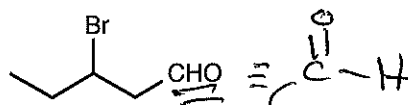
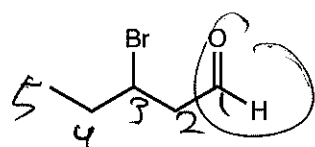
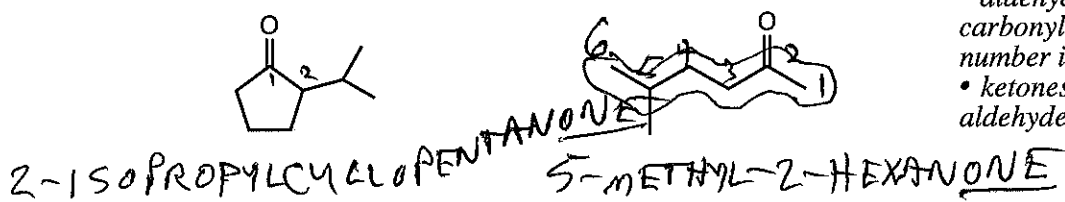
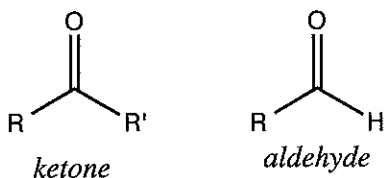


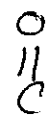
## Chapter 20: Aldehydes and Ketones

[Chapter 20 Sections: 20.1-20.7, 20.9-10.10, 20.13]

### Nomenclature of Aldehydes and Ketones



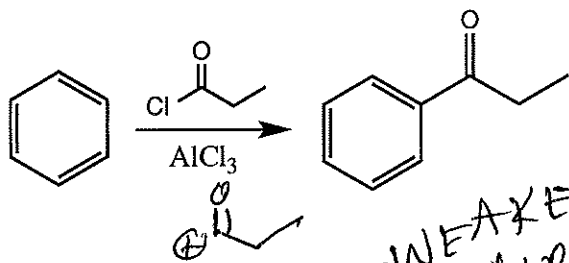
- for both aldehydes and ketones, the parent chain is the longest continuous carbon chain that contains the carbon of the carbonyl group
- numbering (locant) priority is given to the carbonyl carbon
- aldehydes always have the carbonyl group at carbon 1, so a number is not needed
- ketones have the "one" suffix, aldehydes have the "al" suffix



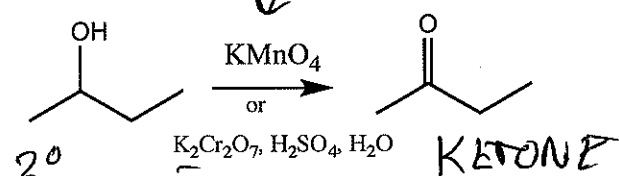
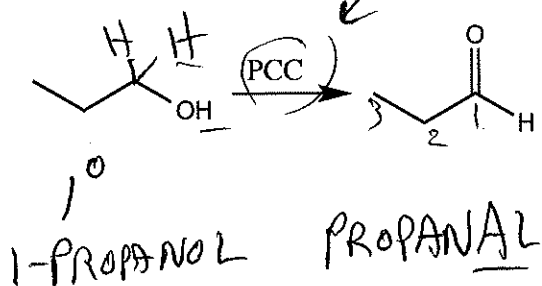
Problems: 1

