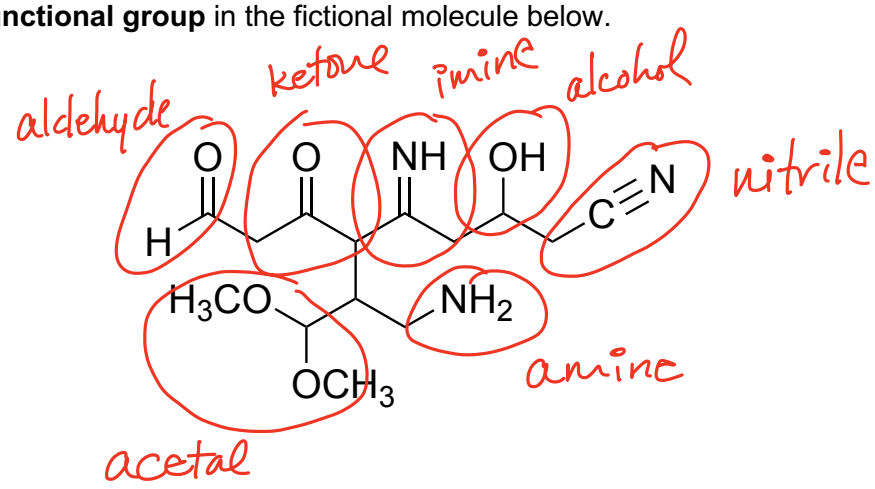
Chapter 18-19 Homework – Addition to Polar pi Bonds

Chapter 18A. Bond Basics

1. to each bond to indicate its polarity.

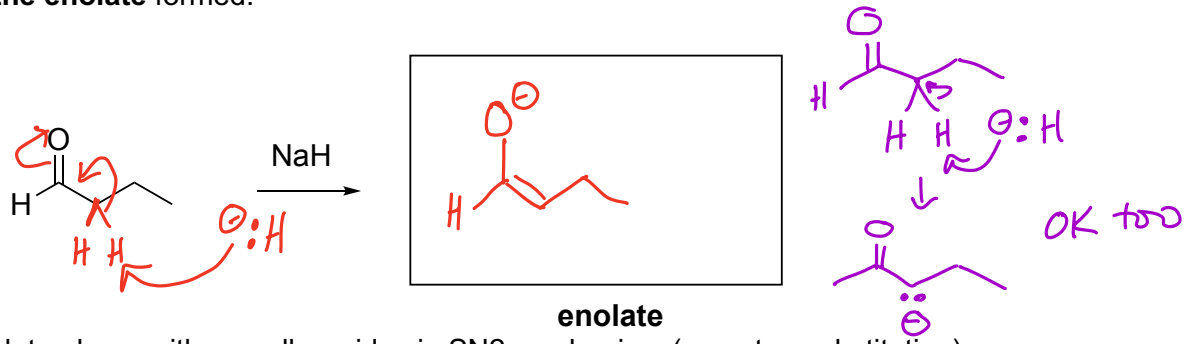
2. **Circle and label each functional group** in the fictional molecule below.

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



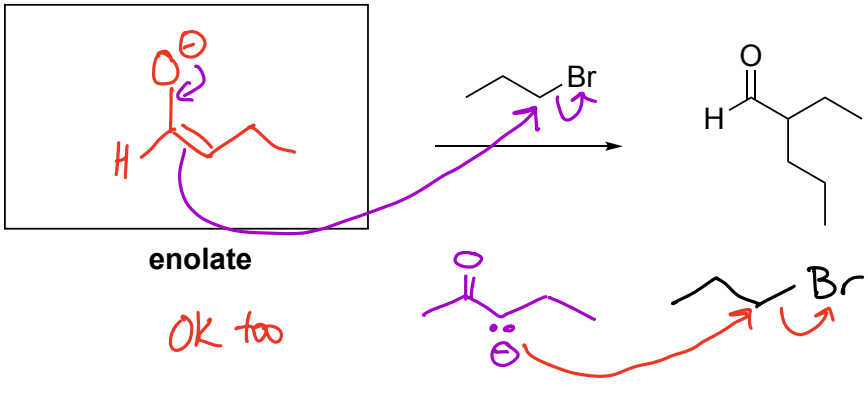
3. Show the mechanism and product for the **alpha-deprotonation of butanal**.

