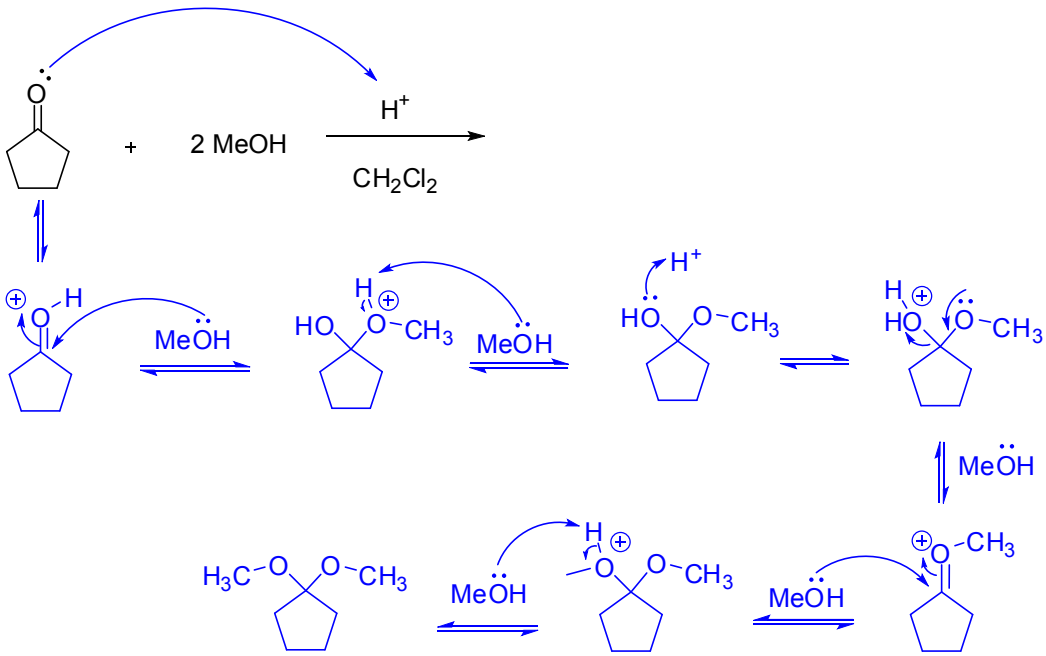
9.

a. Provide a mechanism and product for the following reaction **(5 points)**
b. Identify and name the key intermediate in the reaction **(1 point)**
c. Why is this reaction irreversible overall? **(1 point)**



10.

a. Provide a mechanism and product for the following reaction: **(6 points)**



b. The yield of this reaction was somewhat low.
   i. Suggest *two* ways to improve the yield **(2 points)**
   ii. Briefly rationalize each suggestion. **(2 points)**

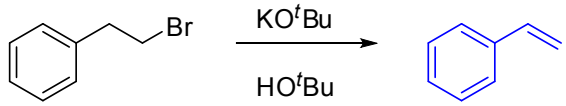
- Add an excess of methanol: this will drive the equilibrium towards products based on Le Chatelier's principle

- Remove water as it forms: this will drive the equilibrium towards products based on Le Chatelier's principle

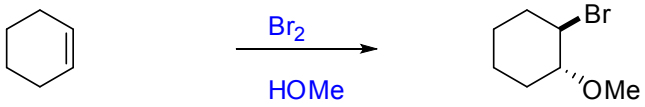
- Use a diol (like 1,2-ethandiol) to generate a cyclic acetal and diminish the entropy effect of starting with 3 molecules and finishing with only 2.

11. Give the missing reagent(s) or the major product of the following reactions: **(10 points—2 points each)**
Note: part marks might be given for incorrect answers with plausible mechanisms

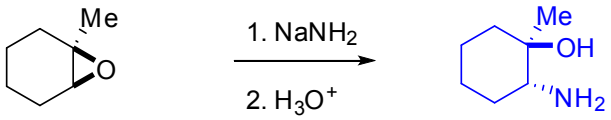
a.



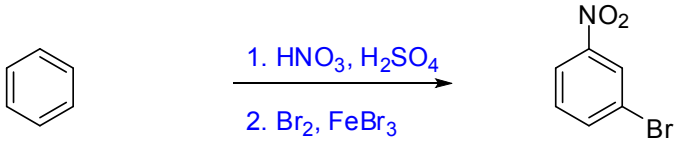
b.