### Review of the Synthesis of Aldehydes and Ketones

#### A. Friedel-Crafts Acylation



#### B. Oxidation of Alcohols (most common method)



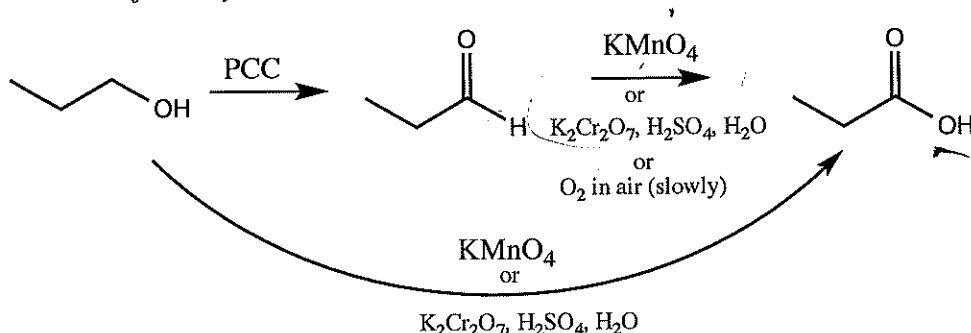
JONES REAGENT

WEAKER OXIDIZING AGENT

STRONGER OXIDIZING AGENTS

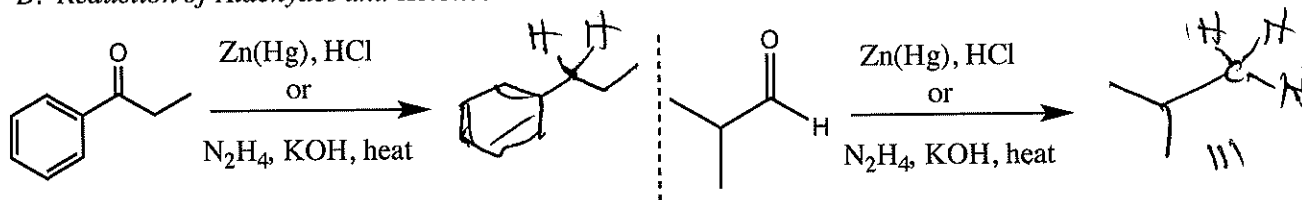
## Review of Reactions of Aldehydes and Ketones

### A. Oxidation of Aldehydes

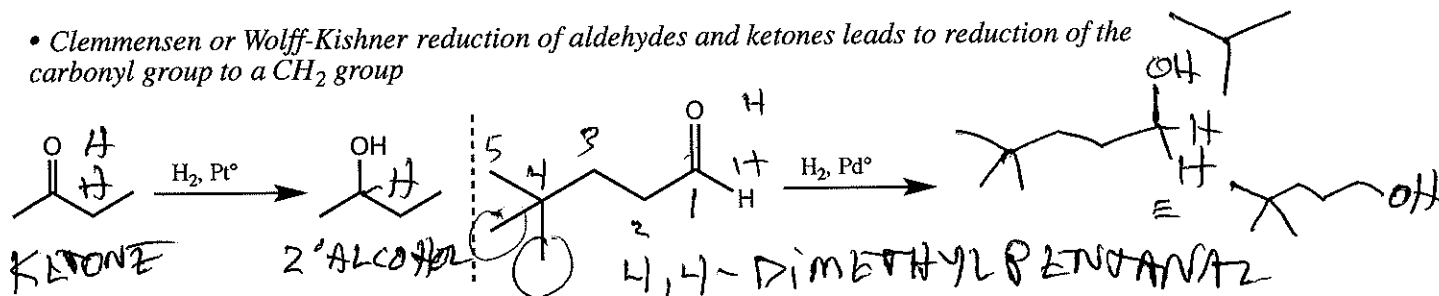


- aldehydes may be oxidized using  $\text{KMnO}_4$  or Jones reagent to the carboxylic acid
- since aldehydes are usually synthesized via oxidation of  $1^\circ$  alcohols, the synthesis of carboxylic acids is usually accomplished via direct oxidation of  $1^\circ$  alcohols with the strong oxidizing agents
- ketones CANNOT be oxidized further

### B. Reduction of Aldehydes and Ketones



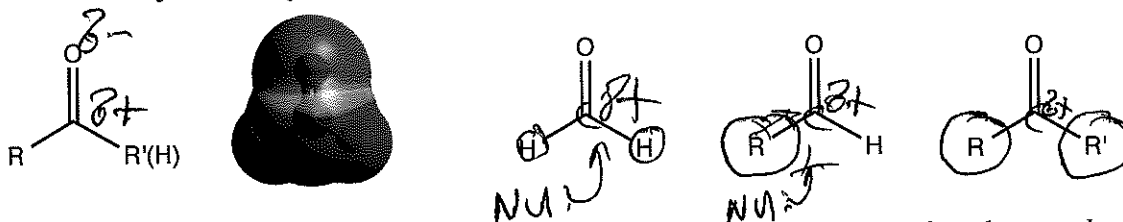
- Clemmensen or Wolff-Kishner reduction of aldehydes and ketones leads to reduction of the carbonyl group to a  $\text{CH}_2$  group



- hydrogenation of ketones forms  $2^\circ$  alcohols (the opposite reaction of the oxidation process)
- hydrogenation of aldehydes forms  $1^\circ$  alcohols

