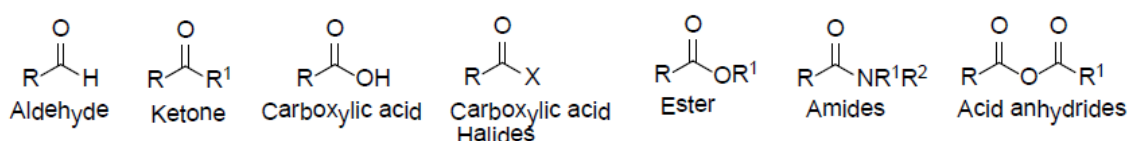


## Aldehydes and ketones

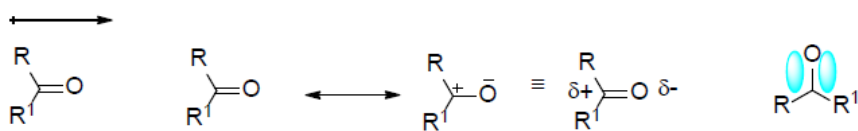
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### 6.1 Introduction

Carbonyl compounds are compounds that contain the carbonyl group, which include aldehydes, ketones, carboxylic acid and its derivatives.



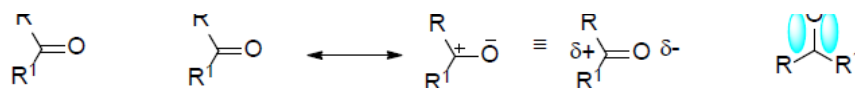
They have dipolar moment as oxygen is more electronegative than carbon. This implies that the carbonyl carbon is slightly positively charged and the carbonyl oxygen is slightly negatively charged. This makes the former susceptible to nucleophilic attack while the latter should be susceptible to attack by electrophiles.



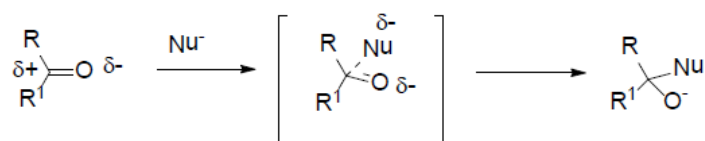
In simple nucleophilic addition reaction, where the rate limiting step is the attack by

# Aldehydes and ketones

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In simple nucleophilic addition reaction, where the rate limiting step is the attack by nucleophile ( $\text{Nu}^-$ ), the rate of the reaction will reduce with electron donating R groups and enhance with electron withdrawing R groups. This is on account of the fact that the positive charge on carbonyl carbon is neutralized progressively on going to the transition state for nucleophilic addition.

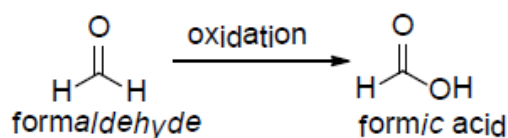


Thus it is further expected that the factors which may cause the delocalization of the positive charge on the carbonyl carbon will render the nucleophilic addition slow. Such factors include conjugation with aromatic rings, double bonds and groups containing unshared pair of electrons. As the addition reaction proceeds, the trigonal carbon is

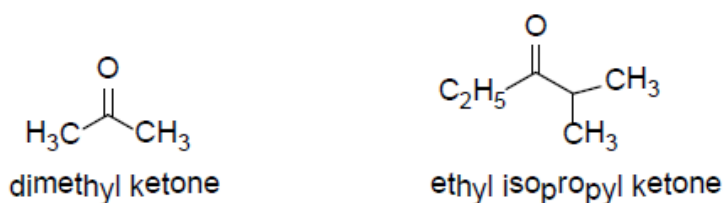
converted to saturated carbon, any increase in steric bulk in the R groups is expected to hinder the rate of the reaction. Thus, carbonyl compounds containing sterically bulky groups tend to react slowly and more reversibly.

## 6.2 Aldehydes and Ketones

Trivially, aldehydes are usually named after the acids they form on oxidation. The *-ic* in the name of the acid is then replaced by *aldehyde* to get the name of the aldehyde.



On the other hand, ketones are named by using the names of the groups attached with the carbonyl group and then adding ketone after the name of groups.



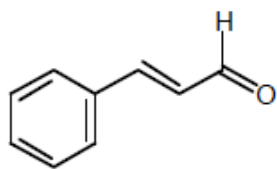
In the *IUPAC* system, aldehydes and ketones are named according to the following procedure:

- The name of the parent hydrocarbon (alkane or alkene or alkyne) is determined while counting the carbonyl carbon as a methyl group for aldehydes and as a methylene group for ketones. The substituents are named as it is done for the hydrocarbon while considering the position of aldehyde as 1-position. For both aldehydes and ketones, the naming is done as in alkanes but keeping in mind the priority sequence and rule of lowest locants.
- The name of the alkane is modified to *alkanal* for an aldehyde. In case of ketones, the name is modified to *alkanone*. The position of the carbonyl group is denoted as numerical prefix to *-one*.

