Structural Elucidation: Infrared (IR) Spectroscopy

CHEM 8B Chapter 16 Homework

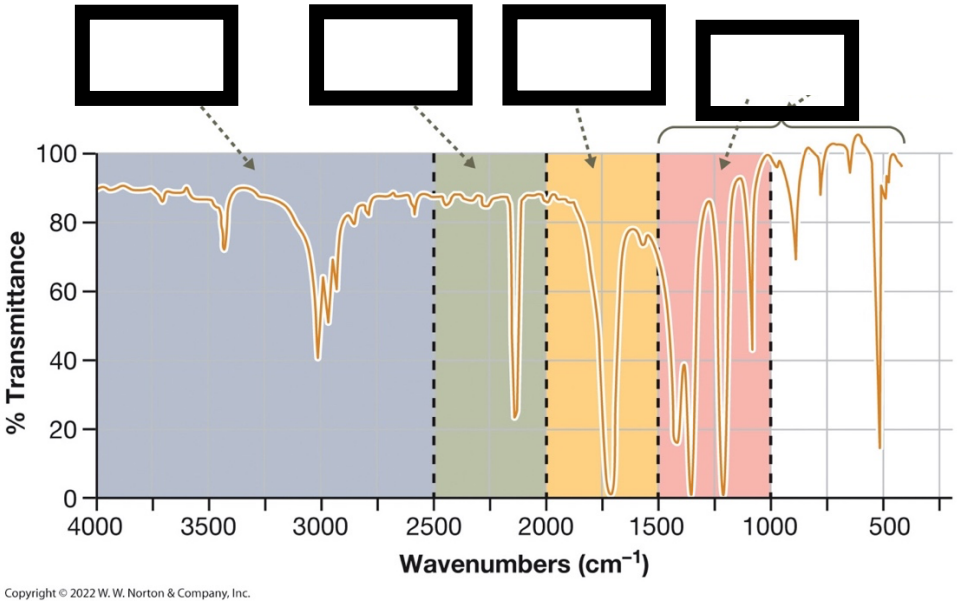
1. Consider the equations below with variables defined.

λ **-** wavelength (distance, m) ν **-** frequency (cycles per second, s^{-1}) **c** - speed of light, 3 x 10^8 m / s	$\nu\lambda = c$ Wavenumber, $\bar{\nu} = \frac{1}{\lambda}$

What is the relationship between <u>wavenumber</u> and <u>frequency</u>? Circle one.

Proportional Inversely proportional

2. Provide one example of a bond that would absorb in **each region** in each box below (ex. O-H, C=C).

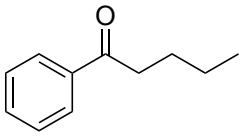


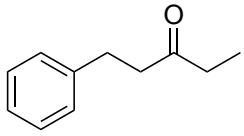
3. Bond length and stretching frequency

⇒ Which has a **longer bond**? Circle one. **O-H** **or** **C=O**

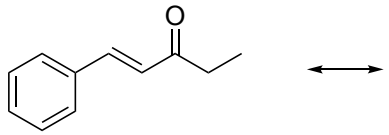
⇒ Which has a **higher stretching frequency** (wavenumber)? Circle one. **C-H** **or** **C≡C**

⇒ Which compound's **C=O** bond has a **lower stretching frequency** (wavenumber)? Circle one.

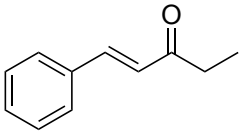


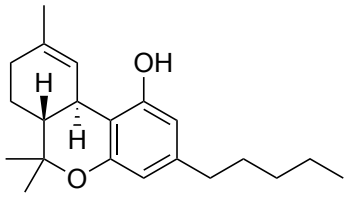


3. Conjugation - Resonance
Used **curved arrow** notation and **draw ONE resonance structure** of the compound below. Be sure to include all charges on atoms where appropriate!

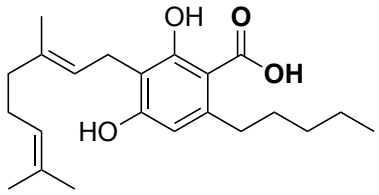


4. Predict IR Peaks: Use **Table 16-1** Characteristic Frequencies of IR absorption to list the **expected bond absorbance range (cm^{-1})** in its IR spectrum.

(a) The **C=O** bond in  _absorbs 1680 – 1750 cm^{-1}_ (worked example)



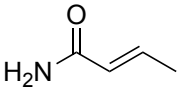
(b) The **O-H** bond in **Tetrahydrocannabinol (THC)** _____



Cannabigerolic Acid (CBGA)

(c) The carboxylic acid (**O-H** and **C=O**) bonds in

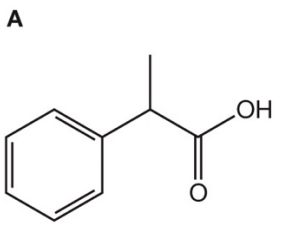
O-H _____ C=O _____

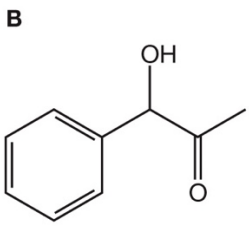
(d) The **N-H** bonds in  _____

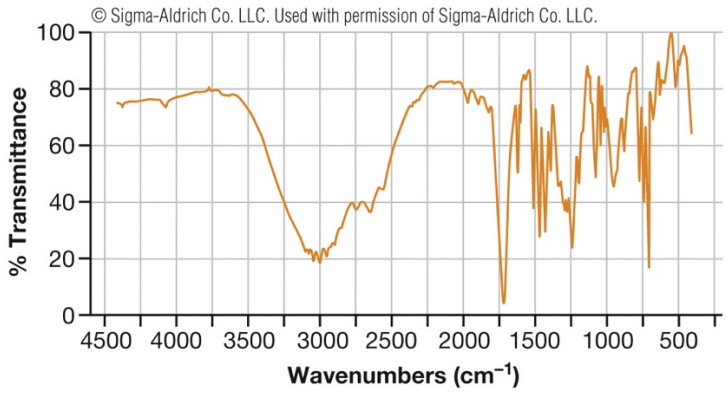
a. How many **N-H peaks** are expected for the compound above? Circle one.

0 1 2 3

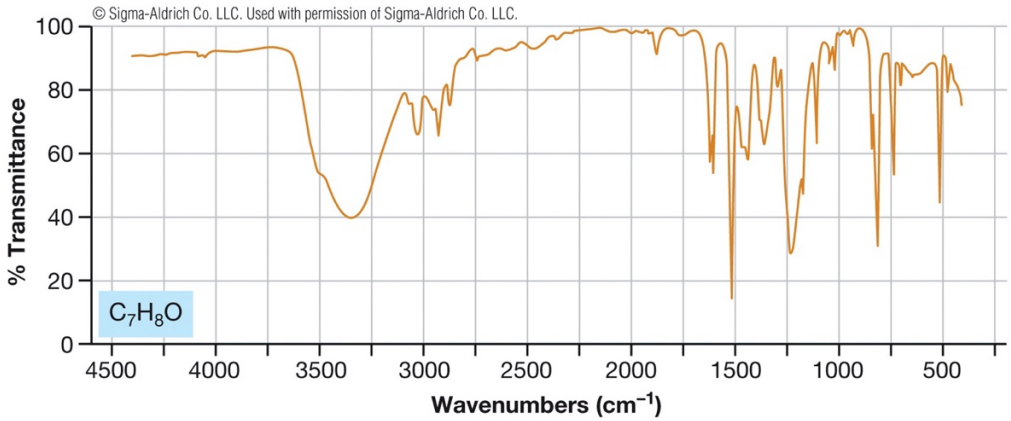
5. Match spectrum to molecule: Which molecule best fits the IR spectrum?







6. Propose TWO possible structures that fit the molecular formula **C_7H_8O** and the IR spectrum below.



(a) What oxygen-containing **functional group** does the compound have? _____

(b) Draw two proposed **structures** for C_7H_8O, one in each box. *Hint: the molecule contains a ring.*

7. Structure elucidation in a chemical reaction, using IR and Mass Spec data analysis of the product. Answer the prompts below to help confirm the structure of a reaction product.

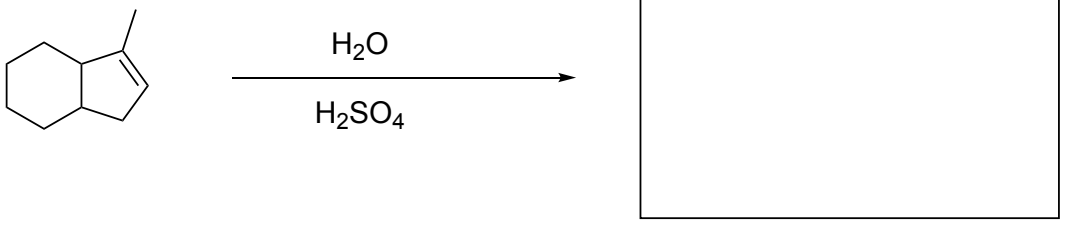
(a) The mass spectrum of the product in the reaction below displays a **M^+ peak = 154**.

What is the molecular the **molecular formula** of the product? _____

(b) The IR spectrum displays a **broad, strong signal at 3250cm^{-1}**.

What is the most likely **functional group** in the product? _____

(c) Draw the structure of the **product** in the box.



7. Structure elucidation in a chemical reaction, using IR and Mass Spec data analysis of the product. Answer the prompts below to guide you to the structure of the reaction product.

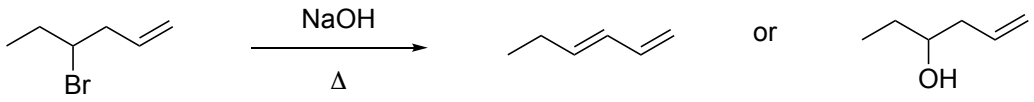
(a) The mass spectrum of the product in the reaction below displays a **M^+ peak = 82**.