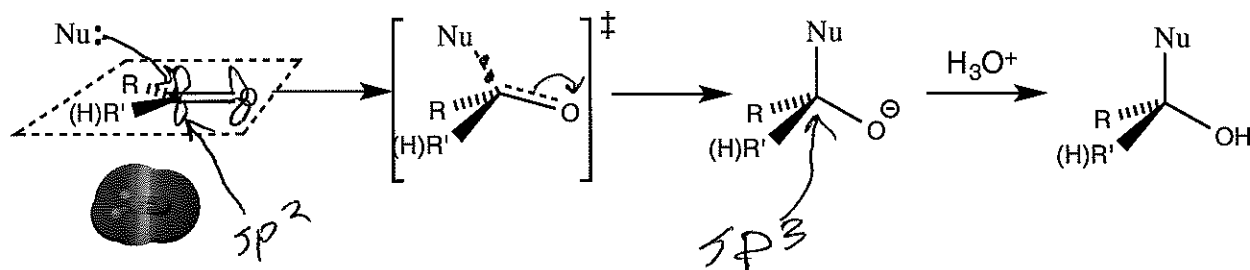
Problems: 2

### General Reactivity of Aldehydes and Ketones



- both aldehydes and ketones have partial positive charge at the carbon of the carbonyl group due to the polar  $\text{C}=\text{O}$  bond
- the partial charge on the aldehyde is greater since it is flanked by a single electron-donating alkyl group
- while both aldehydes and ketones are reactive towards nucleophilic addition, aldehydes are more reactive due to i) the greater partial positive charge and ii) less steric interference

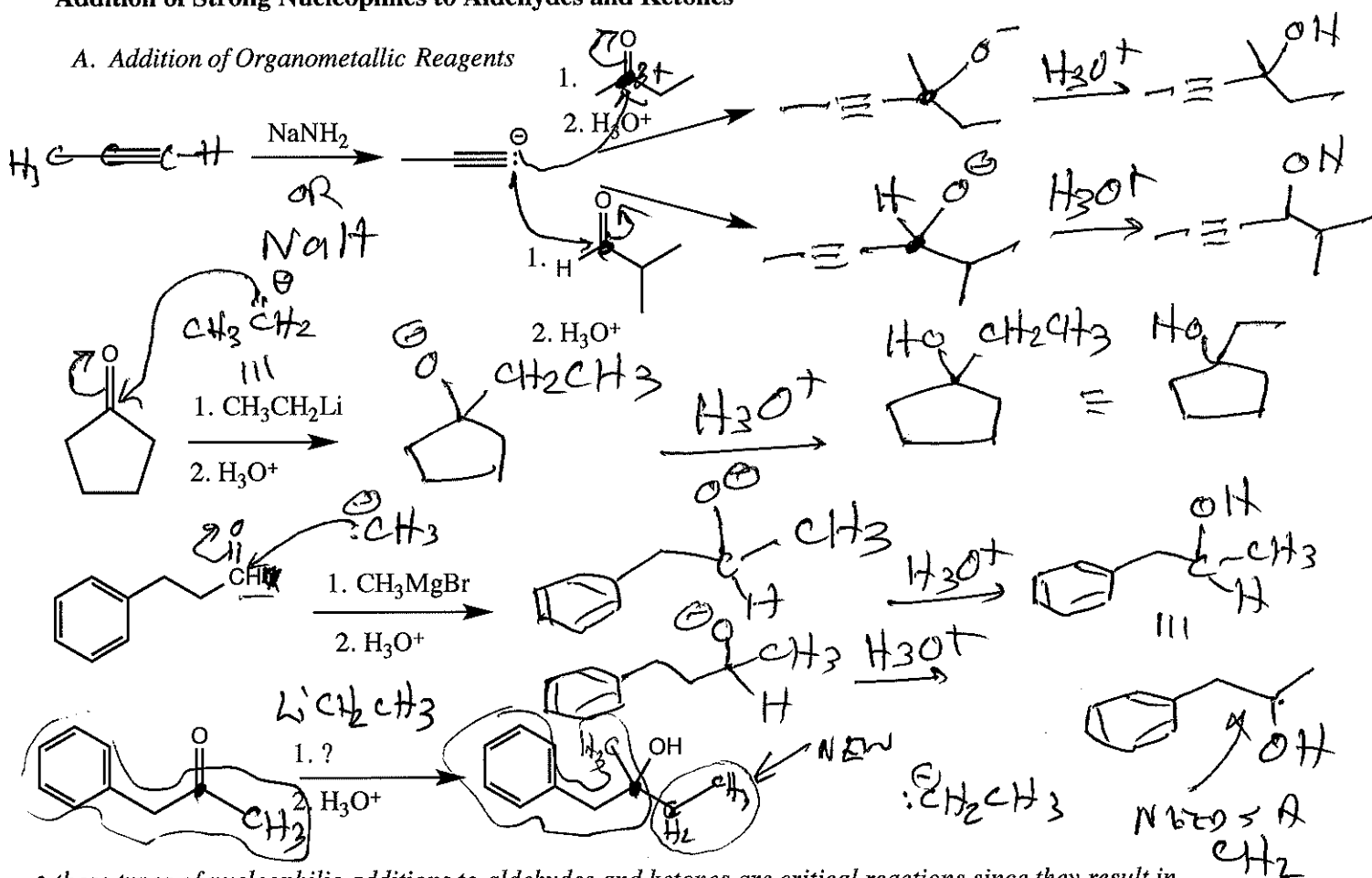
## Mode of Attack of Strong Nucleophiles on the Carbonyl Group of Aldehydes and Ketones



