# Chapter 18-19 Homework – Addition to Polar pi Bonds

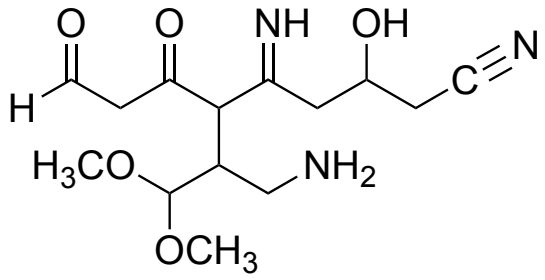
## Chapter 18A. Bond Basics

**1.** to each bond to indicate its polarity.

C–Li  C – Mg  C = O  C = N  O – H  C ≡ N

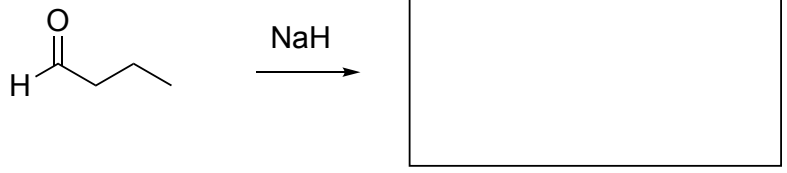
**2. Circle and label each functional group** in the fictional molecule below.

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




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

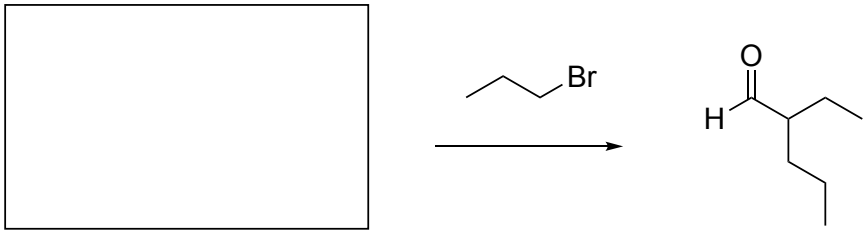
- **Draw the H's** in the alpha position,
- use **curved arrow** notation to show the proton transfer reaction with sodium **hydride**,
- and **draw the enolate** formed.




**enolate**

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

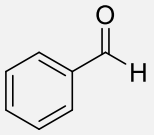
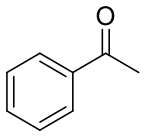
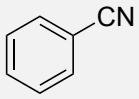
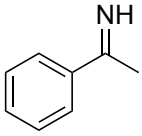
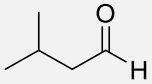
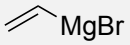
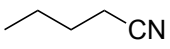
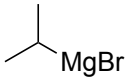
- **Redraw the enolate** from #3 above.
- **Add curved arrows** to explain how the bonds are broken and formed.




**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**<br>*sodium boro**hydride** in methanol* | 1. $NaBH_4$<br>2. $H_2O$<br>*Or*<br>1. $LiAlH_4$<br>2. $H_2O$ | |
| **6** |  **Acetophenone** | **1**. **$LiAlH_4$**<br>**2. $H_2O$**<br>*lithium aluminum **hydride** followed by water* | $NaBH_4$, MeOH<br>*Or*<br>1. $NaBH_4$<br>2. $H_2O$ | |
| **7** |  **benzonitrile** | **1**. **$LiAlH_4$**<br>**2. $H_2O$**<br>*lithium aluminum **hydride** followed by water* | n/a | |
| **8** |  **imine** | **$NaBH_4$**<br>*sodium boro**hydride** in methanol* | 1. $LiAlH_4$<br>2. $H_2O$ | |
| **9** |  **3-methylbutanal** | 1.  <br>2. $H_2O$<br>***vinyl** magnesium bromide followed by water* | 1.  <br>2. $H_2O$ | |
| **10** |  **nitrile** | 1.  <br>2. $H_2O$<br>***Isopropyl lithium** followed by water* | 1.  <br>2. $H_2O$ | |