What is the molecular the **molecular formula** of the product? _____

(b) The IR spectrum displays a **medium-strength signal at 1627 cm^{-1}**.

What is the most likely **functional group** in the product? _____

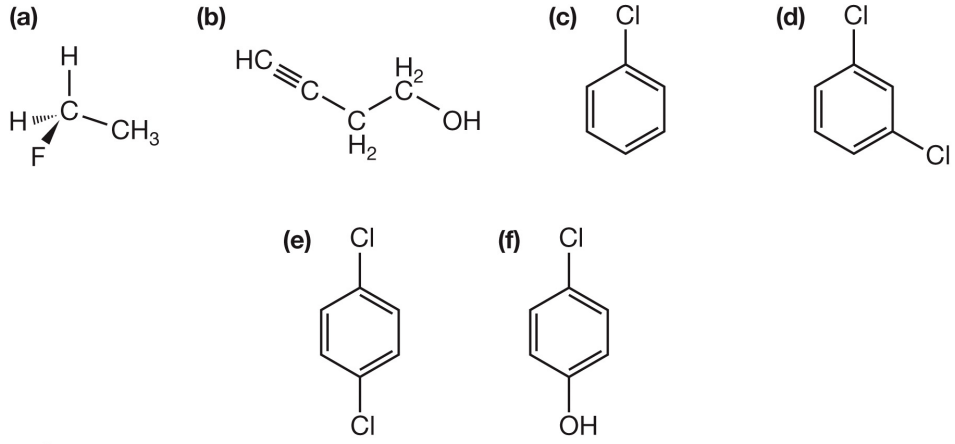
(d) **Circle the major product** of the reaction based on the spectroscopy data above.



Chapter 17 Homework – Nuclear Magnetic Resonance (NMR)

Part A. Carbon Nuclear Magnetic Resonance, ^{13}C NMR

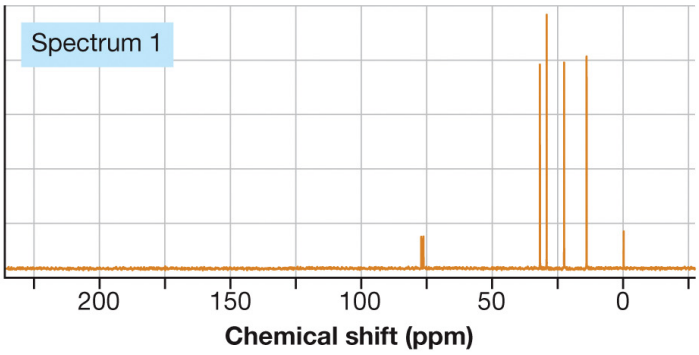
1. **How many signals** are expected in each compound's ^{13}C NMR spectrum?

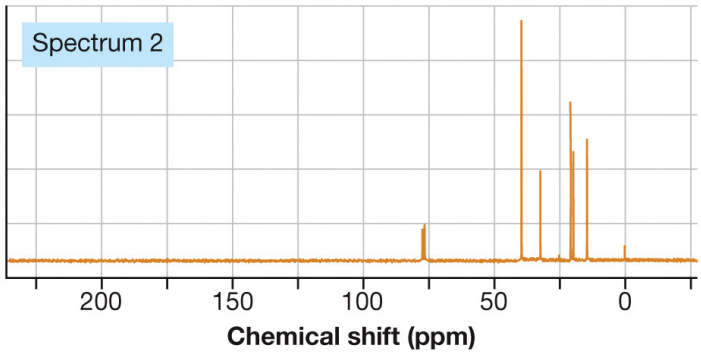


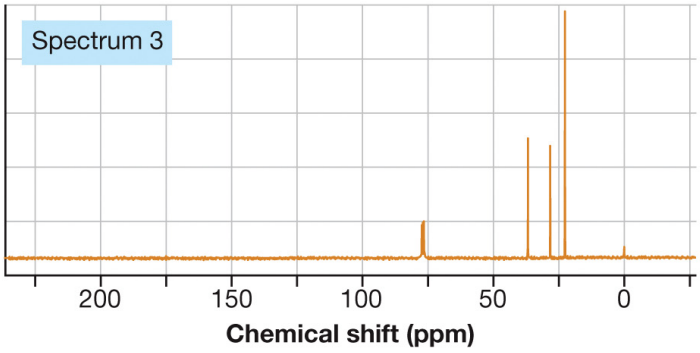
	Number of ^{13}C NMR signals
(a)	
(b)	
(c)	
(d)	
(e)	
(f)	

2. The ^{13}C NMR spectra of three isomers with molecular formula C_8H_{18} are given below. **Match each chemical name to its spectrum (1-3)**. Ignore the peak at 76 ppm (solvent).

Isomer	**Spectrum (1, 2, or 3?)**
2,5-dimethylhexane	
4-methylheptane	
Octane	

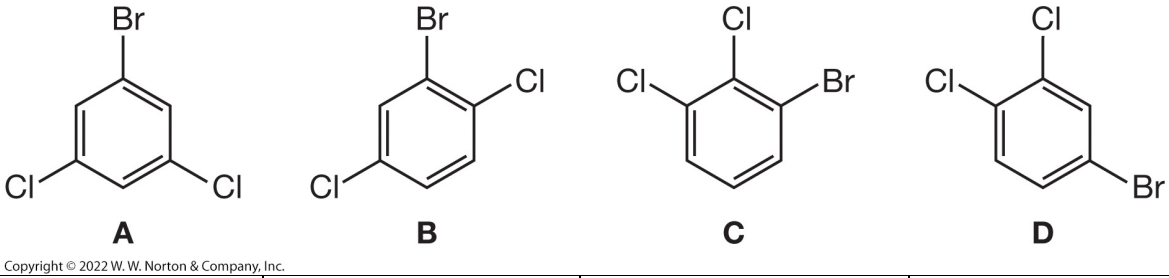






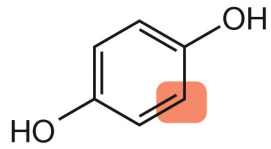
Ch 17A. ^{13}C NMR

3. **How many signals** are expected in each compound's ^{13}C NMR spectrum?



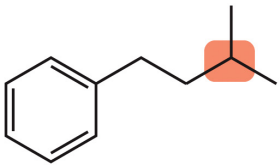
4. Indicate the **approximate chemical shift (range)** of each highlighted carbon in its ^{13}C NMR spectrum (Table 17-5).

(a)



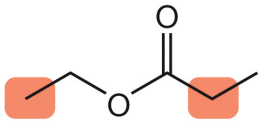
CH

(b)



CH

(c)

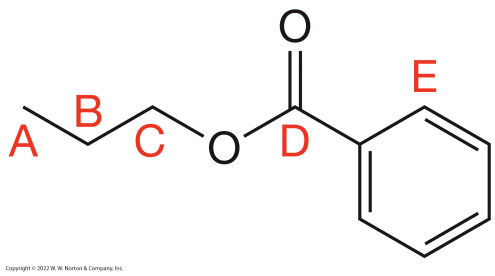


CH_3

20-35

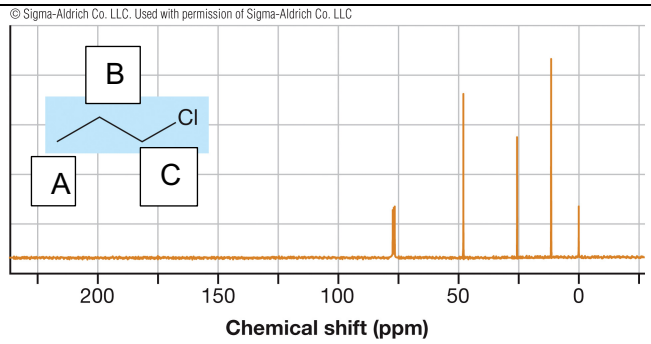
CH_2

5. **Indicate the expected ^{13}C NMR chemical shift range** for each carbon (A-E) in the table below.



Signal	Chemical shift range (ppm) Table 17-5
A	
B	
C	
D	
E	

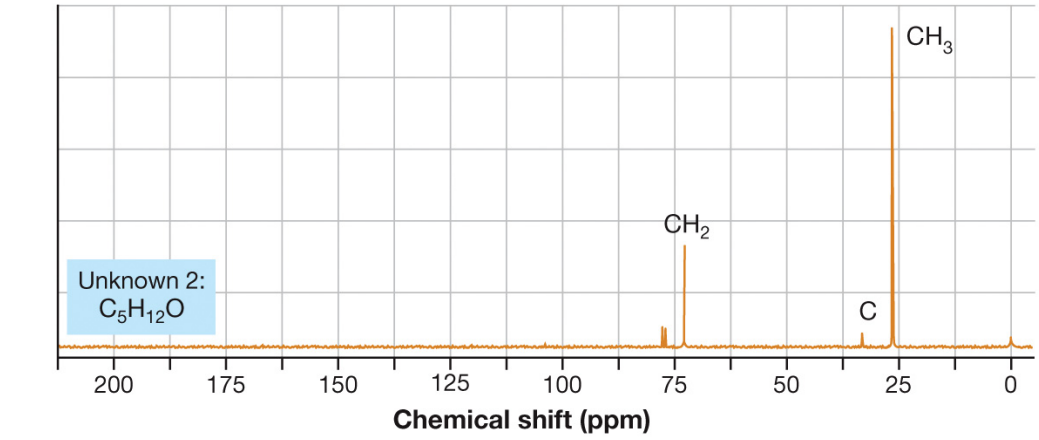
6. 1-chloropropane produced the ^{13}C NMR spectrum shown here. **Match each carbon** in the molecule (letters A-C) to each signal in the spectrum.

