

# Chem 109 C

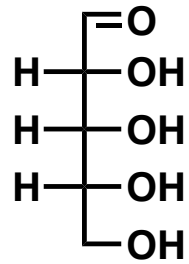
**Fall 2014**

**Armen Zakarian**  
**Office: Chemistry Bldn 2217**

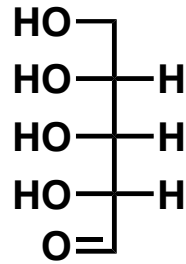
<http://web.chem.ucsb.edu/~zakariangroup/courses.html>

# Carbohydrates: Fischer projections

**manipulation of Fischer projections:**



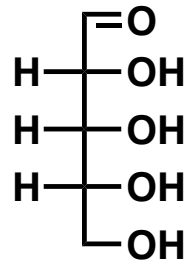
**D-ribose**



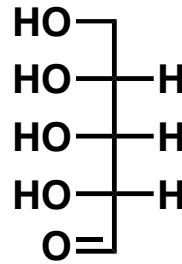
**also D-ribose**

# Carbohydrates: Fischer projections

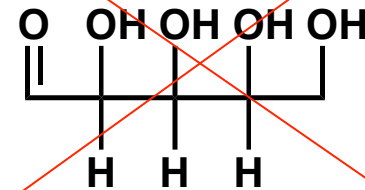
## manipulation of Fischer projections:



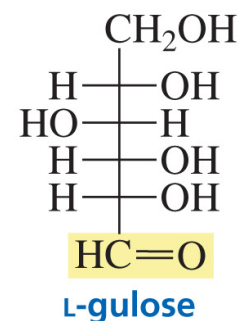
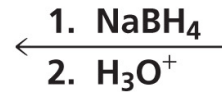
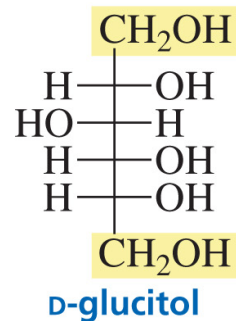
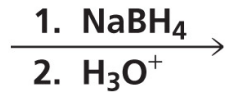
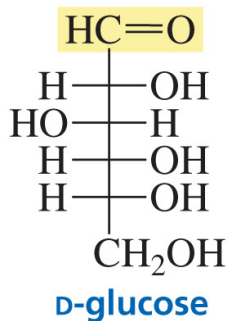
**D-ribose**