- **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.



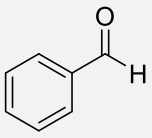
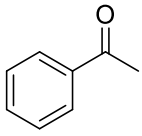
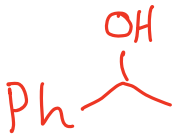
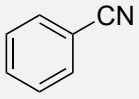
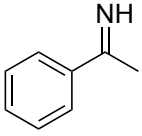
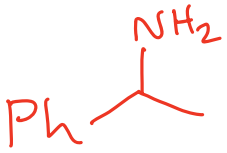
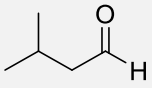
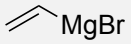
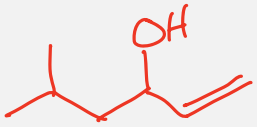
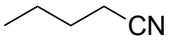
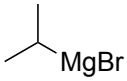
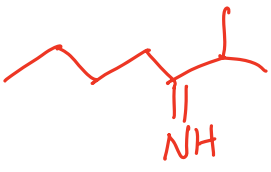
4. React the enolate above with propylbromide via SN2 mechanism (one-step substitution).

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



18B. CARBONYL REACTIONS

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

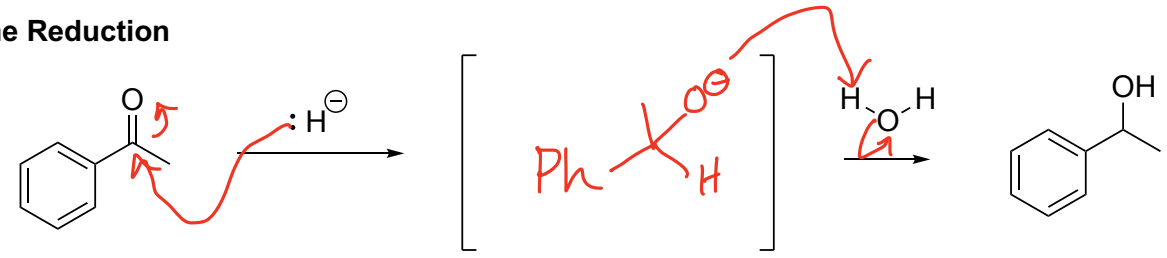
	Starting Material	**Reagents** *& translation* *be able to draw the arrow-pushing mechanism	**Alternate reagents** (same product)	**Draw the Product**
5	 **benzaldehyde** (almond extract)	**$NaBH_4$, MeOH** *sodium boro**hydride** in methanol*	1. $NaBH_4$ 2. H_2O *Or* 1. $LiAlH_4$ 2. H_2O	
6	 **Acetophenone**	**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.

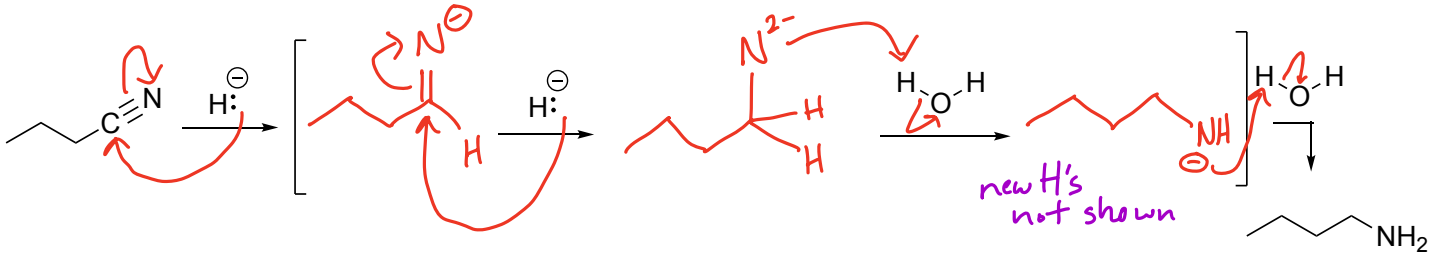
Ch 18C. POLAR Pi BOND ADDITION MECHANISMS

