Organic Chemistry III

後藤 佑樹 (Yuki Goto, Bioorganic Chemistry Lab.)

“Organic chemistry of biomolecules”

Topics

- structure of monosaccharide
  - classification
  - Fischer projection
  - cyclic sugars

done

- reactions of monosaccharide
  - several examples of monosaccharides
  - glycoside formation (glycosylation)
  - protection strategies of monosaccharides

- structure and functions of oligo and polysaccharide

Review of the previous class

Classification of monosaccharide

aldoses/ketoses, pentoses/hexoses

How to understand/draw Fischer projections

4 tips to draw and modify Fischer projections

D/L nomenclature

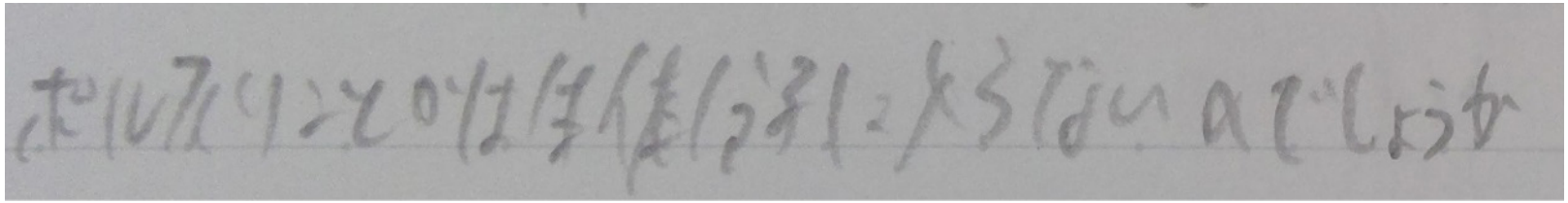
convenient way to categorize stereochemistry of biomolecules

Cyclic forms of sugars

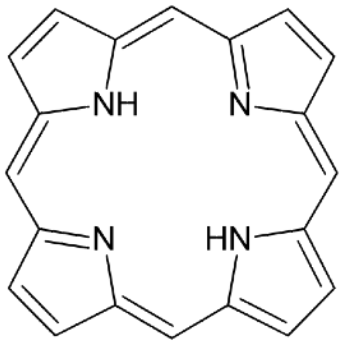
hemiacetal formation, furanoses/pyranoses

anomers, definition of α- and β-anomers

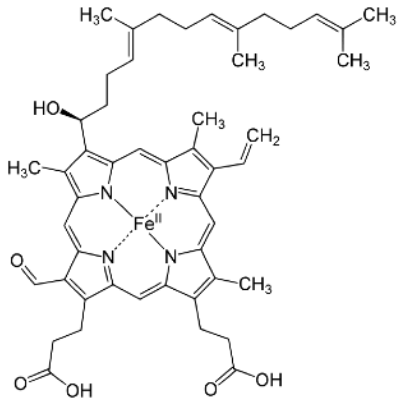
Q and A



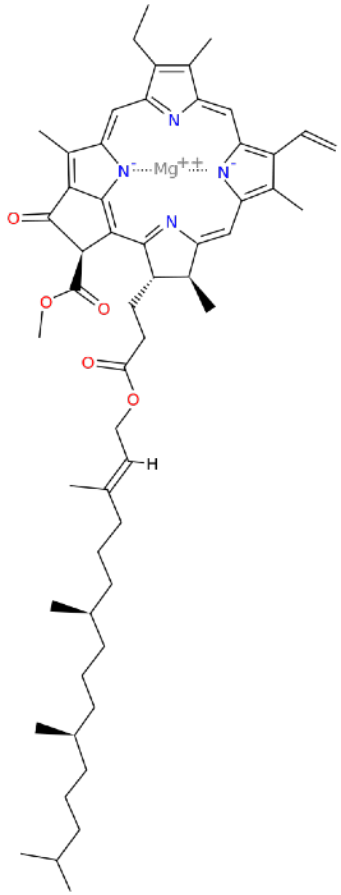
Can porphyrins be considered a type of biomolecule?



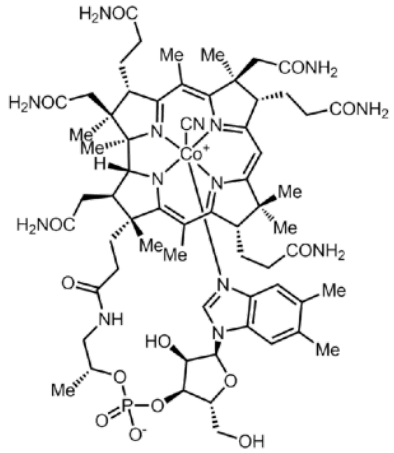
general formula of porphyrins



heme A



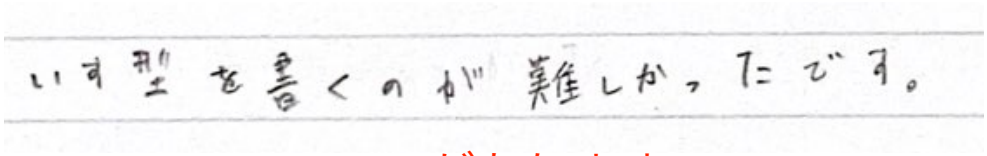
Chlorophyll a



cyanocobalamin (vitamin B_{12})

Q and A

分子進化および生命起源の分野の一大命題
色々研究はあるけど、確定的な説明はいまだ無い（はず）
（ただ、どこかの時点で淘汰圧がかかったのは確かだと思う）



コツがあります。

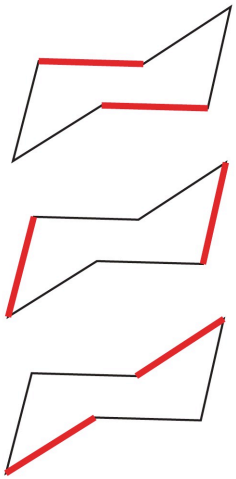
English explanations for this issue are available in Jone's textbook.

English explanations for this issue are available in Jone's textbook.

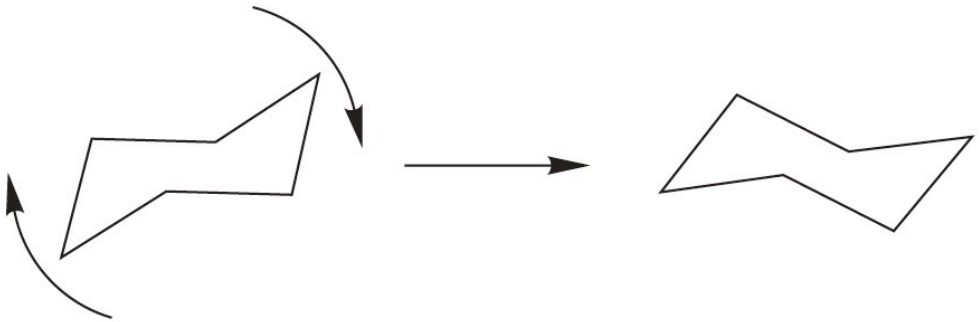
★★

ところで：シクロヘキサンを上手に書くコツ

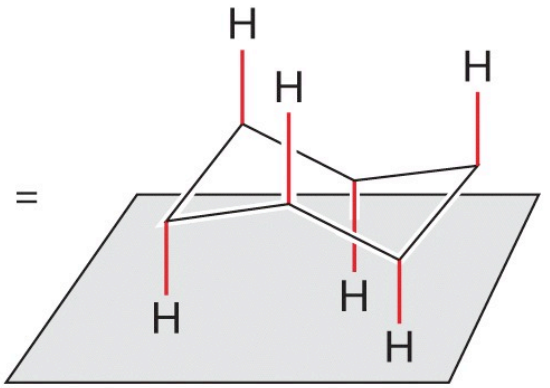
ポイント１
お互いに並行な炭素-炭素結合が3対



ポイント２
ちょっと傾けて書く



ポイント３
アキシアルの結合は全て並行

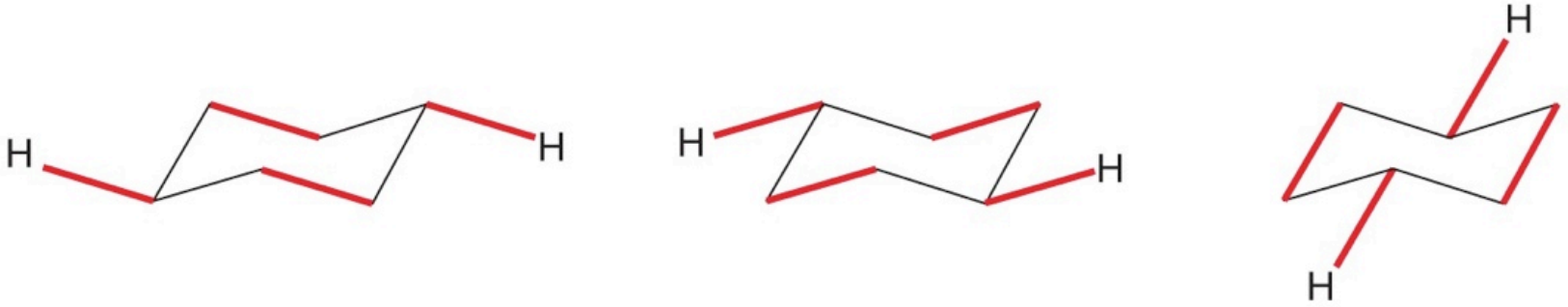


English explanations for this issue are available in Jone's textbook.

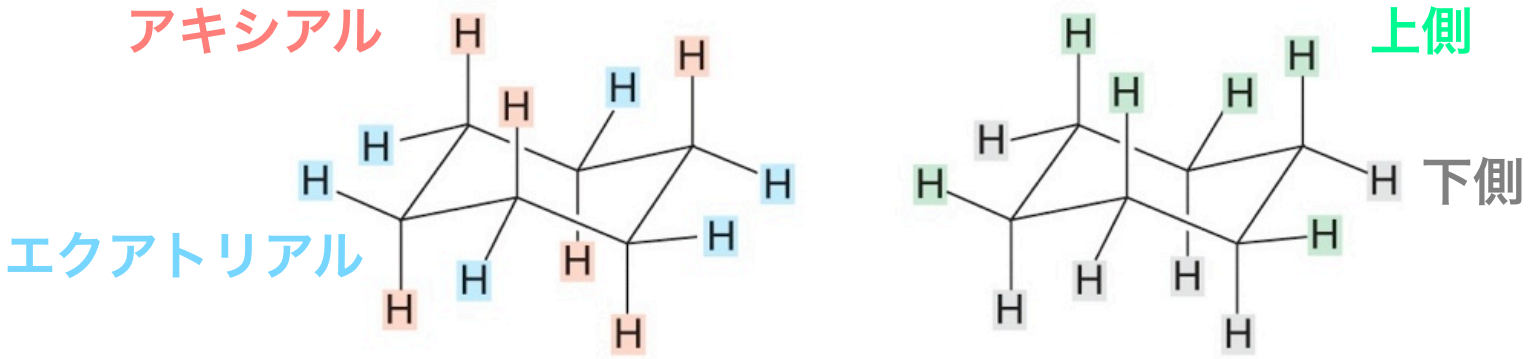
★★

ところで：シクロヘキサンを上手に書くコツ

ポイント４
エクアトリアル結合を書く場合、一つ隣のＣ–Ｃ結合と並行に



ついでに、シクロヘキサンの立体構造をあらためて確認しておこう



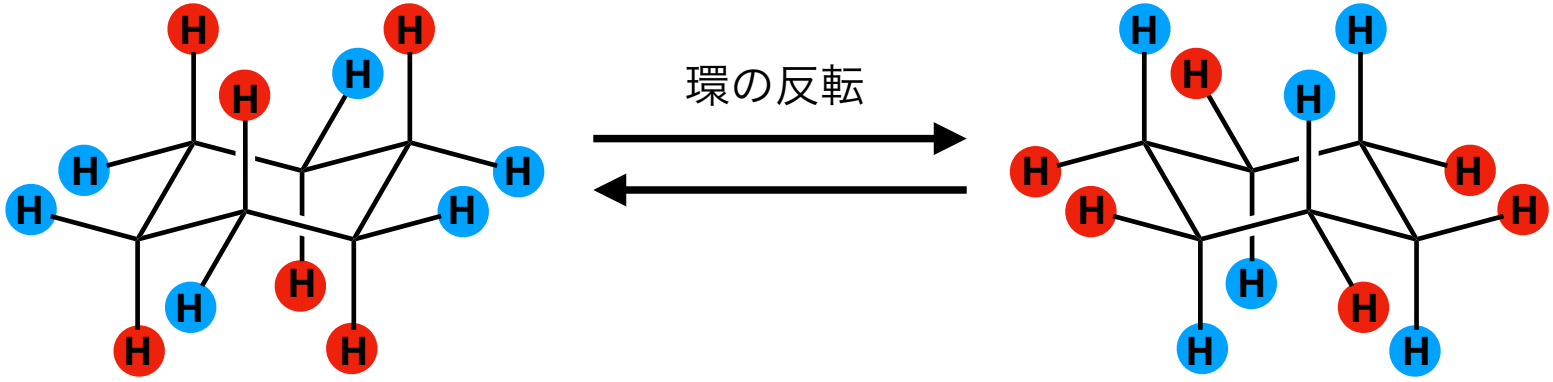
アキシアル/エクアトリアルと上側/下側は独立していることに注意

English explanations for this issue are available in Jone's textbook.

