A/K III

(Hemi-) Acetal Formation

- Rxn w/ ROH
- Carbohydrate Chemistry

Ref 16: 7 ; (Ch.22)

Prob 16: 9 – 11; HMWK #06

Adv Rdg 16: 8 - 9 ; (12: 3 - 8)

Terminology

Hydrate

	Hemiacetals	Acetals
"open"		
general		
aldehyde derived		
"internal"		
general		
aldehyde derived		

General Rxn

Notes:

1.) R_1, R_2 could be H, open chains, rings

2.) R_3, R_4 could be open chains, rings

3.) R_1, R_4 / R_2, R_3 could be rings

4.) all are equilibrium rxns

5.) rxn slow in neutral medium;
can be catalyzed by "acid" or "base"

Rxn Mech.'s

1.) Hemiacetal Form^n

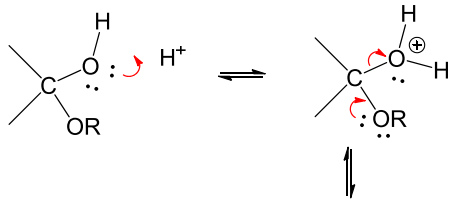
a.) base catalyzed

b.) acid catalyzed

Mech.'s ...

2.) Acetal Form^n

in acid (**not** in base) rxn can go further



Summary

Hemiacetals — formed in acid or base (slowly in neutal medium)
rxn reversible in acid or base

Acetal — formed only in acid
reversible in acid
irreversible (stable) in base

Equilibria can be "shifted"
acc. to Le Chatelier's Principle:

add extra ROH and remove H_2O → acetal

add extra H_2O : aldehyde/ketone are favored (in equil. with hydrate)

$$\text{A/K} + \underset{\text{(xs)}}{\text{ROH}} \xrightleftharpoons{H^+} \text{acetal;}\quad \textit{remove } H_2O$$

$$\text{acetal} + \underset{\text{(xs)}}{\text{HOH}} \xrightleftharpoons{H^+} \text{A/K}$$

$$\left(\rightleftharpoons \text{hydrate}\right)$$

Relevance of "Acetals"

1.) • describes general reactivity of A/K's
• important structural element in carbohydrates/ other natural products

2.) can function as **protecting group** in synthetic schemes

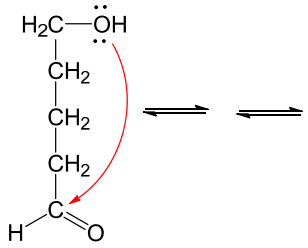
General:

A/K → acetal, prepared in acid
→ do rxn elsewhere on molecule, in base
→ regenerate modified A/K

Ex.

Internal (Cyclic) Hemiacetals

Ex.

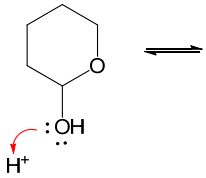


Do detailed mech. as HMWK.

Internal Acetals

- can be formed in presence of ROH/H^+
- hemiacetal → acetal
- mech. as before

Outline of an Ex.



Again, detailed steps as HMWK.

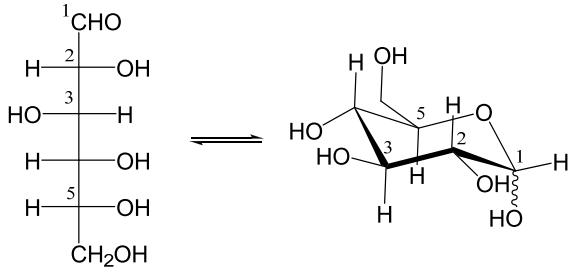
Intro. to Carbohydrate Chem.

(see Solomons Ch. 22 for more details)

e.g.,: sugar, starch, glycogen, cellulose ...

MF: $\approx C_n(H_2O)_n$

Ex. D-Glucose



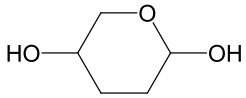
open form internal hemiacetal

Large Carbohydrates

e.g.,: sugar, starch, glycogen, cellulose ...

are "poly" acetals

concepts about basic structure of carbohydrates:



in truth:
there are 5-and 6- membered rings
most carbons carry substituents: OH, CH_2OH
stereochem. is important (ignored here)