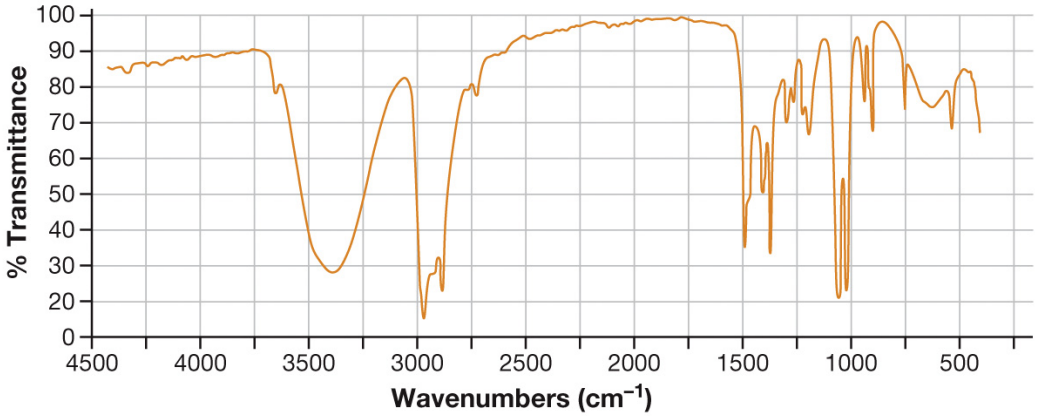


Signal (ppm)	Carbon (A, B, or C)
10	
25	
49	

Ch 17, Part A. ^{13}C NMR

7. **Propose the structure** of the molecule that matches the spectral data below.





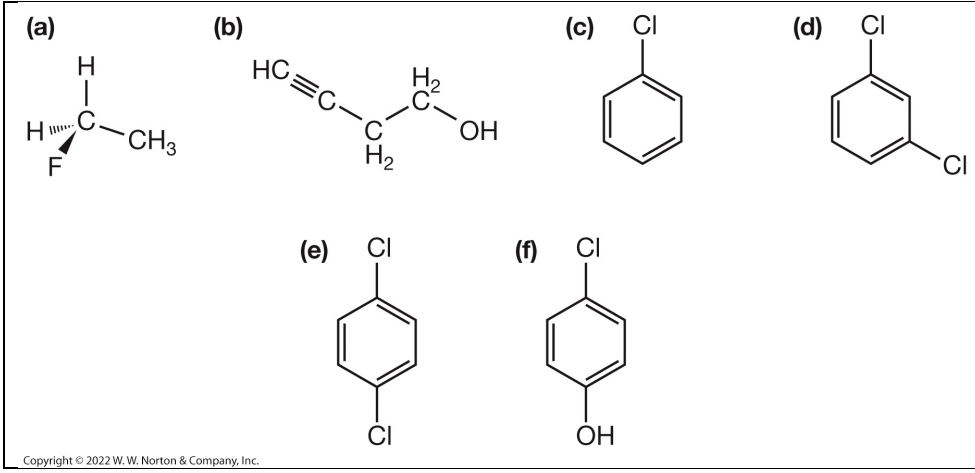
What clues does the **^{13}C NMR** spectrum provide about the structure?

What clues does the **IR spectrum** provide about the structure?

Structure:

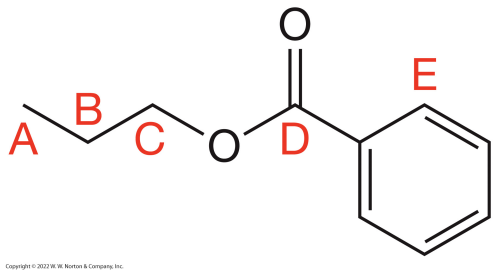
Chapter 17 HW, Part B. Proton Nuclear Magnetic Resonance, ^{1}H NMR

8. **How many signals** are expected in each compound's ^{1}H NMR spectrum?



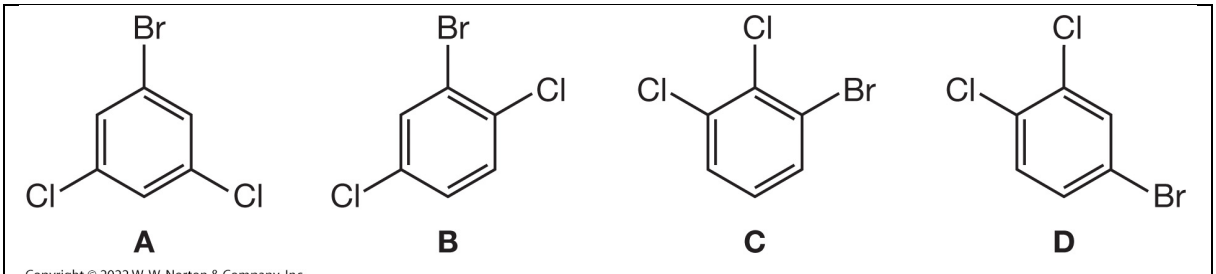
	Number of ^{1}H NMR signals
(a)	
(b)	
(c)	
(d)	
(e)	
(f)	

9. Indicate the **approximate ^{1}H NMR chemical shift** for each carbon (A-E) in the table below.



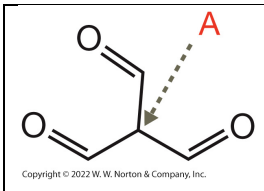
Signal	Chemical shift (ppm) Table 17-1
A	
B	
C	
D	
E	

10. **How many signals** are expected in each compound's ^{1}H NMR spectrum?



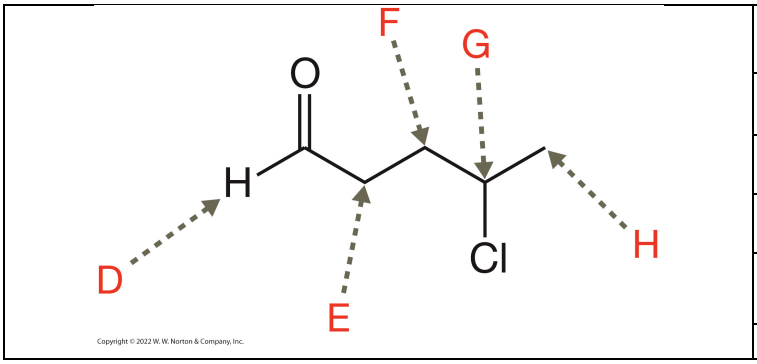
Chapter 17B. ^{1}H NMR

11. Rank protons A-C in order from **largest to smallest chemical shift.** Write the proton's letter in the right column of the table. Then, provide the **integration value** (number of H's) responsible for each signal.



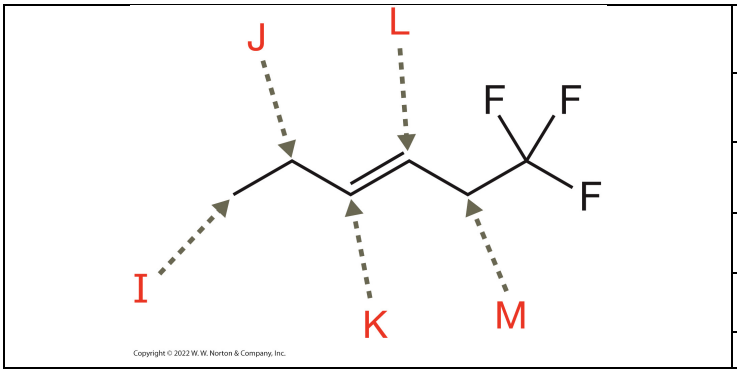
Chemical Shift Rank	Proton (A-C)	Integration (# of H's)
High		
Medium		
Low		

12. Rank protons D-H in order from **largest to smallest chemical shift.** Write the proton's letter in the right column of the table.



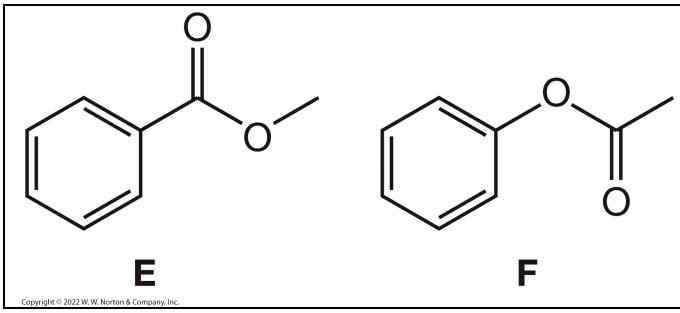
Chemical Shift Rank	Proton (D-H)	Integration (# of H's)
Highest		
Lowest		

13. Rank protons I-M in order from **largest chemical shift to smallest.** Write the proton's letter in the right column of the table.



Chemical Shift Rank	Proton (I-M)	Integration (# of H's)
Highest		
Lowest		

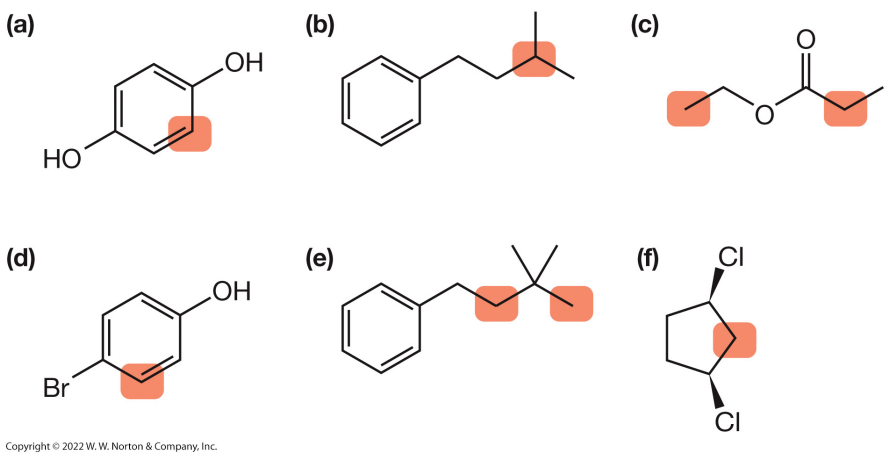
14. Report the approximate **^{1}H NMR** and **^{13}C NMR chemical shifts of just the <u>CH_3 group</u>** in similar benzylic esters **E** and **F** below.