★★

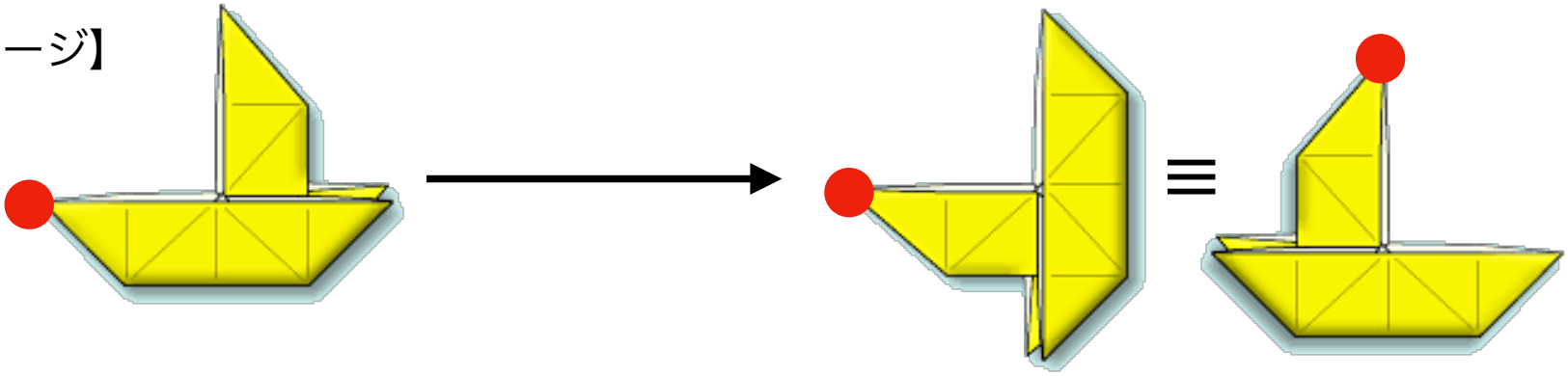
シクロヘキサンの水素置換基

アキシアルとエカトリアルの位置関係は環が反転すると変わる



赤＝アキシアル　　だったのに…　　赤＝エカトリアル　　に！

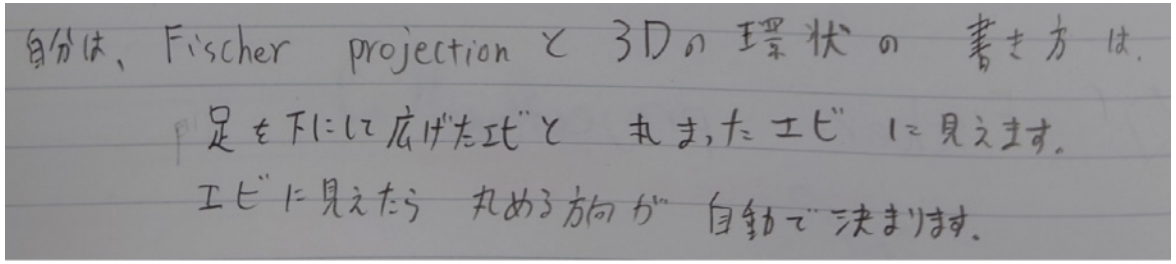
【イメージ】



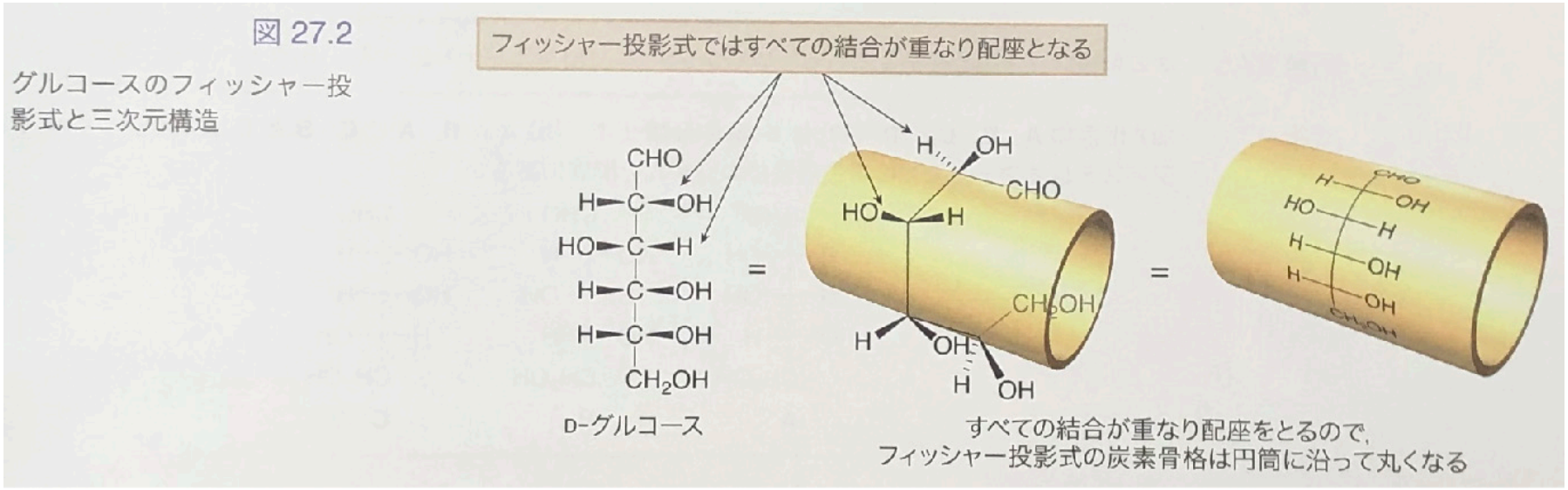
赤 ＝ 舳先　　だったのに…　　赤 ＝ 帆　　に！

3は間違えましたが、魚の骨で考えるやり方がしっくりきました。

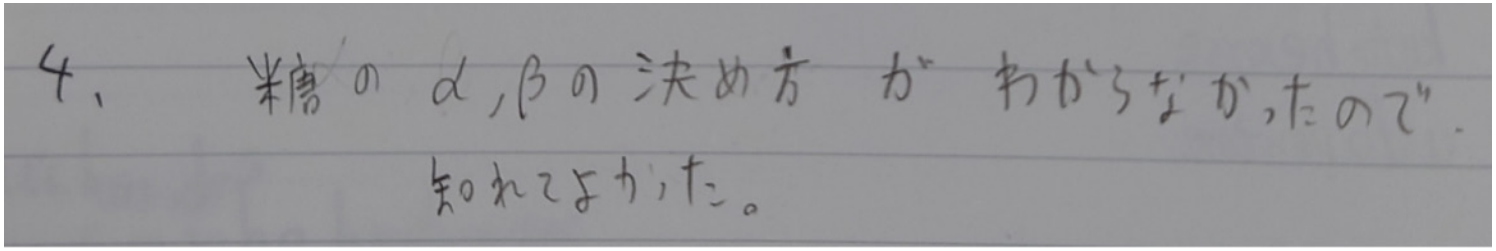
魚の骨をはがして丸めるイメージは自分が思っていたものと全く同じでした。この方法は非常に分かりやすいです。



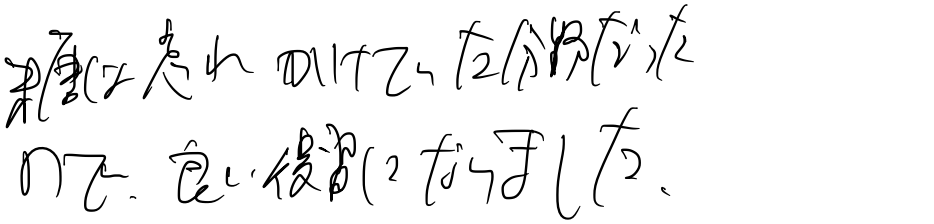
Curling-up shrimp method!