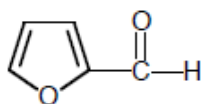
# Aldehydes and ketones

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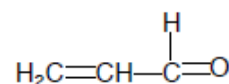
- Traditional names are used for a great many aldehydes and ketones which were recognized as substances long before systems of nomenclature were developed:



cinnamaldehyde

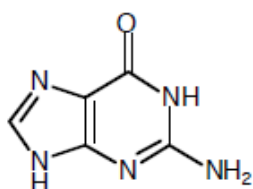


furfural

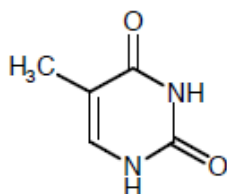


acrolein

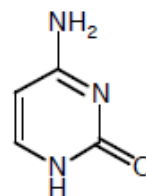
- Three of the four bases which comprise DNA contain carbonyl groups (and all four bases are nitrogen heterocycles, which we will discuss later):



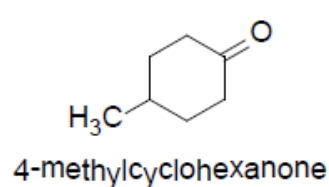
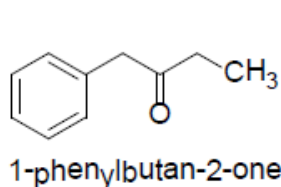
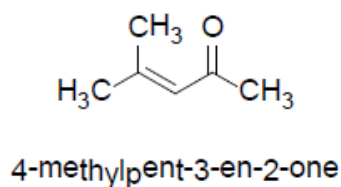
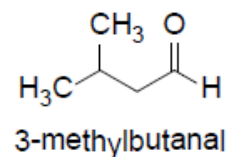
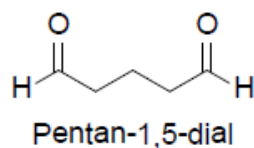
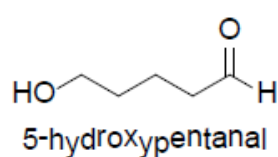
guanine (G)



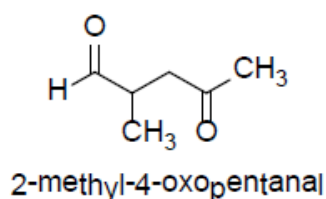
thymine (T)



cytosine (C)



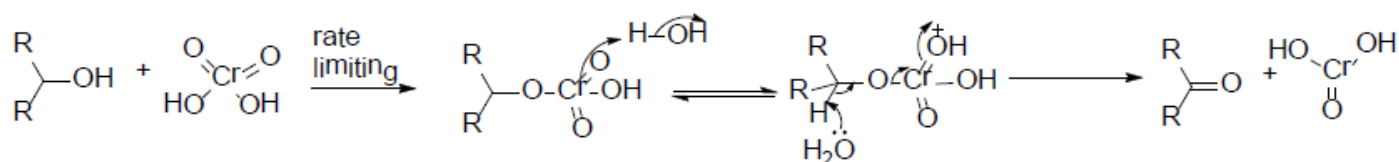
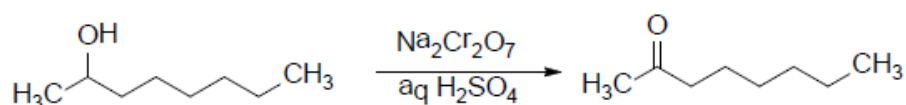
- In cases where both the aldehyde and keto functionalities are present in the same molecule, the aldehyde gets preference and the molecule is suffixed with an *-al*. The position of the keto group is denoted by a numerical prefix and is denoted by used of the word *oxo*.