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

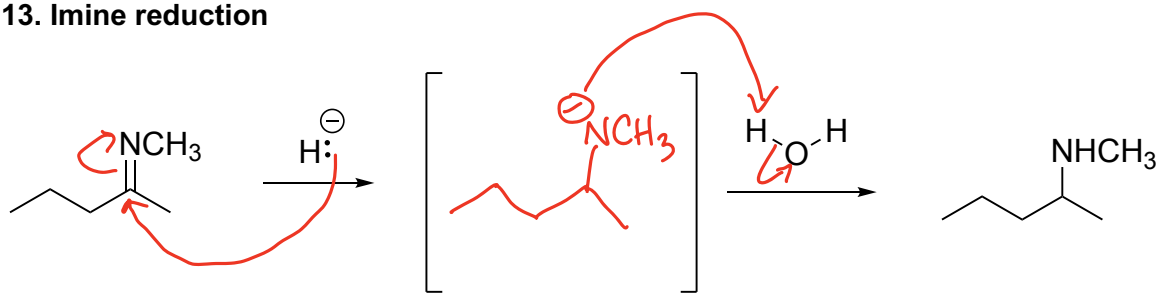
11. Ketone Reduction



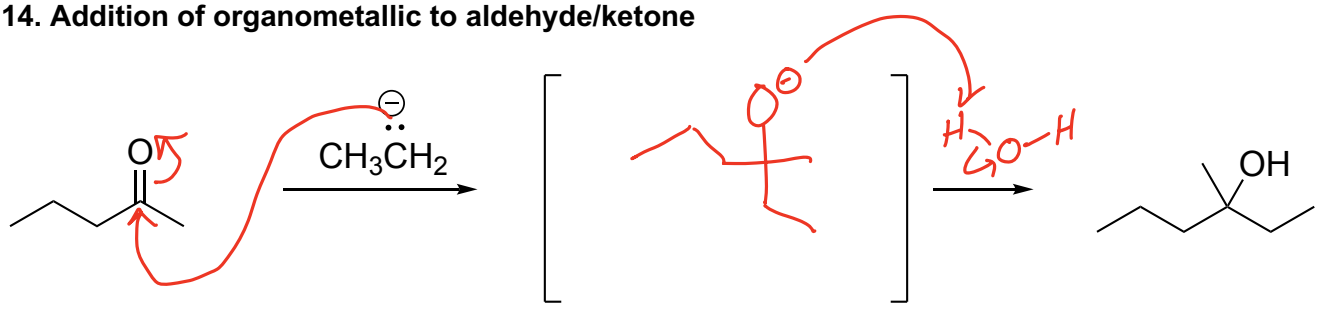
12. nitrile reduction



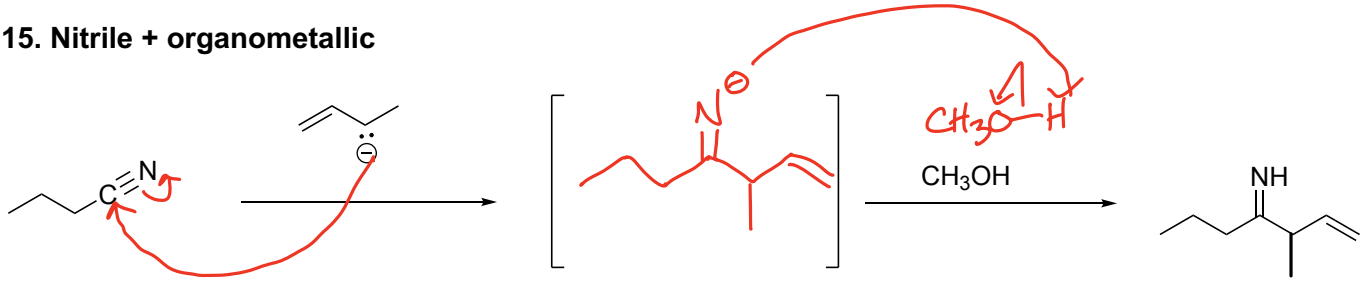
13. Imine reduction



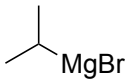
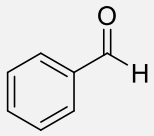
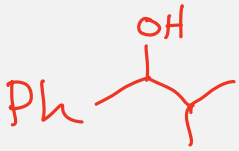
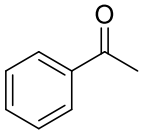
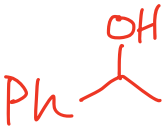
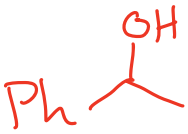
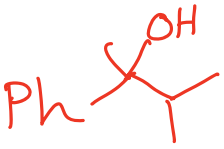
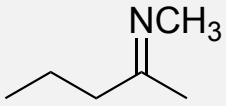
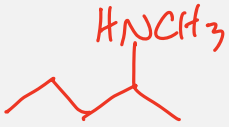
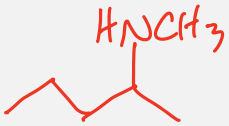
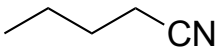
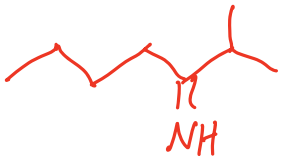