**also D-ribose**



**not D-ribose**

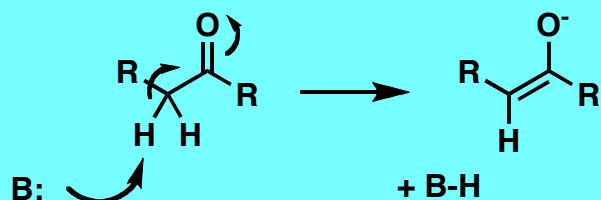


drawn upside down

**an alditol**

# Carbohydrates: Reactions with Bases

fundamental reactivity

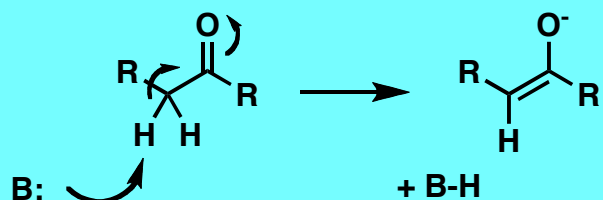


enolate formation: Section 18.2

**base-catalyzed epimerization: *D*-glucose and *D*-mannose**

# Carbohydrates: Reactions with Bases

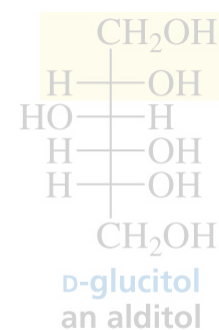
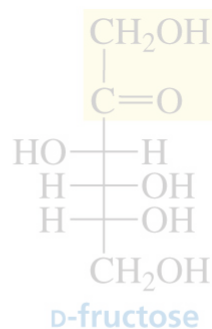
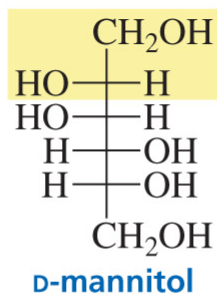
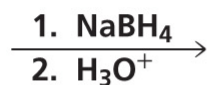
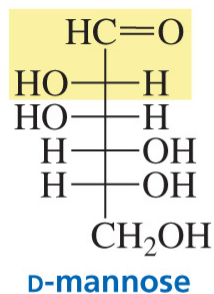
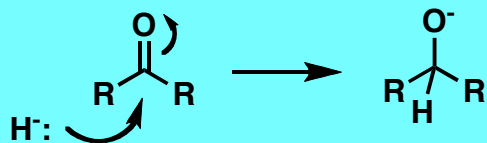
fundamental reactivity



**base-catalyzed enediol rearrangement: *D*-glucose and *D*-fructose**

# Carbohydrates: Reduction

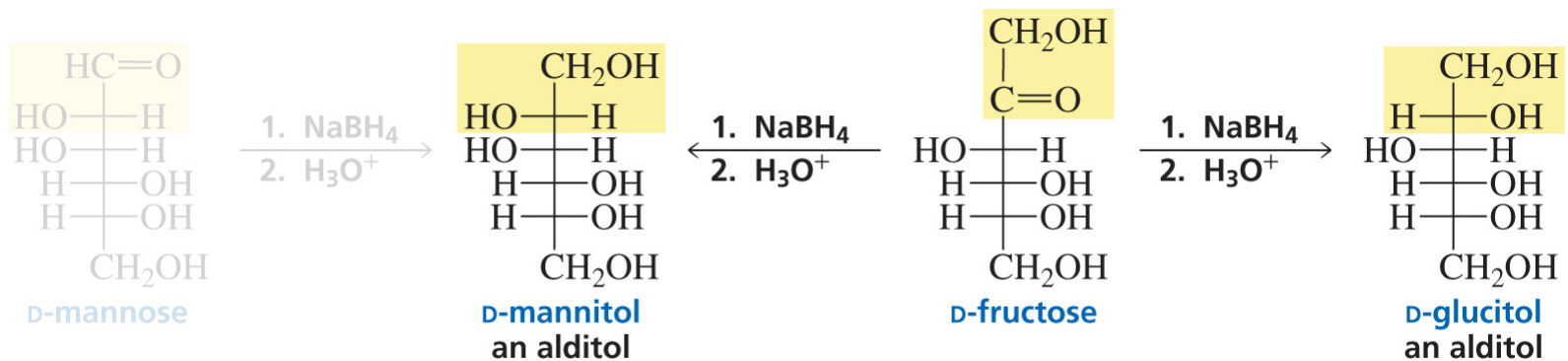
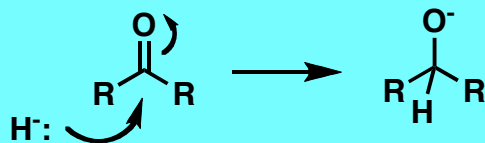
## fundamental reactivity



**an alditol** © 2007 Pearson Prentice Hall, Inc.

# Carbohydrates: Reduction

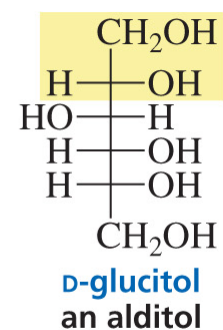
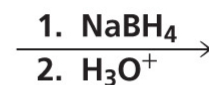
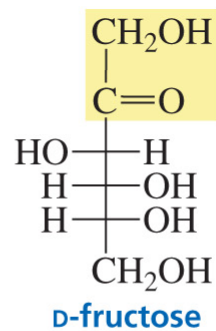
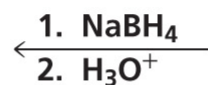
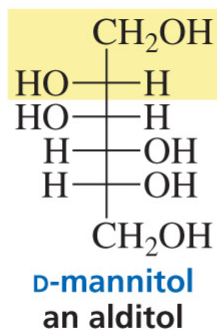
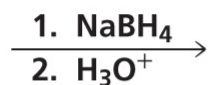
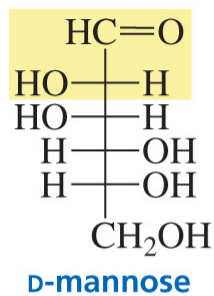
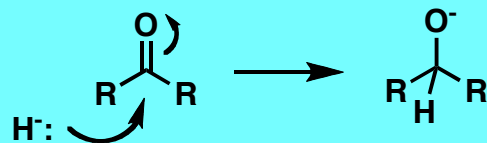
## fundamental reactivity