## 6.2.1 Common Methods for Preparation Aldehydes and Ketones

### 6.2.1.1 Oxidation of Alcohols

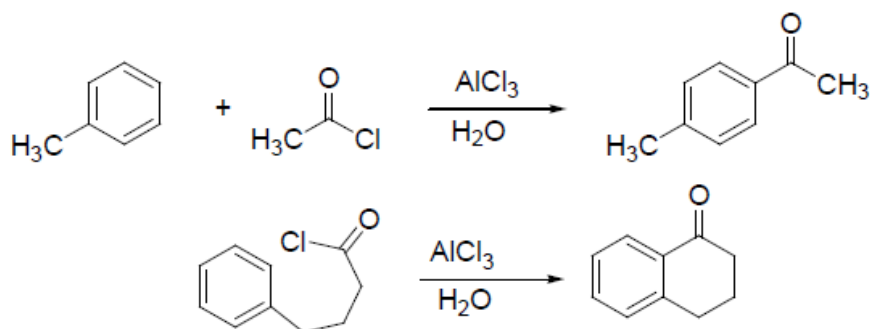
Ketones may be prepared by the oxidation of secondary alcohols in the presence of acid dichromate (Scheme 1). The reaction probably proceeds via the rate limiting formation of a chromate ester followed by decomposition of the ester to give the products.



Scheme 1

## 6.2.1.5 Acylation of Arenes

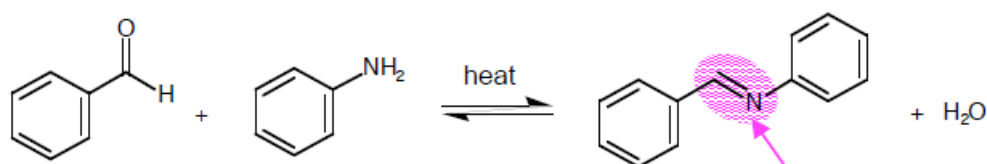
Friedel Craft acylation may be used to prepare alkyl aryl ketones or diaryl ketones (Scheme 7). In this process, an arene is usually treated with an acid halide or acid anhydride in the presence of a Lewis acid catalyst. This reaction is an example of aromatic electrophilic substitution.



## Reaction of aldehyde and ketone

### Reactions of Aldehydes and Ketones with Amines

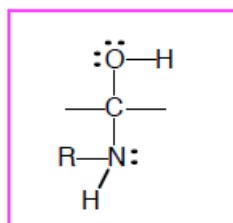
- Aldehydes and ketones react with primary amines to form *imines*, or *Schiff bases*.



An imine is a compound with a **C=N** double bond ( a nitrogen analog of an aldehyde or ketone)

- The mechanism of imine formation involves the nucleophilic addition of the amine to the carbonyl carbon, forming a stable intermediate species called a *carbinolamine*.

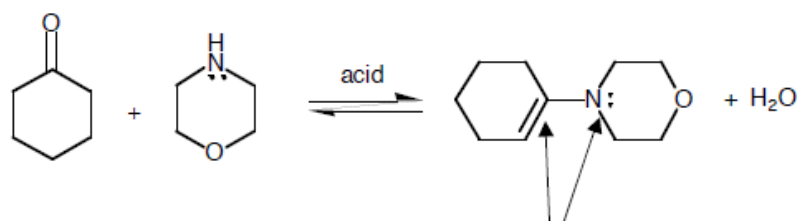
Carbinolamines are compounds with an amine group and a hydroxy group attached to the same carbon.



Carbinolamines are analogous to hemiacetals.

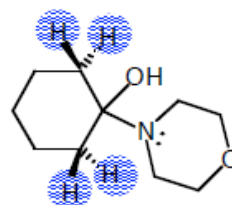
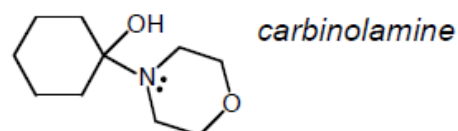
## Reaction of Aldehydes/Ketones with 2° Amines

- Aldehydes and ketones react with secondary amines to form **enamines**.



Enamines have a nitrogen bound to a carbon which is part of a C=C double bond.

- The mechanism involves nucleophilic addition of the amine to the carbonyl to form a carbinolamine.
- Enamines form only if the carbonyl compound has at least one hydrogen on a carbon adjacent to the carbonyl carbon.
- Formation of the alkene may be recognized as an elimination reaction.



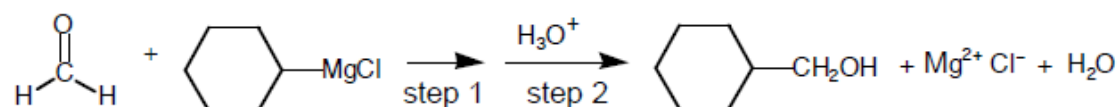


## Addition Using Grignard Reagents

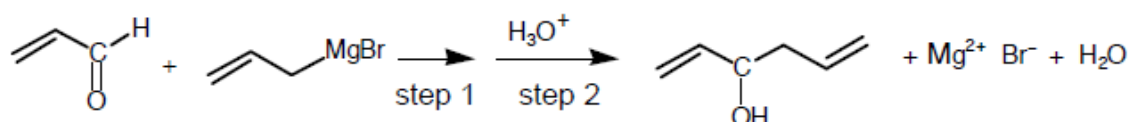
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- Primary, secondary and tertiary alcohols may be formed in the reactions of aldehydes or ketones with Grignard reagents.

