# <u>Chapter 19 Homework – Addition to Polar pi Bonds</u>

19A. NUCLEOPHILIC ADDITION REACTIONS with weak sauce nucleophiles

	Starting Material	Reagents & translation	Draw the Product	
1	O A A A A A A A A A A A A A A A A A A A	HCN hydrogen cyanide	HO CN	
2	0	NH <sub>3</sub> , H <sup>+</sup> <i>Ammonia</i> under acidic conditions	NH	
3	O	<b>H₂NCH</b> <sub>3</sub> , H <sup>+</sup> <i>Methylamine</i> with acid catalyst	NCH3	
4	ОН	CH₃CH₂OH, H <sup>+</sup> excess ethanol under acidic conditions		
5	0	HOCH <sub>2</sub> CH <sub>2</sub> OH, H <sup>+</sup> 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

React each aldehyde or ketone with each reagent and draw the product in the box.	O H	0	O H O
CH₃CH₂OH (2 mol), H <sup>+</sup>	\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	LoX	
HCN	OH CZ	NC OH	OH
HOCH₂CH₂OH, H <sup>+</sup>			
H₂NCH₃, H <sup>+</sup>	NCH <sub>3</sub>	NCH3	O H NCH3
PhNH <sub>2</sub> , H <sup>+</sup>	NPh	NPh  }	NPh

# 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?

- 1. The aldehyde is reacted with alcohol to form an acetal "protecting group",
- 2. then the desired addition reaction takes place on the ketone,
- 3. 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

$$\begin{array}{c|c}
 & 1 \text{ mol} \\
 & H \\
 & H^{+}
\end{array}$$

$$\begin{array}{c}
 & PhMgBr \\
 & Ph \\
 & Ph$$

# 19F. Multi-Step Synthesis

- Each transformation requires at least two synthetic steps to reach the target product.
  - o 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.
  - o 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.
  - o 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