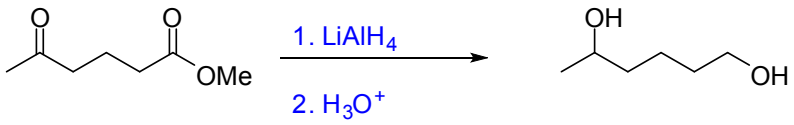
c.



d.

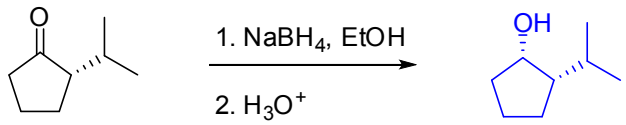


e.

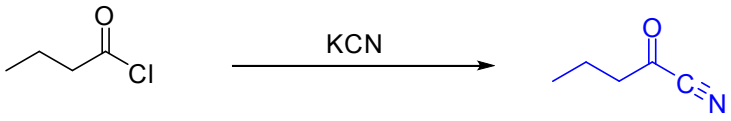


12. Give the major product of the following reactions: **(10 points—2 points each)**
Note: part marks will be given for incorrect answers with plausible mechanisms

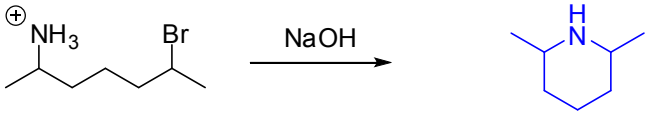
g.



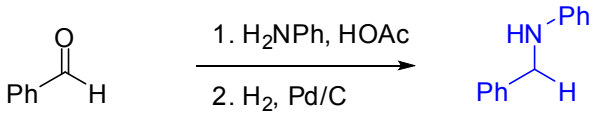
h.



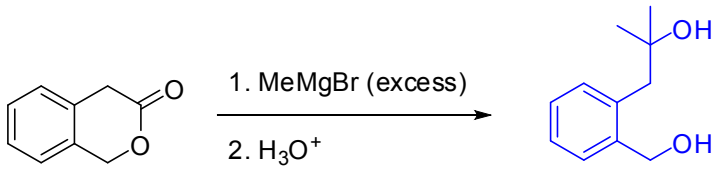
i.



j.

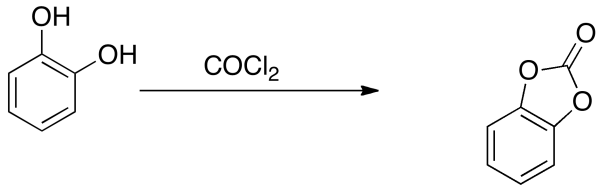


k.

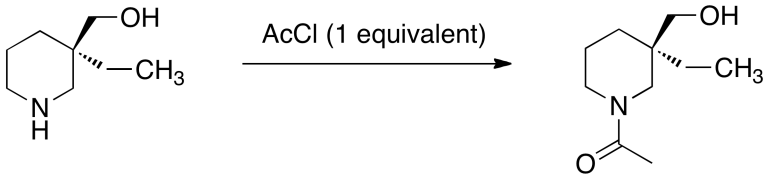


13. Give the major product(s) of each of the following reactions. **(10 points – 2 pts each)**

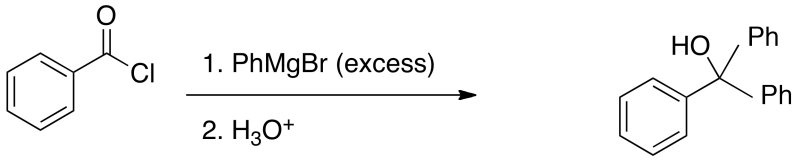
a)



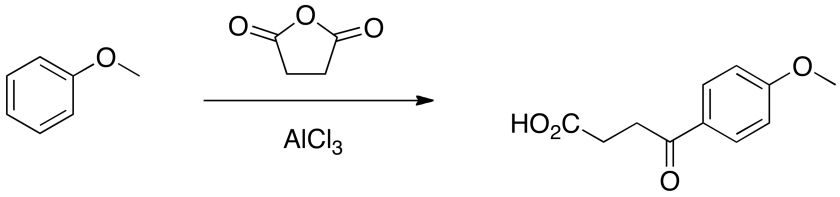
b)



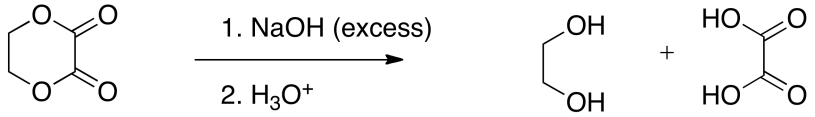
c)



d)

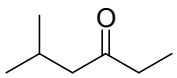


e)



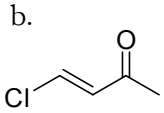
14. How many unique proton signals would be expected in the ^{1}H NMR of the following molecules? **(3 points)**

a.