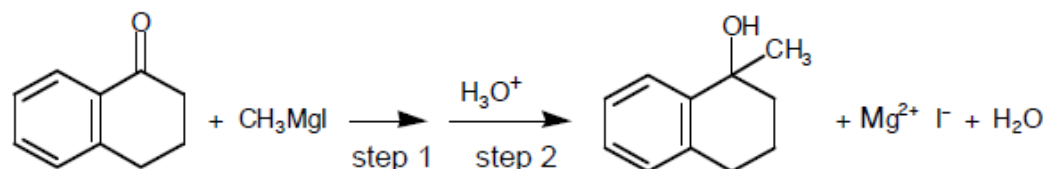
*primary alcohols from formaldehyde*



*secondary alcohols from aldehydes*

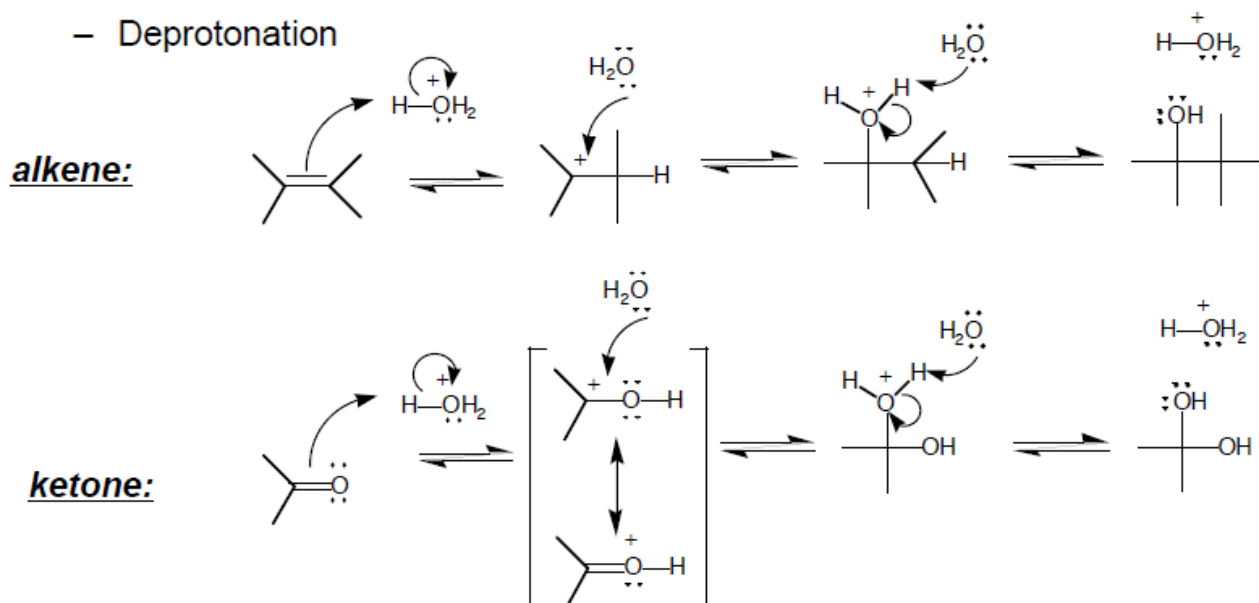


*tertiary alcohols from ketones*



## Addition Under Acidic Conditions

- Addition of water to carbonyl compounds under acidic conditions is analogous to addition of water to alkenes
- The reaction occurs in three steps:
  - Protonation
  - Addition
  - Deprotonation



### 1. oxidation

- prim. alcohol  $\rightarrow$  aldehyde  $\rightarrow$  carboxylic acid
- sec. alcohol  $\rightarrow$  ketone  $\rightarrow$  no more oxidized