	^{1}H NMR (Table 17-1)	^{13}C NMR (Table 17-5)
E		
F		

Chapter 17B. ^{1}H NMR

15. Use the N+1 rule, where N is the number of adjacent H's, to predict **splitting pattern** of the highlighted signal in its ^{1}H NMR spectrum (singlet, doublet, triplet, quartet, pentet, sextet, septet, octet, or nonet).



	Splitting Pattern(s)
(a)	
(b)	
(c)	CH_3 group: CH_2 group:
(d)	
(e)	CH_2 group: CH_3 group:
(f)	

16. **<u>Structural Elucidation</u>**: use the data below to determine the structure of the compound.

		What does each piece of data tell you about the compound?
Formula	C_3H_6O	Any double bonds?
IR	1720 cm^{-1} (broad, strong) 2900 cm^{-1} (sharp, strong)	
^{1}H NMR	One signal… Chemical shift = 2.0 ppm Integration = 6H Splitting = singlet	
^{13}C NMR	δ 207 ppm δ 31 ppm	

Structure:

Chapter 17 HW

17. Structural Elucidation: use the data below to determine the structure of the compound.

<table>
<tr><td>Formula</td><td colspan="3">$C_5H_{12}O$</td><td>What does each signal tell you about the compound?
(show your work in the space below)</td></tr>
<tr><td>IR</td><td colspan="3">3300 cm^{-1}

2900 cm^{-1}</td><td></td></tr>
<tr><td>^{1}H NMR</td><td>Chemical shift</td><td>Integration (# of Hs)</td><td>Splitting</td><td rowspan="6"></td></tr>
<tr><td rowspan="5"></td><td>4.0 ppm</td><td>1</td><td>Broad singlet</td></tr>
<tr><td>3.5 ppm</td><td>2</td><td>Triplet</td></tr>
<tr><td>1.6 ppm</td><td>1</td><td>nonet</td></tr>
<tr><td>1.5 ppm</td><td>2</td><td>quartet</td></tr>
<tr><td>0.9 ppm</td><td>6</td><td>doublet</td></tr>
<tr><td>^{13}C NMR</td><td colspan="3">δ 61 (CH_2)

δ 42 (CH_2)

δ 25 (CH)

δ 23 (CH_3)</td><td></td></tr>
</table>

Structure:

This graded HW set includes problems adapted from the Karty 3 text.

Recommended Problems from Karty 3, Chapter 17 – see Canvas textbook module

- **In-Chapter Problems,** “Your Turn” = 1-4,7,8, 14-16, 20, 21, 24-27, 30
- **End-o-Chapter Problems** = 1-2, 6-9, 11, 12, 21, 24, 25, 29-35, 41, 44, 47, 49, 52, 53
  - Solutions to all problems are now available for FREE in the Canvas textbook module!

Chapter 18-19 Homework – Addition to Polar pi Bonds

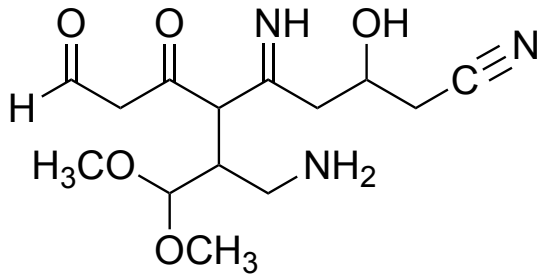
Chapter 18A. Bond Basics

1. to each bond to indicate its polarity.

C–Li C – Mg C = O C = N O – H C ≡ N

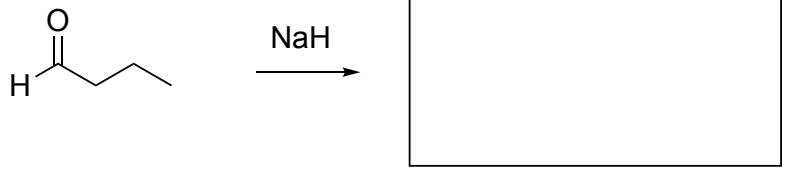
2. Circle and label each functional group in the fictional molecule below.

- Acetal
- Alcohol
- Aldehyde
- Amine
- Imine
- Ketone
- Nitrile



3. Show the mechanism and product for the **alpha-deprotonation of butanal**.

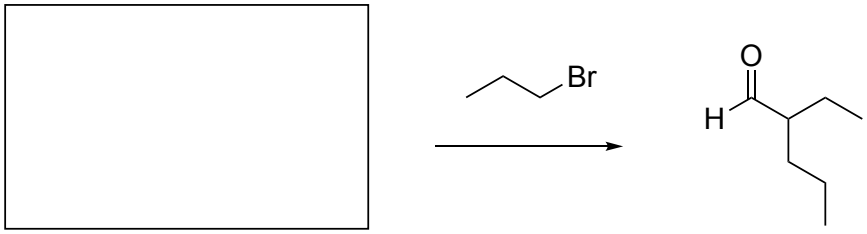
- **Draw the H's** in the alpha position,
- use **curved arrow** notation to show the proton transfer reaction with sodium **hydride**,
- and **draw the enolate** formed.



enolate

4. React the enolate above with propylbromide via SN2 mechanism (one-step substitution).

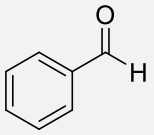
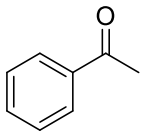
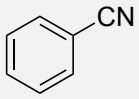
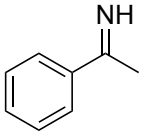
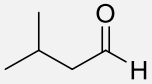
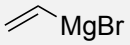
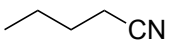
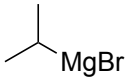
- **Redraw the enolate** from #3 above.
- **Add curved arrows** to explain how the bonds are broken and formed.



enolate

18B. CARBONYL REACTIONS

- Draw the product of each reaction: **starting material + reagents → Product.**

	Starting Material	**Reagents** *& translation* *be able to draw the arrow-pushing mechanism	**Alternate reagents** (same product)	**Draw the Product**
5	 **benzaldehyde** (almond extract)	**$NaBH_4$, MeOH** *sodium boro**hydride** in methanol*	1. $NaBH_4$ 2. H_2O *Or* 1. $LiAlH_4$ 2. H_2O	
6	 **Acetophenone**	**1**. **$LiAlH_4$** **2. H_2O** *lithium aluminum **hydride** followed by water*	$NaBH_4$, MeOH *Or* 1. $NaBH_4$ 2. H_2O	
7	 **benzonitrile**	**1**. **$LiAlH_4$** **2. H_2O** *lithium aluminum **hydride** followed by water*	n/a	
8	 **imine**	**$NaBH_4$** *sodium boro**hydride** in methanol*	1. $LiAlH_4$ 2. H_2O	
9	 **3-methylbutanal**	1.  2. H_2O ***vinyl** magnesium bromide followed by water*	1.  2. H_2O	
10	 **nitrile**	1.  2. H_2O ***Isopropyl lithium** followed by water*	1.  2. H_2O	

Pro-tip: See the REACTION SUMMARY at the end of Chapter 18 class notes.

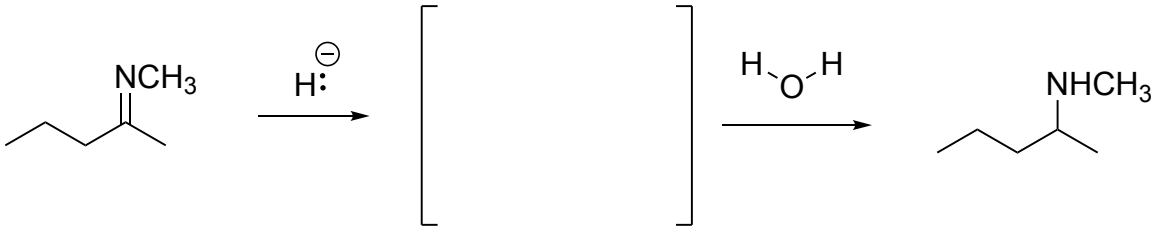
Ch 18C. POLAR Pi BOND ADDITION MECHANISMS

- Draw the arrow-pushing mechanism for the reactions, including all charged intermediates and product.
- Hydride and organometallic reagents are simplified with their nucleophilic form.

