

Chem 109 C

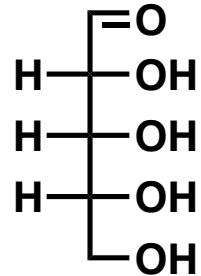
Bioorganic Compounds

**Armen Zakarian
Office: Chemistry Bldn 2217**

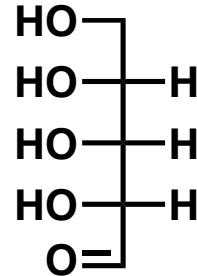
<http://labs.chem.ucsb.edu/~zakariangroup/courses.html>

Carbohydrates: Fischer projections

manipulation of Fischer projections:



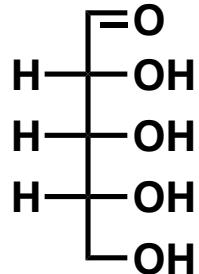
D-ribose



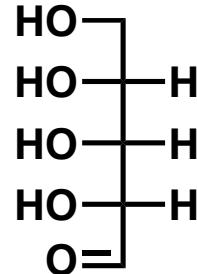
also D-ribose

Carbohydrates: Fischer projections

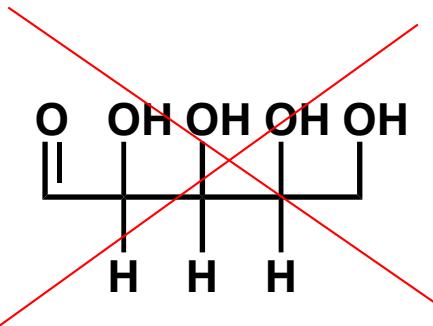
manipulation of Fischer projections:



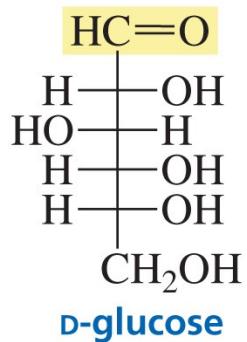
D-ribose



also D-ribose

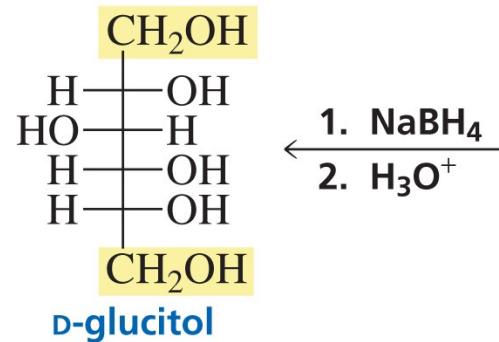


not D-ribose



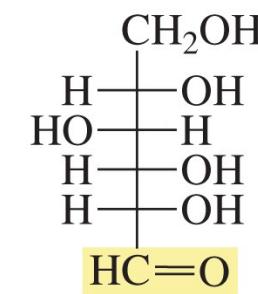
D-glucose

1. NaBH_4
2. H_3O^+



D-glucitol

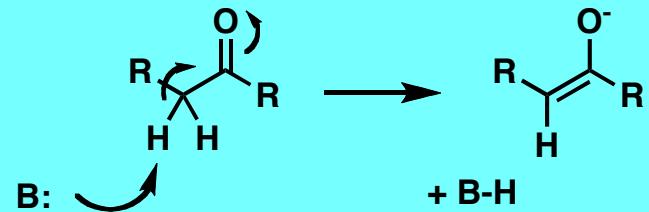
an alditol



L-gulose
drawn upside down

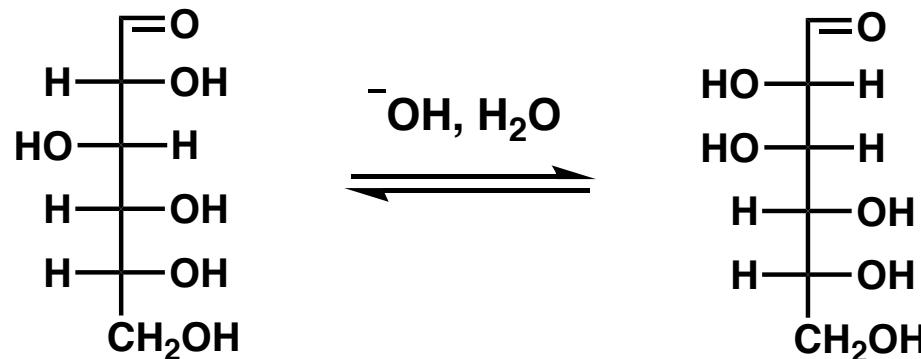
Carbohydrates: Reactions with Bases

fundamental reactivity



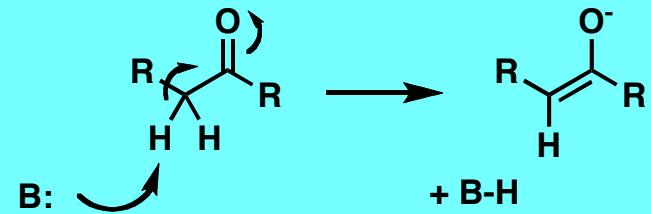
enolate formation: Section 17.3

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

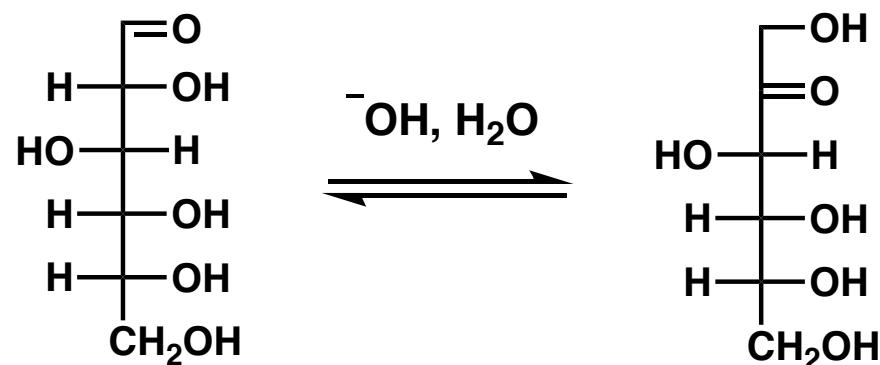


Carbohydrates: Reactions with Bases

fundamental reactivity

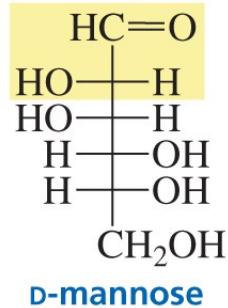
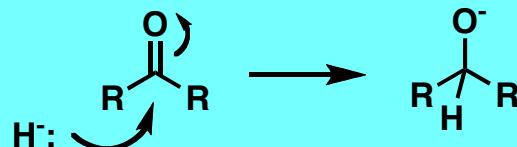


base-catalyzed enediol rearrangement: *D-glucose* and *D-fructose*

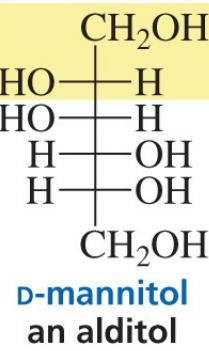


Carbohydrates: Reduction

fundamental reactivity

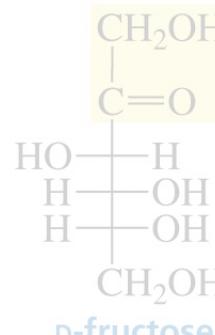


1. NaBH_4
2. H_3O^+



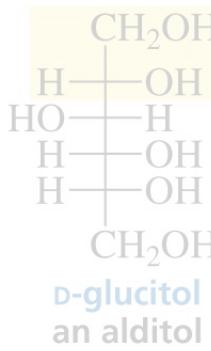
D-mannitol
an alditol

1. NaBH_4
2. H_3O^+



D-fructose

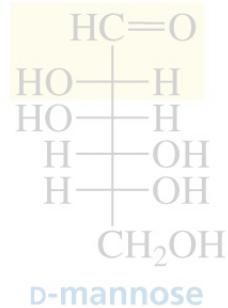
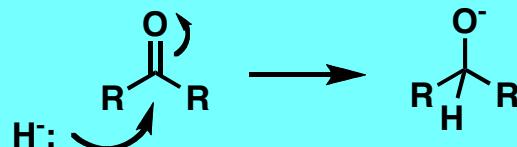
1. NaBH_4
2. H_3O^+