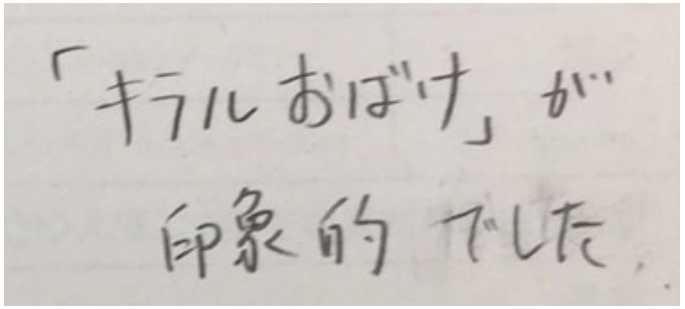


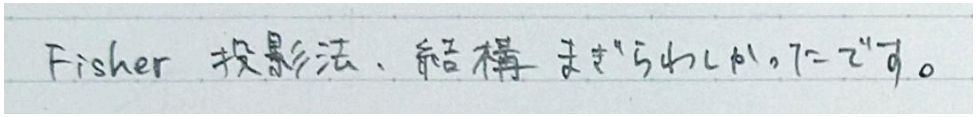
なんでもよいので、自分なりのイメージをもっておくのが大切！



立体化学が苦手なのでしっかり練習したいです。

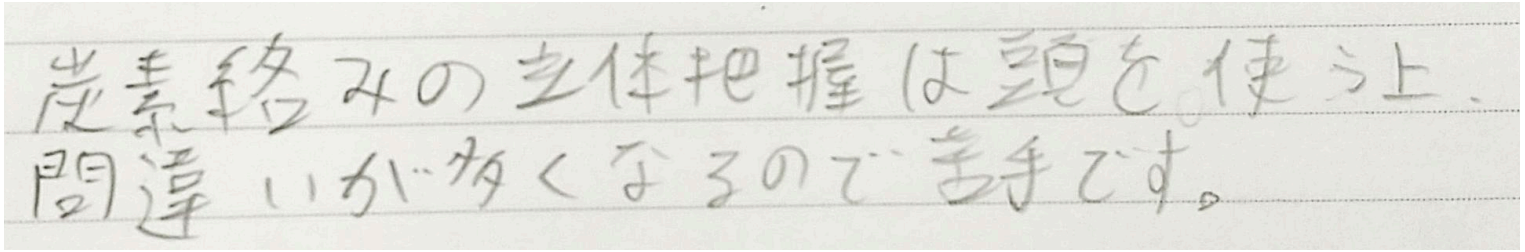






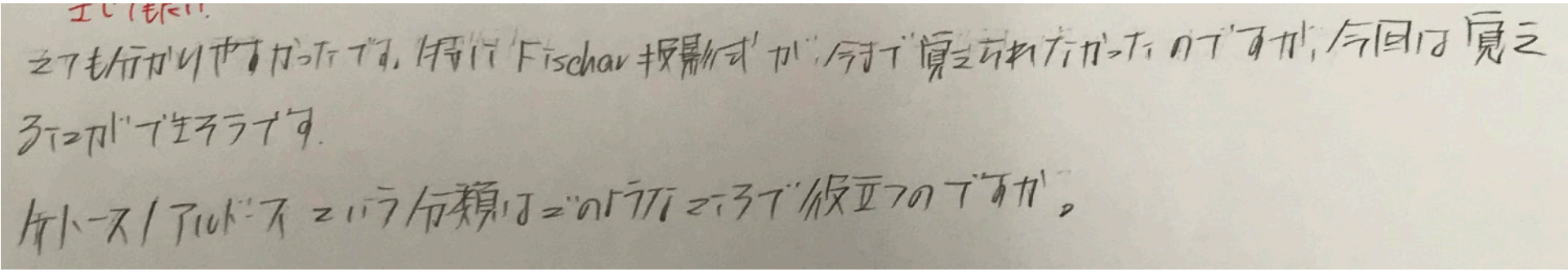
4

命名法とか投影法とか忘れたころに必要になるので鬱陶しいです。



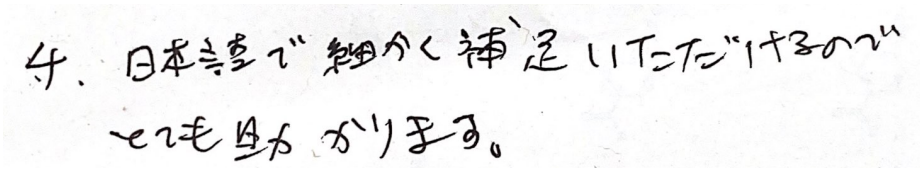
正直、Fisher投影法自体は、、、むしろ、立体化学の練習として重要かと。

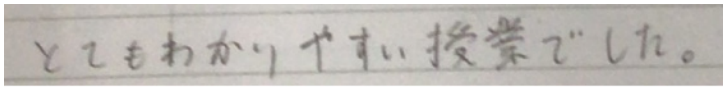
Q and A

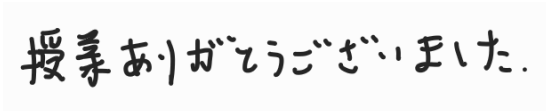


役にたつ？ことはないかもしれませんが、
命名法なので知っていないと、話が通じないことがあると思います。
そういう意味では役にたつ？

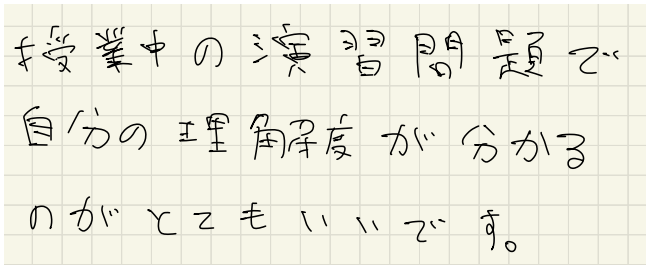
間の休み助かります。
美味しいの話、説得力があって面白かったです。





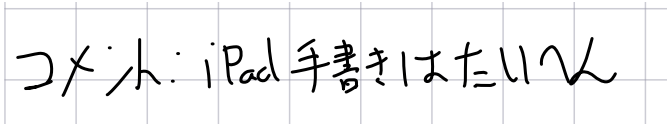


こちらこそ。
頑張って下さい。

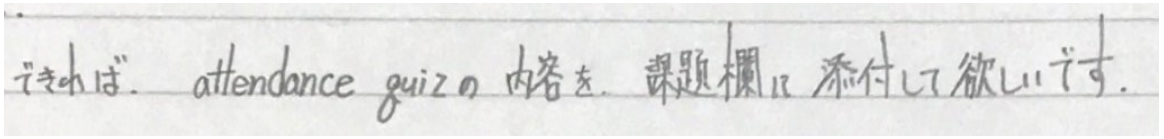


2限の終了時間は一応11:55だと思います

ごめん！勘違いしてた。今日から気をつけます。



紙に書いて、写真とって画像
アップでもOKですよ。



attendance quizの内容は
quizとしてハンドアウトに記
載しています。

授業の進行に合わせて、、、
あと、出席なので、、、

自分が把握できていないだけかもしれませんが、りばけには
関西弁の先生が少ないので新鮮でした。

吉村 英哲先生
京都府出身（たぶん）

平田 岳史先生
兵庫県出身

Topics

- structure of monosaccharide
  - classification
  - Fischer projection
  - cyclic sugars

- reactions of monosaccharide
  - several examples of monosaccharides
  - glycoside formation (glycosylation)
  - protection strategies of monosaccharides

- structure and functions of oligo and polysaccharide

Reaction of monosaccharides - 1

Simple transformation of functional groups

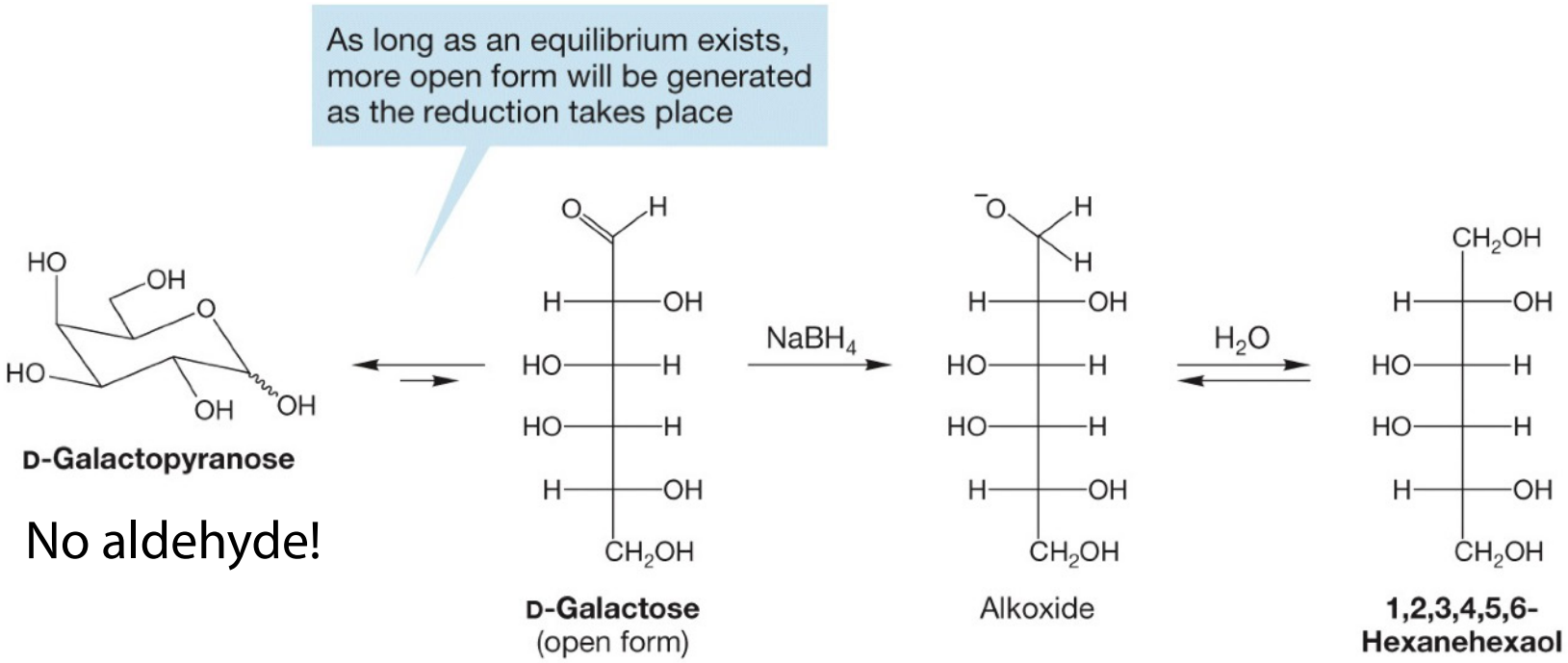
functional groups in sugars	**possible reactions**
aldehydes	**reduction to alcohol** **oxidation to carboxyl group**
alcohols	**alkylation to ethers** **acylation to esters**

Review quiz: Give an example(s) of reagents/conditions to achieve each transformation.

Reaction of monosaccharides - 1

Simple transformation of functional groups

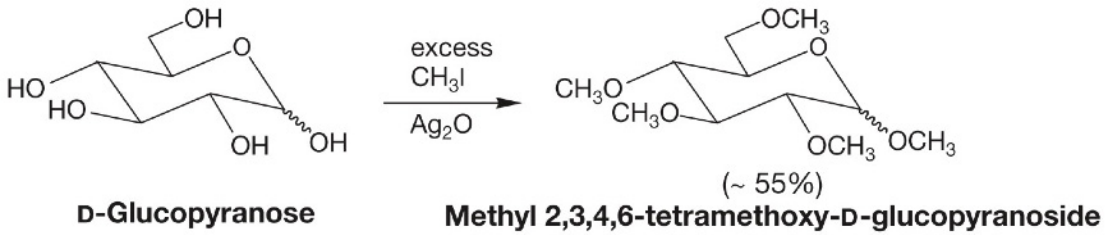
e.g. reduction of the terminal aldehyde to alcohol



Reaction of monosaccharides - 1

Simple transformation of functional groups

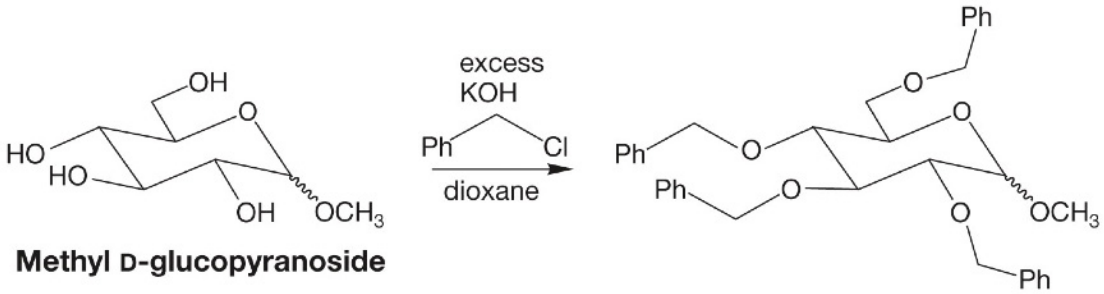
e.g. alkylation of hydroxy groups



D-Glucopyranose

(~ 55%)

Methyl 2,3,4,6-tetramethoxy-D-glucopyranoside



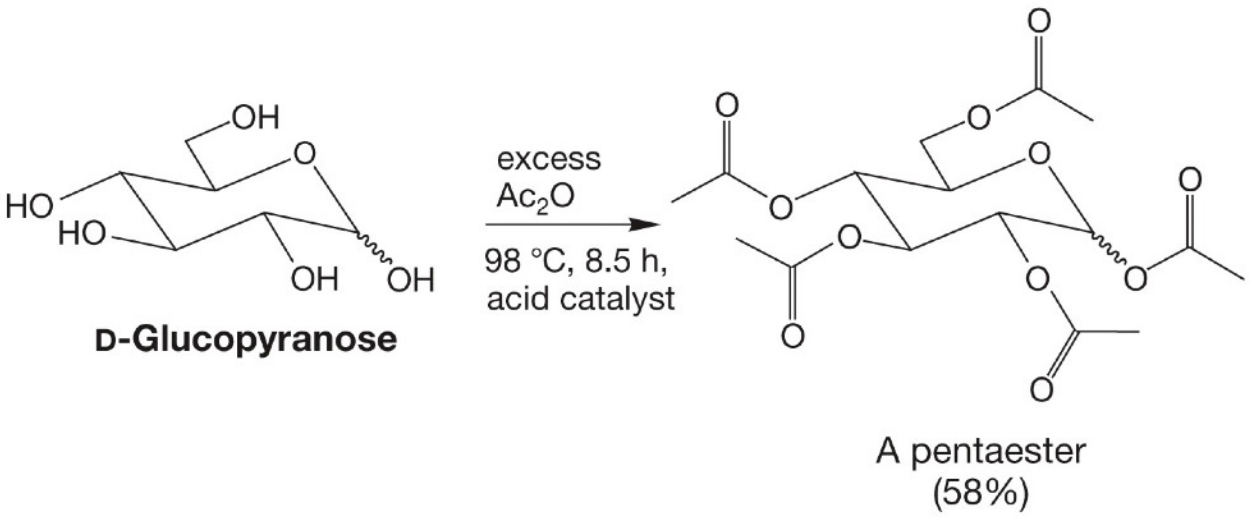
Methyl D-glucopyranoside

"Williamson ether synthesis" (~ 95%)

Reaction of monosaccharides - 1

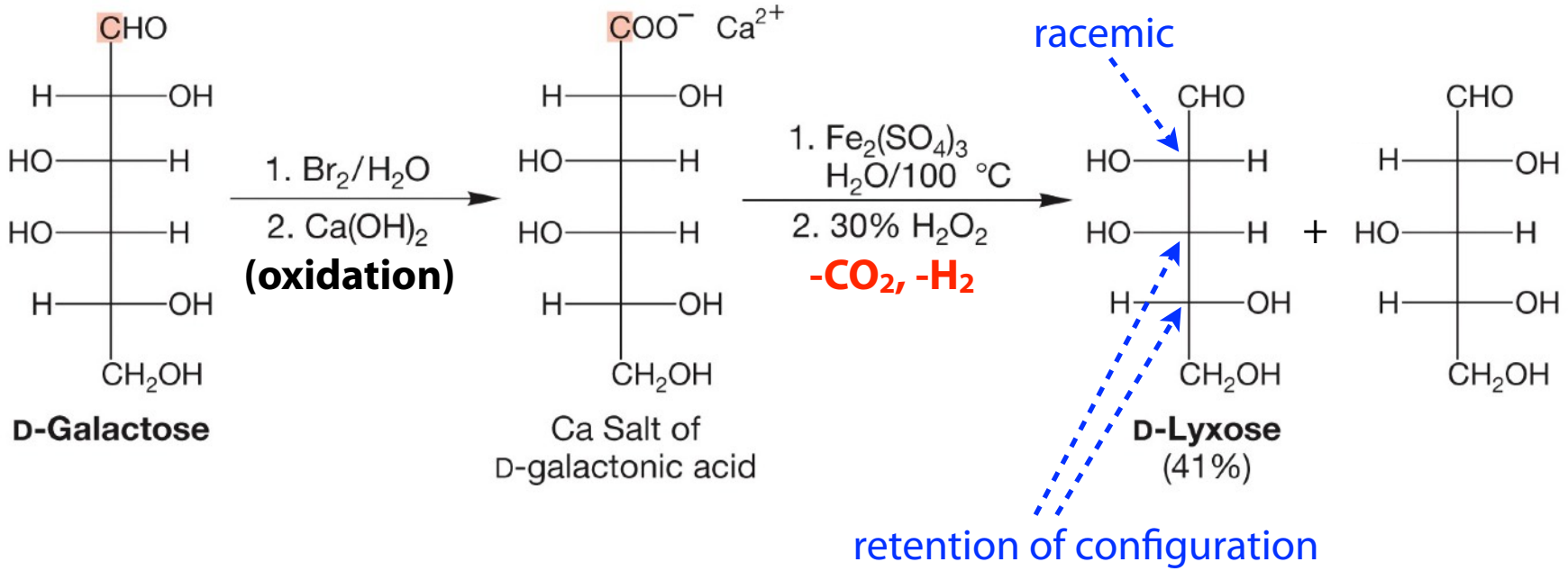
Simple transformation of functional groups

e.g. acylation of hydroxy groups



Reaction of monosaccharides - 2

Truncation of chains in monosaccharides (Ruff degradation)