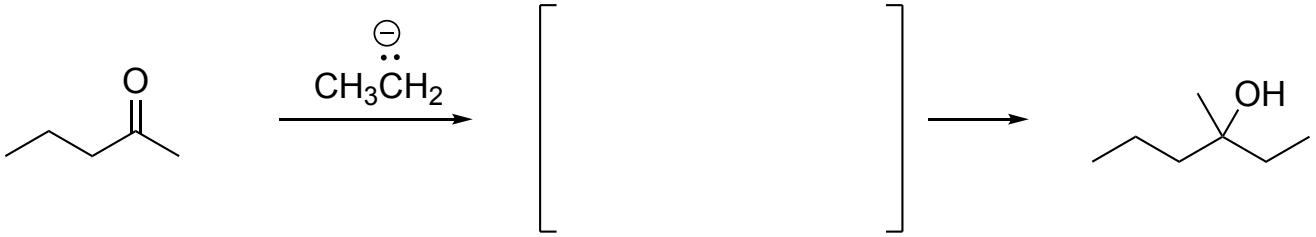
11. Ketone Reduction

12. Nitrile reduction

13. Imine reduction

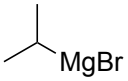
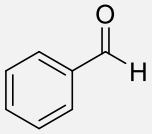
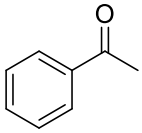
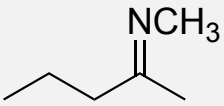
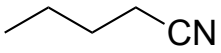
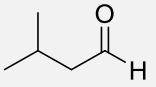
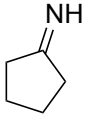


14. Addition of organometallic to aldehyde/ketone



15. Nitrile + organometallic

18D. Mix & Match with Reaction Bootcamp!

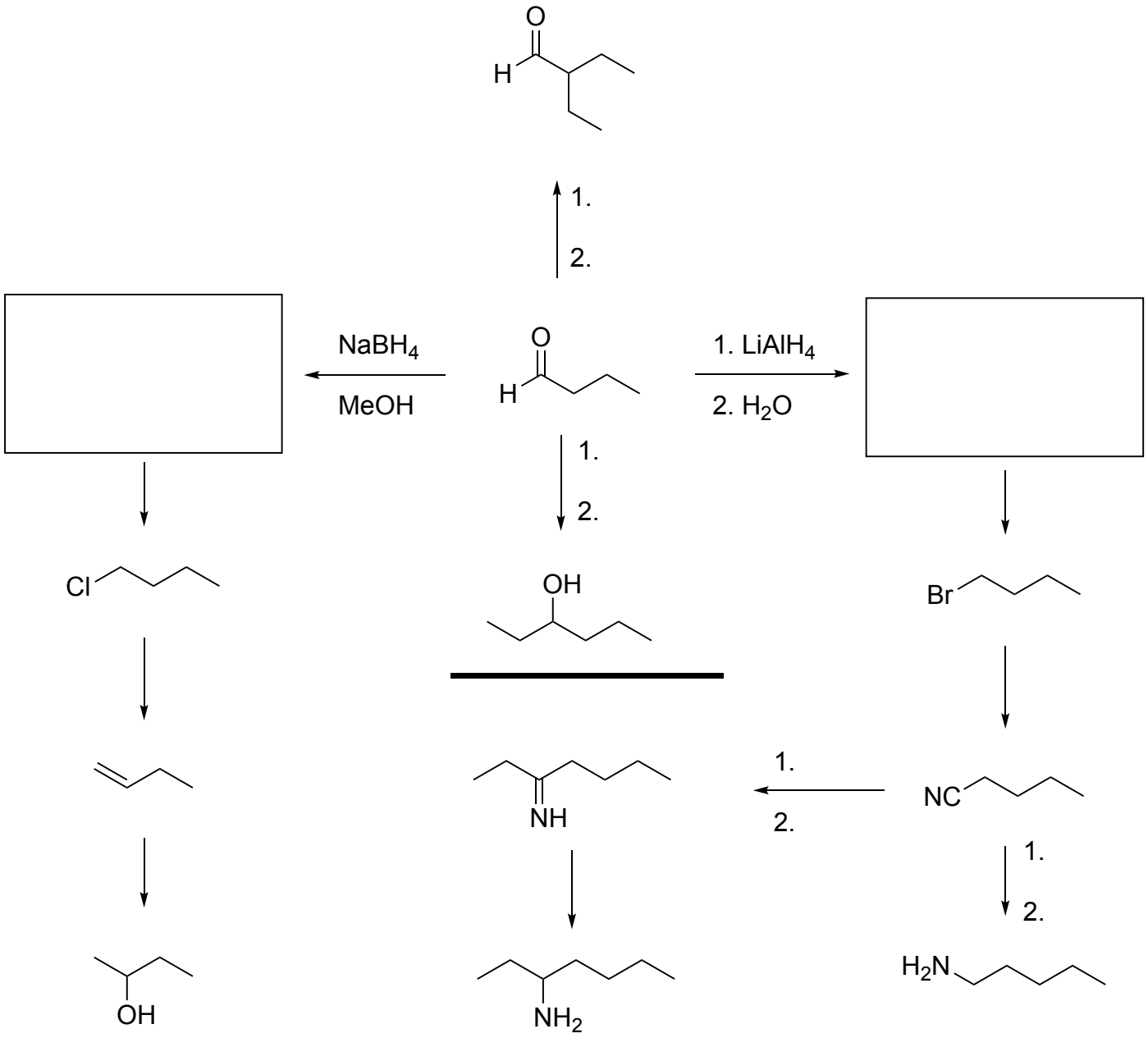
	React each carbonyl compound with each reagent and draw the product in the box	$NaBH_4$, MeOH	1. $LiAlH_4$ 2. H_2O	1.  2. H_2O
16	 **benzaldehyde** (almond extract)			
17	 **Acetophenone**			
18	 **imine**			**NO REACTION**
19	 **pentanenitrile**	**NO REACTION**		
20	 **3-methylbutanal**			
21	 **imine**			**NO REACTION**

18E. Reaction Puzzle - “training wheels” for multi-step synthesis

The “puzzle” below covers Chapter 18 and previous reactions. Take it one step at a time.

Draw the missing products in the boxes and **add missing reagents** to the arrows.

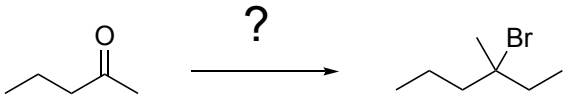
When the reagents need to be separated into steps, the numbers are provided for you.



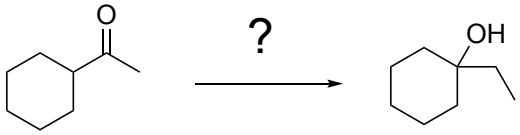
18F. Multi-Step Synthesis

- Each transformation requires **at least two synthetic steps** to reach the target product.
  - These problems were designed to use no more than four reactions.
  - There are multiple pathways and it's ok if you use a feasible pathway with more than four steps ☺
- Show each set of **reagents and reaction products** on the journey.
  - Mechanisms are not required, but may be helpful.
- If there is a mixture of products (ex. *major* and *minor*), assume the minor product can be removed.
  - You can just draw the desired *major* product.

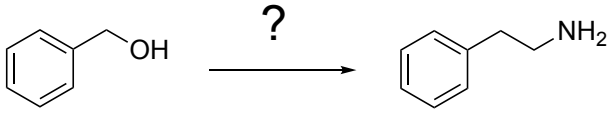
22.



23.

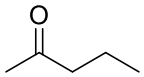
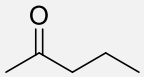
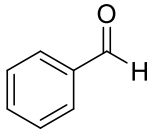
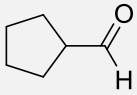
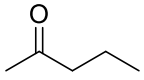


24.



Chapter 19 Homework – Addition of Weak Nucleophiles to Polar pi Bonds

19A. NUCLEOPHILIC ADDITION REACTIONS with weak-sauce nucleophiles

	Starting Material	Reagents *& translation*	Draw the Product
1		**HCN** *hydrogen cyanide*	
2		**NH_3**, H^+ ***Ammonia** under acidic conditions*	
3		**H_2NCH_3**, H^+ ***Methylamine** with acid catalyst*	
4		**CH_3CH_2OH,** H^+ *excess **ethanol** under **acidic** conditions*	
5		**$HOCH_2CH_2OH$**, H^+ ***1,2-ethanediol** under acidic conditions*	

19B. ACIDIC NUCLEOPHILIC ADDITION MECHANISMS

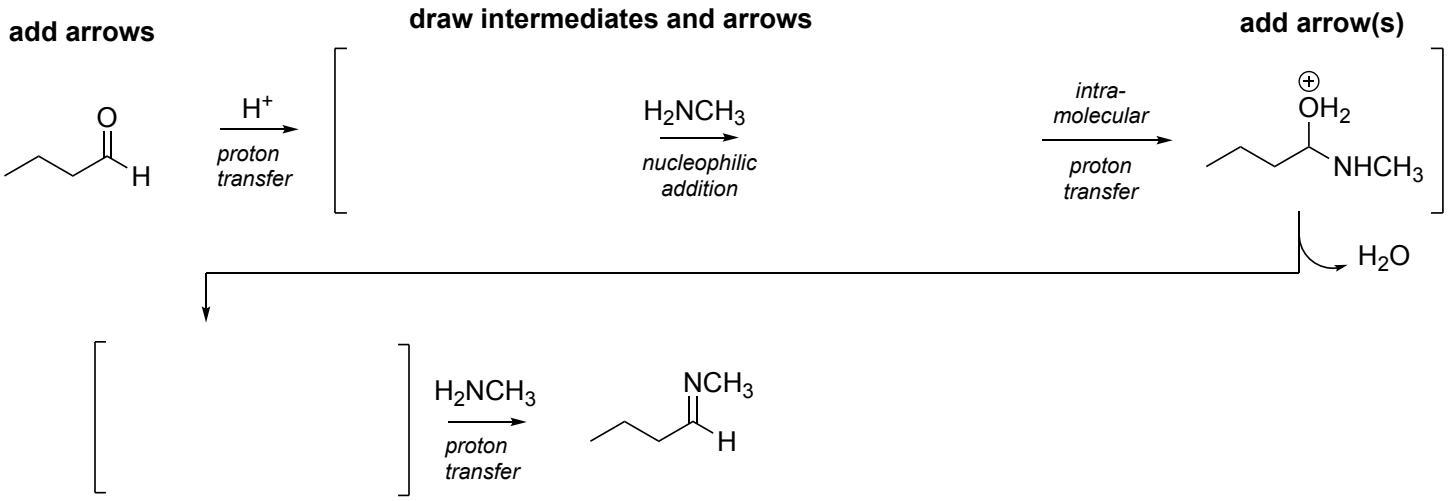
- Draw the arrow-pushing mechanism for each reaction, including all charged intermediates and product.