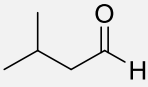
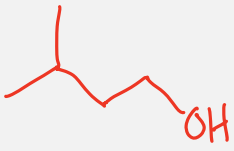
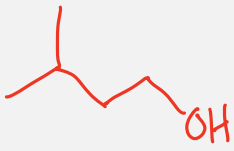
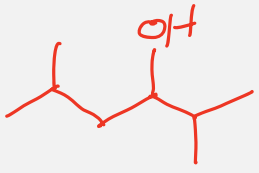
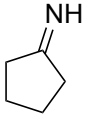
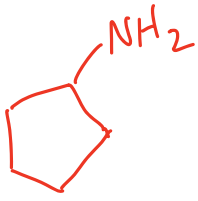
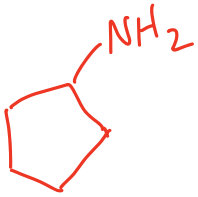
14. Addition of organometallic to aldehyde/ketone



15. Nitrile + organometallic



18D. Mix & Match with Reaction Bootcamp!

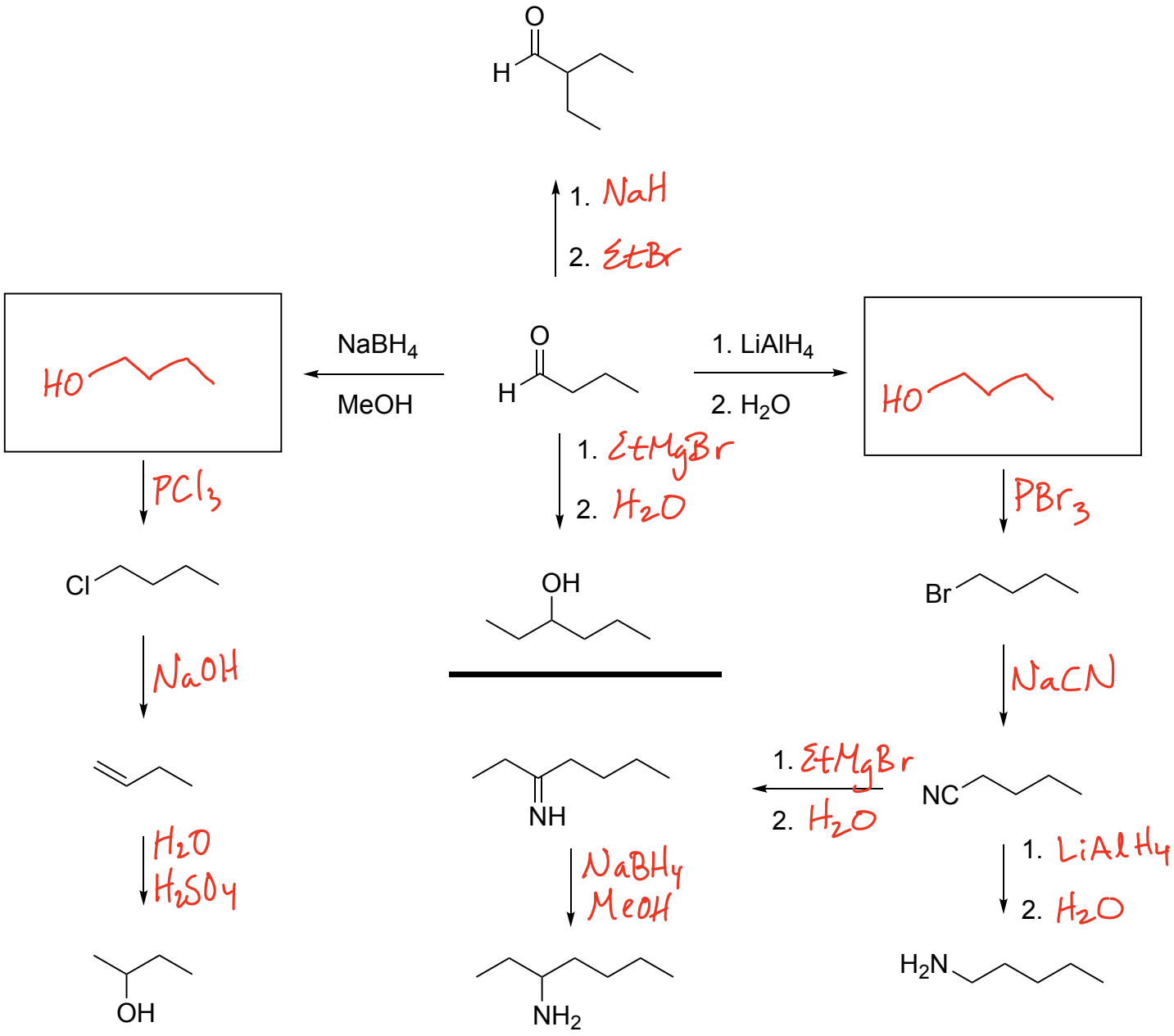
React each carbonyl compound with each reagent and draw the product in the box		$NaBH_4$, MeOH	1. $LiAlH_4$ 2. H_2O	1.  2. H_2O
16	 **benzaldehyde** (almond extract)			
17	 **Acetophenone**			
18	 **imine**			NR.
19	 **pentanenitrile**	NR		
20	 **3-methylbutanal**			
21	 **imine**			N.R.