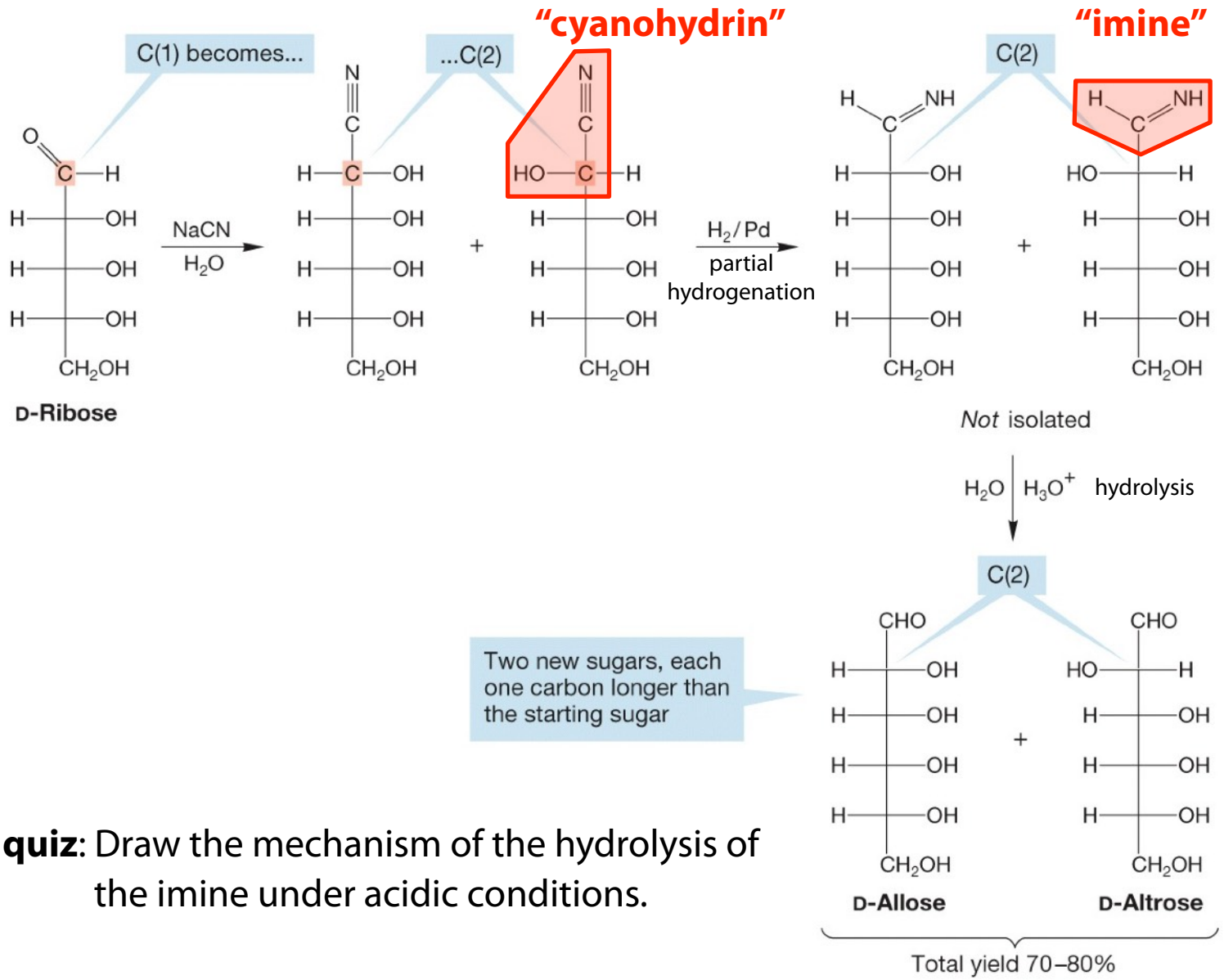


Note; Br2 acts as a mild oxidant.

Whereas the aldehyde is oxidized, hydroxy groups are intact.

Reaction of monosaccharides - 3

Elongation of chains in monosaccharides (Kiliani-Fischer synthesis)

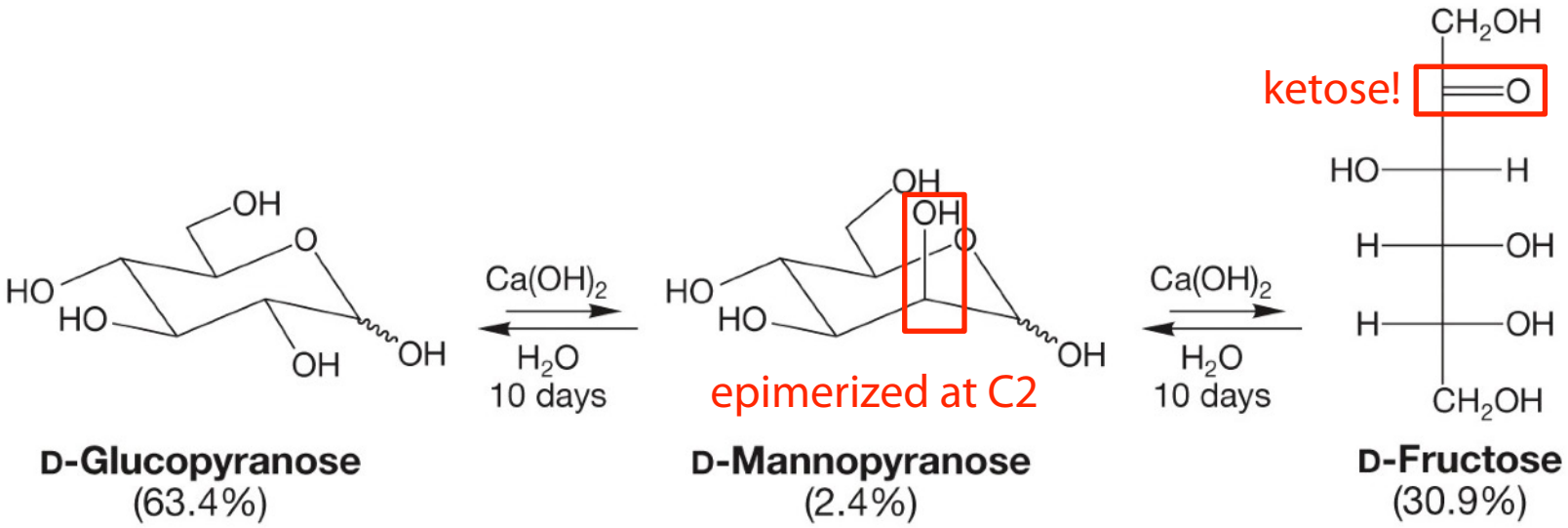


Review quiz: Draw the mechanism of the hydrolysis of the imine under acidic conditions.

Reaction of monosaccharides - 4

Epimerization under basic conditions (Lobry de Bruijn-Alberda van Ekenstein reaction)

D-glucose can be slowly converted to D-mannose and D-fructose under basic conditions!

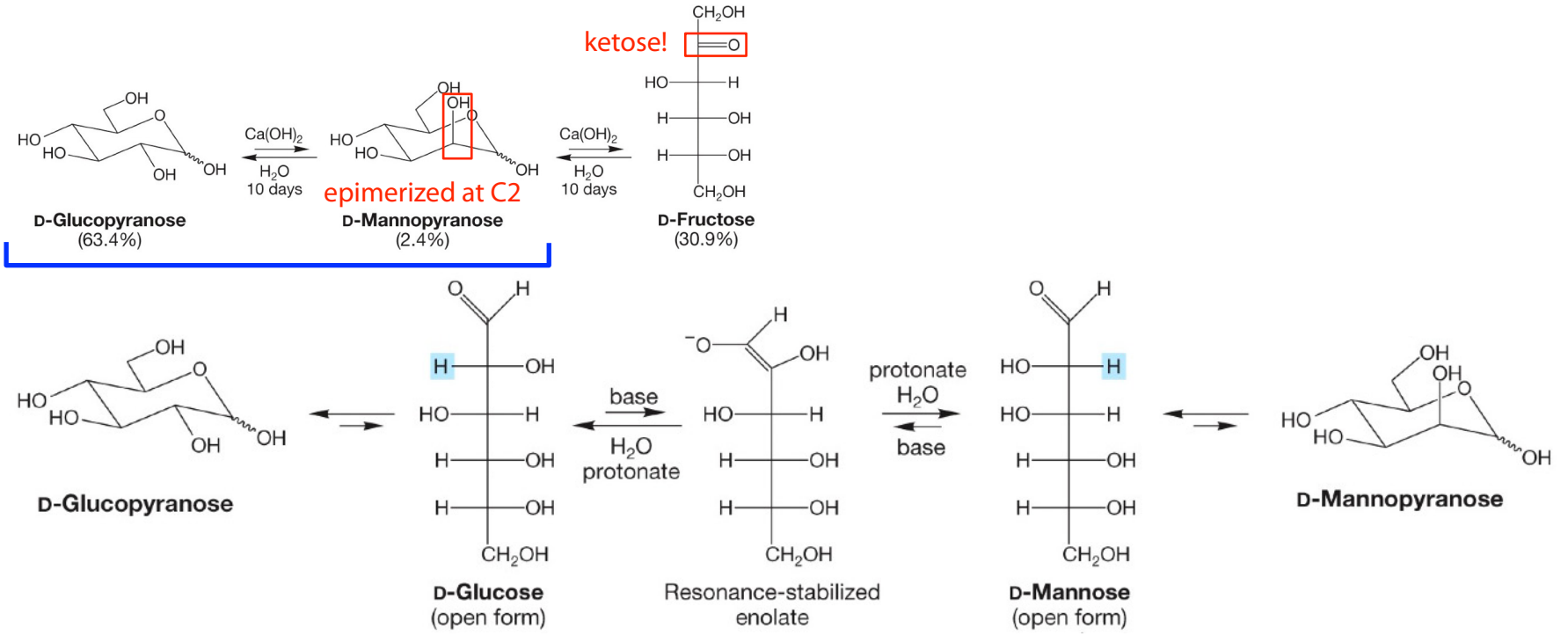


How!?

Quiz-6: Although D-fructose (open chain form) is here shown to emphasize it is a ketose, it actually exists in the pyranose and furanose form. Draw Fischer projections for the pyranose and furanose forms of D-fructose.

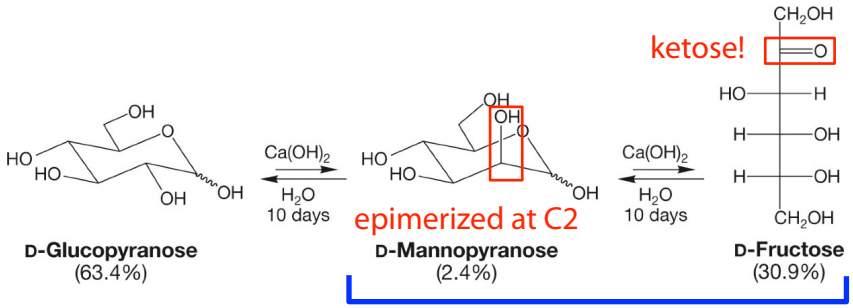
Reaction of monosaccharides - 4

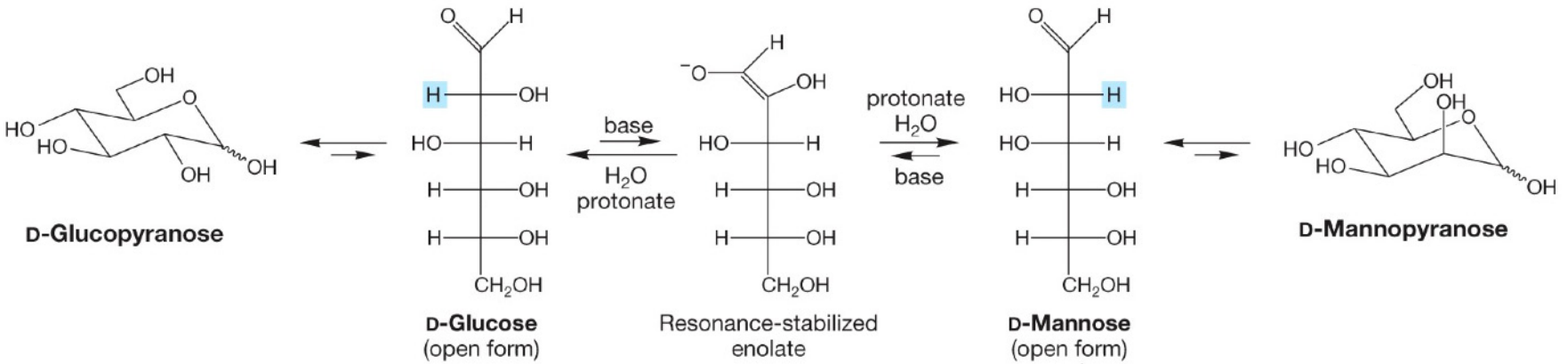
Epimerization under basic conditions (Lobry de Bruijn-Alberda van Ekenstein reaction)