7. Cyanohydrin formation

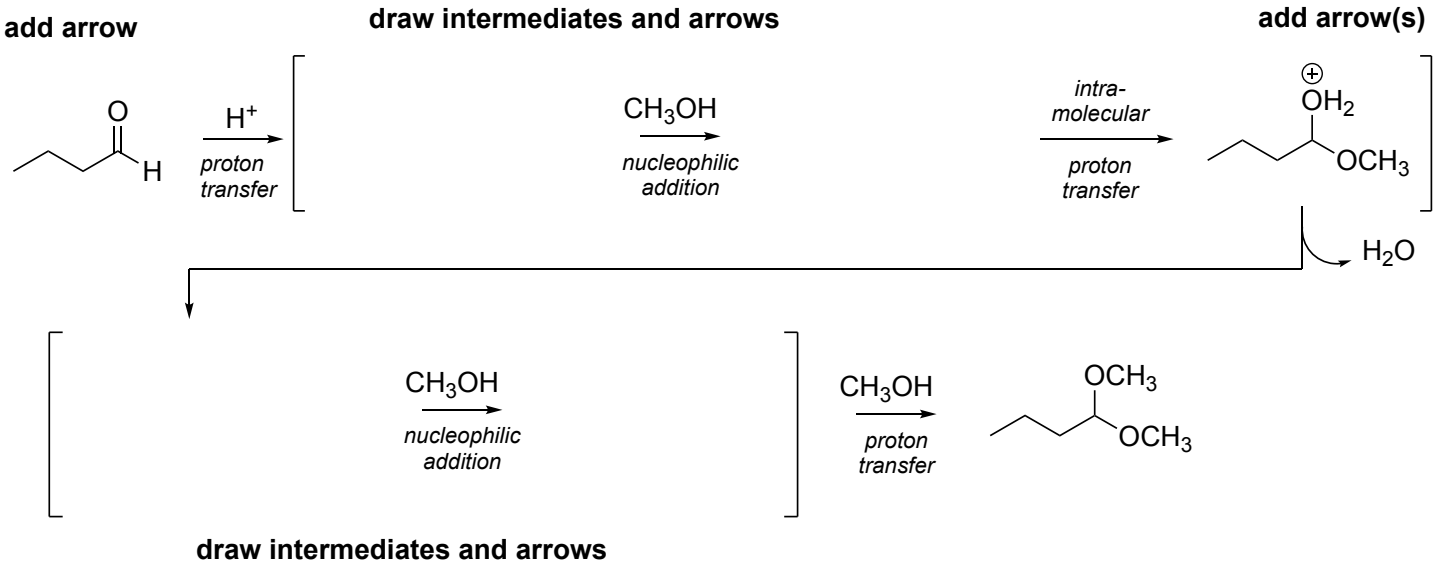
19C. NUCLEOPHILIC ADDITION & DEHYDRATION MECHANISMS

- Draw the arrow-pushing mechanism for each reaction, including all charged intermediates and product.

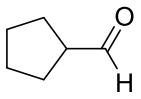
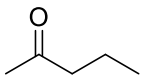
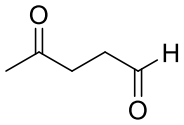
8. Imine mechanism



9. Acetal Mechanism



19D. Mix & Match with Reaction Bootcamp!

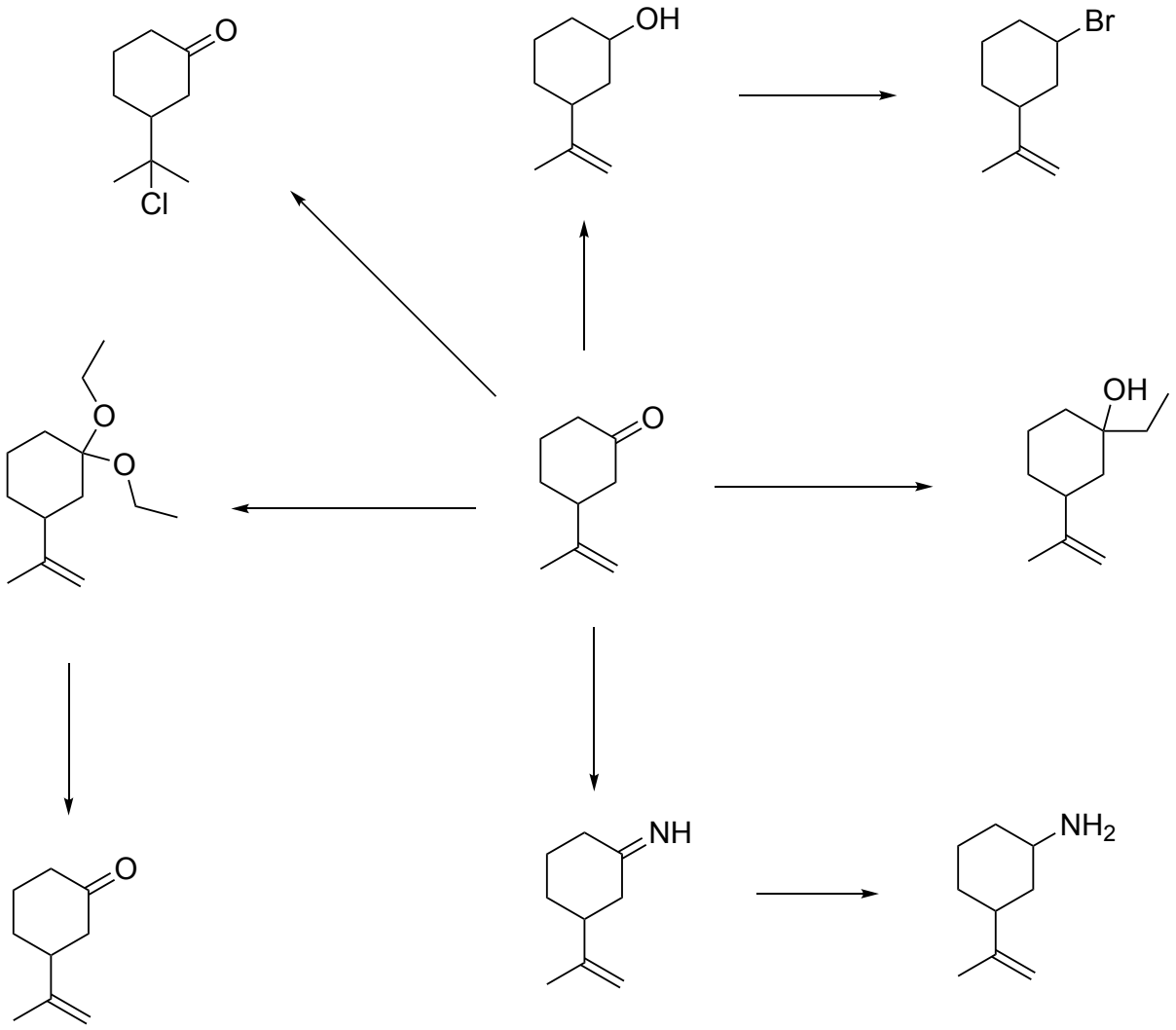
React each **aldehyde or ketone** with each **reagent** and **<u>draw the product</u>** in the box.			
CH_3CH_2OH (2 mol), H^+			
HCN			
$HOCH_2CH_2OH$, H^+			
H_2NCH_3, H^+			
$PhNH_2$, H^+			

19E. Reaction Puzzle - “training wheels” for multi-step synthesis

The “puzzle” below covers Chapter 19 and previous reactions. Take it one step at a time.

Add all missing reagents to the arrows.

- Hydride and organometallic addition reactions require a separate, second step for addition of water.
- Be sure to add those numbers for separate steps (1…. 2….) where applicable for full credit.



19F. Chemoselective Reaction Puzzles - "training wheels" for multi-step synthesis

Aldehydes are more reactive than ketones, but what if you want the ketone to react instead?