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

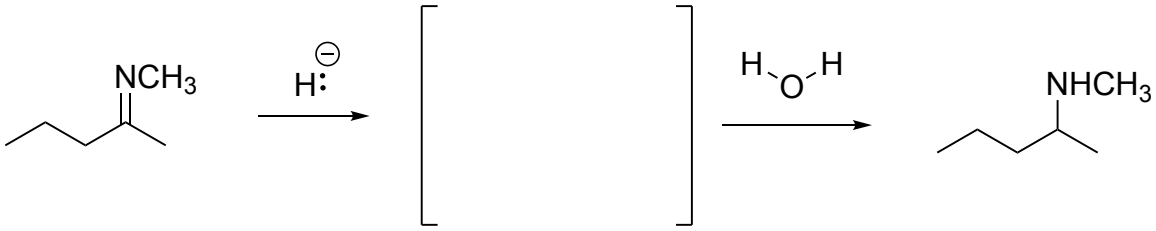
## Ch 18C. POLAR Pi BOND ADDITION MECHANISMS

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

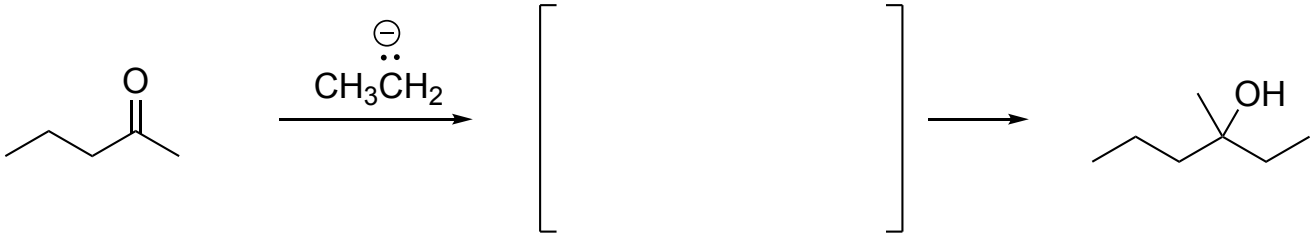
### 11. Ketone Reduction


### 12. Nitrile reduction


### 13. Imine reduction

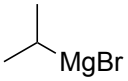
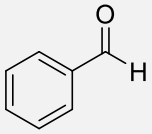
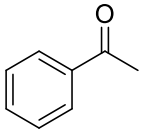
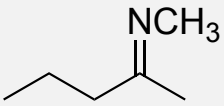
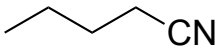
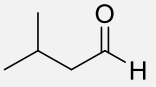
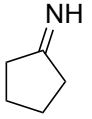