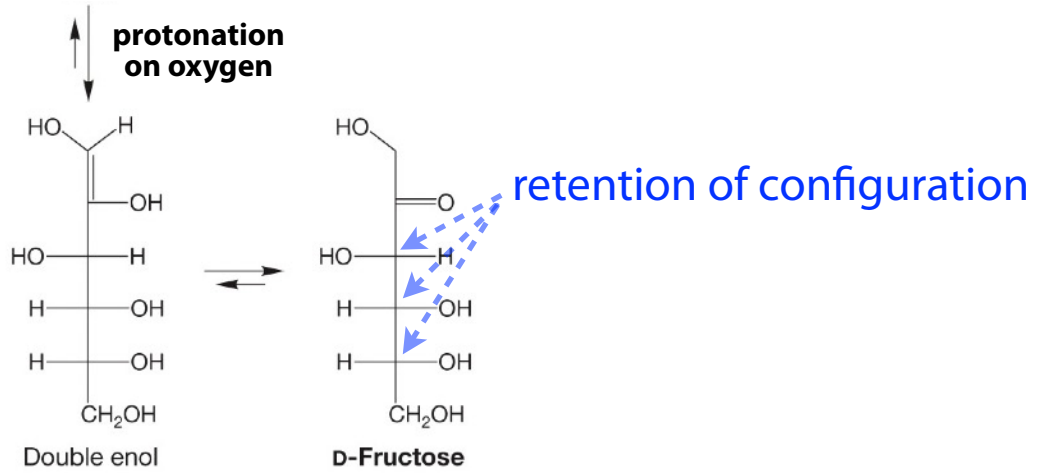


Reaction of monosaccharides - 4

Epimerization under basic conditions (Lobry de Bruijn-Alberda van Ekenstein reaction)



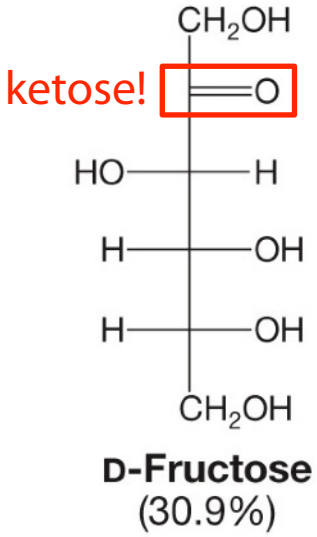




Reaction of monosaccharides - 4

Epimerization under basic conditions (Lobry de Bruijn-Alberda van Ekenstein reaction)

D-glucose can be slowly converted to D-mannose and D-fructose under basic conditions!



D-Fructose
(30.9%)

pyranose form **furanose form**

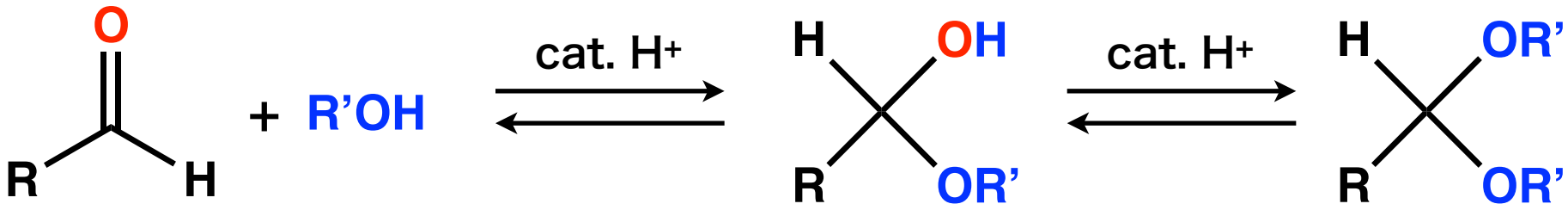
Quiz-6: Although D-fructose (open chain form) is shown here to emphasize it is a ketose, it actually exists in the pyranose and furanose form. Draw Fischer projections for the pyranose and furanose forms of D-fructose.

Reaction of monosaccharides - 5

Synthesis of glycosides

If glucose is reacted with alcohols, what can occur?

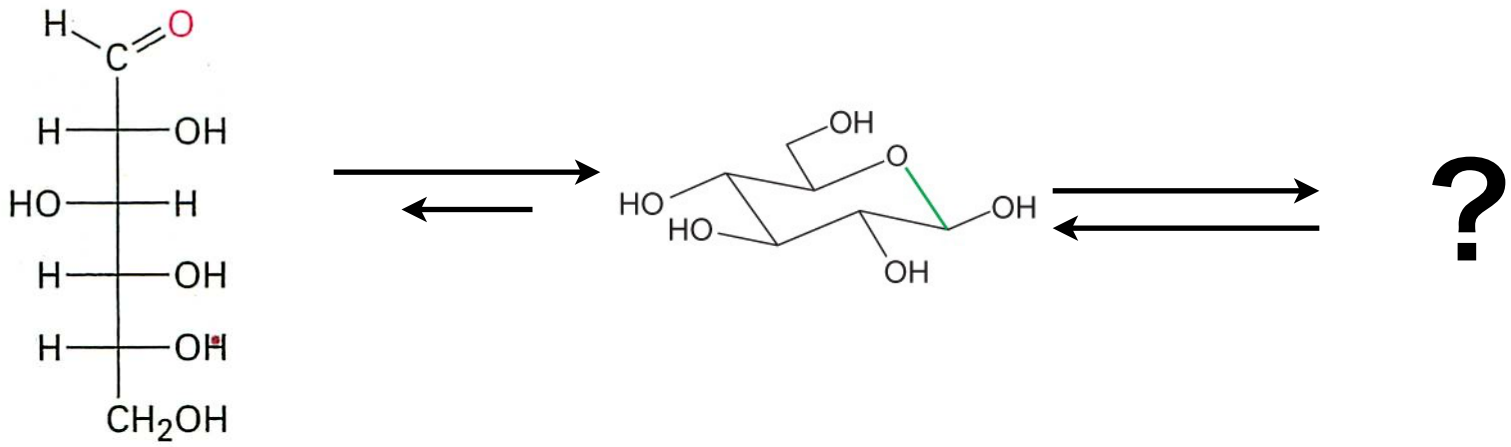
Remind this



hemiacetal

acetal

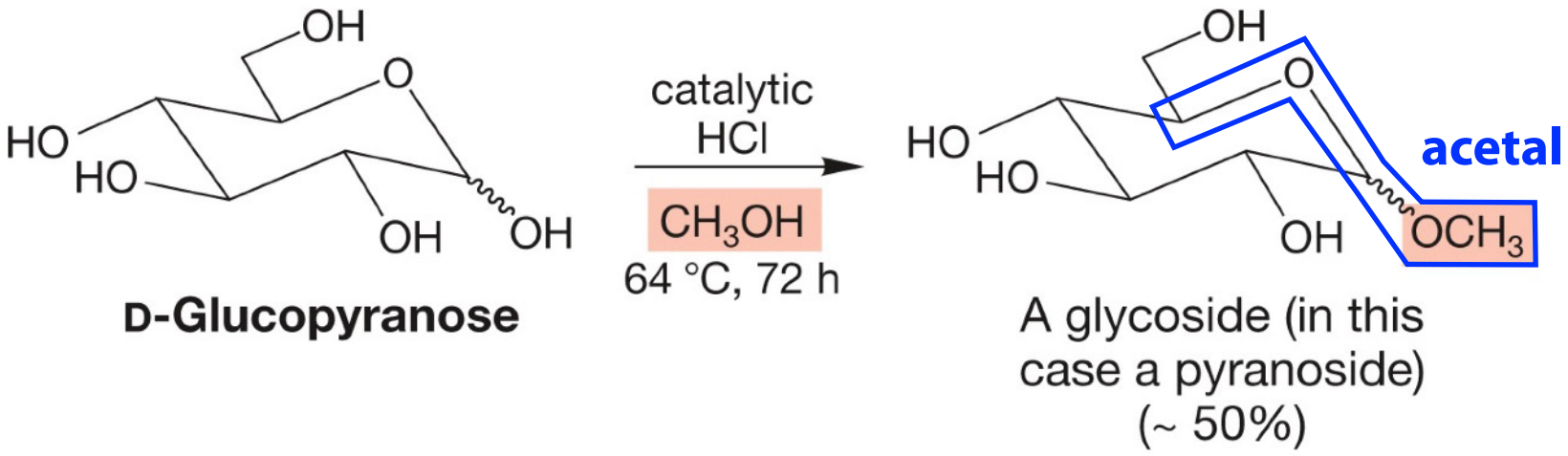
in sugar chemistry, **cyclic form** **glycoside**



Reaction of monosaccharides - 5

Synthesis of glycosides

If glucose is reacted with alcohols, what can occur?



glycosides: (in a narrow sense,) acetal forms of sugars on the anomeric position

nomenclature - giving the alkyl group followed by the sugar name with the "-ose" replaced with "-oside"

e.g. the name of the glycoside above is "methyl D-glucopyranoside"

Review quiz: Draw the mechanism of the glycoside formation under acidic conditions.

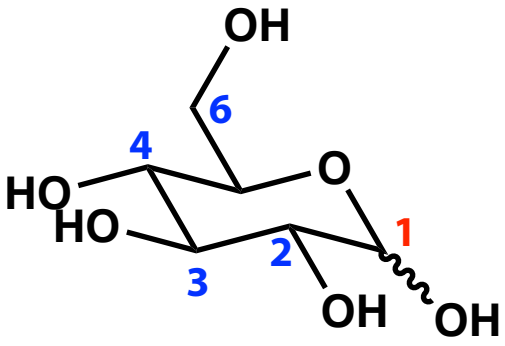
Topics

- structure of monosaccharide
  - classification
  - Fischer projection
  - cyclic sugars

- reactions of monosaccharide
  - several examples of monosaccharides
  - glycoside formation (glycosylation)
  - protection strategies of monosaccharides

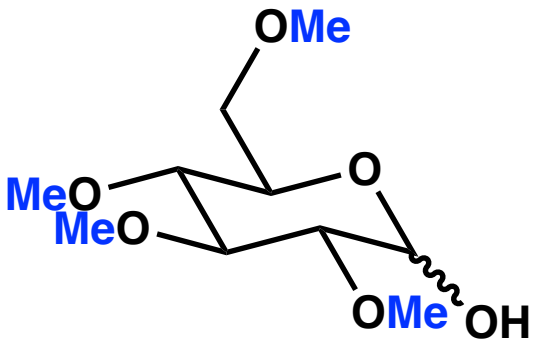
- structure and functions of oligo and polysaccharide

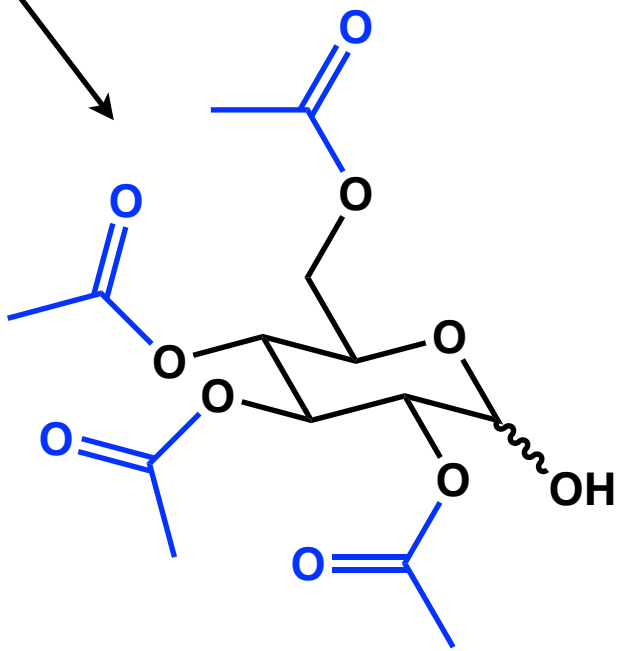
Selective protection of monosaccharides



D-glucopyranose

How?

