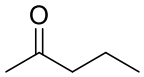
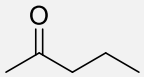
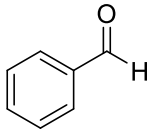
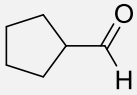
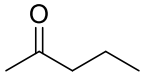
# Chapter 19 Homework – Addition of Weak Nucleophiles to Polar pi Bonds

**19A. NUCLEOPHILIC ADDITION REACTIONS** with weak-sauce nucleophiles

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

## 19B. ACIDIC NUCLEOPHILIC ADDITION MECHANISMS

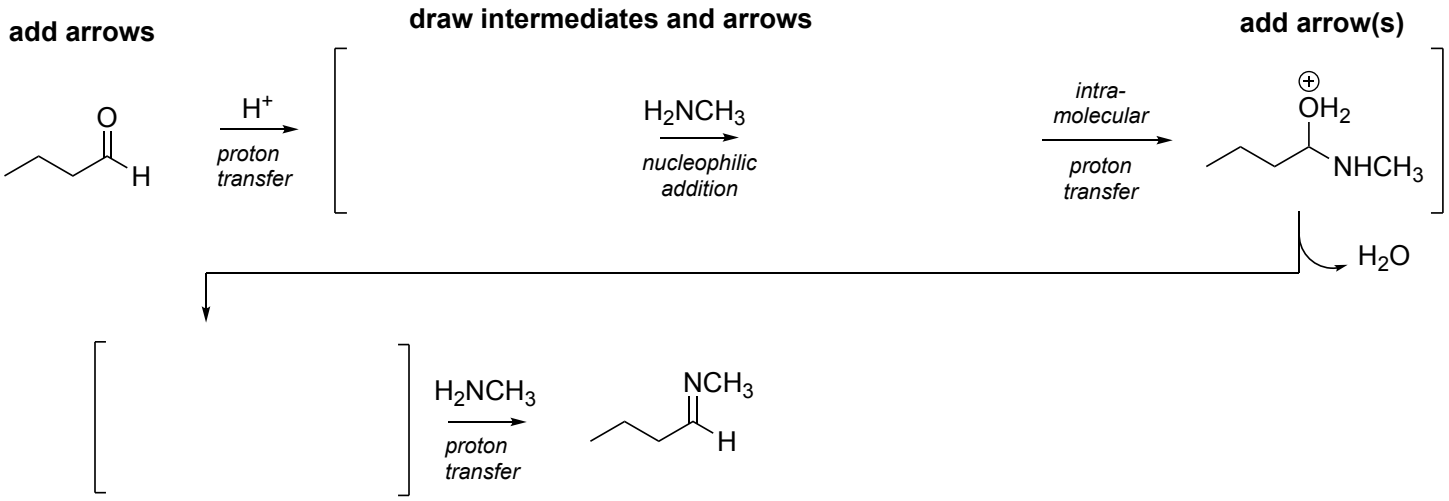
- Draw the arrow-pushing mechanism for each reaction, including all charged intermediates and product.