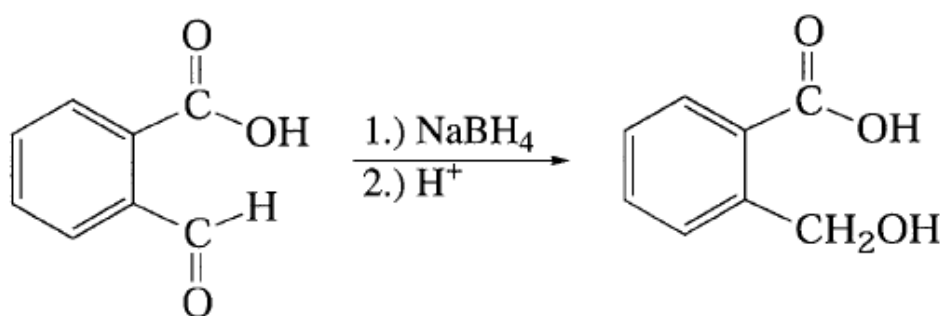
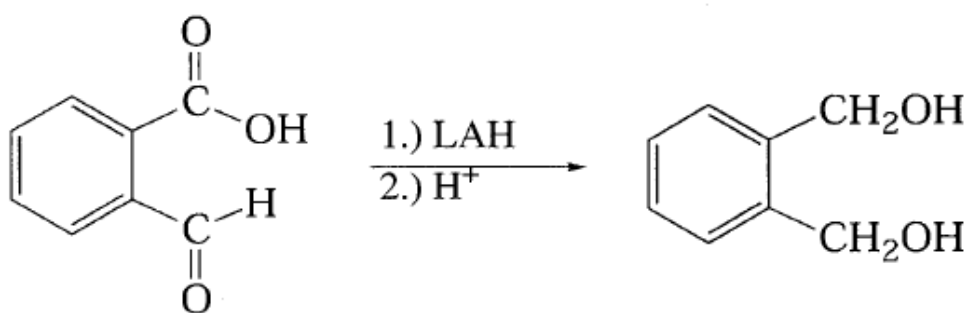
Tollens' reagent:  $[Ag(NH_3)_2]^+ \rightarrow Ag$



Benedict's or **Fehling's solution**:  $Cu^{2+}(l) \rightarrow Cu_2O(s)$

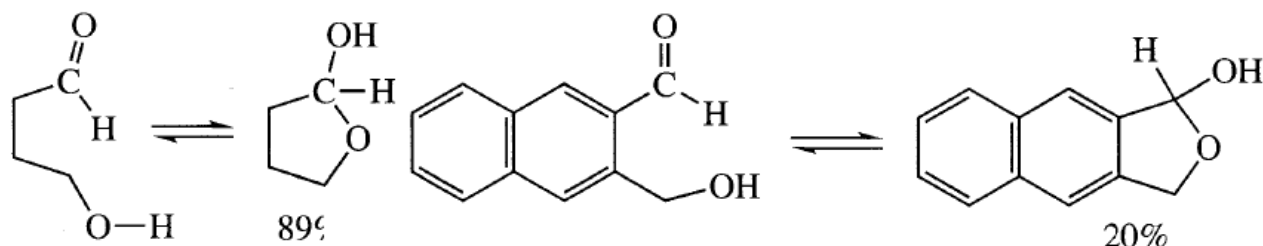
## 2. reduction

- aldehyde  $\rightarrow$  primary alcohol
- ketone  $\rightarrow$  secondary alcohol

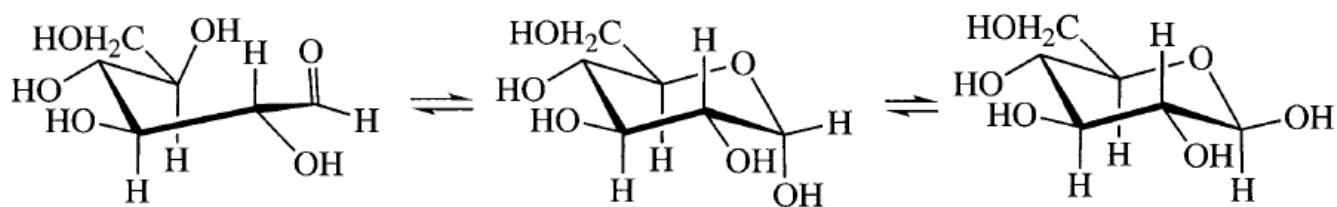


## 5. Hemiacetals are the key to understanding the carbohydrates (“sugars”)

- Ring-chain tautomerism of hemiacetals result in stable rings under special conditions



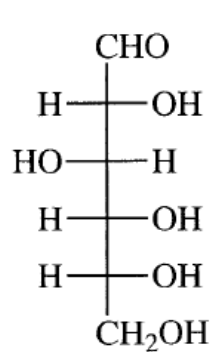
- Stable rings are commonly seen among sugars



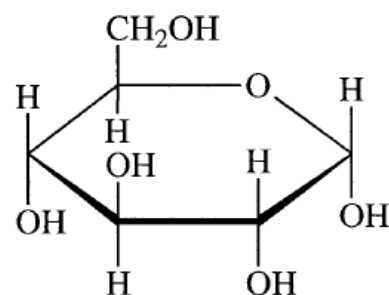
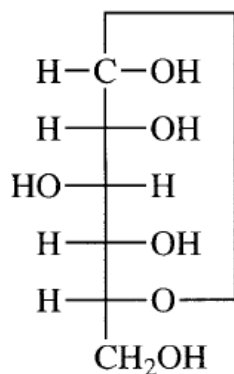
Glucose in its acyclic form.