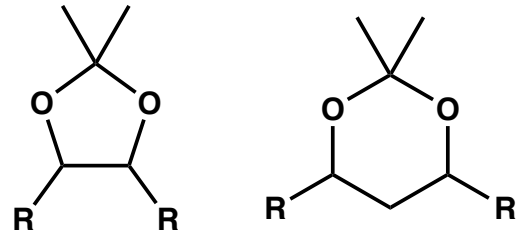


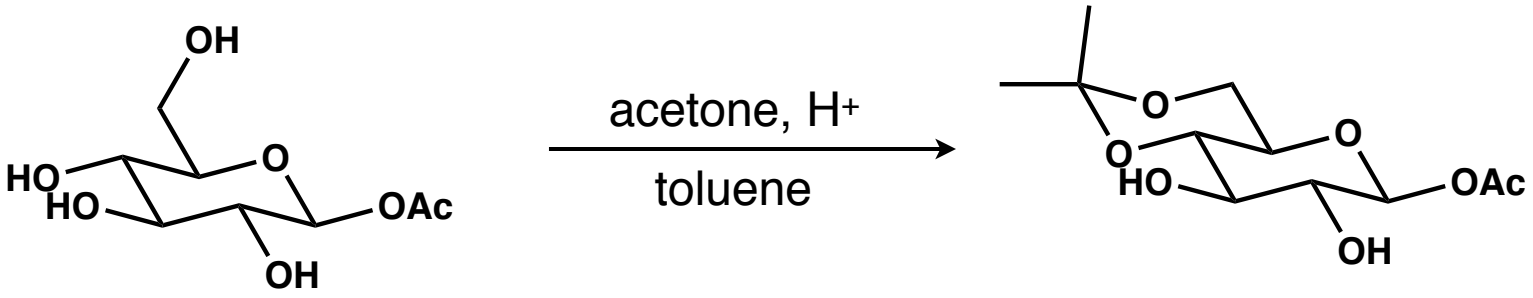


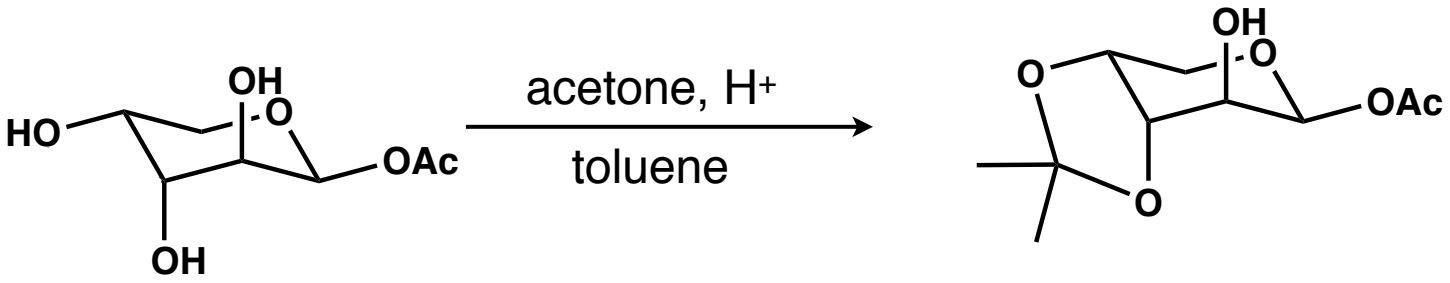
Review quiz: Draw the mechanism of the last reaction.

Selective protection of monosaccharides

acetonide - protective group of 1,2- and 1,3- diols



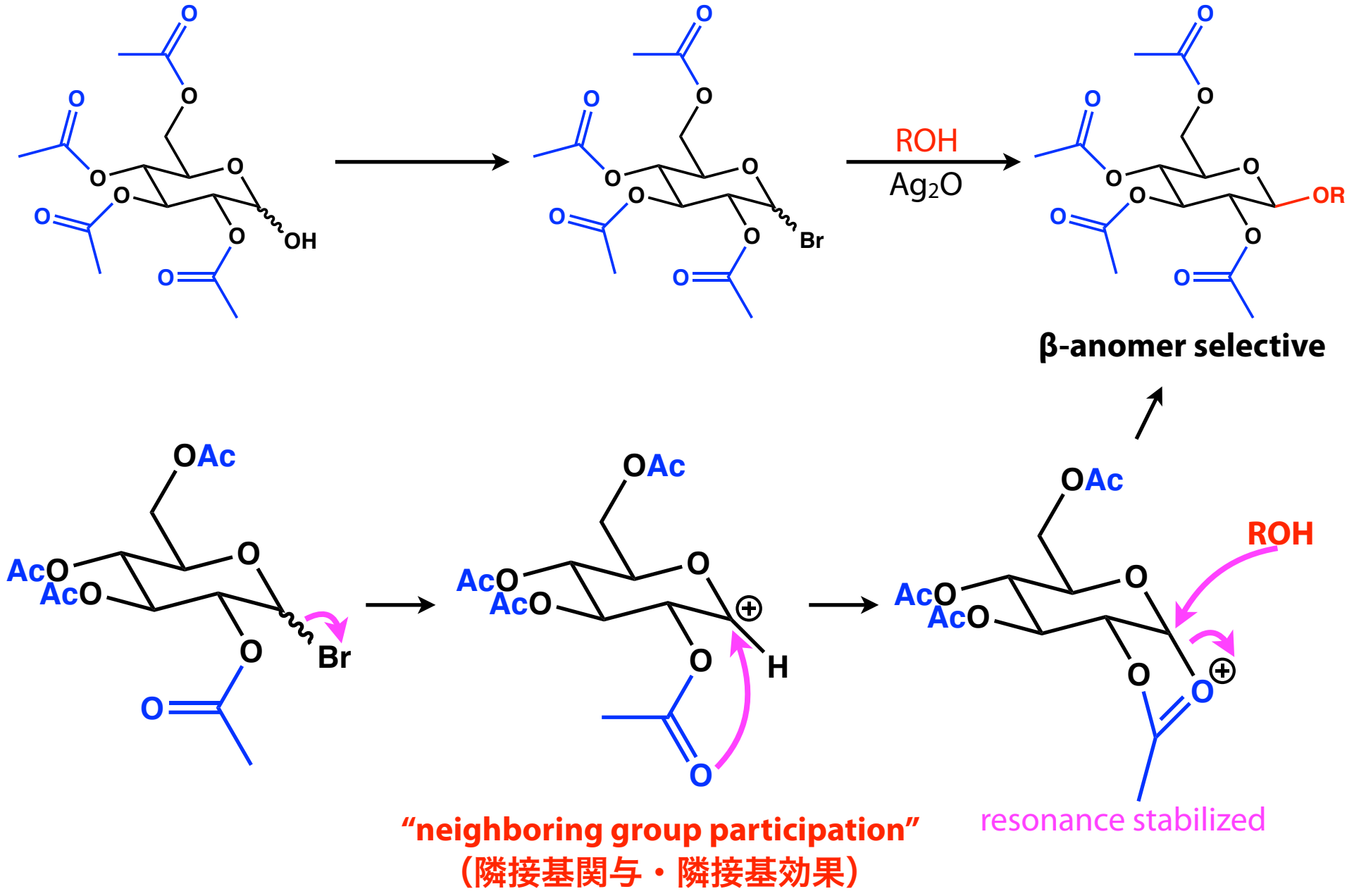




Only *syn* 1,2-diols can be protected by acetonide.

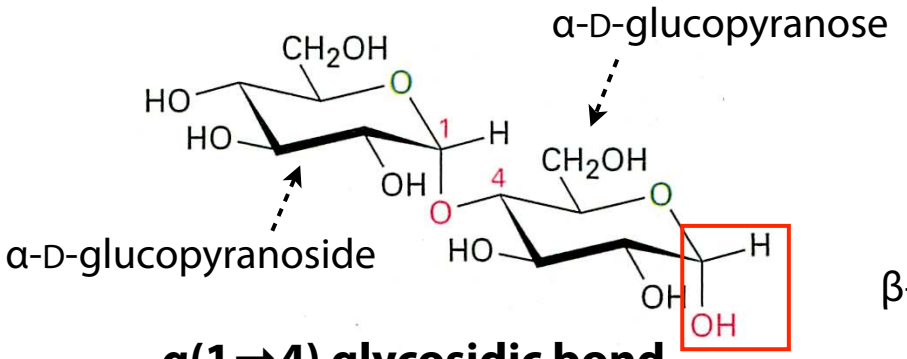
Review practice: Draw the mechanism of protection and deprotection of acetonide group.

Stereoselective glycosylation



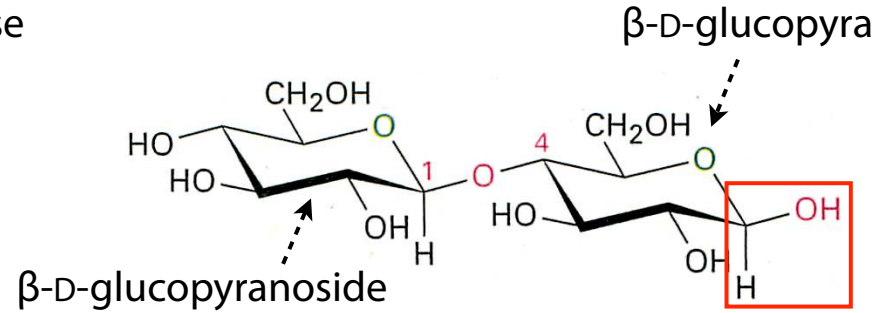
If ROH in glycosylation is a sugar … disaccharides

Dimers of D-glucopyranose



α(1→4) glycosidic bond

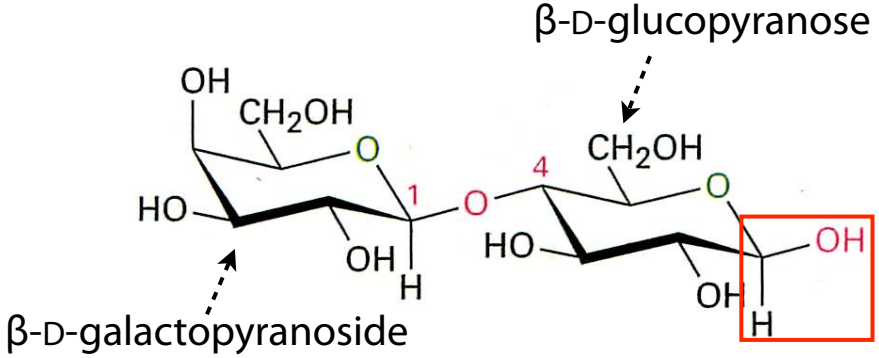
(maltose)



β(1→4) glycosidic bond

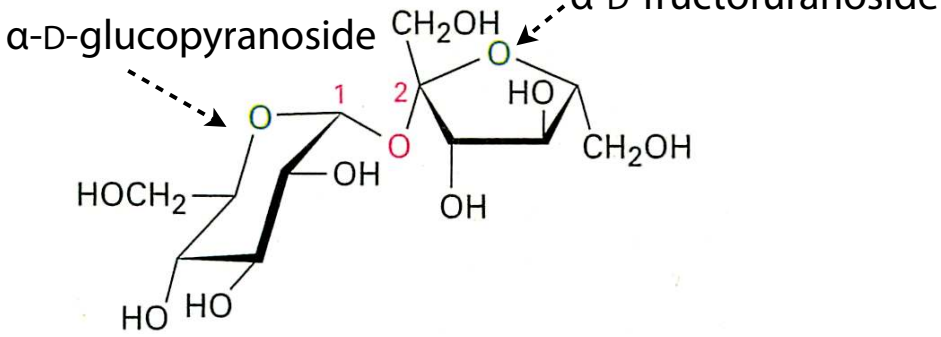
(cellobiose)

lactose （乳糖）



β(1→4) glycosidic bond

sucrose（ショ糖、砂糖）



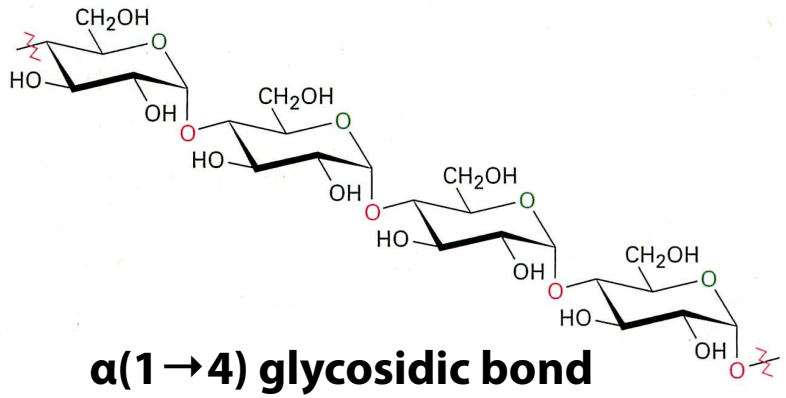
α(1→2) glycosidic bond

Two important polysaccharides

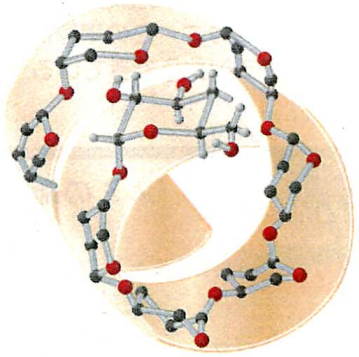
Both are polymers of D-glucopyranose

see 3D structures

amylose（デンプンの構成要素）

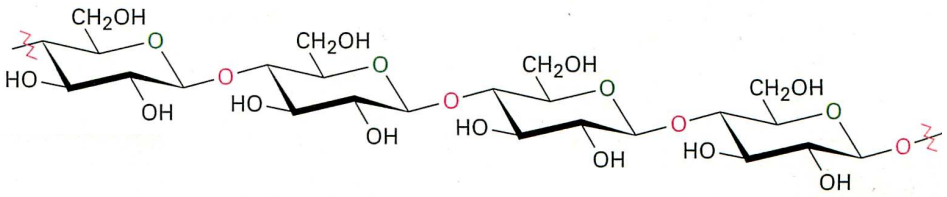


α(1→4) glycosidic bond

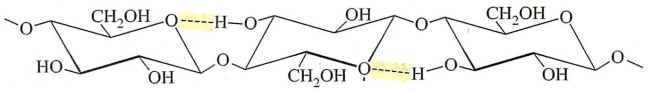


helical structure of amylose
(good energy source)

cellulose



β(1→4) glycosidic bond



planar structure of cellulose
(we cannot digest this)

topics- roles of polysaccharides in organisms

energy storage - amylose, glycogen, etc.