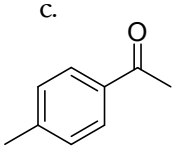
5

b.



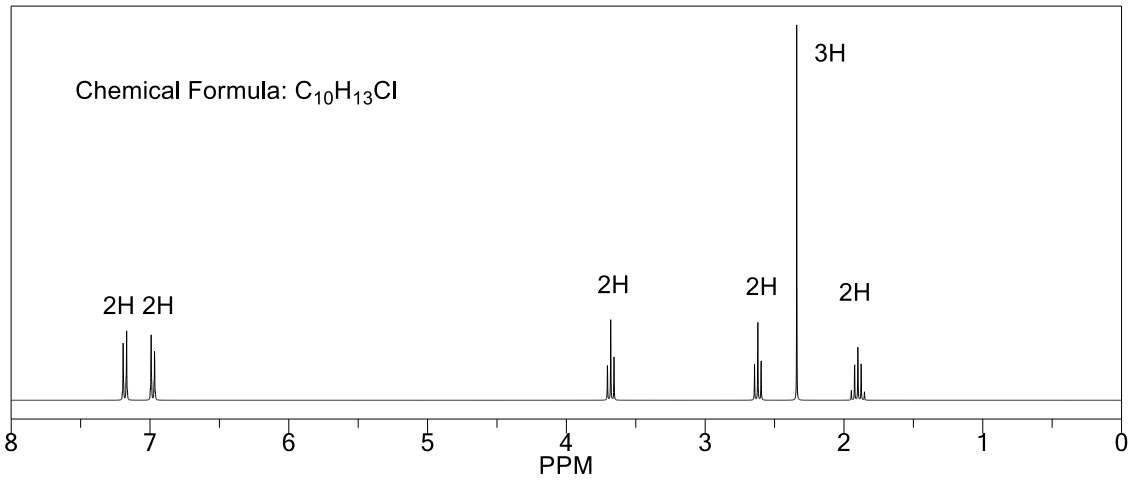
3

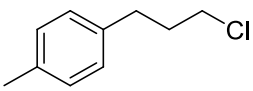
c.



4

15. Determine the structure of the compound represented in the NMR spectrum below. **(6 points)**



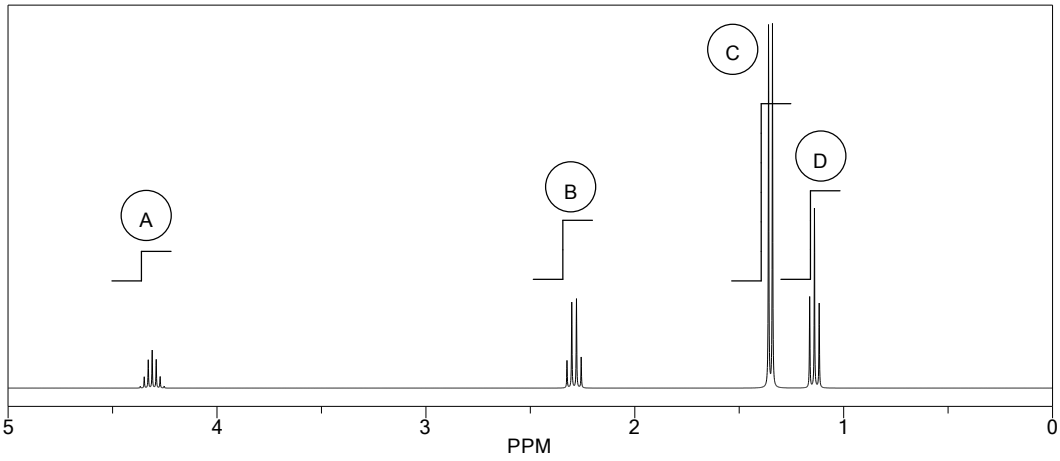


16.