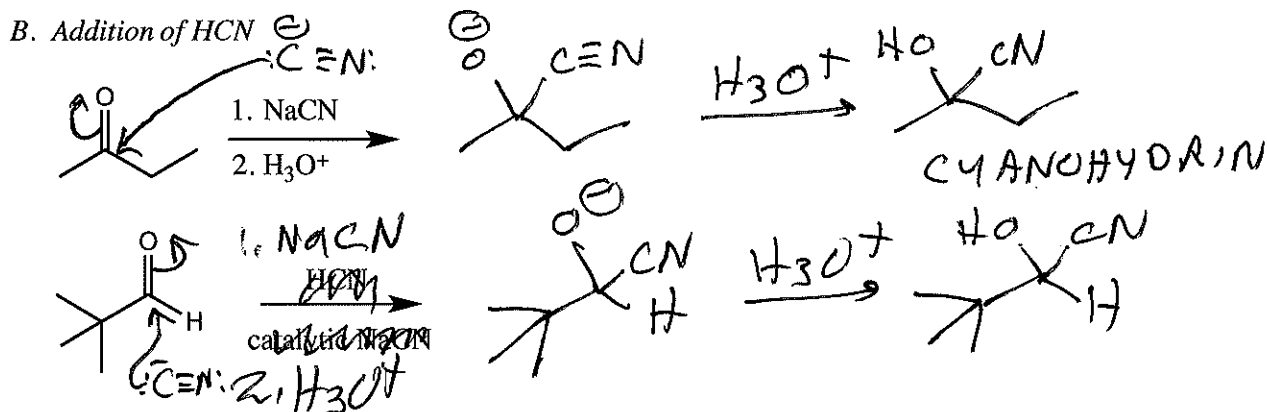
- nucleophiles attack the partially positively charged carbon of the carbonyl group by pushing electrons into the polarized pi bond
- the pi electrons are forced onto the electronegative oxygen atom
- these reactions are often followed up by addition of acidic water ( $\text{HCl}$ ,  $\text{H}_2\text{O}$  or  $\text{H}_3\text{O}^+$ ) to protonate the negatively charged oxygen and form a neutral product