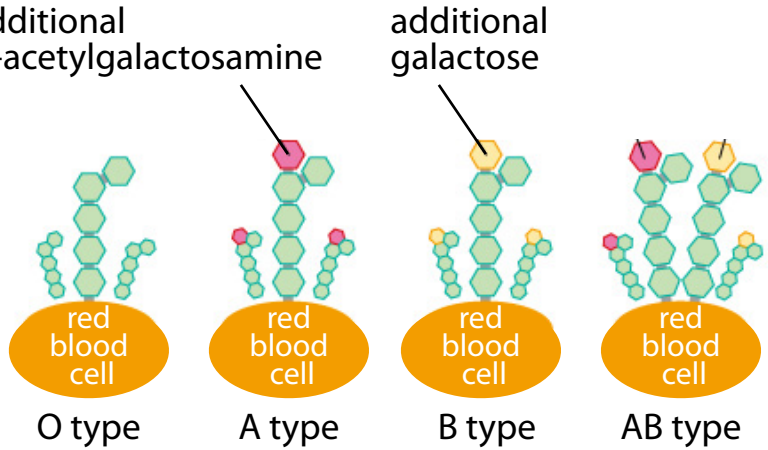
structural skeleton - cellulose, chitin, etc.

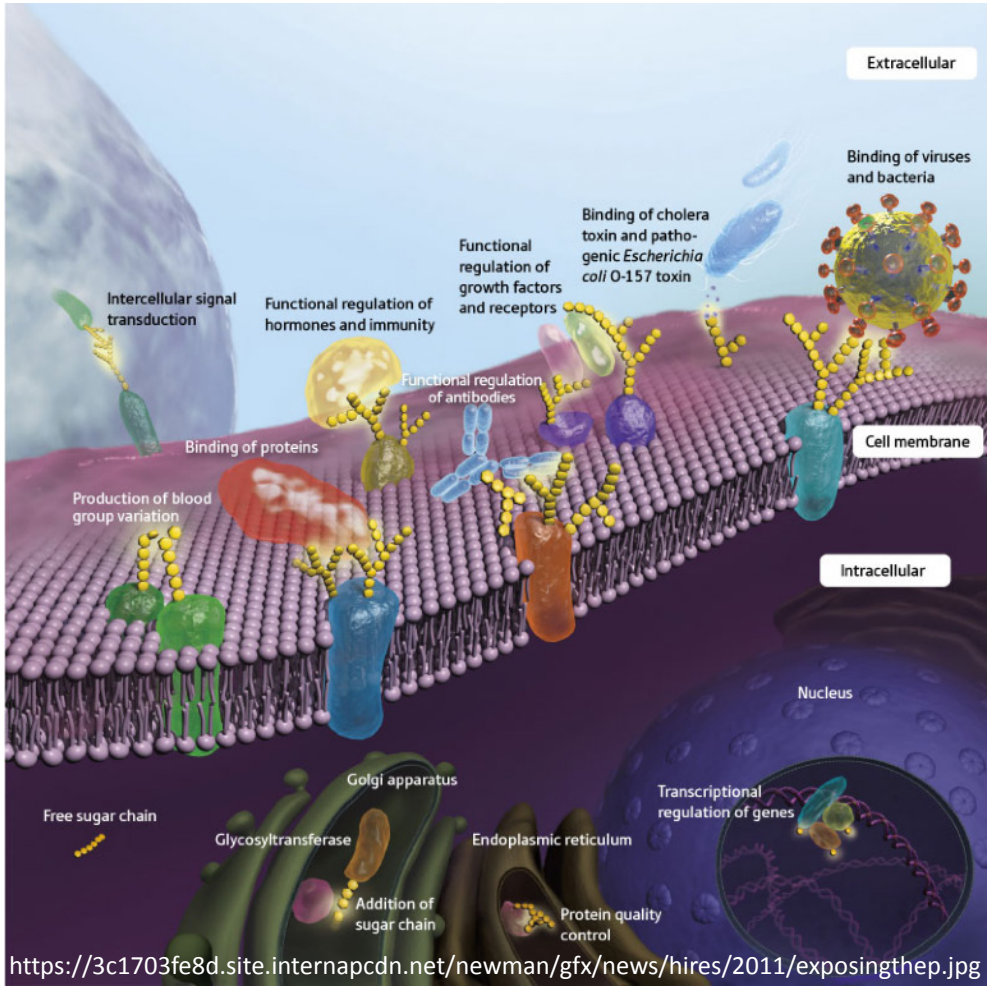
regulation of cellular events

Many different polysaccharide chains are found on exterior surface of cells.

Different cells display different poly saccharine chain on the surface.

They play important roles in
- definition/recognition of cellular types
- infection of viruses
- regulation of growth factors

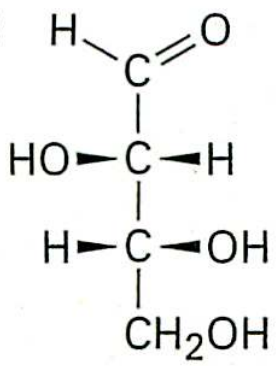




Classification of monosaccharide

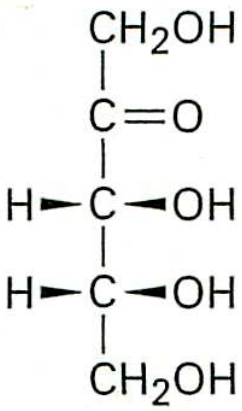
Quiz-1: Classify the following monosaccharides

(a)



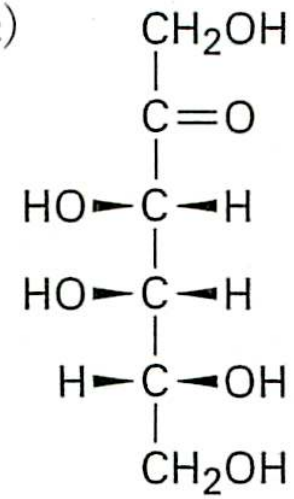
トレオース
threose

(b)



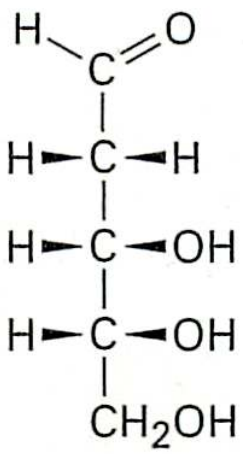
リブロース
ribulose

(c)



タガトース
tagatose

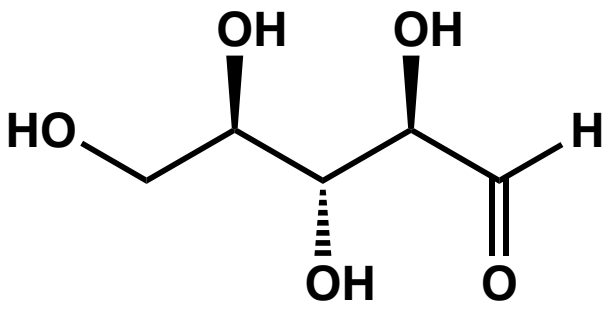
(d)

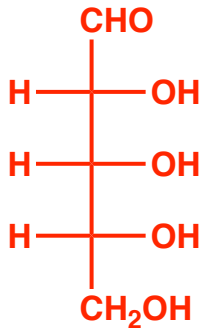


2-デオキシリボース
2-deoxyribose

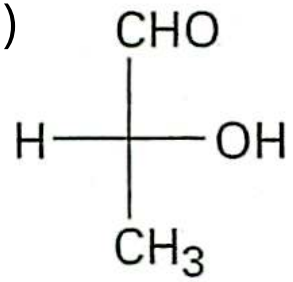
aldotetrose **ketopentose** **ketohexose** **aldopentose**

Fischer projection drawing



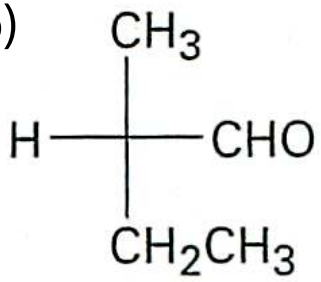


(a)

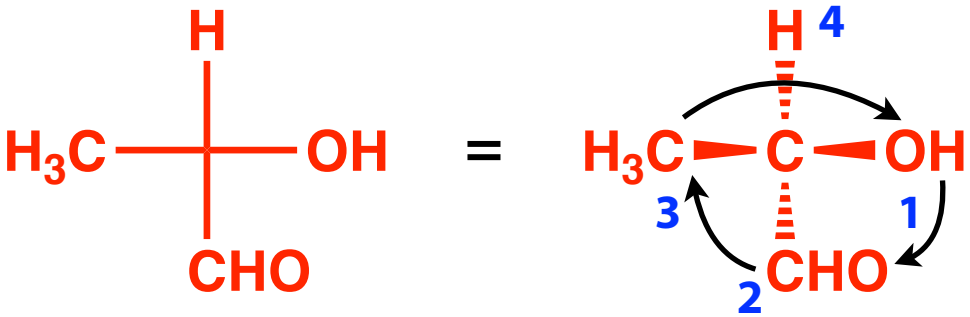


(*R*)

(b)

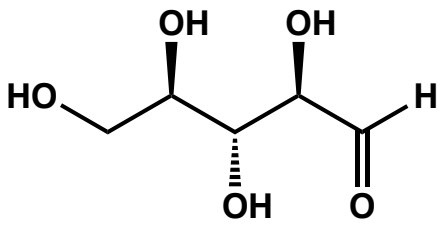


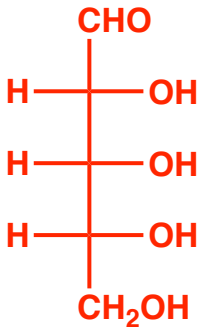
(*S*)



Fischer projection drawing

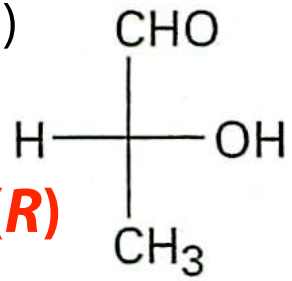
Quiz-2: Draw the Fischer projection of the sugar below.





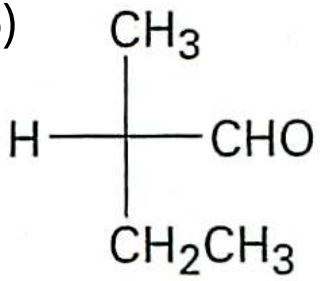
Quiz-3: Designate the stereogenic carbon of the following compounds as either (*R*) or (*S*).

(a)

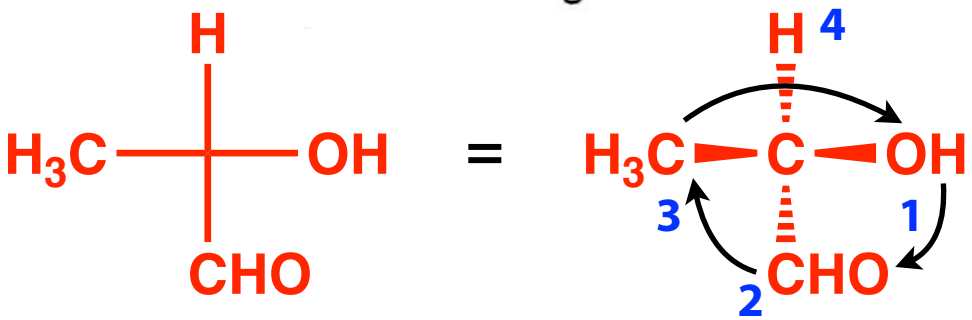


(*R*)

(b)

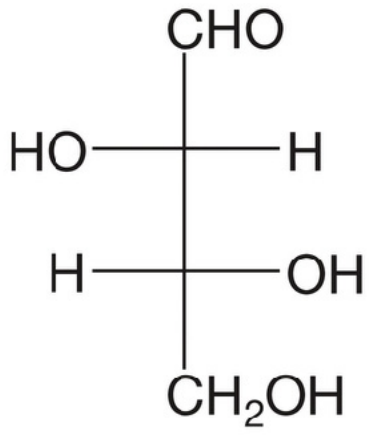


(*S*)

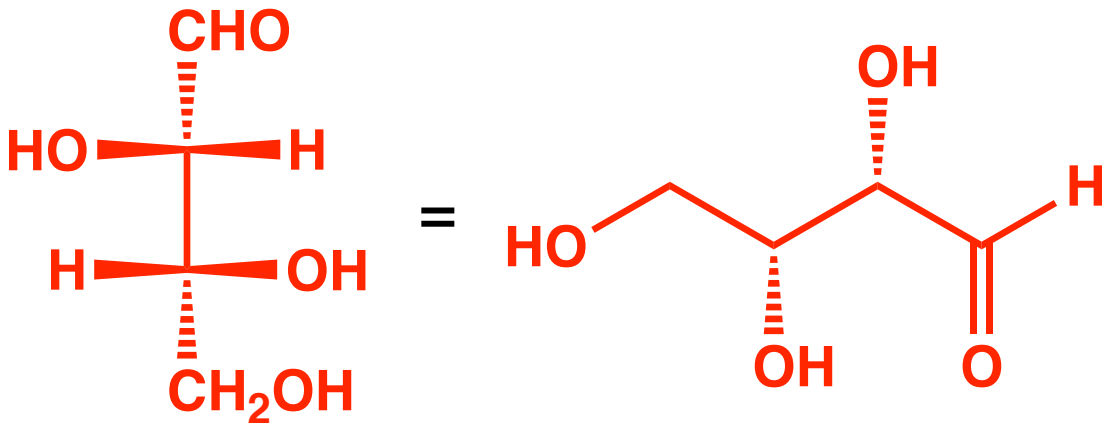


Fischer projection drawing

Quiz-4: Use solid-wedge and dashed-wedge notation to write 3D representation for the following molecule shown in Fischer projection.