I. The aldehyde is reacted with alcohol to form an acetal "protecting group",

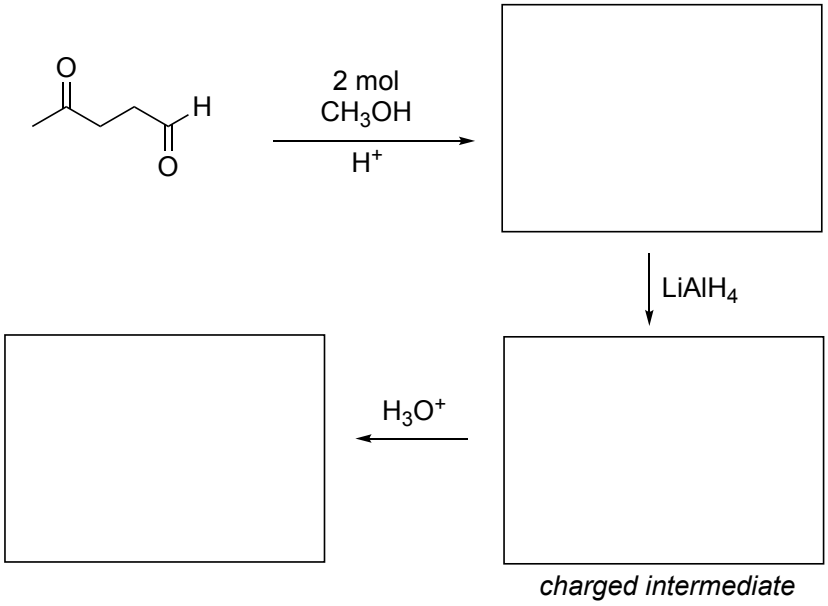
II. then the desired addition reaction takes place on the ketone,

III. and finally the acetal is removed (hydrolyzed) to reveal the original aldehyde.

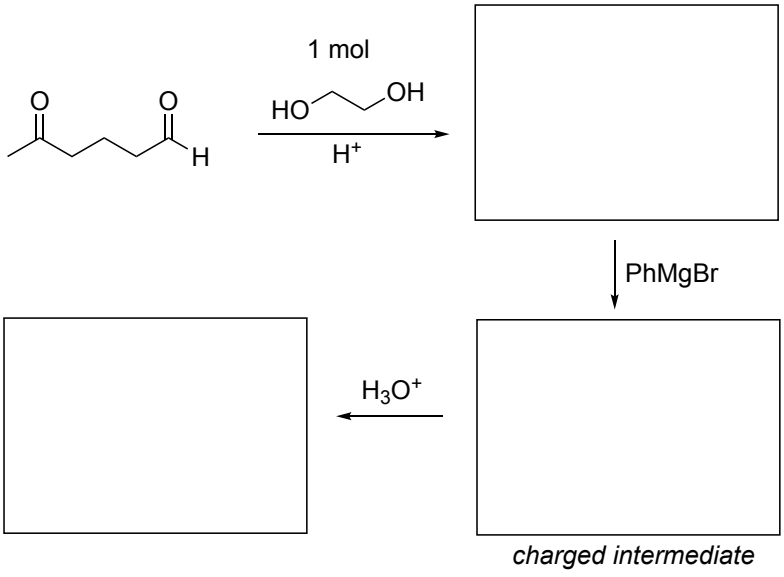
Cool, right?!

Draw the missing products of each reaction in the boxes.

11. Chemoselective reduction



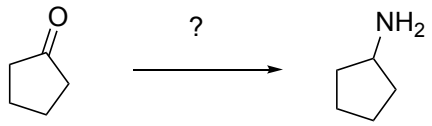
12. Chemoselective organometallic addition



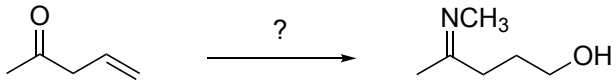
19F. Multi-Step Synthesis

- Each transformation requires **at least two synthetic steps** to reach the target product.
  - These problems were designed to use no more than three reactions.
  - There are multiple pathways and it's ok if you use a feasible pathway with more than three steps ☺
- Show each set of **reagents and reaction products** on the journey.
  - Mechanisms are not required, but may be helpful.
- If there is a mixture of products (ex. *major* and *minor*), assume the minor product can be removed.
  - You can just draw the desired *major* product.

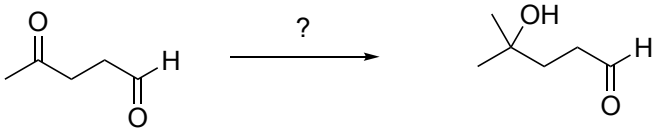
13. Ketone to amine



14. Conjugated ketone to alpha-chloro-imine

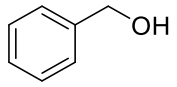
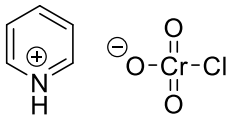
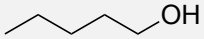
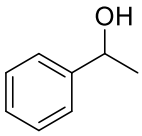
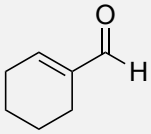
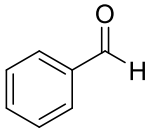


15. Chemoselective organometallic addition – see "training wheels" on pg 5

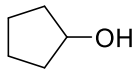
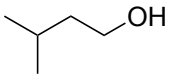
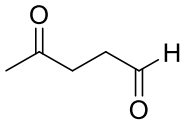


Chapter 20 Homework – Redox Reactions

20A. REDOX Reactions

	Starting Material	Reagents *& translation*	Draw the Product
1		 **pyridinium chlorochromate** (PCC) ***PCC**: Pyridinium chlorochromate in methylene chloride solvent*	
2		**$NaCrO_4$** *Chromic Acid* or **$KMnO_4$** *Potassium permanganate* *Reagents may also be listed as…* 1. $KMnO_4$, KOH 2. H_2O, HCl	
3		PCC	
4		**1 mole H_2, Pd** *1 mole of hydrogen gas over palladium catalyst* *Alternate metals to Pd: platinum (Pt) or nickel (Ni)*	
5		**$NaCrO_4$** or **$KMnO_4$**	

20B. Mix & Match with Reaction Bootcamp!
Not all molecules react with all reagents – look out for seven combinations that result in "NO REACTION".

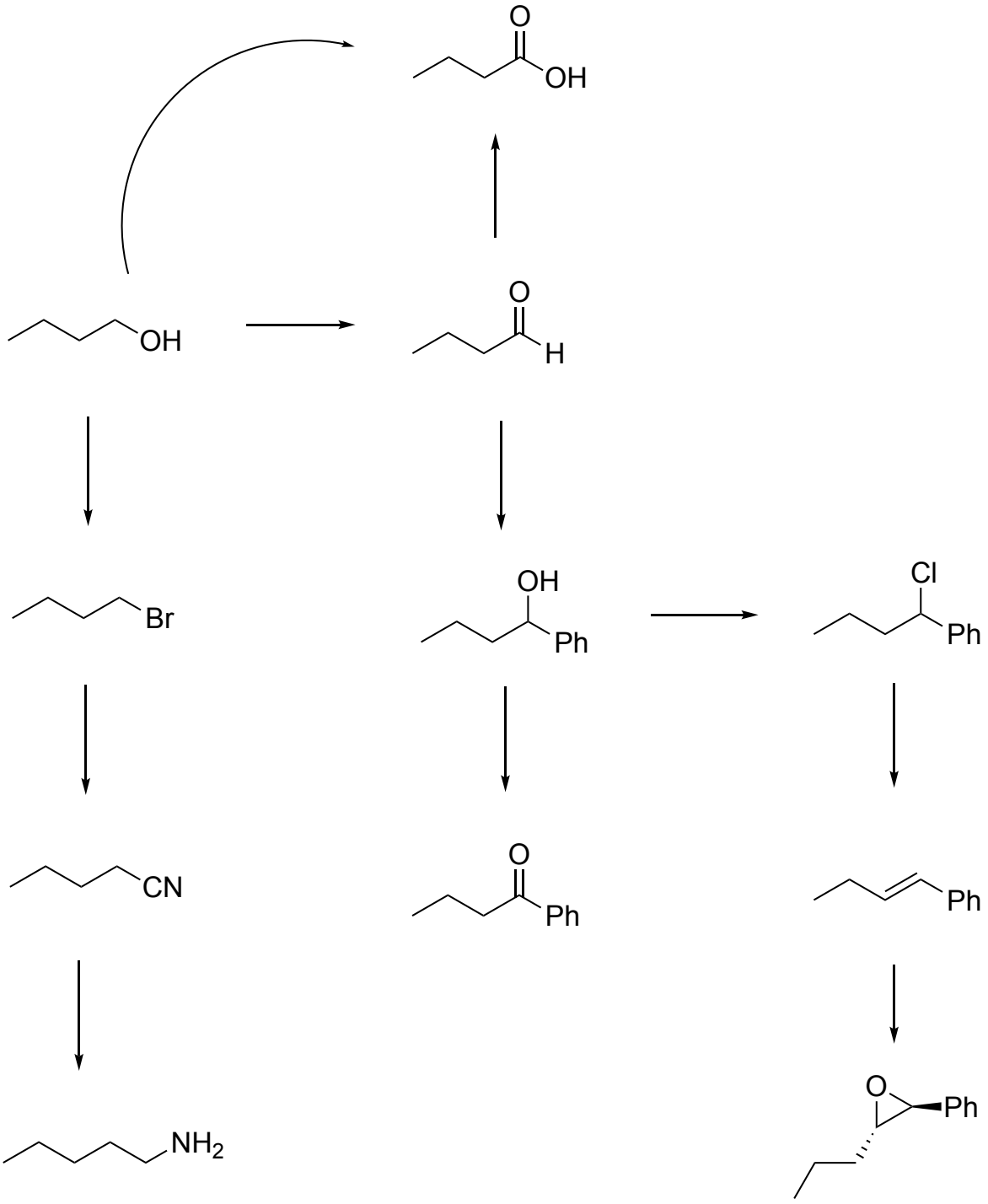
React each **molecule** with each **reagent** and **draw the product** in the box.			
PCC			
$NaCrO_4$			
1. $LiAlH_4$ (excess) **2. H_2O**			
1 mole H_2, Pt			
$NaBH_4$ (1 mol) **CH_3OH**			

20D. Reaction Puzzle - “training wheels” for multi-step synthesis

The “puzzle” below covers Chapter 20 and previous reactions. Take it one step at a time.

Add all missing reagents to the arrows.