## Addition of Strong Nucleophiles to Aldehydes and Ketones

### A. Addition of Organometallic Reagents

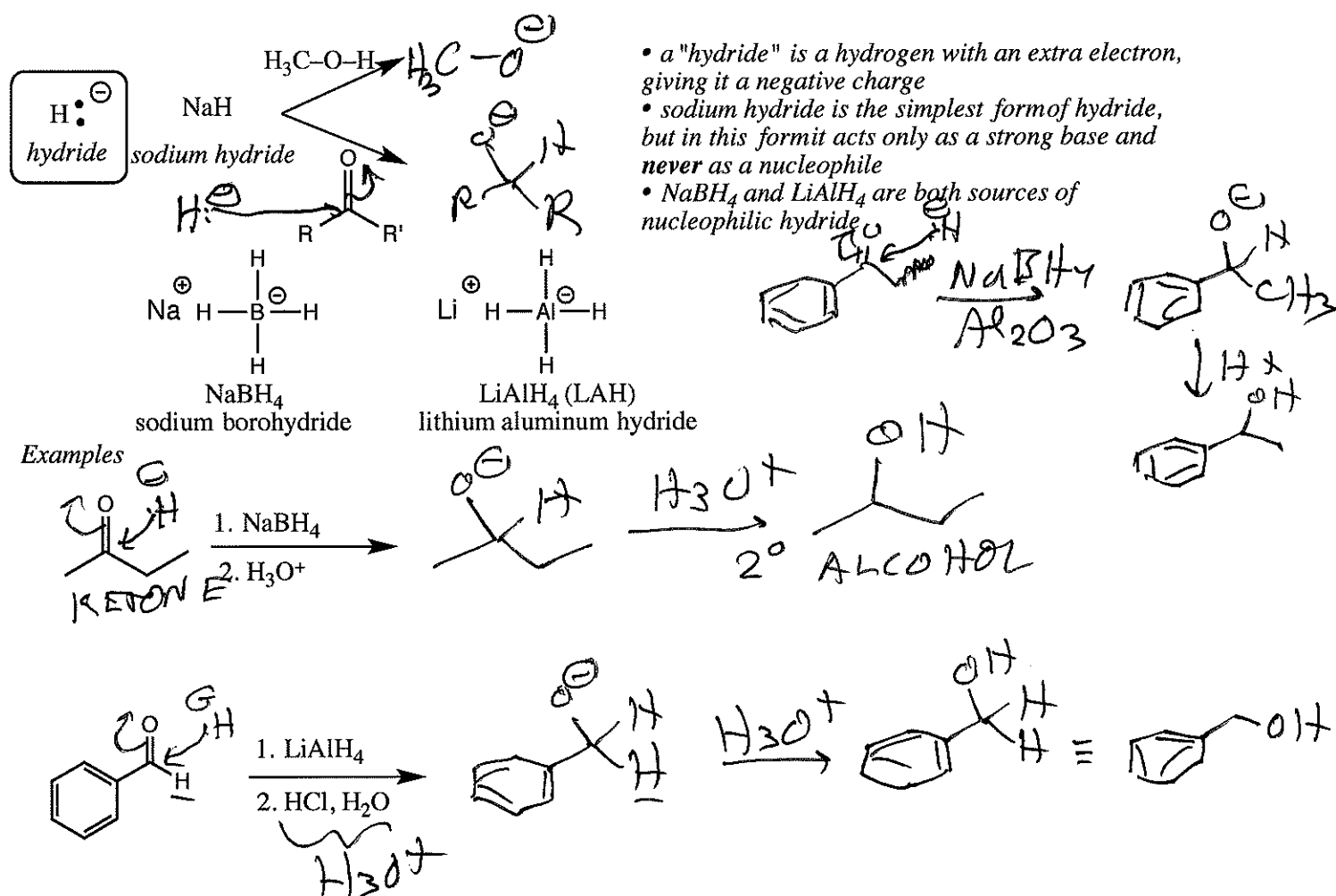


- these types of nucleophilic additions to aldehydes and ketones are critical reactions since they result in the formation of NEW C-C bonds!
- these reactions, therefore, provide a way in which to create larger molecules from readily available smaller molecules



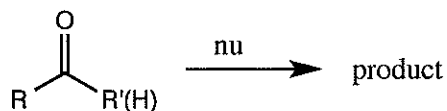
- there are two methods for addition of HCN to a carbonyl group. The net result is the same
- the product of addition is referred to as a "cyanohydrin" to reflect the presence of both the cyanide AND hydroxyl groups
- as with the organometallics, this reaction forms a new C-C bond

C. Addition of Hydride (hydride reduction)



- reduction of aldehydes with either  $\text{NaBH}_4$  OR  $\text{LiAlH}_4$  results in the formation of 1° alcohols
- reduction of ketones with either  $\text{NaBH}_4$  OR  $\text{LiAlH}_4$  results in the formation of 2° alcohols

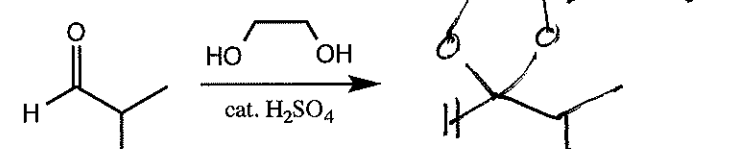
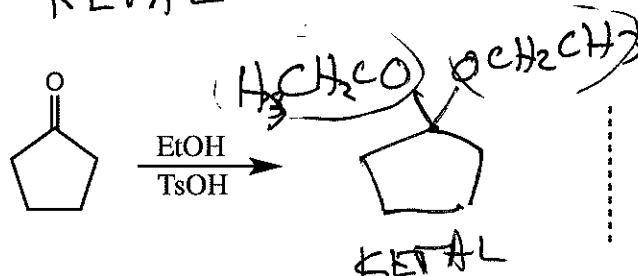
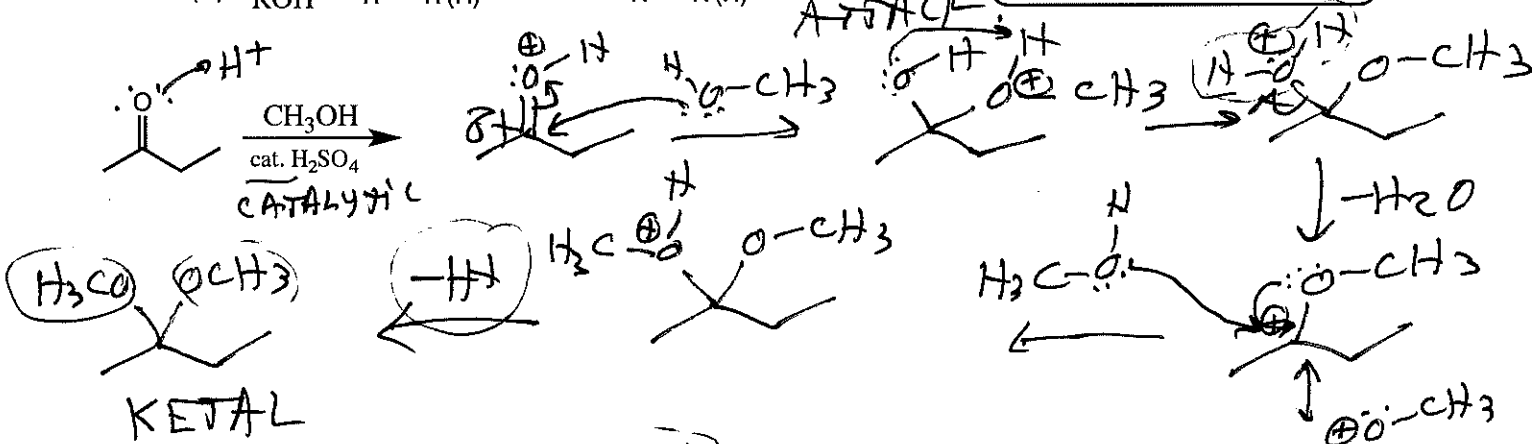
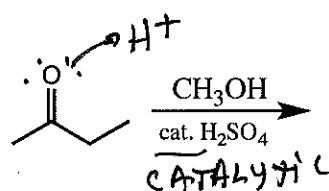
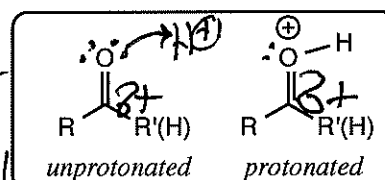
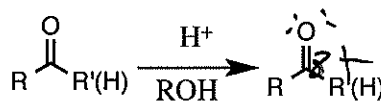
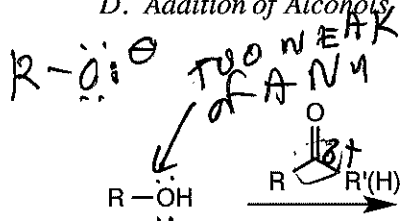
## Summary of Nucleophilic Addition Reactions of Aldehydes and Ketones