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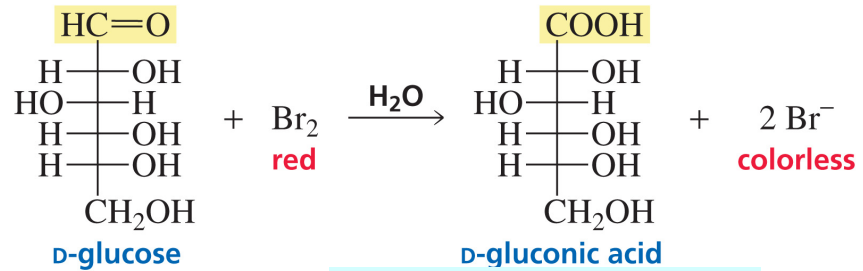
# Carbohydrates: Reduction

## fundamental reactivity



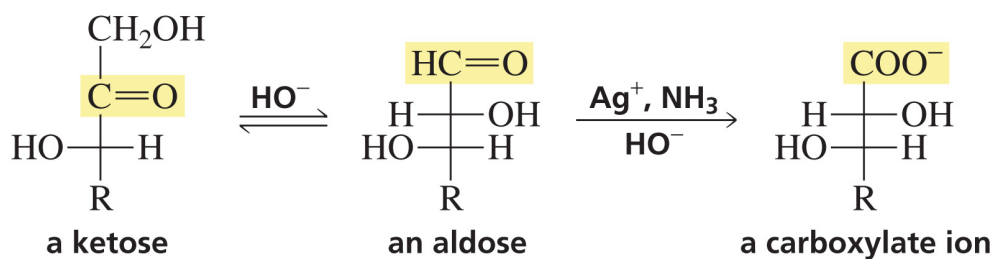
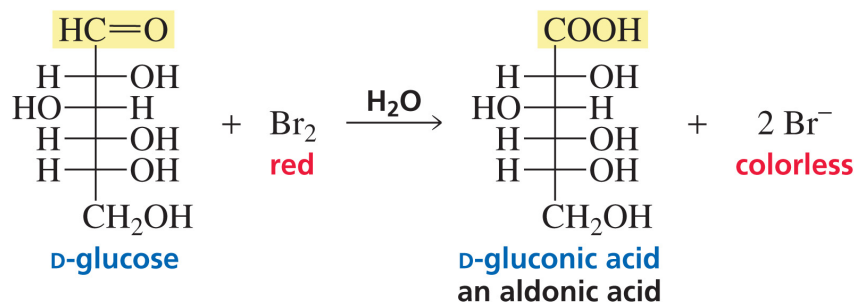