Glucose in its  $\alpha$ -form.

Glucose in its  $\beta$ -form.



Fischer projections



Haworth Projection

# Aldehydes and ketones

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- Sugars are classified by the number of carbon atoms in the chain
- There are three-carbon, four-carbon, five-carbon and six-carbon sugars

**Table 17.1**

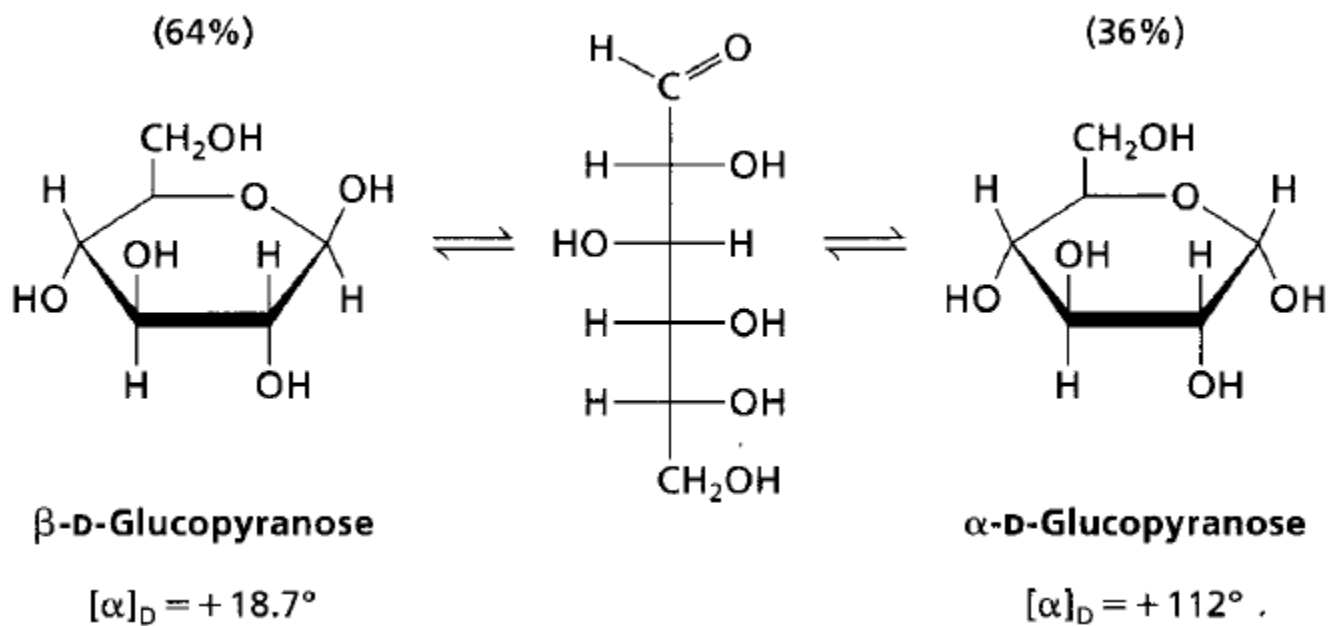
Structures and names of common carbohydrates.

Common carbohydrates				
$\begin{array}{c} \text{CHO} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{C} = \text{O} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	
<b>D-Glyceraldehyde</b>	<b>Dihydroxyacetone</b>	<b>D-Erythrose</b>	<b>D-Threose</b>	
$\begin{array}{c} \text{CHO} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\   \\ \text{H} - \text{C} - \text{H} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$
<b>D-Ribose</b>	<b>2-Deoxy-D-ribose</b>	<b>D-Xylose</b>	<b>D-Arabinose</b>	<b>D-Lyxose</b>
<b>Building blocks for RNA and DNA</b>				
$\begin{array}{c} \text{CHO} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{C} = \text{O} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	
<b>D-Allose</b>	<b>D-Gulose</b>	<b>D-Glucose</b>	<b>D-Fructose</b>	
$\begin{array}{c} \text{CHO} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\   \\ \text{HO} - \text{C} - \text{H} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{H} - \text{C} - \text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$
<b>D-Galactose</b>	<b>D-Idose</b>	<b>D-Mannose</b>	<b>D-Talose</b>	<b>D-Altrose</b>

- Sugars may be **aldoses** (contain an aldehyde) or **ketoses** (contain a ketone)