nucleophile	catalyst	type of product	Structure
$\text{H}^-$ (hydride, $\text{NaBH}_4$ or $\text{LiAlH}_4$ )	none	alcohol (1° from aldehyde, 2° from ketone)	$\text{R}-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-\text{R}'(\text{H})$
$\text{R}^-$ (Grignard, alkyllithium)	none	alcohol (2° from aldehyde, 3° from ketone)	$\text{R}-\overset{\text{R}}{\underset{\text{OH}}{\text{C}}}-\text{R}'(\text{H})$
$\ominus\text{C}\equiv\text{N}$ (cyanide)	none	cyanohydrin	$\text{R}-\overset{\text{NC}}{\underset{\text{OH}}{\text{C}}}-\text{R}'(\text{H})$

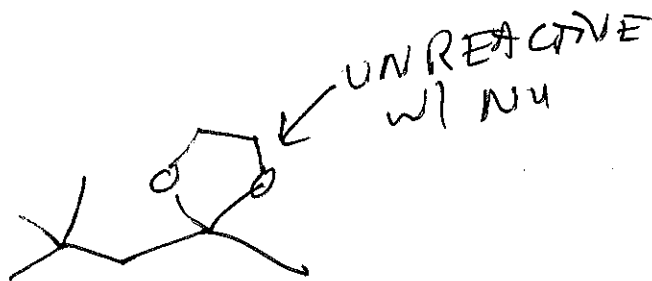
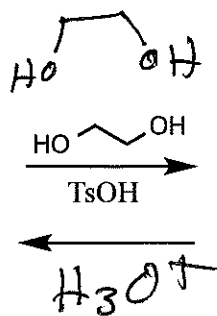
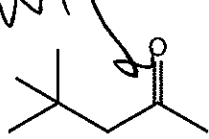
### D. Addition of Alcohols

- alkoxides are strong nucleophiles but alcohols are poor nucleophiles
- alcohols will not react with aldehydes or ketones in the absence of an acid catalyst
- an acid catalyst protonates a lone pair of the oxygen atom of the carbonyl group
- protonation increases the partial positive charge on the carbon and enhances the reactivity of the carbonyl towards nucleophilic addition
- under acidic conditions, aldehydes and ketones will react with the weaker alcohol nucleophile
- the most common acid catalysts are  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  or para-toluenesulfonic acid ( $\text{TsOH}$ )

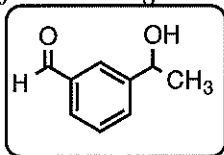


- reaction of aldehydes or ketones with alcohols under acid catalysis results in the addition of TWO equivalents of the alcohol to the carbonyl group. The product is called a "ketal" from a ketone and an "acetal" from an aldehyde
- if a diol such as ethylene glycol is used, both ends of the diol add across the carbonyl group to form a cyclic ketal
- cyclic ketals are the most often utilized type of ketal