### 7. Cyanohydrin formation

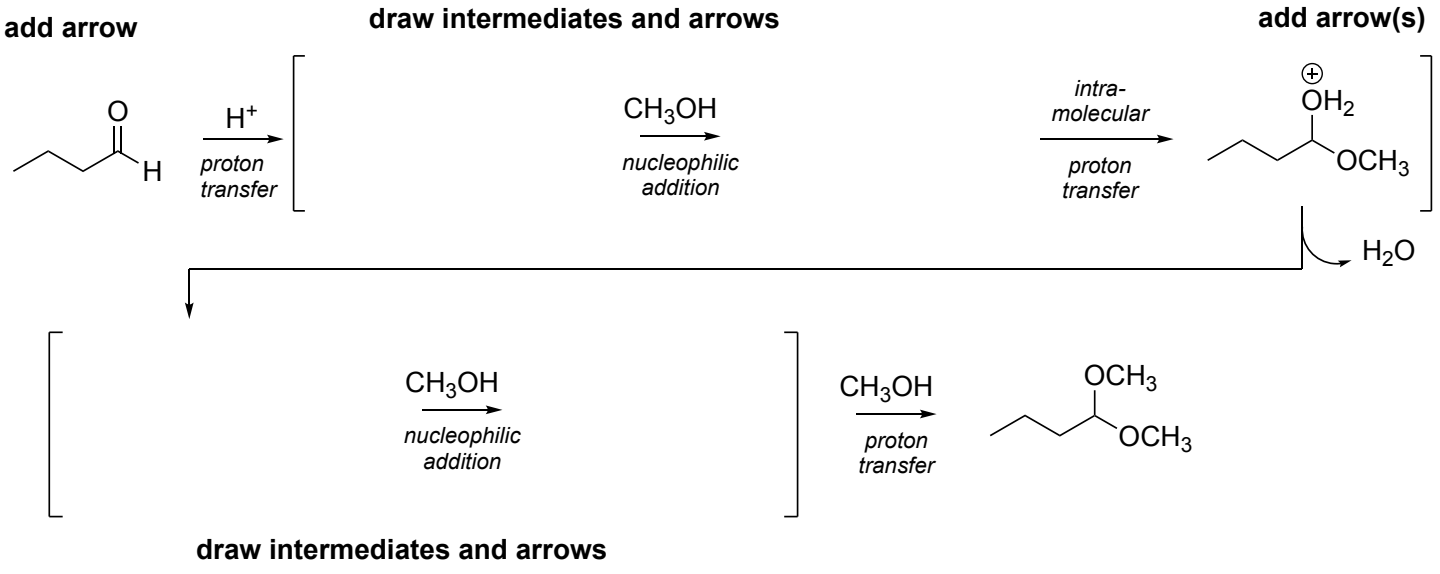

## 19C. NUCLEOPHILIC ADDITION & DEHYDRATION MECHANISMS

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

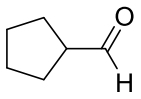
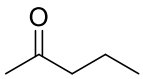
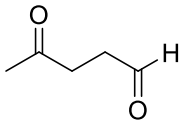
### 8. Imine mechanism




### 9. Acetal Mechanism



**19D. Mix & Match with Reaction Bootcamp!**

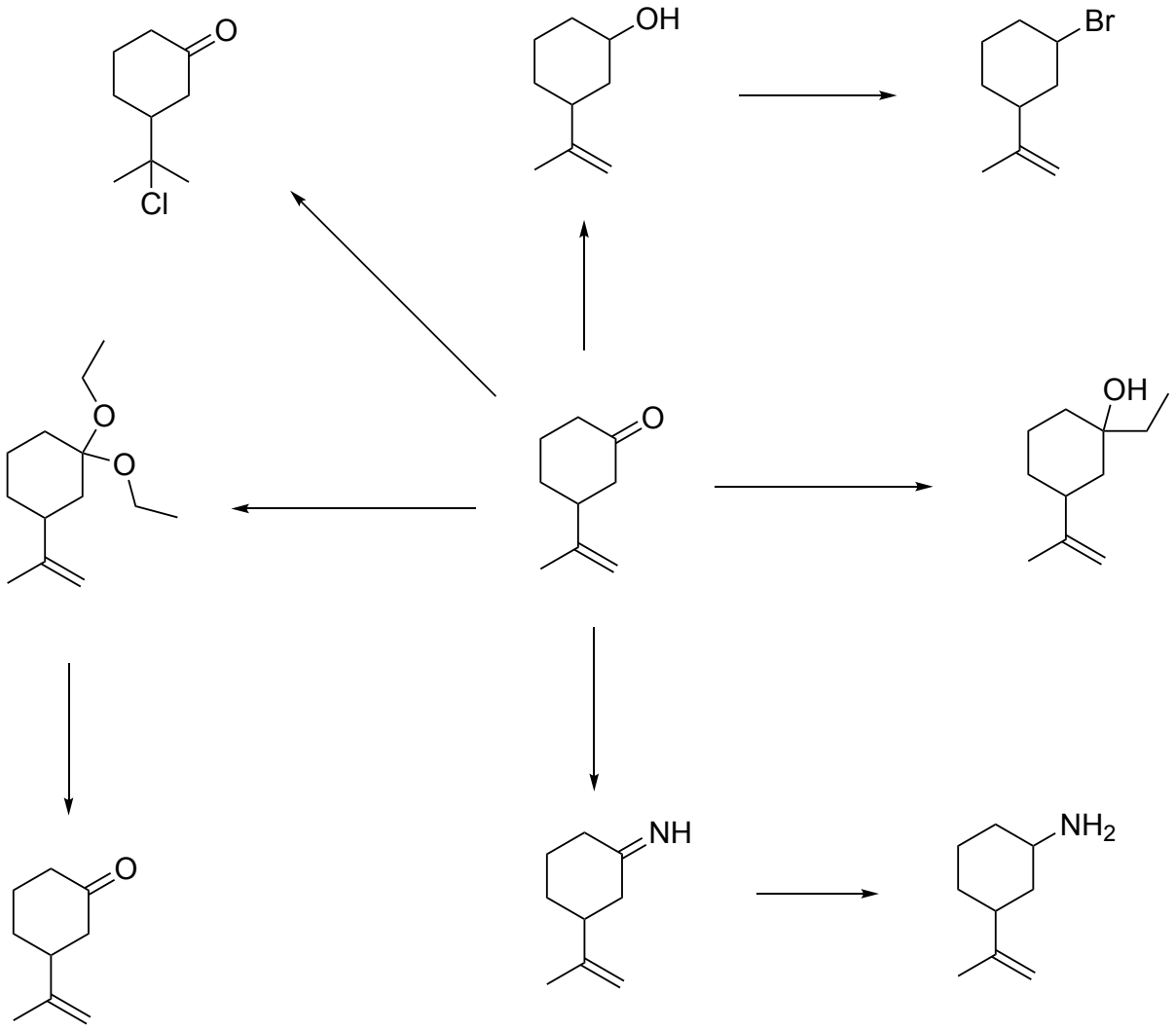
| React each **aldehyde or ketone** with each **reagent** and **<u>draw the product</u>** in the box. |  |  |  |
|---|---|---|---|
| **$CH_3CH_2OH$ (2 mol), $H^+$** | | | |
| **HCN** | | | |
| **$HOCH_2CH_2OH$, $H^+$** | | | |
| **$H_2NCH_3$, $H^+$** | | | |
| **$PhNH_2$, $H^+$** | | | |