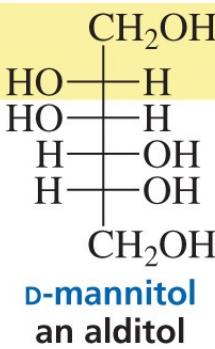
D-glucitol
an alditol

Carbohydrates: Reduction

fundamental reactivity

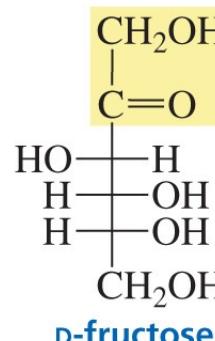


1. NaBH₄
2. H₃O⁺



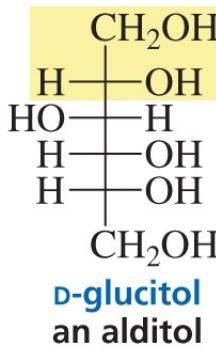
D-mannitol
an alditol

1. NaBH₄
2. H₃O⁺



D-fructose

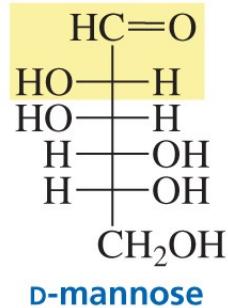
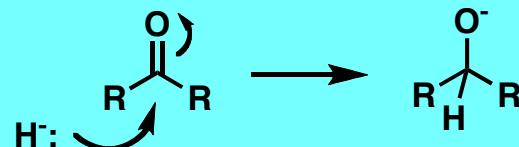
1. NaBH₄
2. H₃O⁺