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.

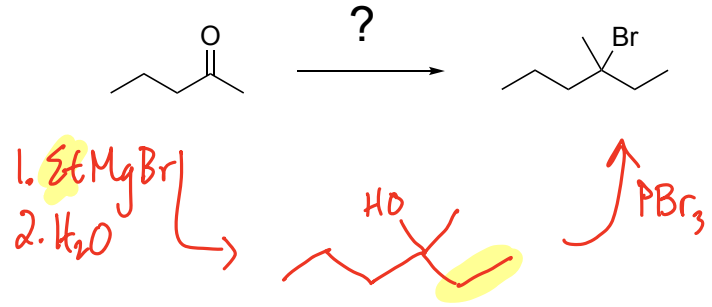
When the reagents need to be separated into steps, the numbers are provided for you.



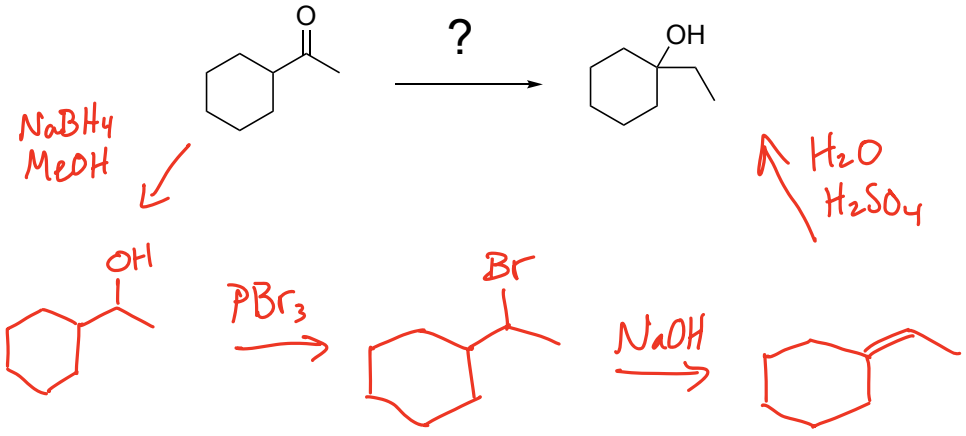
18F. Multi-Step Synthesis

- 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.