**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",

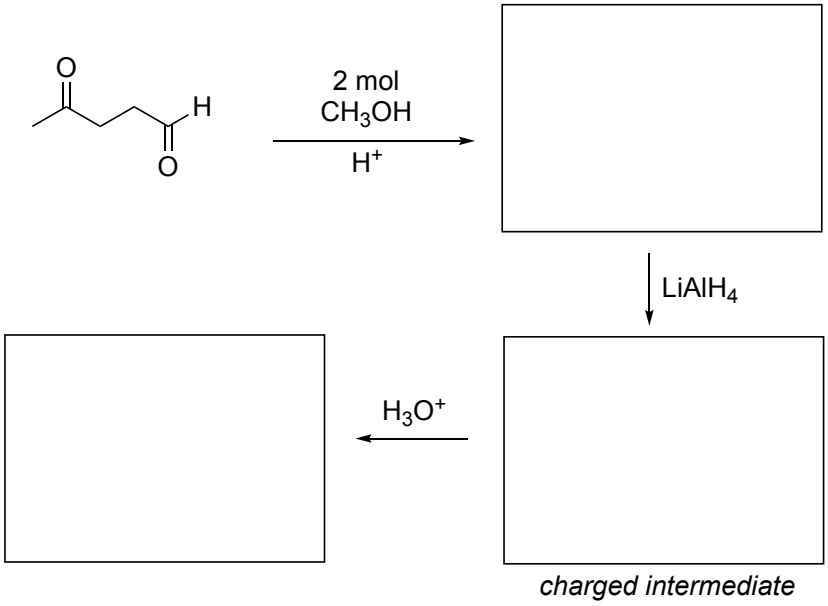
**II.** then the desired addition reaction takes place on the ketone,

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

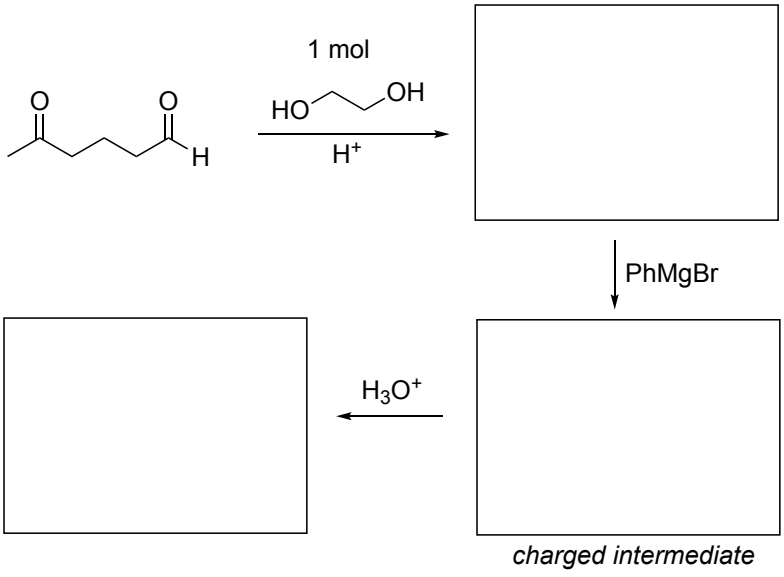
Cool, right?!

**Draw the missing products** of each reaction in the boxes.

**11. Chemoselective reduction**



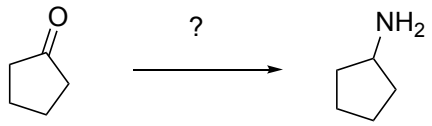

**12. Chemoselective organometallic addition**



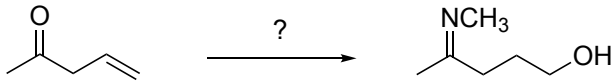
## 19F. Multi-Step Synthesis

- 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