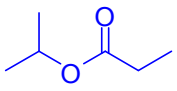
a. What is the structure of the unknown compound whose molecular formula is $\mathbf{C_6H_{12}O_2}$? The ^{1}H NMR spectrum of this compound is below. **(2 points)**

b. Justify your answer by accounting for all information given. **(10 points)**

Note: the infrared spectrum showed a number of absorbances from 2879 – 2960 cm^{-1}, and a strong absorbance at 1734 cm^{-1}.



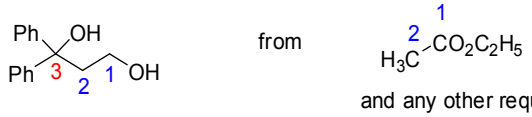
Peak	Chemical shift	Integra-tion	Multi-Plicity	Comments/Ideas
A	~ 4.3	1H	m (n=many)	CH—O
B	~2.3	2H	q (n=3)	CH_3–CH_2—C=O
C	~1.4	6H	d (n=1)	2 × CH_3-CH
D	~1.1	3H	t (n=2)	CH_3—CH_2



2 points

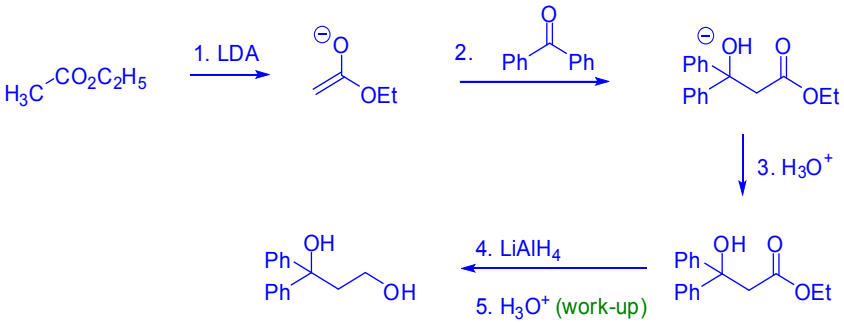
17. Propose a synthesis of the following molecule from the starting materials shown. An aldol reaction must be employed as part of the route (retrosynthesis is not required). **(6 points)**

- The ester has been reduced to an alcohol
- Carbon 2 has lost one hydrogen

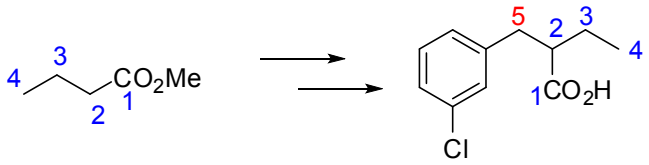


- There is a 1,3-relationship between the two oxygens--aldol reaction!
- The 2-3 bond is a new C-C bond

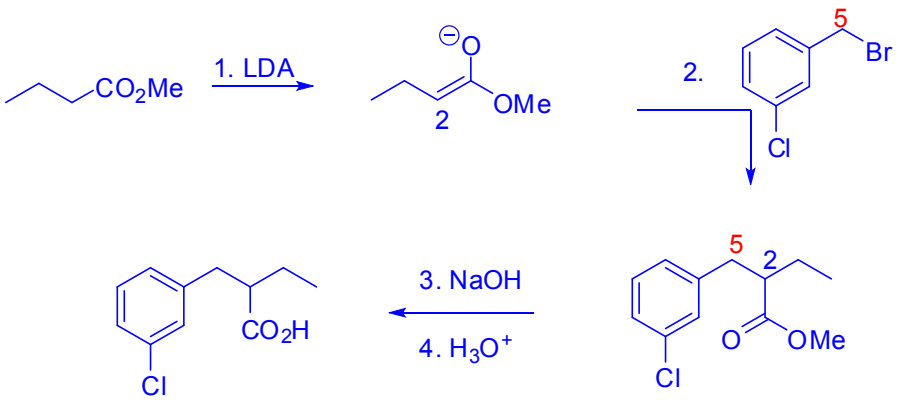
> Note: When an analysis/brainstorming is required, identify all the bonds that have been broken and formed between starting materials and products, and give suggestions (brainstorm) the types of reactions that might be appropriate. When brainstorming, your goal should be to generate many ideas, not to be "right." You should aim to have the "right" reactions once you are actually writing down the synthesis. Even then, chemists usually write down many posibilities before picking the one that looks best.