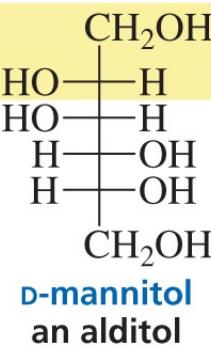
D-glucitol
an alditol

Carbohydrates: Reduction

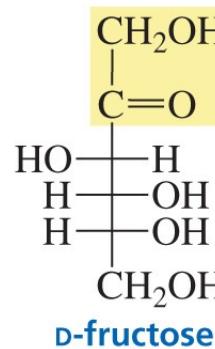
fundamental reactivity



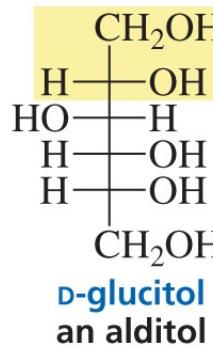
1. NaBH₄
2. H₃O⁺



1. NaBH₄
2. H₃O⁺

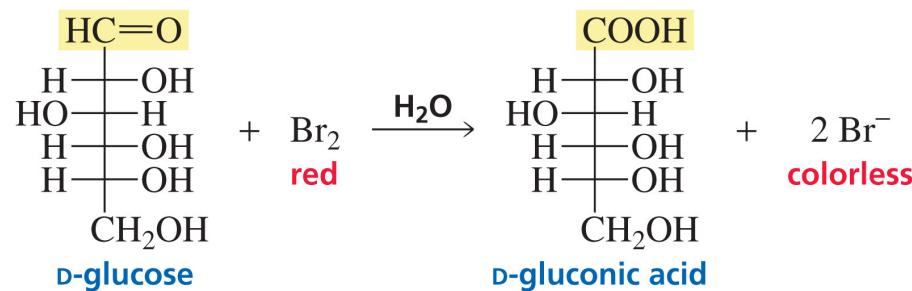


1. NaBH₄
2. H₃O⁺



Carbohydrates: Oxidation, three methods

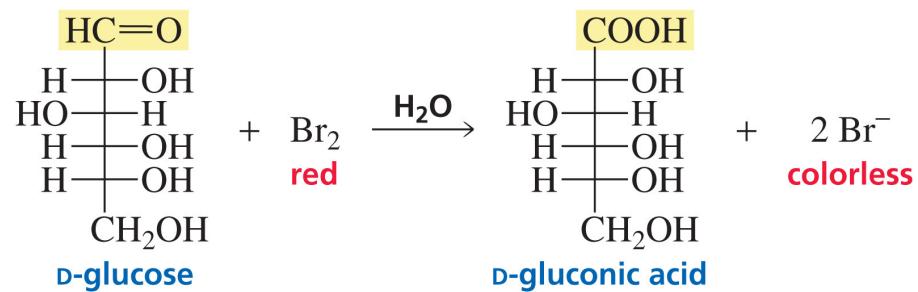
1



an aldonic acid

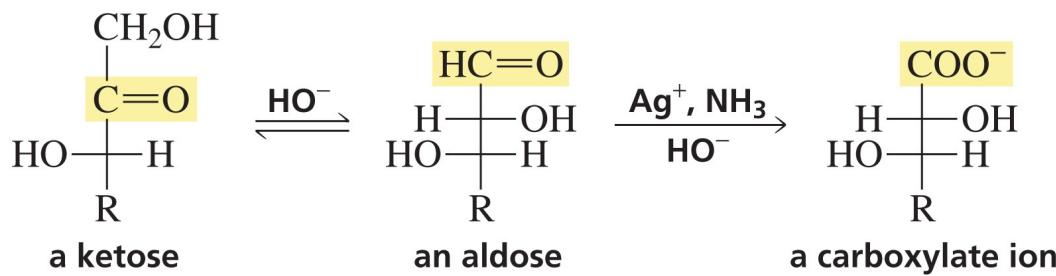
Carbohydrates: Oxidation, three methods

1



an aldonic acid

2

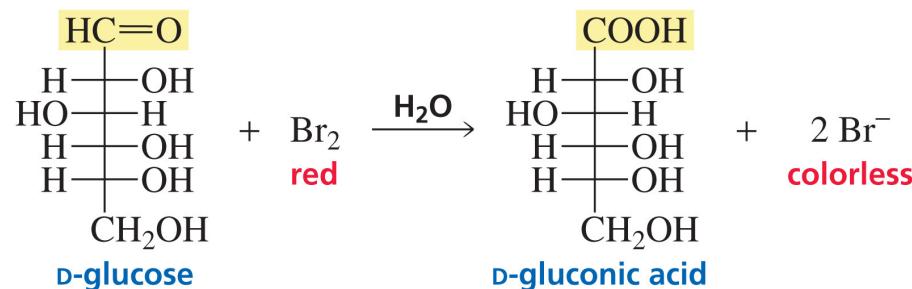


“Tollens test”



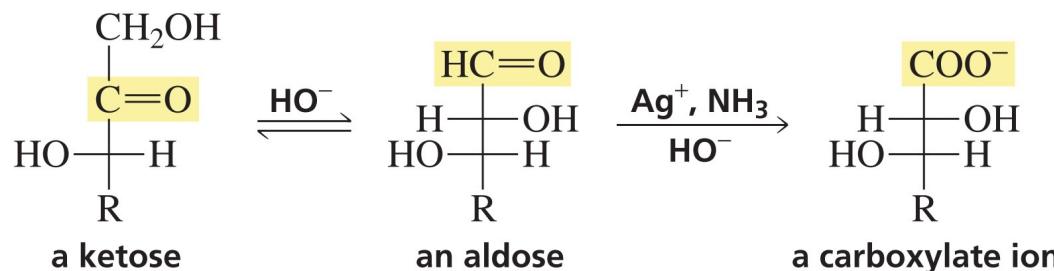
Carbohydrates: Oxidation, three methods

1



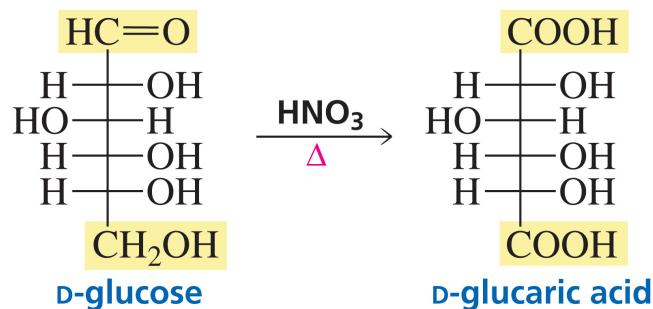
an aldonic acid

2



“Tollens test”

3



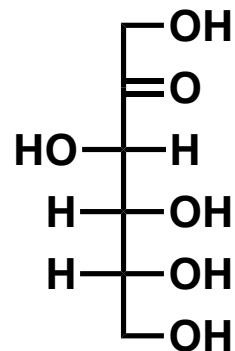
an aldaric acid



Carbohydrates: Oxidation

PROBLEM 9

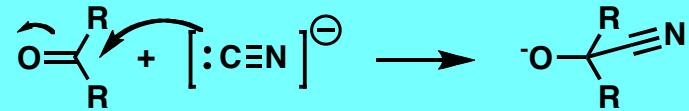
Show how an enediol rearrangement can move the carbonyl group of fructose from C-2 to C-3