# Carbohydrates: Oxidation



Copyri **an aldonic acid**

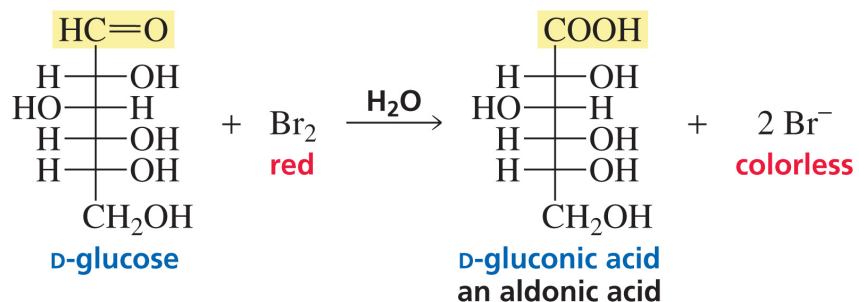
# Carbohydrates: Oxidation



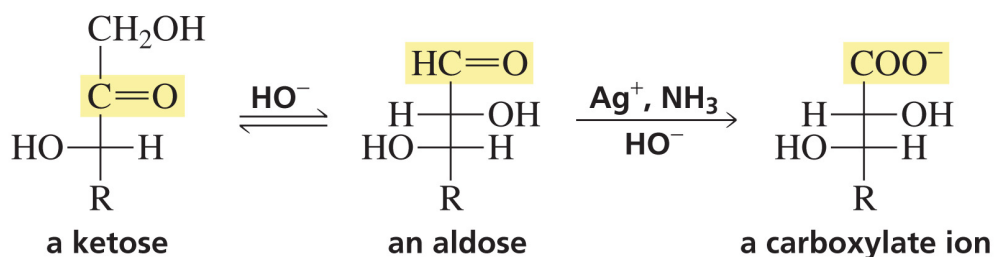
**“Tollens test”**

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# Carbohydrates: Oxidation

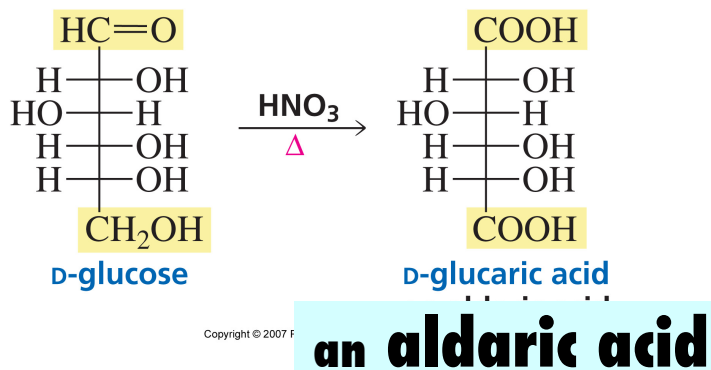


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“Tollens test”

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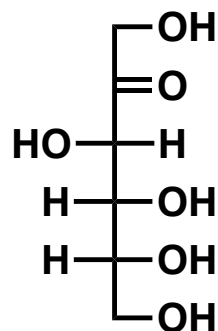


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# Carbohydrates: Oxidation

## PROBLEM 9

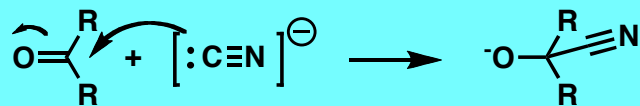
Show how an enediol rearrangement can move the carbonyl group of fructose from C-2 to C-3