18. Propose a synthesis of the following molecule using the reagents described (retrosynthesis is not required). **(6 points)**

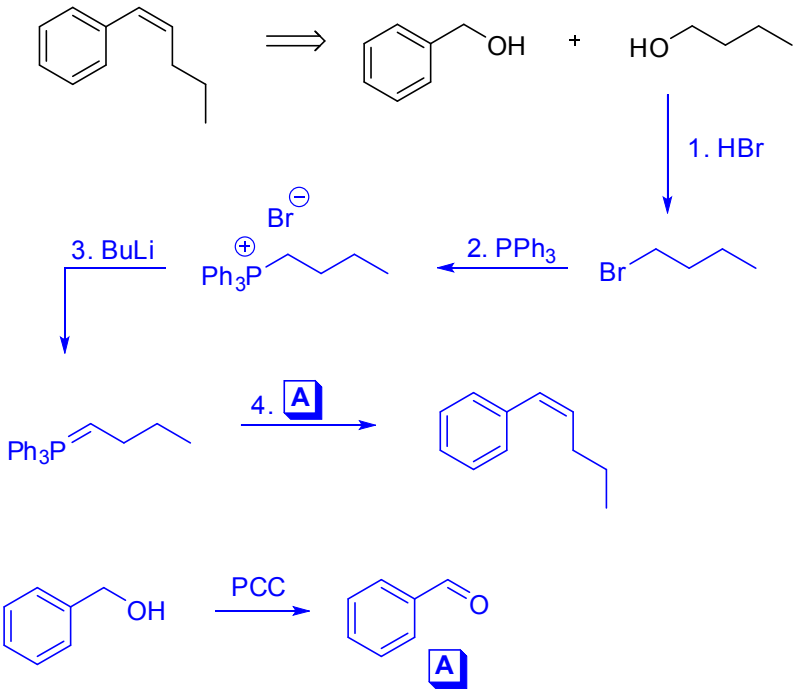


- The ester has been converted to a carboxylic acid (hydrolyzed)
- Carbon 2 has lost a H (deprotonation)
- There is a new C-C bond between carbons 2 and 5



19. Design a synthesis of (*Z*)-hept-3-en-2-one from benzyl alcohol and 1-butanol **(8 points)**. A brainstorming/analysis IS required (bonds broken/formed, atoms added/removed, stereochemistry, & regiochemistry) **(4 points)**. A retrosynthesis is not required.

Analysis (Brainstorming in brackets): - New C=C bond between benzylic carbon and alpha carbon from alcohol (E2 or Wittig?). Proton removed from benzylic position and alpha carbon from alcohol (Acid/base or E2?). Alcohols removed (S_N2—make OHs into good leaving groups?).



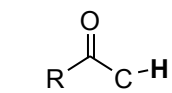
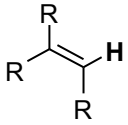
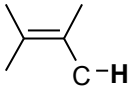
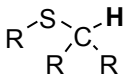
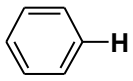
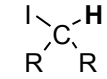
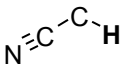
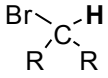
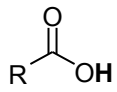
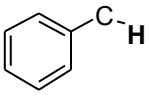
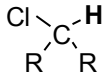
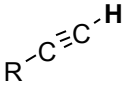
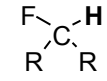
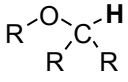
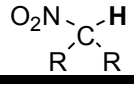
Appendices:

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												

IR: K**ey Absorptions (cm^{-1}):**

C-H	Alkyl	C-H	2850-2960	m, sharp
Alcohol		R**O-H**	3200-3650	s, broad
Carboxylic acid		RC(=O)**O-H**	2500-3300	s, broad
Amine		R_2**N-H**	3300-3500	s, broad
Carbonyl		R_2**C=O**	1650-1780	s, sharp
Nitrile		R**C≡N**	2220-2260	v, sharp
Alkynyl		C≡**C-H**	~3300	m, sharp
Alkynyl		**C≡C**	2100-2260	v, sharp

NMR – Key chemical shifts (ppm):

R-C-CH_n	0.7 - 1.7		2.2 - 2.9		4.5 - 7.0
	1.6 - 2.6		2.0 - 3.0		6.5 - 8.0
	2.1-2.5		2.0 - 4.0		9.0 - 10.0
	2.1 - 3.0		2.7 - 4.1		11.0 - 12.0
	2.3 - 2.7		3.1 - 4.1		
	1.7 - 2.7		4.2 - 4.8		
			3.0 - 5.0		
			4.1 - 4.3