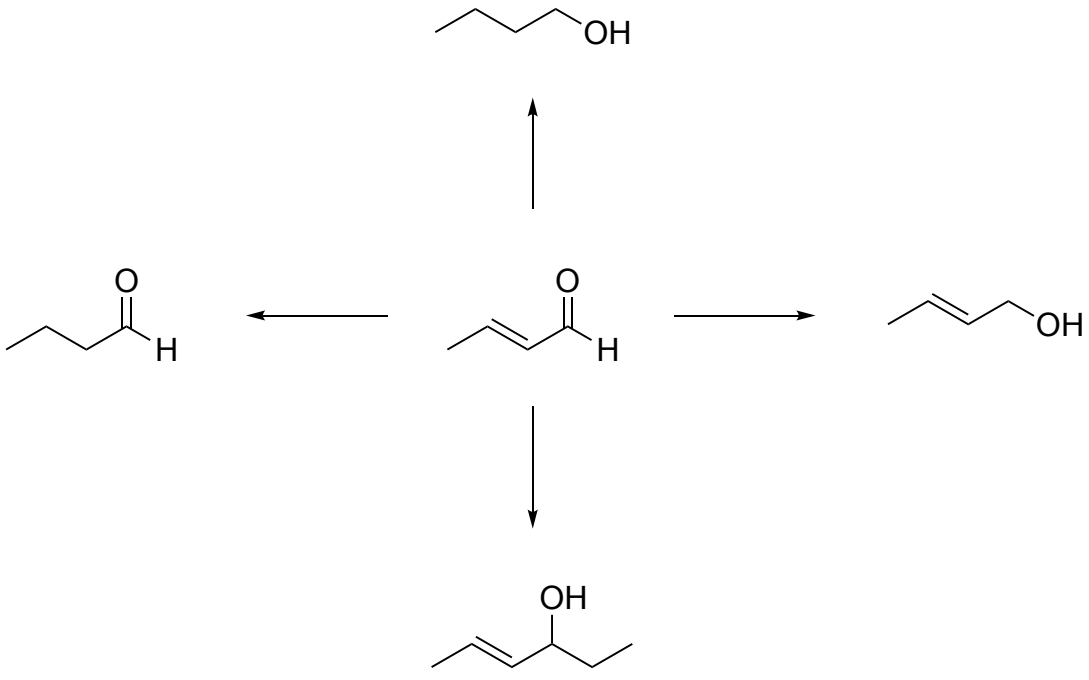
- Hydride and organometallic addition reactions require a separate, second step for addition of water.
- Be sure to add those numbers for separate steps (1…. 2….) where applicable for full credit.



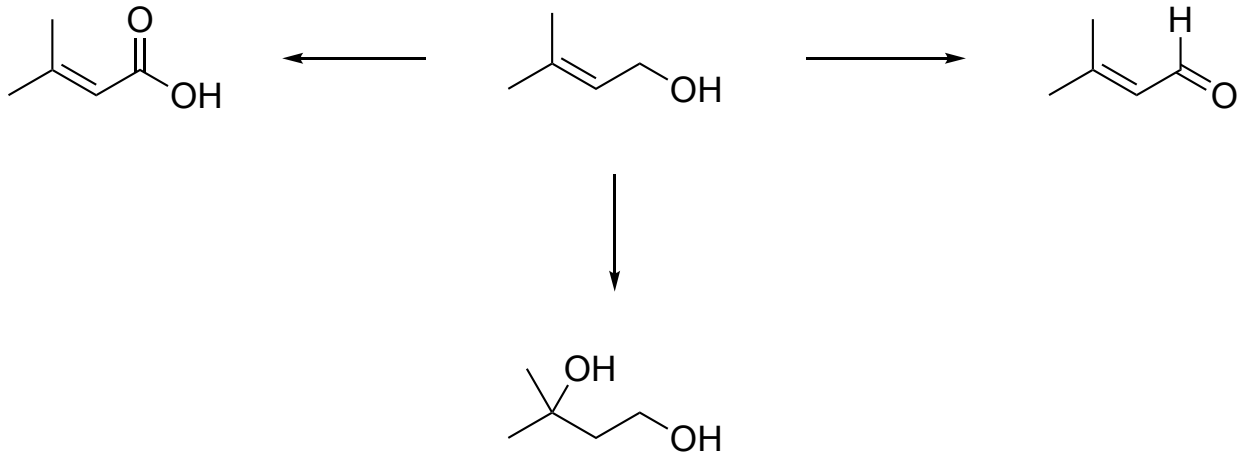
20E. Chemoselective Readuction Puzzles - “training wheels” for multi-step synthesis

- Fill in the proper **reagent** over the arrows below.
- Include the **amount** of each reagent added (1 mole or 2 moles).

11. Aldehyde & Alkene



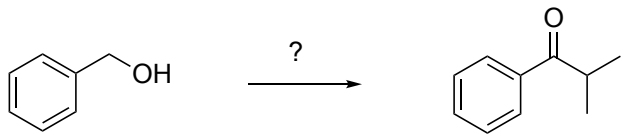
12. Alcohol & Alkene



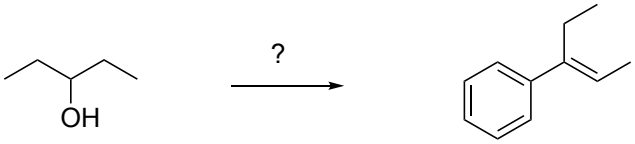
20F. Multi-Step Synthesis

- Each transformation requires **at least two synthetic steps** to reach the target product.
    - All problems below require an organometallic reagent to add carbons. Be sure you're using it with the correct type of functional group!
    - These problems were designed to use no more than four reactions. There are multiple pathways and it's ok if you use a feasible pathway with more than four steps ☺
- Show each set of **reagents and reaction products** on the journey.
- Mechanisms are not required, but may be helpful.
- If there is a mixture of products (ex. *major* and *minor*), assume the minor product can be removed.

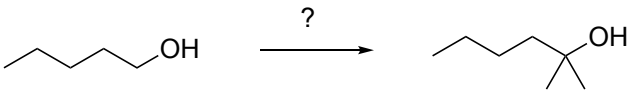
13.



14.

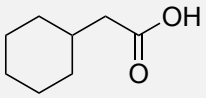
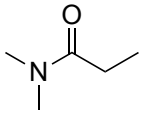
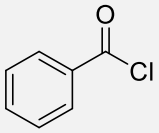
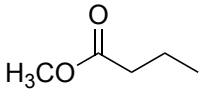
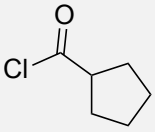
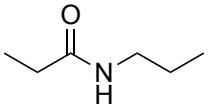
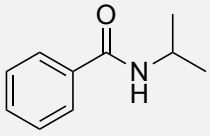


15.



Chapter 22 Homework – Carboxylic Acids & Friends

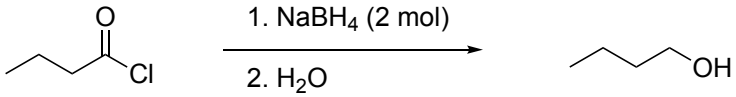
20A. HYDROGEN & OXYGEN NUCLEOPHILES.
Draw the product of each reaction: **starting material + reagent → Product.**

	Starting Material	Reagents *& translation*	Draw the Product
1		**1. xs $LiAlH_4$** **2. H_2O** *Excess lithium aluminum* ***hydride,*** *followed by water*	
2		**1. xs $LiAlH_4$** **2. H_2O**	
3		**xs $NaBH_4$, MeOH** *sodium boro****hydride*** *in methanol*	
4		**1. xs $LiAlH_4$** **2. H_2O**	Draw both organic products
5		**H_3O^+, Δ** *Aqueous acid and heat*	
6		**H_3O^+, Δ**	Draw both organic products
7		**H_3O^+, Δ**	Draw both organic products

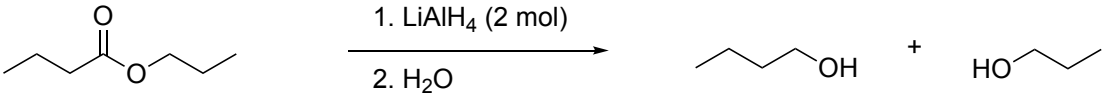
22B. Mechanisms – Acid Derivatives with hydrogen and oxygen nucleophiles.

- Draw the arrow-pushing mechanism for each reaction, including all charged intermediates and product.

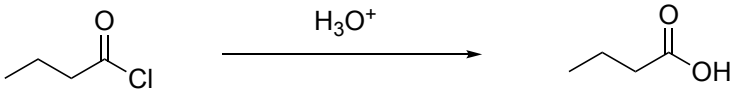
8. Acid chloride reduction with excess LAH



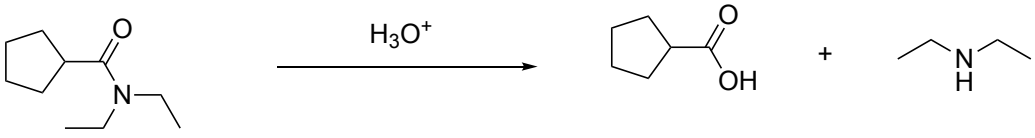
9. Ester reduction with excess LAH



10. Acid chloride hydrolysis

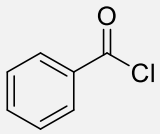
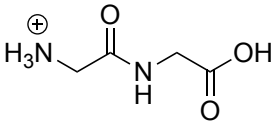
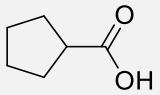
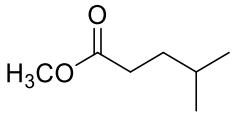
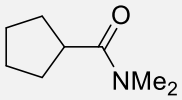
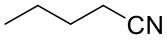


11. Amide hydrolysis



22C. Nucleophilic Acyl Substitution – Mix & Match with Reaction Bootcamp!

- Draw the product(s) of each reaction: **starting material + reagent → Product(s)**
- **Look out for "No Reaction"** – when the reagent does not react with the starting material

	React each molecule with each reagent and draw the product in the box	**xs $NaBH_4$, MeOH**	**H_3O^+**	**1. xs $LiAlH_4$ 2. H_2O**
12				
13	 dipeptide			
14				
15				
16				
17			SKIP - reaction not covered in 8B	