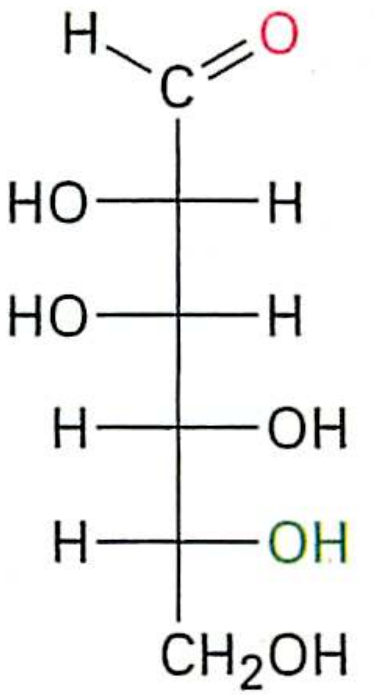


II



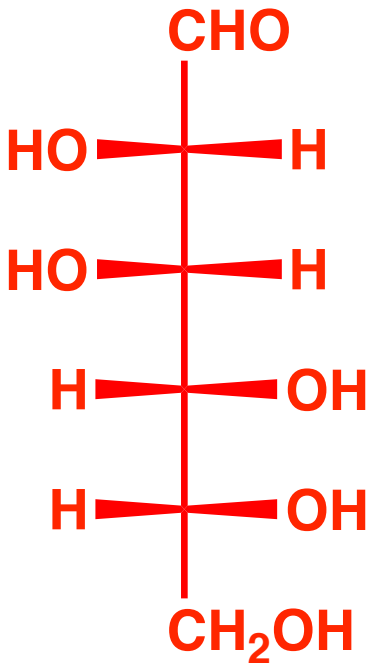
Formation of cyclic sugars via hemiacetal formation

Quiz-5: Here is the Fischer projection of D-mannose.
Draw the structure of β-D-mannopyranose in chair structure.



D-mannose

=



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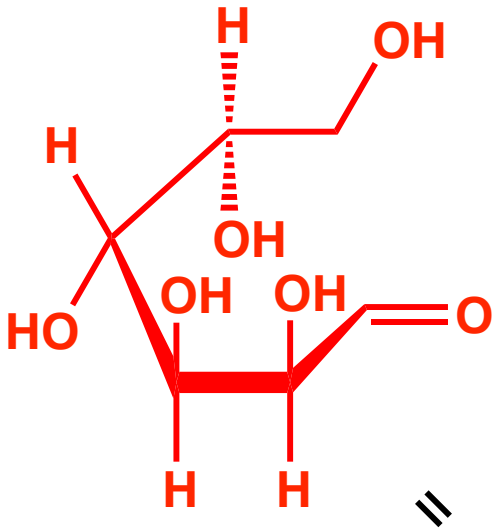

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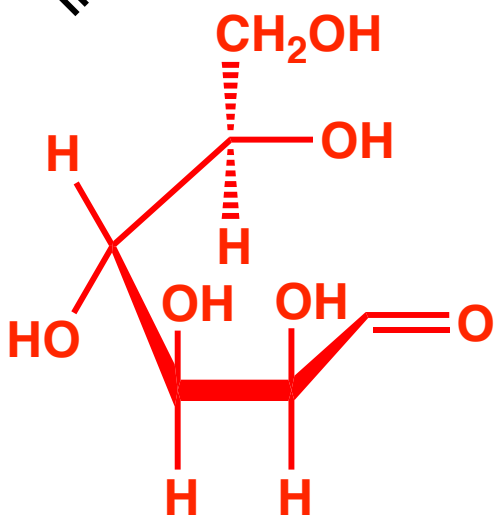

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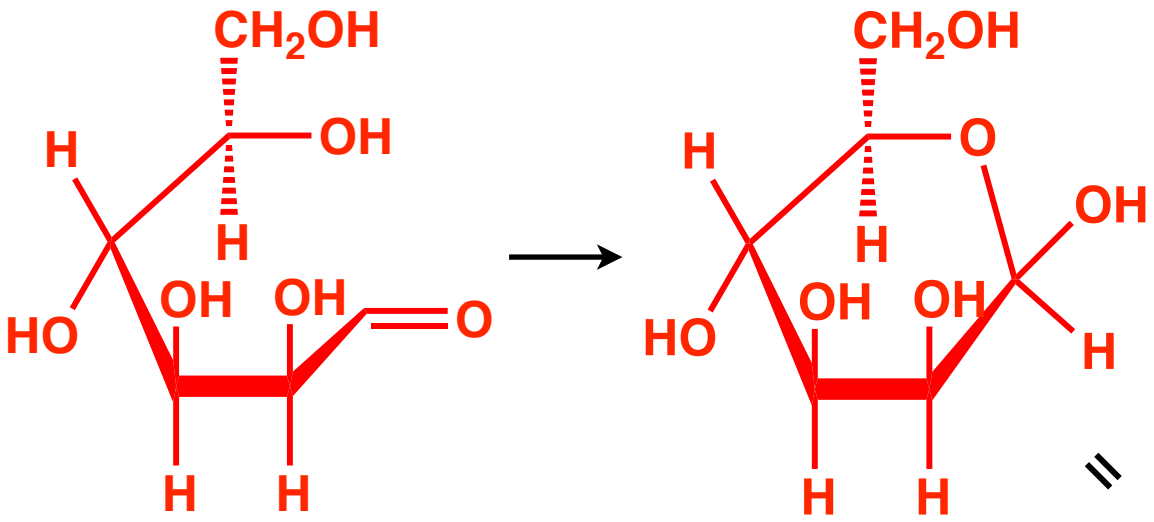

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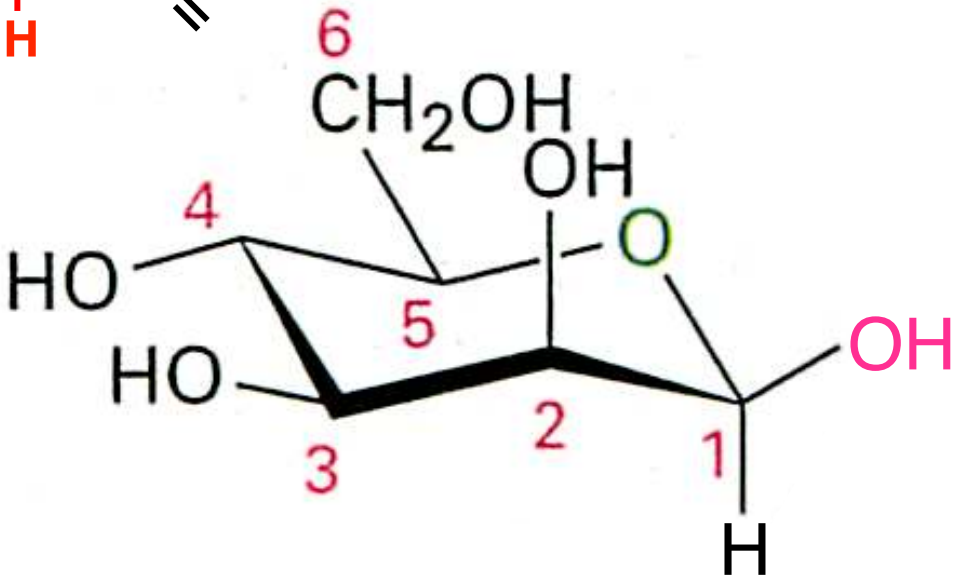

Formation of cyclic sugars via hemiacetal formation

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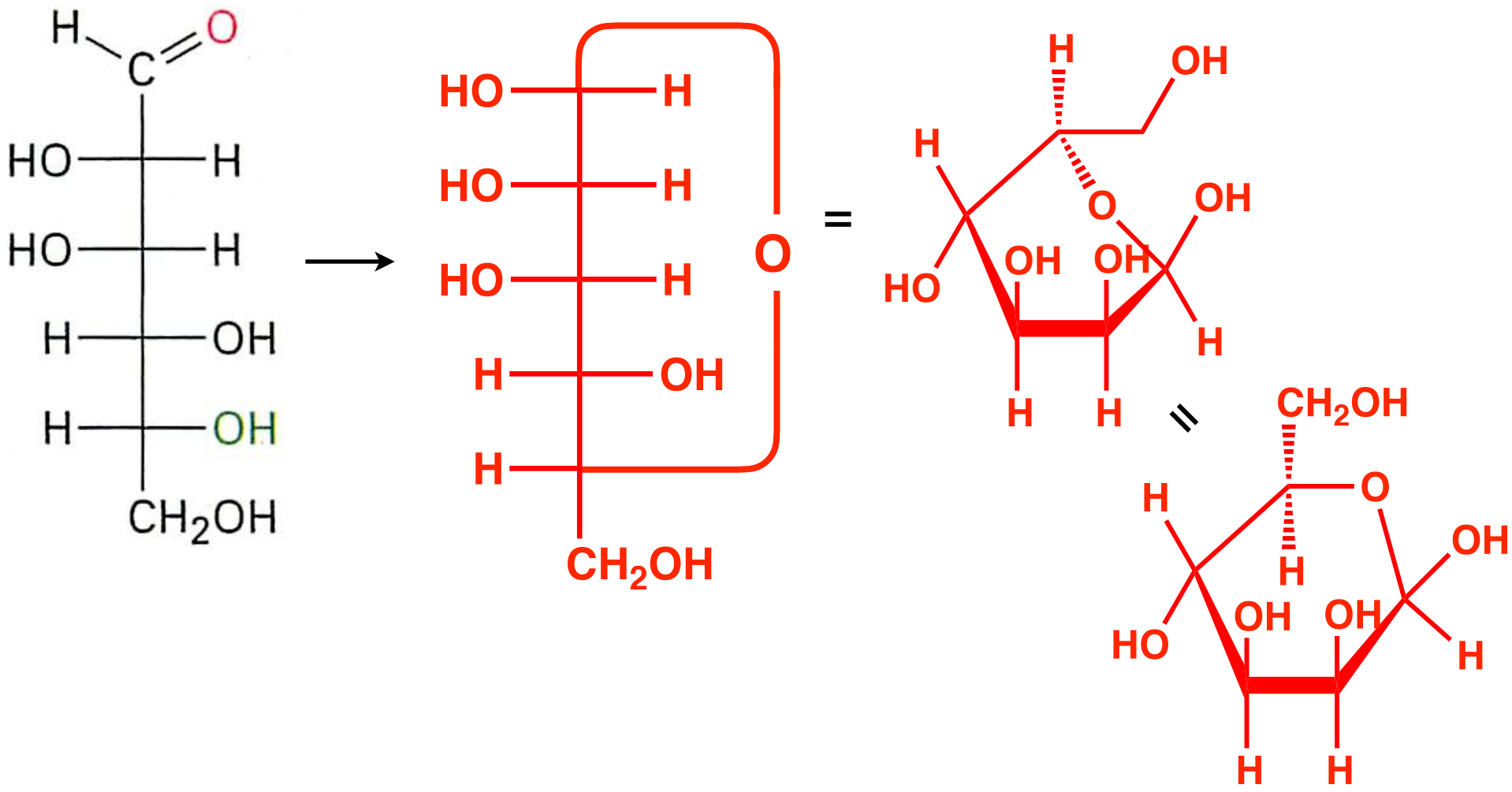

Formation of cyclic sugars via hemiacetal formation

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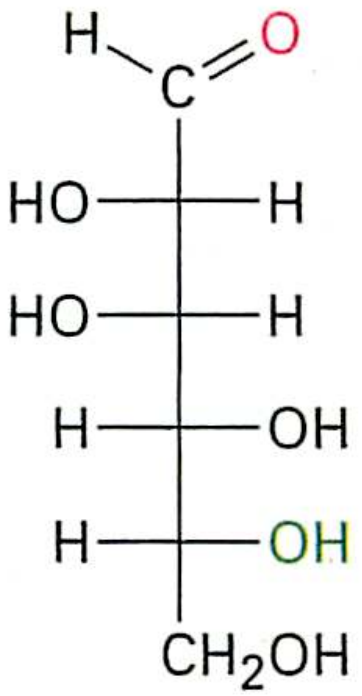
Draw the structure of β-D-mannopyranose in chair structure.



D-mannose