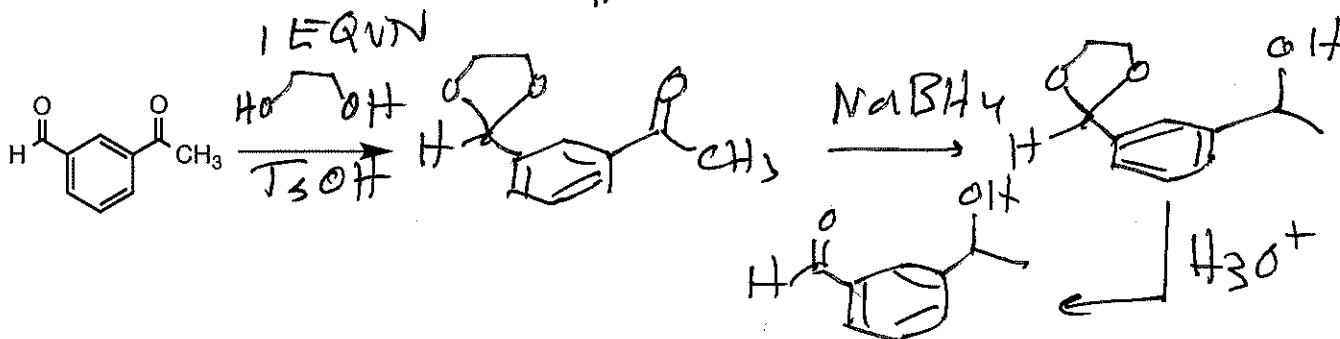
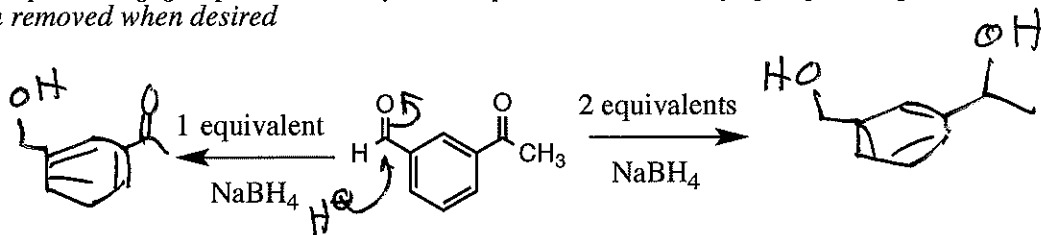
SUBJECT TO REACTION WITH Nu



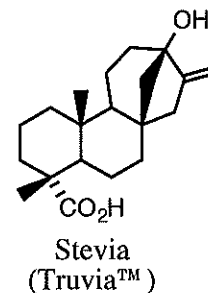
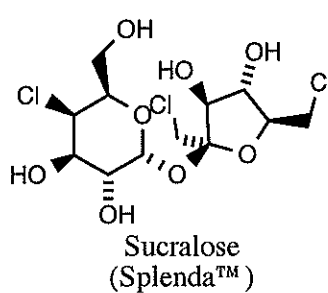
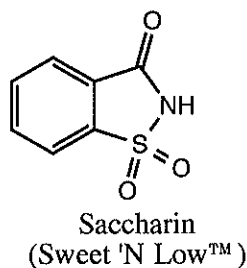
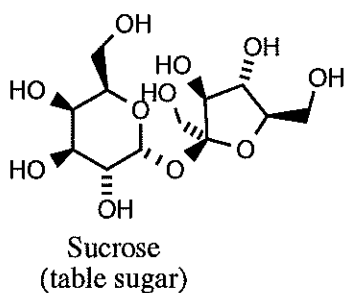
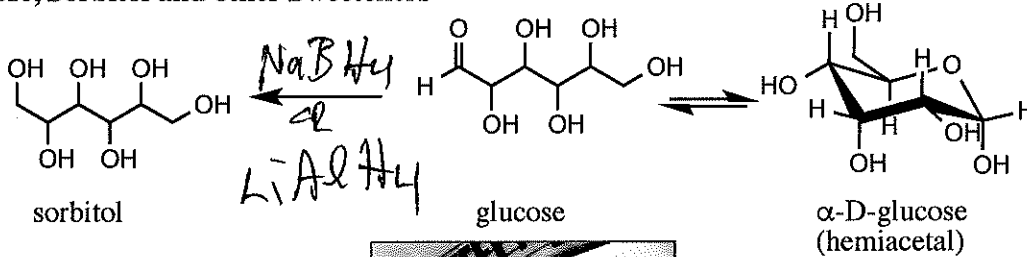
- ketals are "ether-like" compounds that behave like ethers, i.e., they are fairly unreactive
- the ketal formation process can be reversed by addition of water under acidic conditions
- ketals act as carbonyl "protecting groups" in that they can be placed on a carbonyl group to keep it from reacting and then removed when desired