### 14. Addition of organometallic to aldehyde/ketone




### 15. Nitrile + organometallic

**18D. Mix & Match with Reaction Bootcamp!**

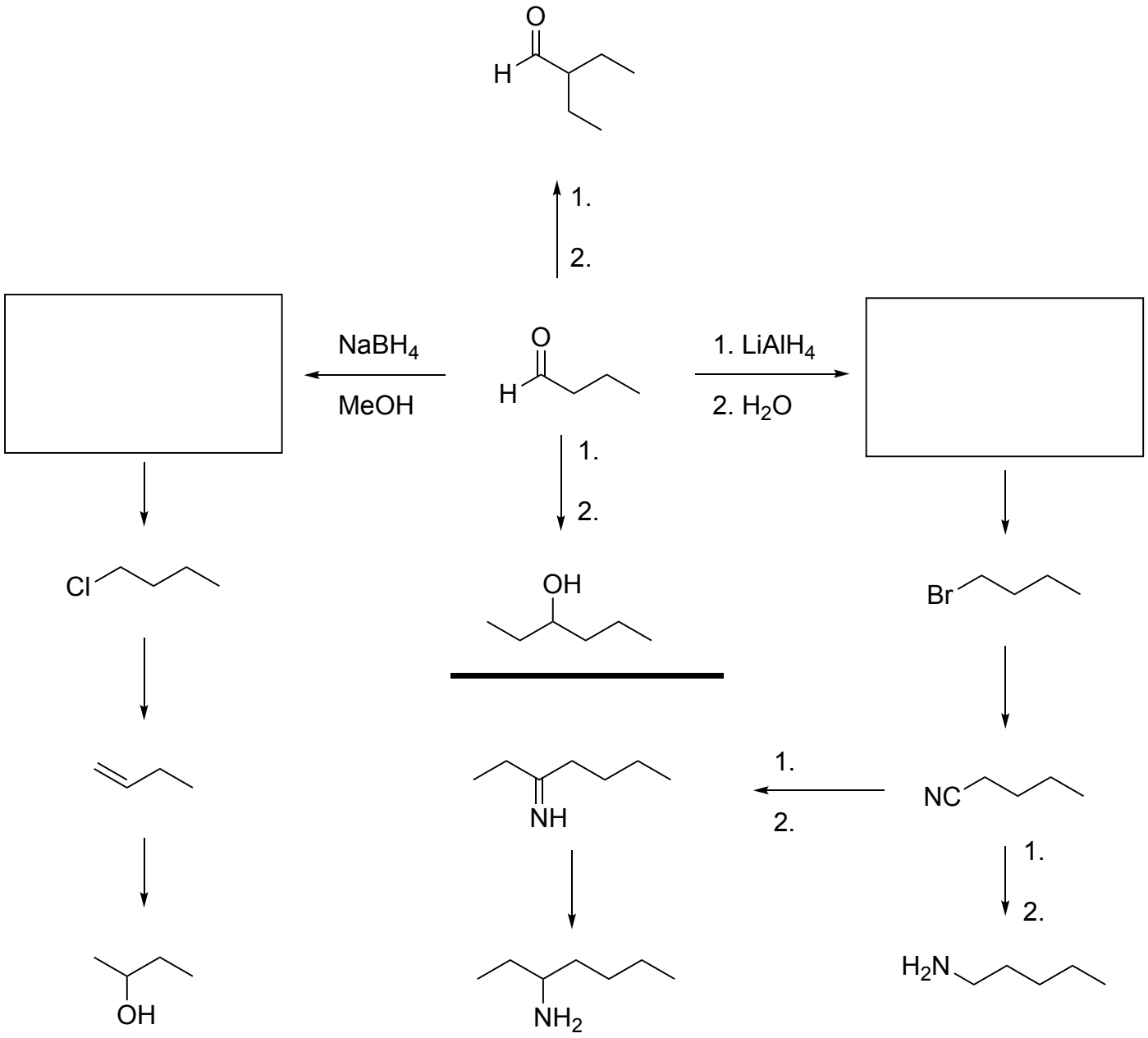
| | React each carbonyl compound with each reagent and draw the product in the box | $NaBH_4$, MeOH | 1. $LiAlH_4$<br>2. $H_2O$ | 1.  <br>2. $H_2O$ |
|---|---|---|---|---|
| **16** |  <br>**benzaldehyde**<br>(almond extract) | | | |
| **17** |  <br>**Acetophenone** | | | |
| **18** |  <br>**imine** |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

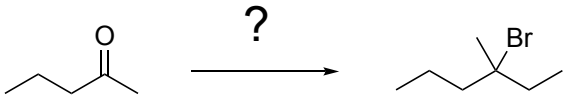
When the reagents need to be separated into steps, the numbers are provided for you.



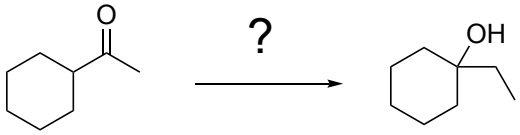
## 18F. Multi-Step Synthesis

- 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.**