**D-fructose**

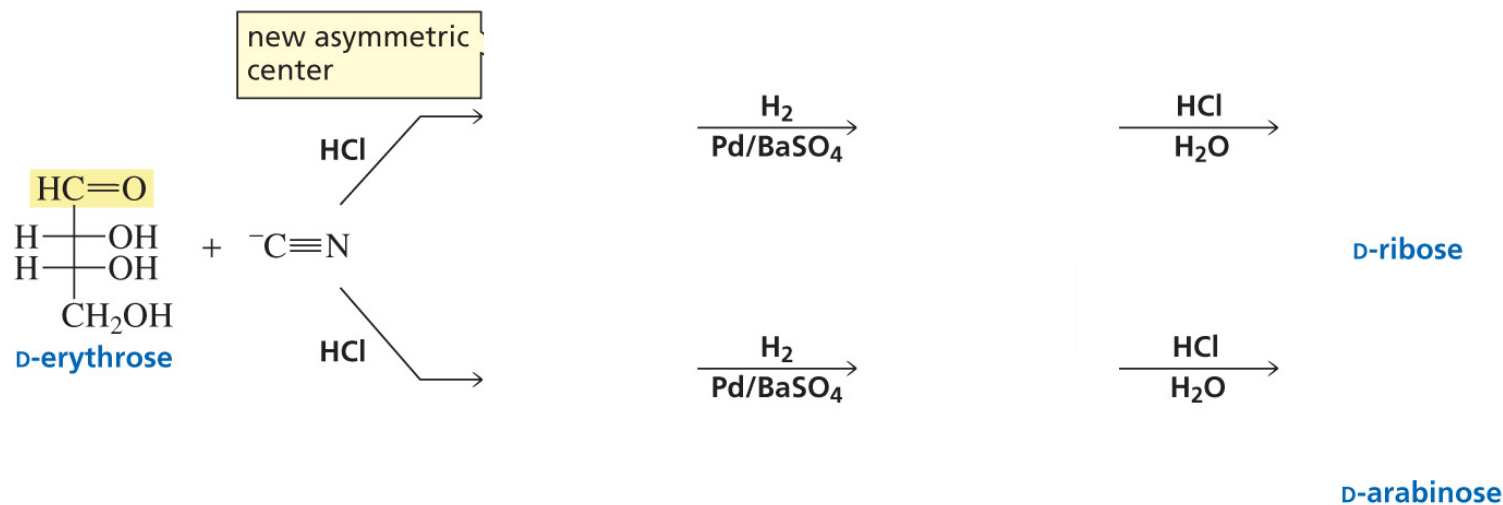
# Carbohydrates: Lengthening the Chain

## fundamental reactivity



## Kiliani-Fischer synthesis:

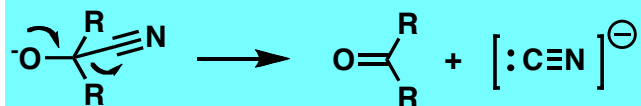
the modified Kiliani-Fischer synthesis



- Steps/Reagents:
1. NaCN, HCl;
  2. H<sub>2</sub>, Pd/BaSO<sub>4</sub>
  3. HCl, H<sub>2</sub>O

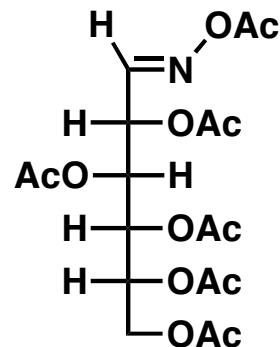
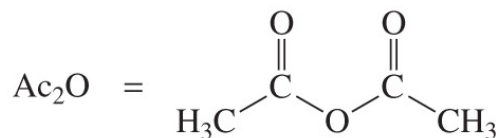
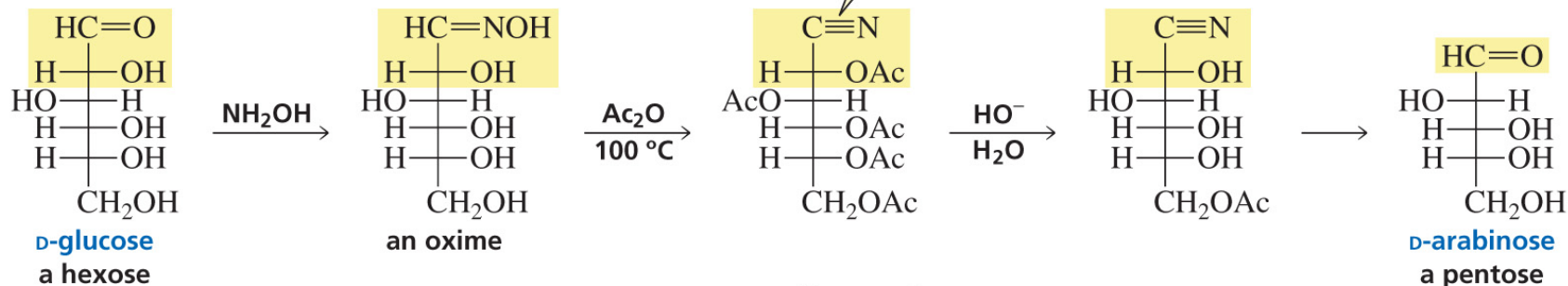
# Carbohydrates: Shortening the Chain

## fundamental reactivity



## Wohl degradation:

the Wohl degradation



- Steps/Reagents:
1.  $\text{NH}_2\text{OH}$ ;  $\text{H}^+$
  2.  $\text{Ac}_2\text{O}$ ,  $100\text{ }^\circ\text{C}$
  3.  $\text{NaOH}$ ,  $\text{H}_2\text{O}$