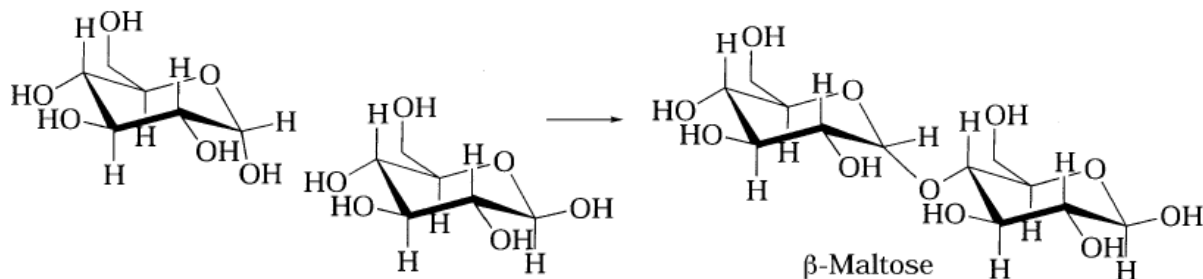
# Aldehydes and ketones

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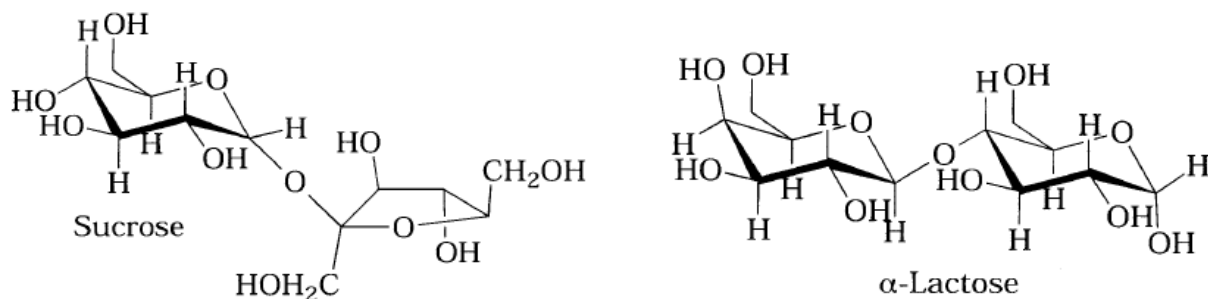


## Sugar Chemistry

- Acetal derivatives are made by addition of alcohol to aldehyde carbonyl groups
- The alcohol can be from another sugar, producing di- and polysaccharides

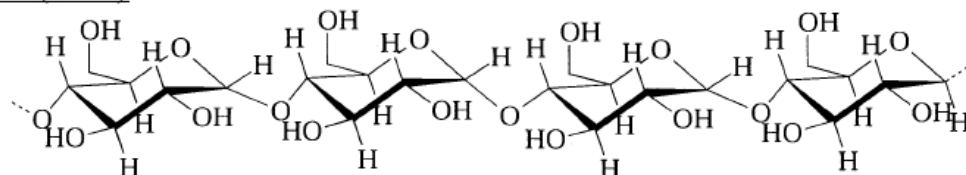


- Sucrose and Lactose are common disaccharides

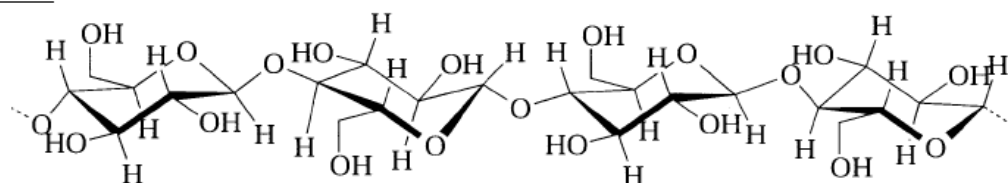


- Carbohydrates are polysaccharides:

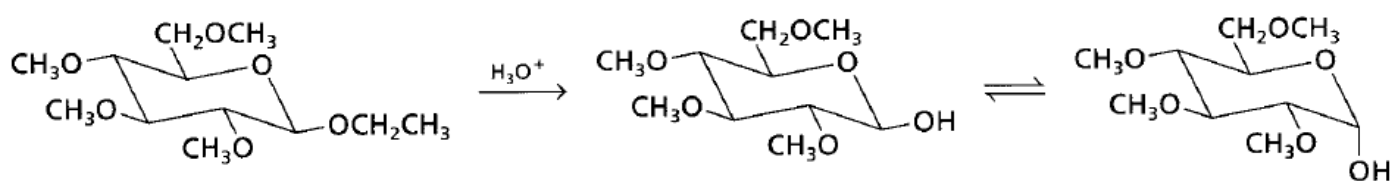
### Amylose (starch)