D-fructose

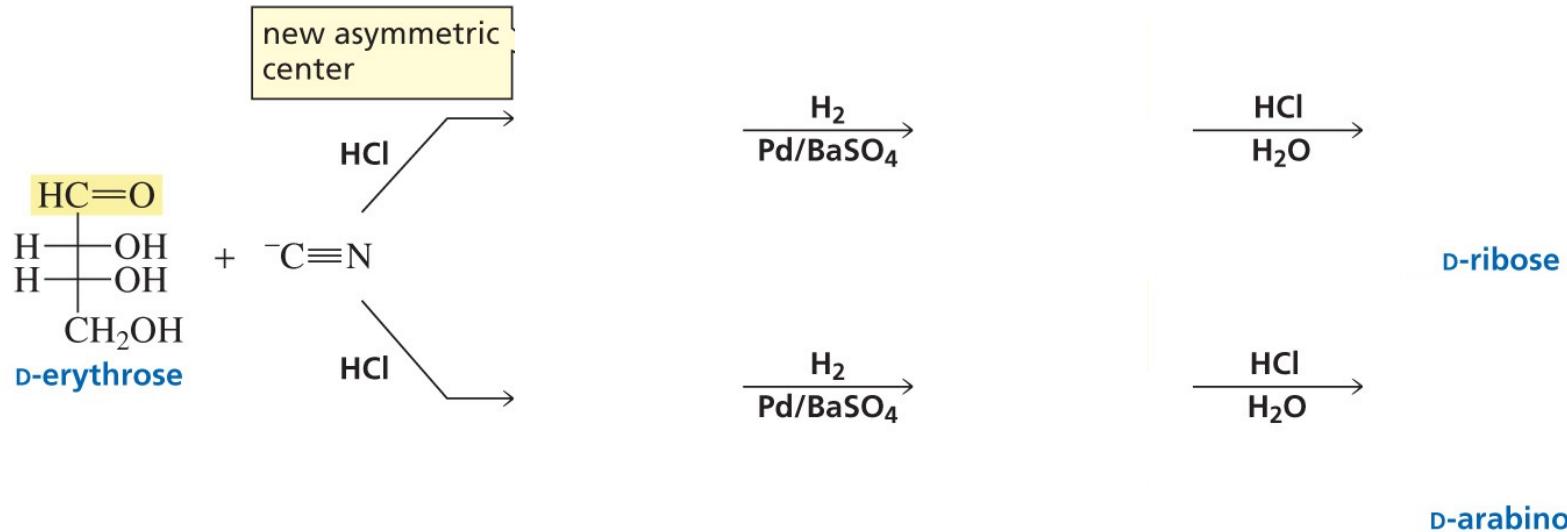
Carbohydrates: Lengthening the Chain

fundamental reactivity



Kilian-Fischer synthesis:

the modified Kilian–Fischer synthesis

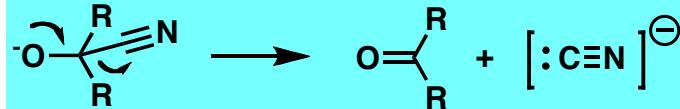


Steps/Reagents:

1. NaCN, HCl;
2. H₂, Pd/BaSO₄
3. HCl, H₂O

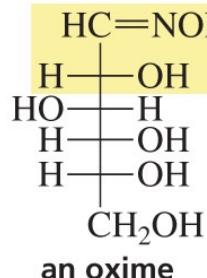
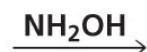
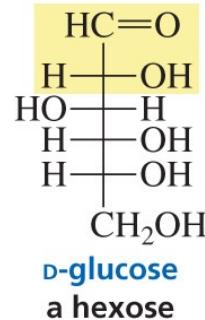
Carbohydrates: Shortening the Chain

fundamental reactivity

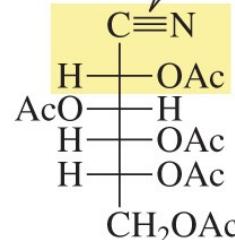
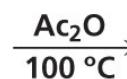


Wohl degradation:

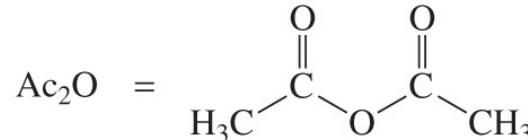
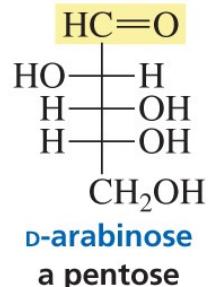
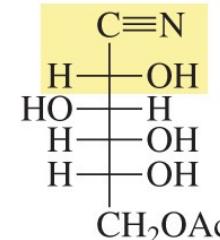
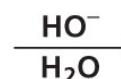
the Wohl degradation



an oxime

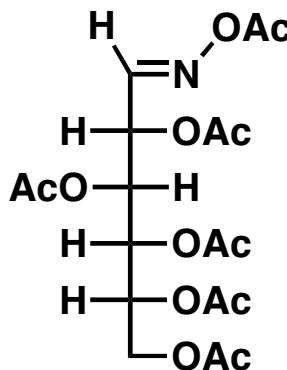


a cyano group



Steps/Reagents:

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



Carbohydrates

PROBLEM 16. What two monosaccharides can be degraded to

a. D-arabinose

b. D-ribose

c. L-arabinose