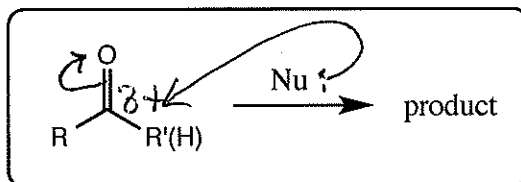
target molecule



Glucose, Sorbitol and other Sweeteners



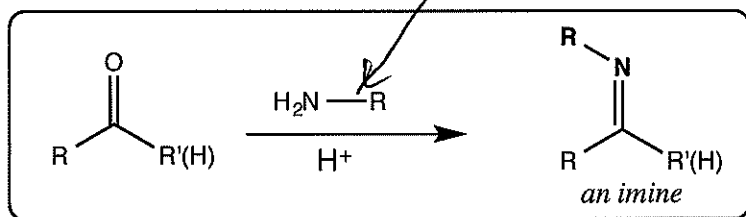
## Summary of Nucleophilic Addition Reactions of Aldehydes and Ketones



nucleophile	catalyst	type of product
<i>single addition reactions</i>		
$\text{H}^-$ (hydride, $\text{NaBH}_4$ or $\text{LiAlH}_4$ )	none	alcohol (1° from aldehyde, 2° from ketone) 
$\text{R}^-$ (Grignard, alkyllithium) $\text{R}-\text{C}\equiv\text{C}^-$	none	alcohol (2° from aldehyde, 3° from ketone) 
$\text{C}\equiv\text{N}^-$ (cyanide)	none	cyanohydrin 
<i>double addition reactions</i>		
$\text{ROH}$ (alcohols) 	$\text{H}^+$	acetals KETAL  
<i>addition-elimination reactions</i>		
$(\text{Ph})_3\text{P}=\text{CR}_2$ (Wittig reagents)	none	alkene 
$\text{R}-\text{NH}_2$ (1° amine)	$\text{H}^+$ sometimes	imine 

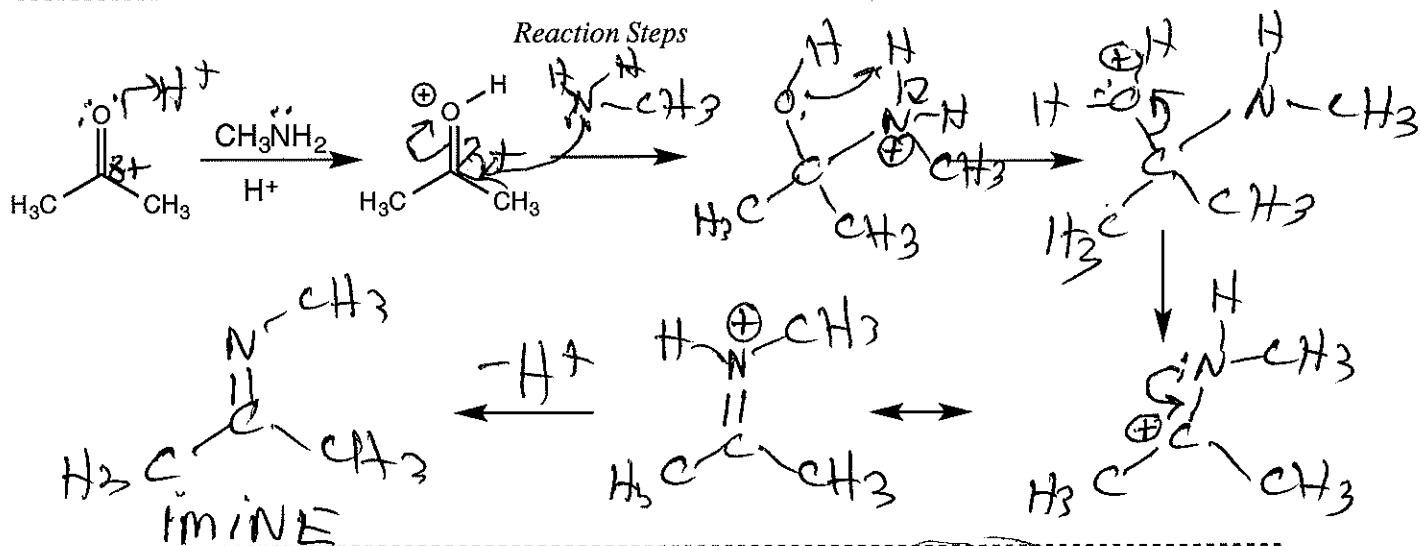
B. Imine Formation

Overall Reaction:



- when a 1° amine reacts with a ketone or aldehyde, an imine product results
- an acid catalyst [usually TsOH or HCl] is often needed
- the final product is replacement of the C=O double bond by a C=N double bond

Reaction Steps



Examples