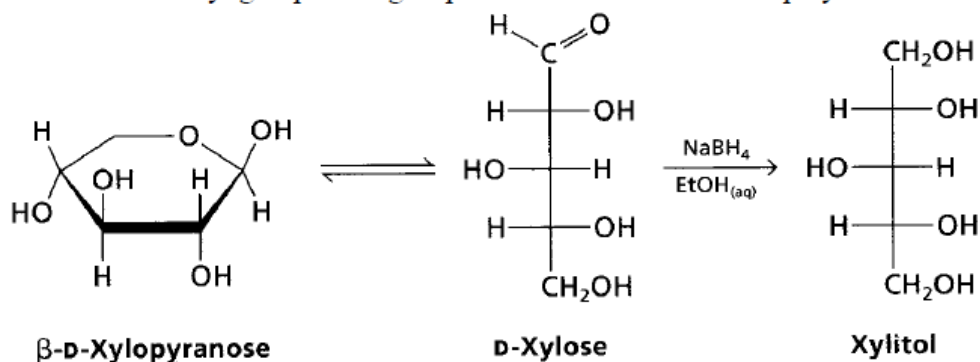
### Cellulose



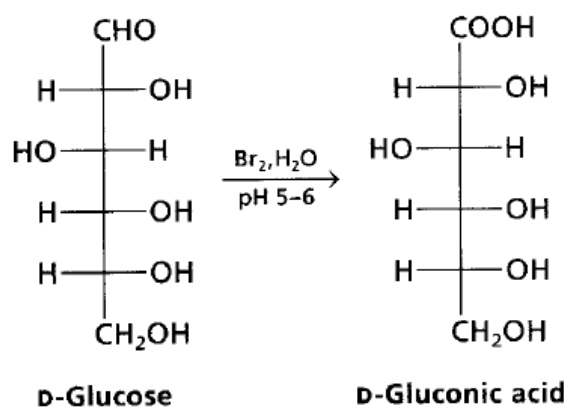
- Polysaccharides are hydrolysed to sugars under acid conditions *because* they are acetals



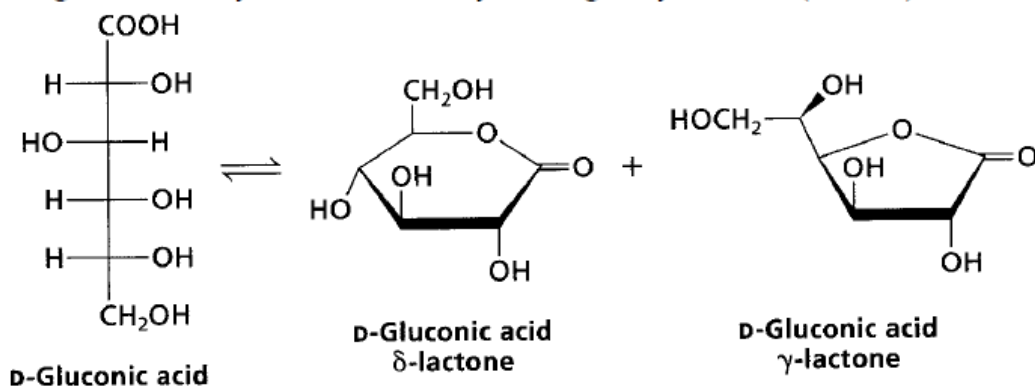
- Reduction of the carbonyl groups of sugars produces alditols which are polyols



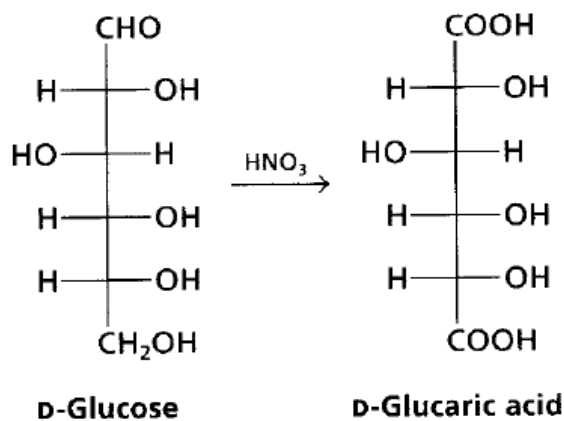
- Oxidation of sugars leads to: carboxylic acids using aqueous  $\text{Br}_2$



- Such long-chain carboxylic acids can also cyclise to give cyclic esters (lactones)



- With concentrated nitric acid, dicarboxylic acids also called aldaric acids are produced





# Aldehydes and ketones

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